# Russian Chemical Reviews, Volume 46 (1977)

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# Proton Transfer Reactions in the Excited Electronic States of Aromatic Molecules

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Proton transfer reactions involving electronically excited aromatic molecules are examined and the methods for the determination of the acidities of aromatic molecules in various electronic excited states are discussed and compared. The proton phototransfer reactions in protic and aprotic solvents and in the solid phase as well as intramolecular proton phototransfer are considered separately. Particular attention is devoted to the degradation of the electronic excitation energy in proton phototransfer reactions.
The bibliography includes 186 references.

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## I. INTRODUCTION

Considerable advances have been achieved during the last two decades in studies on the chemical reactions of electronically excited molecules. Many important characteristics of the reactions occurring in excited electronic states have been elucidated[1,2]. Photoexcitation of molecules leads to a significant change of their electronic structure and reactivity. Among the reactions of excited molecules, the acid–base processes involving the addition or elimination of a proton are of particular interest. Proton phototransfer is the simplest example of a heterolytic reaction and is extremely convenient for the investigation of the general characteristics of the reactions of electronically excited molecules. Phototransfer reactions are used in lasers and masers[3,4] and in photochromic materials[5,6].

Two types of proton transfer reactions are known. Proton transfer via a system of hydrogen bonds (between two heteroatoms) proceeds both in the ground and in the excited electronic states almost without activation energy and with very high rate constants—up to $10^{10}$–$10^{11}$ litre $mole^{-1}$ $s^{-1}$. In the absence of a hydrogen bond (when at least one of the reactants is a CH acid or a C base), a considerable activation energy is characteristic of the proton transfer reactions and the rate constants are less

than $10^7$ litre mole$^{-1}$ s$^{-1}$. The mechanisms of these two types of proton transfer reactions are significantly different[7]. In the excited electronic states, proton transfer via a system of hydrogen bonds usually takes place with retention of the electronic excitation (adiabatically). In proton phototransfer reactions involving CH acids and C bases, electronic excitation is lost. This review is devoted to reactions involving the phototransfer of a proton via a system of hydrogen bonds. The acid–base properties of electronically excited organic molecules, proton transfer reactions in liquid and solid solutions, and processes involving the degradation of the electronic excitation energy in proton phototransfer are considered.

## II. THE ACID–BASE PROPERTIES OF THE EXCITED ELECTRONIC STATES

When an organic molecule absorbs light and passes to an excited state, the electron density is redistributed. In particular, in molecules containing an N, O, or S heteroatom, the density of the lone electron pair at the heteroatom increases or decreases, which causes a change in the acid–base properties of the organic molecule.

The change in acid–base properties occurring on photoexcitation was observed comparatively long ago. As early as 1931, Weber[8] observed a change in the fluorescence spectrum of 1-naphthylamine-4-sulphonate as the acidity of the solution was altered, although the absorption spectrum remained unchanged. Förster[9-11] attributed this phenomenon to a change in the acid–base properties of the molecules in the excited state. Later, the problem of the acid–base properties of electronically excited molecules and of proton phototransfer was investigated in detail by Weller[12-14]. Terenin and Karyakin observed proton phototransfer in solid layers in 1947[15]. The p$K$ values corresponding to the excited states of numerous compounds have now been determined and are listed in Table 1.

The p$K$ of the excited states are determined by various spectroscopic methods. Some of these will now be briefly considered.

1. The method based on the so called Förster cycle[10] can be called the thermodynamic method. The attainment of protolytic equilibrium in the excited state is not necessary in this method; it is sufficient to know the spectroscopic characteristics of the starting materials and the final products of the photoprotolytic dissociation.

By considering the diagram in Fig. 1, where $\Delta H$ and $\Delta H^*$ are the enthalpies of dissociation in the ground and excited states respectively and $\Delta E_{AH}$ and $\Delta E_{A^-}$ are the differences between the energies of the two states of the undissociated and dissociated forms respectively, one can write

$$\Delta H - \Delta H^* = \Delta E_{AH} - \Delta E_{A^-}. \quad (1)$$

Assuming further that the entropies of protolytic dissociation in the ground and excited states are equal, we obtain

$$\ln \frac{K^*}{K} = \frac{\Delta E_{AH} - \Delta E_{A^-}}{RT}, \quad (2)$$

where $K$ and $K^*$ are the equilibrium constants for protolytic dissociation in the ground and excited states respectively. If the energy difference is expressed in terms of the difference in wavenumbers ($\Delta\nu$, cm$^{-1}$) and the numerical value of $R$ is substituted, then we have at room temperature ($T$ = 298 K)

$$pK = pK^* + 2.1 \cdot 10^{-3} \Delta\nu. \quad (3)$$

**Table 1.** The acid dissociation constants of organic compounds in various electronic states in aqueous solutions.

| Compound | p$K(S_0)$ | p$K(S_1)$ | $\Delta$p$K(S_1)$ | Method | Refs. | p$K(T)$ | Method | Refs. |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| **OH Acids** | | | | | | | | |
| Phenol | 10.0 | 4.1 | — | 1c | 30* | 8.5 | 1d | 29* |
| | — | 5.7 | — | 1c | 28* | — | — | — |
| Phenol (in ethanol) | 11.97 | 6.3 | — | 1a | 70* | 10.5 | — | 70 |
| *p*-Bromophenol | 9.36 | 3.1 | — | 1c | 29 | 7.7 | 1d | 29 |
| | — | 2.9 | — | 1c | 30 | — | — | — |
| | — | 3.1 | — | 1c | 20** | — | — | — |
| *p*-Cresol | 10.3 | 4.3 | — | 1c | 20** | 8.6 | 1d | 29 |
| *p*-Methoxyphenol | 10.24 | 5.7 | — | 1c | 30 | 8.4 | 1d | 29 |
| *p*-Phenoxysulphonate | 8.97 | 2.3 | — | 1c | 30 | 7.5 | 1d | 29 |
| | — | 2.4 | — | 1c | 20** | — | — | — |
| 1-Naphthol | 9.23 | 2.0 | — | 1a | 98 | — | — | — |
| | 10 | 2.68 | — | 2a | 86 | — | — | — |
| | — | — | 7.65 | 1c | 86 | — | — | — |
| | 9.6 | 0.7 | — | 1a | 91 | — | — | — |
| | — | 2.37 | — | 2a | 91 | — | — | — |
| 2-Naphthol | 9.49 | 2.81 | — | 2a | 98 | 8.1 | 2c | 83 |
| | — | 2.5 | — | 1a | 98 | — | — | — |
| | — | 3.0 | — | 2a | 103 | — | — | — |
| | — | 3.2 | — | 2a | 104 | — | — | — |
| | — | 3.4 | — | 1a | 104 | — | — | — |
| | — | 3.0 | — | 1a | 30 | — | — | — |
| | — | 3.07 | — | 1c | 91 | — | — | — |
| 2-Naphthol-5-sulphonate | 9.18 | 0.73 | — | 2a | 12** | — | — | — |
| 2-Naphthol-6-sulphonate | 9.10 | 1.66 | — | 2a | 98** | — | — | — |
| 1-Naphthol-2-sulphonate | 9.58 | 0.4 | 9.2 | 2b | 77* | 7.9 | 1d | 77 |
| Naphthalene-1-sulphonic acid | −10.6 | −3.7 | — | 2b | 52* | — | — | — |
| 2,7-Dihydroxynaphthalene | 9.37 | 8.20 | — | 1a | 91* | — | — | — |
| | — | −1.0 | — | 1b | 91 | — | — | — |
| | — | 3.37 | — | 1c | 91 | — | — | — |
| | — | 2.65 | — | 2a | 91 | — | — | — |
| | — | 2.46 | — | 2a | 86 | — | — | — |
| 1-Hydroxypyrene | 8.7 | 3.2 | — | 1a, 1b | 84 | — | — | — |
| 3-Hydroxypyrene-5,8,10-trisulphonate | 7.10 | 1.0 | — | 1a | 98** | — | — | — |
| Benzoic acid | 4.16 | 9.5 | — | 1c | 30* | — | — | — |
| (Benzoic acid) H$^+$ | −7.3 | 0 | — | 2a | 99 | — | — | — |
| | −7.26 | 1.62 | — | 1a | 35* | — | — | — |
| | — | −2.0 | — | 1a | 53** | −4.9 | 1d | 53 |
| Salicylic acid | | | | | | | | |
| -COOH | — | — | −1.5 | 1a | 87* | — | — | — |
| -OH | — | — | −0.2 | 1a | 87* | — | — | — |
| Methyl salicylate (-OH) | — | — | 6.1 | 1a | 87 | — | — | — |
| 2-Naphthoic acid | 4.21 | 11.5 | — | 1c | 30* | — | — | — |
| | 4.2 | 6.6 | — | 1a | 82*, 83* | — | — | — |
| (2-Naphthoic acid)H$^+$ | −6.9 | 1.5 | — | 2a | 99* | — | — | — |
| | −8.0 | 1.4 | — | 2b | 48* | — | — | — |
| Anthracene-1-carb xylic acid | 3.7 | 6.9 | — | 1a | 82* | 5.6 | 2c | 82* |
| (Anthracene-1-carboxylic acid)H$^+$ | −8.5 | 1.7 | — | 2b | 75* | — | — | — |
| (Anthracene-9-carboxylic acid)H$^+$ | −7.4 | −3.1 | — | 1c | 73** | — | — | — |
| Pyrene-1-carboxylic acid | 4 | 8.1 | — | 1a, 1b | 84 | 5.2 | 2c | 84 |
| 1-Hydroxyanthraquinone | 9.3 | — | — | — | — | 8.8 | 2c | 56* |
| 1-Hydroxyfluorene | 9.3 | — | — | — | — | 8.4 | 2c | 56* |
| (Anisole)H$^+$ | −6.8 | −5 | — | 1a | 38 | — | — | — |
| (Acetophenone)H$^+$ | −6.15 | 7.02 | — | 1a | 35 | — | — | — |
| | −6.0 | 1.0 | — | 2a | 99 | — | — | — |
| (Benzophenone)H$^+$ | −5.7 | −3.6 | — | 1c | 45* | −0.4 | 1d | 45* |
| | — | — | — | — | — | 1.5 | *** | 78** |
| *p*-Hydroxybenzophenone | 6.5 | −4 | — | **** | 72 | 3.5 | **** | 72 |
| Flavone (basicity) | −1.33 | −5.4 | — | 1c | 44* | — | — | — |
| (Xanthone)H$^+$ | −4.1 | 0.96 | — | 2b | 55** | 3.0 | 2d | 55 |
| (Coumarin)H$^+$ | — | −5.3 | — | 1b | 57* | — | — | — |
| | — | −7.4 | — | 1a | 57 | — | — | — |
| Tyrosine (-COOH) | 2.3 | — | 5 | 1a | 42 | — | — | — |
| **NH Acids** | | | | | | | | |
| 2-Aminopyridine | — | 12.0 | — | 1b | 66* | — | — | — |
| (2-Aminopyridine)H$^+$ | 6.86 | 8.95 | — | 1c | 64* | — | — | — |
| (2-Aminopyridine)H$_2^{2+}$ | −7.6 | −19.8 | — | 1a | 66* | — | — | — |
| (2-*trans*-Styrylpyridine) H$^+$ | 4.98 | 11.4 | — | 1c | 51* | — | — | — |
| (Quinoline)H$^+$ | 4.9 | — | −5.0 | 1a | 23 | 6.0 | 2c | 83 |
| (Quinoline)H$^+$ (in ethanol) | 4.12 | 9.5 | — | **** | 70 | 4.8 | — | 70 |
| (Isoquinoline)H$^+$ | 5.14 | 7.5 | — | 1c | 91* | — | — | — |
| 2-Aminoquinoline | — | 12.7 | — | 2b | 62* | — | — | — |
| (5-Aminoquinoline)H$^+$ | — | 10.9 | — | 1c | 59* | — | — | — |
| (6-Aminoquinoline)H$_2^{2+}$ | 1.2 | −11.2 | — | 1a | 58* | — | — | — |
| (Acridine)H$^+$ | 5.45 | 10.3 | — | 1a | 102** | 5.6 | 2c | 83 |
| (Acridone)H$^+$ | −0.6 | 0.92 | — | 2a | 101** | — | — | — |
| (1-Azaphenanthrene)H$^+$ | 5.2 | 11.5 | — | 1a, 1b | 84* | 7.0 | 2c | 84** |
| | 4.75 | 10.5 | — | 1c | 49* | 7.4 | 1d | 49* |
| (2-Azaphenanthrene)H$^+$ | 4.6 | 9.4 | — | 1a, 1b | 84 | 4.6 | 2d | 84 |
| (3-Azaphenanthrene)H$^+$ | 5.38 | 9.5 | — | 1c | 49 | 7.2 | 1d | 49 |
| (4-Azaphenanthrene)H$^+$ | 4.2 | 11.0 | — | 1a, 1b | 84 | 5.7 | 2c | 84** |
| (9-Azaphenanthrene)H$^+$ | 4.6 | 9.6 | — | 1a, 1b | 84 | 5.7 | 2c | 84** |
| (5,6-Diazaphenanthrene)H$^+$ | 2.2 | −0.07 | — | 2b | 100 | — | — | — |
| (*o*-Phenanthroline)H$^+$ | 4.85 | 12.7 | — | 1b | 34** | 6.7 | 1d | 43 |
| (*o*-Phenanthroline)H$_2^{2+}$ | −1.4 | −2.2 | — | 1b | 34** | −3.8 | 1d | 43 |
| 1-Naphthylamine | — | 13.5 | — | 1c | 95 | — | — | — |
| (1-Naphthylamine)H$^+$ | 3.9 | −4 | — | 1a | 91 | — | — | — |
| (2-Naphthylamine)H$^+$ | 4.07 | −1.5 | — | 2a | 11, 94 | 3.3 | 2c | 83* |

Table 1 cont'd.

| Compound | $pK(S_0)$ | $pK(S_1)$ | $\Delta pK(S_1)$ | Method | Refs. | $pK(T)$ | Method | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 2-Naphthylamine | — | 12.2 | — | 2a | 11 | — | — | — |
| | — | 12.3 | — | 1c | 95 | — | — | — |
| | 14 | 11.86 | — | 2b | 50* | — | — | — |
| (1-Aminoanthracene)$H^+$ | 3.3 | −5.5 | 8.8 | 1a | 85 | 3.5 | 1c | 85** |
| (2-Aminoanthracene)$H^+$ | 3 45 | −5.4 | 8.8 | 1a | 85 | 3.0 | 1d | 85** |
| (9-Aminoanthracene)$H^+$ | 2.7 | −6.1 | 8.8 | 1a | 85 | 3.0 | 1d | 85 |
| (1-Aminopyrene)$H^+$ | 2.8 | −5.8 | — | 1a, 1b | 84 | 3.5 | 2d | 84 |
| (4-Aminopyrene)$H^+$ | — | — | −2 | 2a | 96 | — | — | — |
| 3-Acetamidopyrene-5,8,10-trisulphonate | 13.9 | 6.9 | — | 2a | 97** | — | — | — |
| Indole | — | 12.3 | — | 2b | 90 | — | — | — |
| | — | — | 7.5 | 1c | 68 | — | — | — |
| (Indole)$H^+$ | −3.5 | 2.1 | — | 2b | 90 | — | — | — |
| (1-Methylindole)$H^+$ | −2.32 | 1.8 | — | 2b | 90* | — | — | — |
| (Benzimidazole)$H^+$ | — | — | −6.3 | 1c | 68 | — | — | — |
| (Indazole)$H^+$ | — | — | −5.0 | 1c | 68 | — | — | — |
| (Benzotriazole)$H^+$ | — | — | −2.4 | 1c | 68 | — | — | — |
| Carbazole | 21.1 | 11.9 | — | 2b | 92 | — | — | — |
| (Carbazole)$H^+$ | — | −1.3 | — | 2b | 92 | — | — | — |
| (ArN = NPh)$H^+$ | −3.00 | 13.62 | — | 1a | 35* | — | — | — |
| (Phenazine)$H_2^{2+}$ | −4.3 | 4.1 | — | 1c | 79 | — | — | — |
| (Phenazine)$HMe^{2+}$ | −3.5 | 3.3 | — | 1c | 79 | — | — | — |
| (Phenazine)$H_2^+$ | 3.8 | 8.5 | — | 1c | 79 | — | — | — |
| (Phenazine)$HMe^+$ | 5.7 | 10.4 | — | 1c | 79 | — | — | — |
| (1-Amino-2-naphthol)$H^+$ | 4.0 | 0.6 | — | **** | 60* | — | — | — |
| (Quinoline-2-carboxylic acid) $H_2^{2+}$ | — | −6.4 | — | 2b | 76* | — | — | — |

*The acidities of related compounds are also quoted in the relevant paper.

**The acidities determined by other methods are also quoted in the relevant paper.

***$pK$ was determined from data on the variation of the rate constants for the destruction of triplet states with the acidity of the medium.

****The method of determination is not indicated.

There are literature data for the acidity constants of naphthols [111], hydroxyquinolines [36,39,40,61,65,67,74,88,93], 8-mercaptoquinoline [69], aminoquinolines [108], nitroquinolines [43], aminoanthracenes [109], nitrobenzene [70], azo- and azoxy-benzenes [33], 5,6-diazaphenanthrene [89], indolizidine [37], lumiflavin [63], thionine [54,71,80], warfarin [106], riboflavin [107], azures [54], fluoroscein and dichlorofluorescein [41], purines [46], and many other compounds [110,112-115].

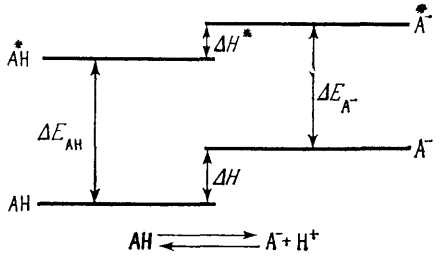



Figure 1. A simplified energy level diagram for acid dissociation in the ground and excited electronic states.

In this equation $\Delta\nu$ is determined experimentally. It is noteworthy that, first, the above equation is applicable only when the entropies of protolytic dissociation in the ground and excited states are equal. The discrepancy between the values of $pK^*$ measured by this method and the values obtained by other procedures is sometimes attributed to the failure of precisely this condition [16]. Secondly, $\Delta\nu$ refers to purely electronic transitions between the zero vibrational sublevels of the corresponding electronic levels (0–0 transition). Since it is difficult to determine the frequency of the 0–0 transition (and hence also its shifts) for compounds in solutions, one usually measures the shift of the maxima in the absorption spectra of the acid and basic forms (method 1a) or in the fluorescence spectra of these forms (method 1b). The average shift in the absorption and fluorescence spectra (method 1c) is also frequently used. This procedure can be applied to determine the $pK$ of triplet states. In this case, the shift of the short-wavelength maximum in the phosphorescence spectrum is determined experimentally assuming it to be the shift of the frequency of the 0–0 transition (method 1d).

2. The method based on the measurement of the intensity or quantum yields of the fluorescence under steady-state conditions has been developed in detail by Weller [12]. Consider the mechanism of the photoprotolytic dissociation of an acid AH:

$$\begin{array}{ccc} A^*H & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & A^- + H^+ \\ h\nu \uparrow \; k_f \downarrow \; k_d & & k_f' \downarrow \; k_d' \\ AH & & A^- \end{array} \qquad (4)$$

Using the method of steady-states, the following expressions can be obtained for this mechanism:

$$\frac{\varphi}{\varphi_0} = \frac{1 + k_{-1}\tau_0'[H^+]}{1 + k_{-1}\tau_0'[H^+] + k_1\tau_0}, \qquad (5)$$

$$\frac{\varphi\,\varphi_0'}{\varphi'\varphi_0} = \frac{1}{k_1\tau_0} + \frac{k_{-1}\tau_0'}{k_1\tau_0}[H^+], \qquad (6)$$

where $\varphi$ is the quantum yield of the fluorescence of the undissociated form for certain specific pH values. $\varphi'$ the quantum yield of the fluorescence of the dissociated form at the same pH values, $\varphi_0$ the quantum yield of the fluorescence of the undissociated form in the absence of the protolytic reaction, $\varphi_0'$ the quantum yield of the fluorescence of the dissociated form in an alkaline solution, $k_1$ and $k_{-1}$ are the rate constants for the forward and reverse reactions, $k_f$ and $k_f'$ the rate constants for the processes involved in the fluorescence of the undissociated and dissociated forms, $k_d$ and $k_d'$ the rate constants for the monomolecular non-radiative deactivation processes for the undissociated and dissociated forms, and $\tau_0 = 1/(k_0 + k_d)$ and $\tau_0' = 1/(k_f' + k_d')$ the decay times of the fluorescence of the undissociated and dissociated forms respectively.

Having plotted $\varphi\varphi_0'/\varphi'\varphi_0$ against $[H_3O^+]$, it is possible to obtain the rate constants $k_1$ and $k_{-1}$ as well as the photoprotolytic dissociation equilibrium constant $K^* = k_1/k_{-1}$ (method 2a). A necessary condition for the applicability of method 2a is the establishment (at least partially) of the acid–base equilibrium in the excited state. In certain cases, it is necessary to allow for the contribution of the deviation from the steady state to the kinetics of the protolytic dissociation. Eqn. (6) then assumes the form

$$W\frac{\varphi\,\varphi_0'}{\varphi'\varphi_0} - (1 - W) = \frac{1}{k_1\tau_0} + \frac{k_{-1}\tau_0'}{k_1\tau_0}[H^+], \qquad (7)$$

where $1 - W$ is the fraction of molecules reacting immediately after excitation before the establishment of the steady state. $W$ can be calculated from the changes in the relative fluorescence quantum yields as a function of the

pH of the solution by the method of successive approximations, provided that the corresponding diffusion coefficients are known[17].

The method in which the pH of the solution at the point of inflection in the plot of the relative fluorescence quantum yield against pH is adopted as p$K^*$ (method 2b) is sometimes used. However, it has been shown[18,19] that this method frequently does not yield the true value of p$K^*$. According to Eqn. (5), the pH at the point of inflection ($pH_{\frac{1}{2}}$) in the $\varphi/\varphi_0$–pH plot is†

$$pH_{1/2} = \lg \frac{k_{-1}\tau_0'}{|1 + k_1\tau_0|}. \quad (8)$$

When $k_1\tau_0 \gg 1$, we have in this case

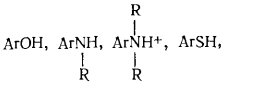
$$pH_{1/2} = pK^* + \lg \frac{\tau_0'}{\tau_0}. \quad (9)$$

Thus $pH_{\frac{1}{2}} \simeq pK^*$, provided that $\tau_0 \simeq \tau_0'$, but in this case it is better to use the more accurate method 2a. Method 2b is used when one of the forms (AH or $A^-$) does not fluoresce, but under these conditions the error is particularly large. Suppose that $A^-$ does not fluoresce. This implies that $\varphi_0' < 10^{-4}$ and $\tau_0' < 10^{-12}$ s and if $\tau_0 = 10^{-8}$ s, then $pH_{\frac{1}{2}} < pK^* - 4$. The point of inflection method is used to determine the p$K$ values for triplet molecules, since during the lifetime of the triple state there is sufficient time for the establishment of the protolytic equilibrium. The pH at the point of inflection in the plot of the intensity of the triplet–triplet absorption (method 2c) or phosphorescence (method 2d) against the pH of the solution is adopted as the value of p$K(T)$.

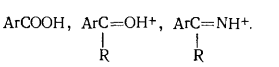
Measurements of the p$K^*$ for aromatic hydroxy-compounds led to the conclusion[20] that methods 2b and 1c usually yield similar results, which do not agree with the results obtained by method 1a, the difference being outside the limits of experimental error. It is assumed that the difference is caused by the relaxation of the solvent molecules during the lifetime of the excited molecule. The frequencies of the 0–0 transitions in the absorption and fluoresence spectra will then differ. This is confirmed by measurements of the p$K^*$ in solid solutions[20], where solvent relaxation is hindered. In this case, all three methods yield similar results.

The difference between p$K$ values for the ground and excited states can reach several orders of magnitude. According to the charge-transfer theory[21], such a jump in acidity is a consequence of the mixing of the configuration of the corresponding electronically excited state with the possible configuration of the charge-transfer (CT) state, which has a higher energy. The degree of mixing is greater the smaller the difference between the energies of the two states, so that $\Delta pK\,(S_0 - S_1) > \Delta pK\,(S_0 - T)$. However, when this theory is used, one cannot explain the similarity of the p$K$ values for the ground and triplet states found experimentally. The resonance theory predicts[22] that the relative contribution of the CT structure compared with that of the biradical structure should be greater in the $S_1$ state than in the triplet state. This theory readily explains small changes in the p$K^*$ values for the singlet states of aromatic carboxylic acids on the grounds that these compounds have only one resonance structure incorporating the C=O bond. It has also been shown theoretically[23,31,32] that acidity can both increase and decrease on photoexcitation.

Examination of Table 1 shows that the acidity of excited singlet states increases for compounds in which the dissociated proton is in the $\alpha$-position:



and decreases for compounds where the dissociated proton is in the $\beta$-position:



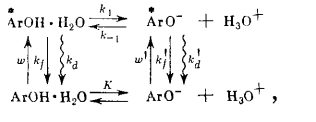
The basicity of amines of the aniline type decreases in the singlet excited state, while that of amines of the acridine type increases. A similar tendency has been observed for the triplet state, but is less pronounced.

Many interesting results may be obtained using the Hammett equations. It has been noted for phenol derivatives, 2,4-dinitrophenylhydrazones, and other benzene derivatives[24-28] that there is a linear relation between $\Delta\nu$ (in the absorption spectrum) and the $\sigma$ constant for the substituent (in the ground state). Hence it follows[16] that, since the variation in the p$K$ for the ground states of these compounds obeys the Hammett equation, the p$K^*$ should also obey this equation. Such correlation has been obtained for a series of *meta*- and *para*-substituted phenols[29]. The change in $\rho$ for these compounds relative to the ground state indicates[16] a change in the electronic interaction in the excited state.

For many compounds, the p$K^*$ of the deuterated form is smaller than the value of the non-deuterated form[30].

## III. PROTON PHOTOTRANSFER REACTIONS IN PROTIC SOLVENTS

Proton phototransfer reactions were first discovered and investigated in aqueous solutions. Förster[10,11] investigated similar reactions for solutions of hydroxy-derivatives of pyrene and naphthalene in water. The sharp increase in the acidity of these compounds on excitation leads to their dissociation during the lifetime of the excited state with formation of the excited ions of the conjugate base and the hydronium ion. These systems were investigated in detail by Weller[47,97,98,102,116], who studied the fluorescence spectra of many aromatic hydroxy-compounds, aromatic amines, and heterocyclic bases over a wide pH range. In many cases, the equilibrium in the excited state is not established completely owing to the competition of radiative and non-radiative deactivation processes involving the excited molecules. A typical curve for the pH dependence of the fluorescence of the dissociated and undissociated forms is illustrated in Fig. 2 (for 2-naphthol). The general mechanism of all dark and photochemical processes occurring in aqueous solutions of hydroxy-derivatives of aromatic compounds may be formulated as follows:



(10)

where $w$ and $w'$ are the rates of light absorption by the undissociated molecules and ions respectively. The variation of the relative fluorescence quantum yields of the dissociated and undissociated forms with hydrogen ion

†At the point of inflection, $\varphi/\varphi_0$ is equal to half the sum of the relative quantum yields of the AH fluorescence in acid and alkaline media.

concentration is described by Eqns. (5) and (6). A similar variation of the relative fluorescence quantum yields of the protonated and non-protonated forms with hydroxide ion concentration has been observed for bases whose proton-accepting properties are more marked in the excited state than in the ground state (for example, in the case of acridine).

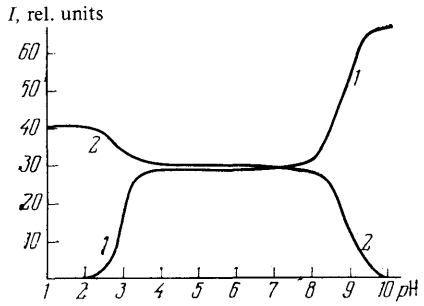



Figure 2. pH dependence of the fluorescence intensity ($I$) of the dissociated (curve *1*) and undissociated (curve *2*) forms of 2-naphthol in aqueous solution [176].

We shall consider in greater detail the 2-napthol–water system. The rate of protolytic dissociation of excited 2-napthol is fairly low compared with the rates of fluorescence and non-radiative deactivation and the majority of the excited 2-napthol molecules are deactivated without dissociating. In the pH range 3–8, the equilibrium in the excited state of this system is therefore not fully established. The activation energy for the dissociation of excited 2-napthol molecules is 16.8 kJ $mol^{-1}$. The rate-limiting stage in the proton transfer in this system is probably the reorientation of the water molecules of the solvation shell, which requires an activation energy. The rate of the reverse reaction is probably limited by diffusion. In the dissociation of excited 2-napthol, an appreciable kinetic isotope effect is observed [103]. The dissociation rate constants are $5.29 \times 10^7$ and $1.3 \times 10^7$ $s^{-1}$ in $H_2O$ and $D_2O$ respectively, while the corresponding rate constants for the reverse reactions are $5.5 \times 10^{10}$ and $3.5 \times 10^{10}$ litre $mol^{-1}$ $s^{-1}$. The influence of isotope substitution is significantly greater for the forward reaction than for the reverse reaction, where the effect can be to a large extent accounted for by the difference between the diffusion coefficients of the ions in $H_2O$ and $D_2O$. It is still not clear whether the decreased rate constant for the dissociation of excited 2-napthol in $D_2O$ is associated with an increase in the activation energy owing to the smaller vibrational energy of the zero level of the O–D bond compared with the O–H bond or with the decrease of the pre-exponential factor. The influence of isotope substitution on the protolytic dissociation equilibrium constants of excited aromatic hydroxy-compounds has been investigated [30].

The proton-accepting properties of water as well as its ability to give up a proton are fairly weak, so that the stronger bases and acids present in solution may compete with water in the reaction with excited proton donors and acceptors:

$$Ar^*OH + B \underset{k_A}{\overset{k_B}{\rightleftarrows}} Ar^*O^- + BH^+. \qquad (11)$$

The variation of the fluorescence quantum yields of the protonated and non-protonated forms with hydrogen ion (or hydroxide ion) concentration and with the concentration of the added base (or acid) can be described as follows [174]:

$$\frac{\varphi}{\varphi_0} = \left(1 + \frac{k_1\tau_0 + k_B[B]\tau_0}{1 + k_{-1}\tau_0'[H_3O^+] + k_A[BH^+]\tau_0'}\right)^{-1}, \qquad (12)$$

$$\frac{\varphi'}{\varphi_0'} = \left(1 + \frac{1 + k_{-1}\tau_0[H_3O^+] + k_A[BH^+]\tau_0'}{k_1\tau_0 + k_B[B]\tau_0}\right)^{-1}. \qquad (13)$$

Table 2. The rate constants for the proton phototransfer reactions in protic solvents.

| Acid | Base | Solvent | $T$, °C | $10^{-8}$ $k^{**}$ litre $mole^{-1}$ $s^{-1}$ | Refs. |
|---|---|---|---|---|---|
| 2-Naphthol* | $H_2O$ | $H_2O$ | 20 | 0.44 (1) | 86 |
| $H_3O^+$ | 2-Naphthoxide* | $H_2O$ | 20 | 490 (2) | 86 |
| 1-Naphthol* | $H_2O$ | $H_2O$ | 20 | 0.81 (1) | 86 |
| $H_3O^+$ | 1-Naphthoxide* | $H_2O$ | 20 | 390 (2) | 86 |
| 1,2-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 1.8 (1) | 86 |
| $H_3O^+$ | 1,2-DHN ion* [a] | $H_2O$ | 20 | 400 (2) | 86 |
| 1,5-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 0.4 (1) | 86 |
| $H_3O^+$ | 1,5-DHN ion* | $H_2O$ | 20 | 320 (2) | 86 |
| 1,7-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 0.32 (1) | 86 |
| $H_3O^+$ | 1,7-DHN ion* [a] | $H_2O$ | 20 | 430 (2) | 86 |
| 1,8-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 0.5 (1) | 86 |
| $H_3O^+$ | 1,8-DHN ion* [a] | $H_2O$ | 20 | 360 (2) | 86 |
| 2,3-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 0.28 (1) | 86 |
| $H_3O^+$ | 2,3-DHN ion* [a] | $H_2O$ | 20 | 470 (2) | 86 |
| 2,6-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 0.16 (1) | 86 |
| $H_3O^+$ | 2,6-DHN ion* [a] | $H_2O$ | 20 | 410 (2) | 86 |
| 2,7-DHN* [a] | $H_2O$ | $H_2O$ | 20 | 1.25 (1) | 86 |
| $H_3O^+$ | 2,7-DHN ion* [a] | $H_2O$ | 20 | 310 (2) | 86 |
| (Acridine)$H^+$* | $OH^-$ | $H_2O$ | 25 | 185 (2) | 102 |
| (Acridine)$H^+$* | $NH_3$ | $H_2O$ | 25 | 0.25 (2) | 102 |
| $H_3O^+$ | 2-Naphthoxide* | $H_2O$ | 25 | 480 (2) | 98 |
| 2-Naphthol* | $C_2H_5COO^-$ | $H_2O$ | 25 | 28.6 (2) | 98 |
| 2-Naphthol* | $C_3H_7COO^-$ | $H_2O$ | 55 | 27.6 (2) | 98 |
| 2-Naphthol* | $CH_3COO^-$ | $H_2O$ | 25 | 29.0 (2) | 98 |
| $H_3PO_4$ | 2-Naphthoxide* | $H_2O$ | 25 | 29.1 (2) | 116 |
| 2-Naphthol* | $HCOO^-$ | $H_2O$ | 25 | 24.0 (2) | 98 |
| 2-Naphthol* | $H_2PO_4^-$ | $H_2O$ | 25 | 6.0 (2) | 116 |
| HCOOH | 2-Naphthoxide* | $H_2O$ | 25 | 0.33 (2) | 98 |
| $H_3O^+$ | 1-Cyano-2-naphthoxide* | $H_2O$ | 25 | 210 (2) | 116 |
| $NH_4^+$ | Acridine* | $H_2O$ | 25 | 5.7 (2) | 102 |
| $H_3BO_3$ | Acridine* | $H_2O$ | 25 | 3.8 (2) | 116 |
| $Mg(H_2O)_n^{2+}$ | Acridine* | $H_2O$ | 25 | 0.94 (2) | 116 |
| 2-Naphthol* | $H_2O$ | $H_2O$ | 25 | 0.53 (1) | 103 |
| 2-Naphthol* | $D_2O$ | $D_2O$ | 25 | 0.13 (1) | 103 |
| $H_3O^+$ | 2-Naphthoxide* | $H_2O$ | 25 | 550 (2) | 103 |
| $D_3O^+$ | 2-Naphthoxide* | $D_2O$ | 25 | 350 (2) | 103 |
| $H_2O$ | Benzoquinoline* | $H_2O$ | 25 | 0.07 (1) | 117 |
| (Benzoquinoline)$H^+$* | $H_2O$ | $H_2O$ | 25 | 120 (2) | 117 |
| 2-Naphthol* | $H_2O$ | $H_2O$ | 25 | 0.45 (1) | 118 |
| 2-Naphthol* | $CH_3COO^-$ | $H_2O$ | 20 | 24.0 (2) | 119 |
| 3-Acetamidopyrene-5,8,9-trisulphonate* | $OH^-$ | $H_2O$ | 25 | 1.48 (2) | 97 |
| " | $(CH_3)_2NH$ | $H_2O$ | 25 | 0.45 (2) | 97 |
| " | $CH_3NH_2$ | $H_2O$ | 25 | 0.46 (2) | 97 |
| " | $(CH_3)_3N$ | $H_2O$ | 25 | 0.22 (2) | 97 |
| " | $NH_3$ | $H_2O$ | 25 | 0.23 (2) | 97 |
| 2-Naphthol | $CH_3COO^-$ | Methanol | 20 | 8.1 (2) | 119 |
| 2-Naphthol | $CH_3COO^-$ | Ethanol | 20 | 5.0 (2) | 119 |

*Excited molecule.
**(1) The rate constant for a pseudounimolecular reaction ($s^{-1}$); (2) the rate constant for a bimolecular reaction (litre $mol^{-1}$ $s^{-1}$).
[a] DHN = Dyhydroxynaphthalene.

Table 2 lists the rate constants for proton phototransfer in protic solvents determined by different investigators. It shows that the rate constants for the proton phototransfer reactions involving oppositely charged ions are of the order of $10^{10}$–$10^{11}$ litre $mole^{-1}$ $s^{-1}$ and depend only slightly on the

chemical nature of the reacting ions. This is evidence in support of the view that the rates of such reactions are diffusion limited. The slight differences between the rate constants are probably caused by the differences between the diffusion coefficients and steric factors.

The rate constants for the dissociation of excited hydroxy-derivatives of aromatic compounds have a wide range of values and depend on the nature of the hydroxy-compound. Weller [122] and Derkacheva [86] noted a linear relation between log $k_1$ and $pK_a^*$ for a series of hydroxy- and dihydroxy-derivatives of naphthalene. The rate-limiting step in these reactions is apparently the actual proton transfer to the polar solvent accompanied by the dielectric relaxation of the latter. The water molecule is a weak proton acceptor and the dissociation of excited aromatic compounds in aqueous solutions proceeds exclusively by virtue of the high polarity of water and the specific solvation of the ions formed. The absence of any appreciable dissociation of excited 2-naphthol molecules in absolute ethanol [123], which is less polar than water, may serve as a confirmation of this hypothesis. Compounds which are more acid, such as excited ammonium derivatives of pyrene, dissociate also in alcoholic solutions [96]. In a study of the dissociation of compounds whose acidity changes in the excited state within the limits of four orders of magnitude (in methanol, ethanol, 1-propanol, and 1-butanol), Weller [96] showed that the ionisation rate constants are almost independent of the nature of the aromatic compound and depend only on temperature and the nature of the solvent. This is direct proof that the rate-limiting stage of proton phototransfer in such systems is the reorientation of the polar solvent molecules. The reactions of excited aromatic hydroxy-compounds with proton acceptors, which are much more powerful than water and alcohols, namely carboxylate anions, proceed at much higher rates than dissociation and their rates are probably limited by diffusion. The rate constants for the reactions of excited 2-naphthol with these bases are almost independent of the basicity of the anions, which varies over a factor of ten, and are equal to $(2.5 - 3.0) \times 10^9$ litre mole$^{-1}$ s$^{-1}$. Proton phototransfer from excited 2-naphthol to the acetate ion proceeds also in alcoholic solutions [119].

The study of the proton phototransfer reaction in protic solvents involves a large class of protolytic reactions, ranging from fairly slow, whose rate is limited by the reorientation of the polar solvent molecules, requiring an activation energy, to rapid reactions, whose rate is limited by diffusion. On photoexcitation, certain compounds dissociate so rapidly that the fluoresence of the undissociated molecules in neutral aqueous solutions is not observed and only the dissociated form fluoresces. As an example, one may quote the 2-naphthylammonium cation [94,124] and 1-naphthol in aqueous solutions [47,86]. The absence of the fluorescence of these compounds in conjunction with the usual emission rate constants (approximately $10^8$ s$^{-1}$) shows that the rate constant for the dissociation of the excited molecules $k \geqslant 10^{11}$ s$^{-1}$.

The high rate constant for proton phototransfer in principle enables this process to compete successfully with the deactivation reactions of the highest excited states and other relaxation processes. Analysing the kinetics of the onset of the fluorescence of the naphthoxide ion following the excitation of 2-naphthol in aqueous solution, Ofran and Feitelson [118] observed that a proportion of the excited 2-naphthol molecules, namely 5%, are dissociated during a period less than 1 ns, i.e. the rate of dissociation of some of the molecules is much higher than that of the others. Since the quantum yield in the formation of excited 2-naphthoxide ions is independent of the wavelength of the exciting light, the rate-limiting stage of such rapid dissociation is probably the rearrangement of the solvent molecules in the solvation shell. Consequently two processes were observed for 2-naphthol—rapid dissociation in the non-relaxed state and fairly slow dissociation in the state corresponding to thermal equilibrium.

In studies on the possibility of photoprotolytic reactions in the higher excited states, Hochstrasser [147] and Shablya [148] showed that the fluorescence quantum yields of the acridinium cation are different on excitation to the first and higher singlet states. The difference disappears when the fluorescence of the acridinium cation is quenched by hydrochloric acid, but persists on quenching by potassium chloride. In order to account for this phenomenon, it has been suggested [147,148] that, on excitation of the acridinium cation to the first ($S_1$) and higher ($S_2$) singlet states, the following equilibria occur:

$$S_1\ C_{13}H_9^*NH^+ \rightleftarrows C_{13}^*H_9N + H^+; \quad (14)$$

$$S_2\ C_{13}H_9^*NH^+ \rightleftarrows C_{13}^*H_9N + H^+. \quad (15)$$

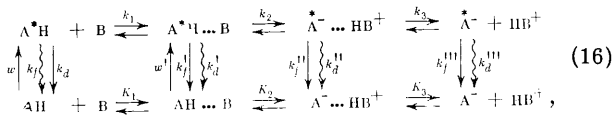
On excitation to the highest singlet states, the fluorescence quantum yield of the protonated form should then be smaller than for excitation to the $S_1$ state in consequence of dissociation and should increase when this process is suppressed, i.e. at a fairly high concentration of $H^+$ ions the quantum yields should be equal on excitation to different electronic states if the main deactivation process of the $S_2$ state is the internal transition $S_2 \rightarrow S_1$. However, the authors of the present review have shown [149] that the equalisation of the fluorescence quantum yields is observed only simultaneously with the quenching of the fluorescence and is not observed when acids such as perchloric, formic, and acetic are used. Furthermore, the equalisation of the fluorescence quantum yields on excitation of different electronic states is observed in systems where acid–base interaction is ruled out, for example on quenching the fluorescence of 2-naphthylamine by ethyl bromide in ethanol. The observed phenomena are probably associated with a change in the probabilities of the intercombination transitions from the highest singlet states to the highest triplet states and not with the shift of the protolytic equilibrium in the highest excited states.

Thus proton phototransfer in protic solvents (water, alcohols) proceeds via a protolytic mechanism with formation of solvated ions as the reaction products. The rate constants for such reactions are in the range $10^7$ to $10^{11}$ s$^{-1}$. In most cases, the proton phototransfer proceeds in the excited singlet state corresponding to thermal equilibrium. However, in some instances rapid proton transfer occurs in the non-relaxed state. The proton phototransfer reactions may be accompanied by non-radiative deactivation of the excited molecules. This phenomenon is examined below.

## IV. PROTON PHOTOTRANSFER REACTIONS IN APROTIC SOLVENTS

The interaction of aromatic hydroxy- and amino-compounds with acids and bases in the ground electronic state in aprotic solvents results in the formation of hydrogen-bonded complexes and ion pairs in which the ions are or are not separated by solvent molecules (depending on the strength of the acid and base and the

polarity of the solvent) [170]. This is manifested clearly in the infrared and near ultraviolet absorption spectra [125,126]. As in the ground state, in the excited state there is a possibility of the formation of excited hydrogen-bonded complexes, excited ion pairs, and excited solvated ions. The general mechanism of the processes occurring in the ground and excited states in aprotic solvents can be represented as follows:



(16)

where $k_f$, $k'_f$, $k''_f$, and $k'''_f$ are the fluorescence rate constants, $k_d$, $k'_d$, $k''_d$, and $k'''_d$ are the rate constants for the non-radiative deactivation of the free form of the fluorescent species, the excited hydrogen-bonded complex, the excited ion pair, and the excited ion respectively, and $K_1$, $K_2$, and $K_3$ are the equilibrium constants for the formation of the hydrogen-bonded complex, the ion pair, and the ion in the ground electronic state respectively. If the base B is fairly weak, proton transfer in the excited hydrogen-bonded complex does not occur and a new complex formation equilibrium is established in many cases during the lifetime of the excited state.

The fluorescence spectra of the hydrogen-bonded complexes differ insignificantly from those of the free molecules (the shift of the maximum is of the order of 500 $cm^{-1}$). The fluorescence of hydrogen-bonded complexes was first observed by Mataga et al. for complexes of 2-naphthol with methyl acetate, ethyl acetate, n-butyl acetate, and ethyl chloroacetate in hexane [127]. When the excited hydrogen-bonded complex fluoresces, it is possible to determine the complex-formation equilibrium constant in the excited state from the fluorescence data (Table 3). Mataga et al. [173] derived the following equation for the concentration dependence of the fluoroscence intensity subject to the conditions that equilibrium is established in the excited state, that there are no induced deactivation processes, and that the fluorescence spectra of the free form and the complex are identical:

$$\frac{1-I_0/I}{[B]} = -K^* + \alpha K^* I_0/I, \qquad (17)$$

where $\alpha$ is the ratio of the fluorescence quantum yields of the hydrogen-bonded complex and the free molecule. In those cases where the excited hydrogen-bonded complex does not fluoresce, it is possible to determine only the rate constant for the quenching of the free molecules. It is then convenient to use the formula taking into account the attainment of equilibrium in the ground state:

$$\frac{\varphi_0/\varphi}{1+K[B]\,\varepsilon_1/\varepsilon} = 1 + k_1\tau_0[B]\ , \qquad (18)$$

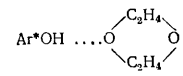
where $\epsilon$ and $\epsilon_1$ are the extinction coefficients of the free form and the hydrogen-bonded complex at the wavelength of the exciting light. A similar situation is observed in the interaction of naphthols and 3-hydroxypyrene with pyridine and $\alpha$-chloropyridine. Weller [122] identified the rate constants for the dynamic quenching of the fluorescence of these compounds by nitrogen-containing heterocycles with the rate constants for the formation of hydrogen-bonded complexes between the excited molecules of the hydroxy-compounds and those of the bases. This is confirmed by the finding that pyridine does not quench the fluorescence of 2-methoxynaphthalene. The quenching effect of pyridine on the fluorescence of 2-naphthol depends significantly on the solvating capacity and polarity of the solvent [120]. The reverse dissociation reaction of the excited hydrogen-bonded complex is usually neglected. The complex formation equilibrium constant in the ground state is as a rule of the order of $10^2$ litre $mol^{-1}$ and increases by 1–2 orders of magnitude on photoexcitation. Since the rate constant for the formation of the hydrogen-bonded complex does not exceed $10^{10}$ litre $mol^{-1}$ $s^{-1}$, the rate constant for the reverse reaction is of the order of $10^6$ $s^{-1}$, i.e. dissociation cannot compete with the radiative and non-radiative deactivation reactions of the excited hydrogen-bonded complex.

Table 3. The equilibrium constants for the formation of hydrogen-bonded complexes in the ground (K) and excited (K*) states.

| Proton-donating molecule | Proton-accepting molecule | Solvent | $K$, litre $mol^{-1}$ | $K^*$, litre $mol^{-1}$ | Refs. |
|---|---|---|---|---|---|
| 2-Naphthol | Pyridine | Benzene | 41 | 84 | 168 |
| 2-Naphthol | Diethylamine | Cyclohexane | 184 | 4620 | 123 |
| 2-Naphthylamine | Pyridine | Benzene | 0.2 | 60 | 168 |
| 2-Naphthylamine | Pyridine | Cyclohexane | 12 | 250 | 121 |
| 2-Naphthylamine | Ethyl acetate | Benzene | 0.26 | 1.8 | 168 |
| 2-Naphthylamine | Butyl acetate | Benzene | 0.1 | 1.8 | 168 |
| 2-Naphthylamine | Butyl acetate | Cyclohexane | 1.1 | 9.8 | 121 |
| 2-Naphthylamine | Triethylamine | Cyclohexane | 1.1 | 10 | 121 |
| Carbazole | Pyridine | Cyclohexane | 14 | 200 | 121 |
| Carbazole | Butyl acetate | Cyclohexane | 9.4 | 66 | 121 |
| Carbazole | Triethylamine | Cyclohexane | 5.5 | 100 | 121 |
| 3-Hydroxypyrene | Pyridine | Benzene | 58 | 270 | 129 |
| 3-Hydroxypyrene | Pyridine | Methylcyclohexane | 220 | 980 | 129 |
| 3-Hydroxypyrene | Pyridine | *o*-Chlorotoluene | 78 | 430 | 122 |
| 3-Hydroxypyrene | α-Chloropyridine | Benzene | 7 | 18 | 122 |
| 3-Hydroxypyrene | α-Chloropyridine | *o*-Chlorotoluene | 8 | 23 | 122 |
| 3-Hydroxypyrene | α-Chloropyridine | Methylcyclohexane | 18.5 | 60 | 122 |

Strong bases such as aliphatic amines interact with excited aromatic hydroxy-compounds, the process involving proton transfer from the excited molecule to the base. This is manifested experimentally by the anomalously large shift of the fluorescence maximum of the proton transfer product relative to the fluorescence maximum in the spectra of hydrogen-bonded complexes. In 1962 Mataga et al. attributed this long-wavelength maximum to the fluorescence of the excited ion pair in which the counterions are joined by a hydrogen bond [171]. Similar phenomena involving an anomalous fluorescence shift have been described by 2-naphthol–aliphatic amine, 3-hydroxy-pyrene–aliphatic amine, 1-naphthol–aliphatic amine, and aromatic aza-compound–carboxylic acid systems [117,123,130–132,172].

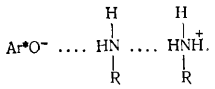
The excited ion pair can be formed in two ways: by the reaction of the excited fluorescent molecules with the base (dynamic pathway) and on excitation of the hydrogen-bonded complexes if the latter are already formed in the ground state (the static pathway). Comparison of the positions of the fluorescence maxima of the photoproduct, the initial excited molecule, and its conjugated base (acid) permits the identification of the proton phototransfer products. In a study of the dependence of the position of the maxima in the fluorescence spectra of 2-naphthol and 3-hydroxypyrene in various solvents (methylcyclohexane, dioxan, triethylamine, and n-butylamine), Weller [130] showed that the fluorescent species are the hydrogen-bonded complex



in dioxan, the contact hydrogen-bonded ion pair

$$Ar^*O^- \ldots HN^+R_3$$

in triethylamine, and the excited ion pair, in which the counterions are separated by hydrogen bonds with a solvent molecule,



in n-butylamine. Nakamizo[117] attributed the long-wavelength band in the fluorescence spectra of the complexes of benzoquinolines with acetic and trichloroacetic acids to emission by the protonated cation of the heterocycle, since the long-wavelength fluorescence spectrum coincided with the fluorescence spectrum of the cation in aqueous solution. In the 2-naphthol–diethylamine system in various solvents, the authors of the review observed the formation of an excited hydrogen-bonded complex, an excited ion pair, and an excited ion (Fig. 3)[123,134,145]. In a study of the temperature variation of the fluorescence spectra of the same system in methylcyclohexane, Krasheninnikov and Shablya[133] found that, when the temperature is reduced, bands with maxima at 365, 392, and 410 nm appear successively; these were assigned to the excited hydrogen-bonded complex, the excited contact ion pair, and the excited naphthoxide ion respectively. The lifetime of the excited ion pairs is in many cases shorter than the lifetime of the excited ions. This difference has been used as a method for the identification of the proton phototransfer products[134].

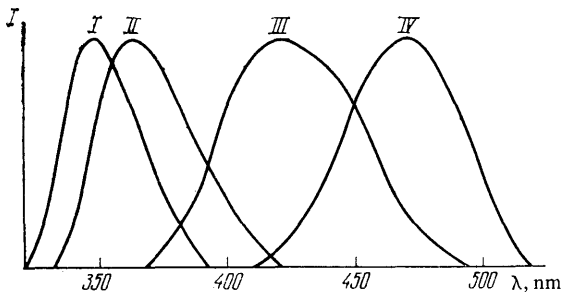
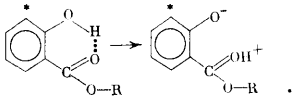



**Figure 3.** The fluorescence spectra of 2-naphthol in hexane (*I*), the hydrogen-bonded complex of 2-naphthol with triethylamine in hexane (II), the 2-naphthol–triethylamine ion pair in toluene (III), and the naphthoxide ion in dimethylformamide (IV).

The nature of the proton phototransfer product depends to a considerable degree on the solvent. For example, in aromatic solvents (benzene, toluene, and *o*-chlorotoluene) the interaction of excited 2-naphthol and 3-hydroxypyrene molecules with triethylamine and diethylamine leads to the formation of excited ion pairs[123,130]. A different situation is observed in cyclohexane solutions[123]. When excited 2-naphthol interacts with diethylamine at low concentrations of the latter, an excited hydrogen-bonded complex is formed, an increase of the concentration of the amine results in marked quenching of the fluorescence, and a new fluorescence band, which has been attributed to the fluorescence of the ion pair, appears only at very high concentrations. When excited 2-naphthol interacts with triethylamine, a broad fluorescence spectrum is observed and is regarded[130] as resulting from the superposition of the fluorescence spectra of the hydrogen-bonded complex and the ion pair, which are in equilibrium. The shift of the equilibrium towards the formation of the ion pair in aromatic hydrocarbons is evidence that these solvents stabilise the ion pair to a greater extent, despite the fact that their dielectric constants hardly differ from those of aliphatic hydrocarbons. The polarisation of the $\pi$-electron system of the aromatic solvent, leading to partial delocalisation of the charges of the ion pair, probably also has a stabilising influence.

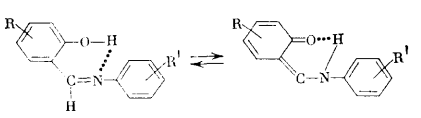
## V. INTRAMOLECULAR PROTON PHOTOTRANSFER REACTIONS

Proton phototransfer can occur not only between two separate molecules of an acid and a base but also between the parts of a single molecule joined by a hydrogen bond. These reactions are observed both in liquid solutions and in the solid phase. The first intramolecular proton phototransfer reaction, involving salicylic acid and its esters, was observed in 1955 by Weller, who subsequently investigated this phenomenon in detail[122,130,138,139]. On excitation, proton transfer occurs in these systems from the hydroxy-group to the carbonyl group with formation of an excited product:

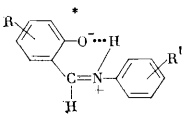


The fluorescence spectra of salicylic acid and its esters consist of two bands—a short-wavelength band corresponding to the emission by the excited initial molecule and the long-wavelength band corresponding to the emission by the form with proton transfer. It is assumed that equilibrium between the two forms is fully established in the excited state. Estimates showed that the energy barrier between the two forms in the excited state of methyl salicylate does not exceed 0.12 kcal mole$^{-1}$. The enthalpy of the reversible interconversion of the two forms is very sensitive to the nature of the substituent in the aromatic ring. The loss of electronic excitation by the form with proton transfer is accompanied by the rapid reverse proton transfer and the regeneration of the initial compound.

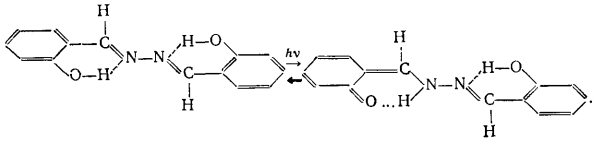
Intramolecular proton phototransfer has been observed in the hydrogen-bonded complex of 2-hydroxy-3-naphthoic acid and pyridine. When this complex is excited, a proton is transferred from the hydroxy-group to the carboxy-oxygen[140-142]. The proton phototransfer reaction occurring with retention of electronic excitation in azomethines with an *ortho*-hydroxy-group in the aldehyde ring has been investigated in detail by Knyazhanskii et al.[186] In solutions of these compounds, there is a tautomeric equilibrium between the benzenoid and quinonoid forms, the equilibrium constant depending on the polarity and proton-donating properties of the solvent:



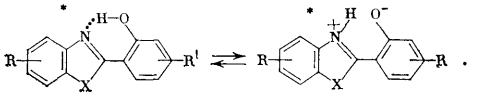
Photoexcitation of the benzenoid form leads to proton phototransfer with formation of an excited ionic form:



which is responsible for the luminescence of the system. A similar intramolecular proton transfer reaction in the salicylaldehyde molecule has been observed by Fassler et al.[6]:

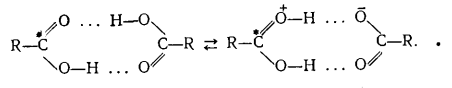


Williams and Heller examined proton phototransfer in 2-hydroxy-derivatives of benzoxazoles, benzothiazoles and benzimidazoles[167]:

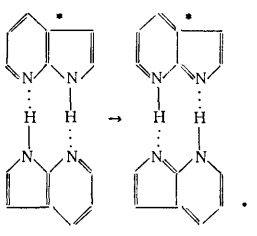


The majority of investigators believe that the form with proton transfer is dipolar and not quinonoid, but the problem has not been finally elucidated.

Proton transfer in dimers can be regarded by convention as intramolecular transfer Hochstrasser[135] observed an appreciable bathochromic shift of the fluorescence of the 1-naphthoic acid dimer in a methylcyclohexane solution at 77 K relative to room temperature. This shift was attributed to the formation of an ion pair as a result of proton transfer in the dimer owing to the sharp increase of the basicity of the carbonyl group:



Solutions of 7-azaindole in solvents incapable of forming hydrogen bonds exhibit two emission bands. Their relative intensities depend on the 7-azaindole concentration, temperature, and the excitation wavelength[136]. It has been suggested that the long-wavelength fluorescence band is due to the emission by the excited tautomeric form of the dimer with double proton transfer via the mechanism



## VI. PROTON PHOTOTRANSFER IN THE SOLID PHASE

Bimolecular processes requiring the migration of the reactants are inhibited in the solid state. Cases of proton phototransfer within hydrogen-bonded complexes[131,132] in 1-naphthol–aliphatic amine systems have been noted. According to the authors, proton phototransfer within the complex is very rapid and leads to the formation of an ion pair in the excited singlet state, which is manifested by the fact that a band, identical with that in the fluorescence spectrum of the naphthoxide ion, appears in the emission spectrum of this system. The phosphorescence spectra of the systems then coincide with the phosphorescence spectrum of 1-naphthol, which shows that the reverse proton transfer takes place after the intercombination transition in the triplet state of the ion pair.

Interesting results were obtained by Terenin and coworkers in studies on the reversible proton phototransfer reactions in frozen solutions of acridine derivatives[145,146]. When 3,6-diaminoacridinium, 3-aminoacridinium, Acridine Orange, and trypaflavinium cations are irradiated with light, the cations dissociate in tetrahydrofuran and toluene at 77 K with formation of the free bases. This photochemical reaction is reversible on raising the temperature. A study of the dependence of the steady-state concentration of the ionic form and of the base on light intensity led the authors to the conclusion that the photochemical reaction proceeds in both directions and that photodeprotonation of the cation is a two-photon process and occurs on excitation to one of the highest triplet states; the reverse reaction, involving the regeneration of the ionic form, is a one-photon process. The quantum yields of both the forward and reverse reactions are low.

The proton phototransfer at 77 K in solid layers obtained by the sublimation of aminoacridines together with various organic acids has been investigated in fair detail. In these systems, protonated forms of the aminoacridines are formed in the ground state, their photolysis resulting in the elimination of a proton and the formation of the base. In this case, the reaction has a one-quantum mechanism[148].

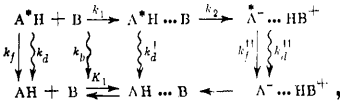
## VII. DEGRADATION OF THE ELECTRONIC EXCITATION ENERGY IN PROTON PHOTOTRANSFER REACTIONS

The deactivation of the excited molecules, associated with the acid–base interaction, was observed for the first time by Mataga et al. in 1957[177] and by Feitelson in 1964[42]. Photochemical acid–base reactions, leading to isotope exchange in C acids and bases, proceed with loss of electronic excitation and lead to the formation of products in the ground state. Induced non-radiative deactivation, competing with the isotope exchange reaction and leading to the loss of excitation without the formation of products, is also observed[151].

For heteroatomic acids and bases, proton phototransfer proceeds in many cases adiabatically, i.e. with retention of electronic excitation. However, in these reactions too non-radiative deactivation of the excited molecules, induced by the acid–base interaction, is observed. Since the proton transfer process involves many stages, non-radiative deactivation can occur at different stages of the reaction. Firstly, the deactivation can proceed when the molecules of the acid and base interact in the step involving the formation of an excited hydrogen-bonded complex. Secondly, there is a possibility of deactivation in the proton transfer stage, where the excited hydrogen-bonded complex is converted into an excited pair. Finally, there is a possibility of the deactivation of the excited ion pair owing to the interaction of the counterions. We shall consider each of the above deactivation pathways in greater detail.

The kinetic mechanism of the proton phototransfer reaction, taking into account the deactivation processes,

is of the following form for systems where the reverse reactions may be neglected[134]:



(19)

where $k_q$ is the rate constant for the induced non-radiative deactivation in the stage involving the formation of the excited hydrogen-bonded complex. On steady-state excitation at the isosbestic point, the dependence of the quantum yields and the fluorescence quenching times for the initial compound and the proton phototransfer product on the reactant (acid or base) concentration can be expressed as follows taking into account complex formation in the ground state:

$$\frac{\varphi_0}{\varphi}\frac{1}{1+K_1[B]} = 1+(k_1+k_q)\tau_0[B], \tag{20}$$

$$\frac{\tau_0}{\tau} = 1+(k_1+k_q)\tau_0[B], \tag{21}$$

$$\frac{\varphi_0\varphi''}{\varphi[B]} = \varphi_1''\frac{\varphi_0}{\varphi}\frac{K_1}{1+K_1[B]} + \varphi_1''k_1\tau_0, \tag{22}$$

$$\frac{\varphi_0}{\varphi}\left(1-\frac{\varphi''}{\varphi_1''}\right) = 1+k_q\tau_0[B], \tag{23}$$

$$\frac{\varphi_1''\tau_0}{\varphi_0\tau_0''} = \frac{k_f''}{k_f}\frac{k_2}{k_2+k_d'}, \tag{24}$$

where $\varphi_0$ and $\varphi$ are the fluorescence quantum yields of the initial compound in the absence and presence of the reactant, $\varphi''$ is the fluorescence quantum yield of the photochemical reaction product, $\varphi_1''$ the fluorescence quantum yield of the photochemical reaction product extrapolated to infinite concentration of the reactant where the entire initial compound is in the ground state in the form of the hydrogen-bonded complex, $k_2/(k_2 + k'_d)$ a quantity characterising the efficiency of the adiabatic proton transfer within the complex, $\tau_0$ and $\tau$ are the lifetimes of the excited initial compound in the absence and presence of the quenching agent, and $\tau_0''$ is the lifetime of the excited product of the photochemical reaction (ion pair). The authors of the present review have shown[134] that, in the 2-naphthol–aliphatic amine systems in polar aprotic solvents (dimethylformamide and acetonitrile), the induced non-radiative deactivation of the excited 2-naphthol molecules by the amine molecules in the stage involving the formation of the excited hydrogen-bonded complex competes to a large extent with the adiabatic reaction [the rate constant $k_q$ for non-radiative deactivation is of the order of $10^9$ litre mol$^{-1}$ s$^{-1}$ (Table 4)]. In solvents of low polarity (benzene, toluene, and dichloroethane), induced non-radiative deactivation was not observed at this stage. In polar solvents, diethylamine and triethylamine also quench the fluorescence of 2-methoxynaphthalene (which is incapable of forming hydrogen bonds with amines), which suggested a donor–acceptor mechanism of the induced non-radiative deactivation.

A study of proton phototransfer from 2-naphthol to various bases in protic solvents showed[119] that the ratio of the rate constants for the reaction and the induced deactivation depends on the type of base‡. Thus the rate constant for the induced non-radiative deactivation in the 2-naphthol–sodium acetate system is negligibly small compared with the rate constant for the adiabatic proton phototransfer. If triethylamine and dimethylhydrazine are used as the bases, the rate constants for proton transfer are comparable to the rate constants for the induced non-radiative deactivation. In the system with potassium benzoate and dimethylaniline, whose molecules contain an aromatic ring, only the quenching of the fluorescence of the neutral form of 2-naphthol is observed. The absence of the fluorescence of the naphthoxide ion in such cases is evidence that the non-radiative deactivation process predominates over the adiabatic proton transfer. It is noteworthy that potassium benzoate and dimethylaniline quench the fluorescence of not only 2-naphthol but also of 2-methoxynaphthalene, the rate constant for the quenching of the fluorescence of 2-methoxynaphthalene by potassium benzoate being close to the corresponding constant for 2-naphthol.

Table 4. The rate constants for the formation of excited ion pairs and ions ($k_1$) and for the non-radiative deactivation ($k_q$) of 2-naphthol in the presence of various bases[119,162].

| Base | Solvent | $10^{-8}(k_1+k_q)$, litre mole$^{-1}$ s$^{-1}$ | $k_1$, litre mole$^{-1}$ s$^{-1}$ | $10^{-8}k_q$, litre mole$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| Triethylamine | Benzene | 20±2 | 20±4 | <4 |
| Diethylamine | Benzene | 41±4 | 41±8 | <8 |
| Triethylamine | Toluene | 23±2 | 23±2 | <2 |
| Diethylamine | Toluene | 34±3 | 34±8 | <8 |
| Piperidine | Toluene | 40±6 | 40±6 | <6 |
| Triethylamine | Dichloroethane | 46±5 | 46±10 | <10 |
| Triethylamine | Acetonitrile | 11±1 | 1.6±0.6 | 9±3 |
| Diethylamine | Acetonitrile | 12±1 | 3.0±0.7 | 9±3 |
| Piperidine | Acetonitrile | 19±2 | 7±2 | 13±4 |
| Triethylamine | Dimethylformamide | 3.3±0.3 | 1.0±0.1 | 2.2±0.2 |
| Triethylamine | Ethanol | 2.0±0.1 | 0.8±0.1 | 1.2±0.1 |
| Dimethylhydrazine | Ethanol | 6.0±0.6 | 2.8±0.3 | 3.2±0.3 |
| *NN*-Dimethylaniline | Ethanol | 44±4 | <0.4 | 44±4 |
| Potassium benzoate | Methanol | 19.5±2.0 | <0.2 | 19.5±2.0 |
| Sodium acetate | Ethanol | 5.0±0.5 | 5.0±0.5 | <0.5 |

In the above systems, excited 2-naphthol molecules behave both as the acid (proton donor) and the electron acceptor. The donor–acceptor interaction can lead to the deactivation of excited molecules[154]. The relative rate constants for the adiabatic proton transfer and the deactivation depend on the relative basicity of the base and on its ionisation potential (its electron-donating properties). On passing from triethylamine ($I$ = 7.8 eV) and dimethylhydrazine ($I$ = 7.75 eV) to dimethylaniline ($I$ = 7.3 eV), the proton transfer rate constant decreases and the deactivation rate constant increases. Similarly, the reaction

‡In protic solvents, where the acid and base form hydrogen-bonded complexes with the solvent, it is impossible to separate experimentally the deactivation processes at various stages, so that the deactivation rate constants determined from the equation

$$\frac{\varphi_0}{\varphi}\left(1-\frac{\varphi''}{\varphi_0''}\right) = 1+\left[k_q + k_1\frac{k_d'}{k_2+k_d'}\right][B]\tau_0 \tag{25}$$

may refer to a combination of processes of different types: deactivation at the stage involving the formation of the excited complex and in the proton transfer step itself.

with the benzoate ion leads to the deactivation of excited 2-naphthol molecules, in contrast to the reaction with the acetate ion, which proceeds adiabatically and leads to proton transfer (the ionisation potentials of acetic and benzoic acids are 10.7 and 8.5 eV respectively). Thus, non-radiative deactivation at the stage involving the formation of the excited hydrogen-bonded complex in the above systems apparently proceeds as a result of the donor–acceptor interaction of the components and competes with the reaction proper.

The quenching of the fluorescence as a result of the formation of hydrogen-bonded complexes has been observed by Cooke and Solomon in a study of the interaction of excited 1- and 2-methoxynaphthalenes with benzoic acid [156]. The introduction of a compound capable of forming a hydrogen bond with benzoic acid, for example, dioxan, reduces the efficiency of the quenching and, at high dioxan concentrations, the quenching vanishes altogether. It is of interest that only monomers and linear (but not cyclic) benzoic acid dimers can quench the fluorescence of methoxynaphthalenes.

Table 5. The relative quantum yields for the formation of excited ion pairs on excitation of the hydrogen-bonded complexes of 2-naphthol with aliphatic amines [134].

| Solvent | Triethylamine | Diethylamine | Piperidine | Benzylamine | t-Butylamine |
|---|---|---|---|---|---|
| Toluene | 1.0 | 0.8±0.1 | 0.6±0.1 | 0.4±0.1 | 0.6±0.1 |
| Dichloroethane | 1.0 | 0.8±0.1 | 0.8±0.1 | — | — |

A number of experimental data, which are treated as proof of the occurrence of non-radiative deactivation in the proton transfer step itself, have been obtained recently. In the excitation of hydrogen-bonded complexes of 2-naphthol with aliphatic amines in aprotic solvents of low polarity, the quantum yield in the formation of the excited ion pair is in many instances less than unity [134] (Table 5). This shows that the degradation of the electronic excitation energy can occur directly in the proton transfer step itself and not as a result of subsequent or competing electron transfer processes.

Förster showed [124] that the excitation of the 2-naphthylammonium cation in aqueous sulphuric acid solutions to the fluorescence of 2-naphthylamine, which is a result of proton transfer to the solvent. At sulphuric acid concentrations where the fluorescence of both forms is observed, the overall fluorescence quantum yield is very low (0.002). The fluorescence quantum yields of 2-naphthylamine in the $H_2SO_4$–$H_2O$ and $D_2SO_4$–$D_2O$ systems at low acid concentrations approach a common limit of 0.26. Both values decrease with increase of acid concentration, but the quantum yield in the deuteriated system decreases much more slowly. In the range of acid concentrations where the fluorescence of the cation may be observed, the fluorescence quantum yield in the deuteriated system is much higher than in the non-deuteriated system. With increase of acidity, the fluorescence quantum yields of the cation increase in both systems and approach one another. In the deuteriated system, the equalisation of the fluorescence quantum yields of the cation and the molecular base occurs at a somewhat lower acid concentration than in the non-deuteriated system. Förster [124] believes that the proton transfer from the excited cation to the solvent makes possible non-radiative deactivation, which is not observed either for the neutral molecule or the cation separately.

However, there are other explanations of the above experimental facts. Schulman and Liedke [143] suggest the existence of at least one non-emitting intermediate complex. This may be a stoichiometric intermediate complex of the naphthylammonium ion and one water molecule. Such a complex may be virtually non-fluorescent owing to the intense internal transition to the ground state. Förster [124] believed that the deactivation could be also caused by the protonation of the aromatic ring of 2-naphthylamine in the singlet state. The excited amine is more sensitive to electrophilic attack by the proton than the cation. The rate of this process should increase with increased acidity of the solution and with increase of the fraction of the neutral amine obtained in the excited state.

Deactivation processes in excited ion pairs have been observed in 2-naphthol–aliphatic amine systems. In particular, the deactivation is manifested by a decreased lifetime of the excited ion pairs compared with the 2-naphthoxide ion in the same solvent and by the marked dependence of the fluorescence quantum yields and the lifetimes of the excited ion pairs on temperature [133,134,161]. In those cases where the molecules of the polar protic solvent quench the fluorescence of the aromatic acid or base, it is difficult to isolate the stage in which the electronic energy is degraded. It has been observed that excited 1-naphthol [162] and indole and its derivatives [178] are effectively quenched by water molecules. In both cases, a decrease of solution temperature and deuteriation of the solvent lead to an appreciable decrease in the rate constant for the non-radiative deactivation. The fluorescence quantum yield and the lifetime of the excited 1-naphthol molecules in aqueous solution increase in the presence of an electrolyte (guanidinium chloride) and a non-electrolyte (sucrose) at high concentrations (of the order of several mole litre$^{-1}$). [169] A similar influence of added salts on the fluorescence of organic compounds has been found for sodium 1-naphthol-4-sulphonate and the ionised forms of indole and its derivatives [179,180]. The authors explain this effect by a decrease in the activity of water when its molecules are bound in the solvation shells of the added salts. The mechanism of the quenching of the fluorescence by water molecules has not been completely elucidated. It is suggested that, when the excited molecule of an aromatic acid or base interacts, there is a possibility of the formation of forms with charge transfer (complete or partial) due to proton or electron transfer [179]. The quenching of the fluorescence of organic molecules by water is probably a general phenomenon.

The study of the temperature variation of the lifetimes of excited ion pairs led to the conclusion that the rate constant for non-radiative deactivation $k''_d$ [see Eqn. (19)] is the sum of two terms, of which the first ($k''_{d_1}$) depends only slightly on temperature and is comparable to the rate constant for the non-radiative deactivation of the 2-naphthoxide ion, while the second component, of the type $k_T = k''_{d_2} \exp(-E/RT)$, is determined by the interaction of the counterions and depends markedly on the nature of the amine and the solvent (Table 6).

Two possible mechanisms of such deactivation have been proposed. In the first, each cycle of the reversible proton transfer in the ion pair is accompanied by the deactivation of some of the molecules [161]. In this case the measured activation energy (of the order of 5–10 kcal

mole$^{-1}$) should correspond approximately to $\Delta H^*$ for the reversible reaction

$$A^*H \ldots B \rightleftarrows \dot{A}^- \ldots\ldots HB^+,$$

and the pre-exponential factor for the deactivation rate constant is equal to the product of the proton transfer rate constant and the probability of the degradation of the energy in the excited hydrogen-bonded complex. The decrease of the activation energy for the quenching processes in ion pairs and the decrease of the pre-exponential factor following the replacement of hydrogen by deuterium are evidence in support of this model. According to another model, the electronic excitation energy is degraded by the donor–acceptor interaction of the counterions in the excited ion pair [133,161]. In this case, the activated quenching mechanism may be associated with the fact that the counterions must overcome an energy barrier (possibly the dissociation of the $-O^-\ldots H-\overset{+}{N}\lessgtr$ hydrogen bond is necessary) in order to achieve a configuration ensuring the maximum probability of rapid electron transfer. The activation energy for the electronic excitation energy degradation processes can then include the dissociation energy of the hydrogen bond between the ions. Such energy degradation in the products of the proton phototransfer reaction leads to the usual quenching via the electron transfer mechanism.

Table 6. The kinetic characteristics of the deactivation processes in excited ion pairs formed by the 2-naphthoxide anion with alkylammonium ions [182].

| Cation | Solvent | lg $k_T$ (20° C) | $E_{act}$, kcal mole$^{-1}$ | lg $k_{d_s}$ |
|---|---|---|---|---|
| $(C_2H_5)_3\overset{+}{N}H$ | Toluene | 8.9±0.1 | 6.4±0.5 | 13.6±0.5 |
| | Triethylamine | 8.7±0.1 | 5.2±0.5 | 12.5±0.5 |
| | Tetrahydrofuran | 7.5±0.2 | 4.7±0.7 | 11.0±1.0 |
| | Butyronitrile | 8.0±0.1 | 5.0±0.5 | 11.7±0.5 |
| $(C_2H_5)_2\overset{+}{N}H_2$ | Toluene | 8.7±0.1 | 10.0±1.0 | 16.0±1.0 |
| | Diethylamine | 8.4±0.1 | 9.3±0.7 | 15.0±1.0 |
| | Tetrahydrofuran | 7.9±0.2 | 6.3±0.5 | 12.5±1.0 |
| $(C_2H_5)_2\overset{+}{N}D_2$ | Toluene | 8.2±0.1 | 6.6±1.0 | 13.0±1.0 |
| | Deuterated diethylamine | 7.4±0.2 | — | — |
| $(CH_2)_5\overset{+}{N}H_2$ | Toluene | 8.6±0.1 | 10.0±1.0 | 16.0±1.0 |
| \|————\| | Tetrahydrofuran | 7.9±0.2 | 6.7±0.5 | 13.0±0.5 |
| $C_6H_5CH_2\overset{+}{N}H_3$ | Toluene | 8.2±0.1 | 8.0±1.6 | 14.0±1.0 |
| | Tetrahydrofuran | 7.9±0.2 | 5.0±1.0 | 12.0±1.0 |
| t-$C_4H_9\overset{+}{N}H_3$ | Toluene | 7.9±0.2 | 6.5±1.0 | 12.0±1.0 |
| t-$C_4H_9\overset{+}{N}H_3$ | Tetrahydrofuran | 8.3±0.1 | 4.0±0.8 | — |

A similar deactivation mechanism, including proton transfer to the hydrogen-bonded complex followed by the donor–acceptor interaction of the counterions, one of which is excited, has been proposed by Ermolaev and coworkers [157,159,182] to explain the complete absence of the fluorescence and phosphorescence of the hydrogen-bonded complexes where both the proton donor and acceptor possess a $\pi$-electron system directly linked to the acid and basic functional groups. The hydrogen-bonded complexes of aromatic hydroxy-derivatives with aromatic heterocycles are examples of such systems [120,122,164,183]. It is suggested that, in the excited hydrogen-bonded complex, there is a fairly high probability of the formation of species with proton transfer, which exhibit electron-donating and electron-accepting properties favourable for electron transfer from the anion to the cation when one of them is in the excited state and the partners have a conjugated $\pi$-electron system. Electron transfer results in the formation of a pair of radicals, which, being unable to move apart in the time available, recombine with formation of a hydrogen-bonded complex in a non-excited state. Proton transfer in the complex is much slower ($10^{-12}$ s) than electron transfer ($10^{-15}$ s). Furthermore, proton transfer is retarded by a potential barrier, whose presence is due to a small difference between the acid–base properties of the partners in the complex, so that it is quite likely that proton transfer is the rate-limiting stage in the quenching process. Apparently these stages are not significantly separated during their occurrence, so that it is impossible to isolate one from the other.

The transfer of a proton and an electron is equivalent to the transfer of a hydrogen atom. In a study of the interaction of 2-naphthol with pyridine in cyclohexane solution by flash photolysis, it was shown [128] that the excitation of the hydrogen-bonded complex did not lead to the formation of any intermediate products, while the reaction of free 2-naphthol molecules in both the first singlet state and the triplet state led to the formation of naphthoxy-radicals, i.e. the fluorescence is quenched via the abstraction of a hydrogen atom from 2-naphthol by pyridine. A similar mechanism of the quenching of fluorescence by the transfer of a hydrogen atom in hydrogen-bonded complexes has been proposed for the benzacridine–phenol system [158]. Mataga and coworkers [184] showed by laser photolysis that, apart from the formation of the excited ion, in the carbazole–triethylamine system in acetonitrile there is a competing process involving the abstraction of a hydrogen atom and the formation of the carbazyl radical. However, the quenching of the carbazole fluorescence by pyridine is not accompanied by the appearance of any unstable intermediate products.

A study of the quenching process in hydrogen-bonded complexes at low temperatures permitted certain conclusions concerning the rate-limiting deactivation stage [159]. When the temperature is reduced from 77 to 4K, the quenching of the fluorescence in 2-naphthol–pyridine and carbazole–pyridine complexes in frozen toluene solutions is found to be diminished. The rate-limiting stage of the deactivation process in such complexes is apparently proton transfer from the acid to the base (pyridine) by tunnelling.

All the processes considered above refer to the singlet excited state. The study of the deactivation processes in the triplet state is complicated by the fact that the latter is formed from the singlet state as a result of an intercombination transition. All the deactivation processes leading to the quenching of the singlet state can therefore decrease the quantum yield of the triplet state. However, this difficulty may be overcome if the triplet state is populated by means of a triplet–triplet energy transfer. Using the method of the triplet–triplet energy transfer from the toluene glassy matrix to the luminescent compound investigated, it has been shown [164] that the phosphorescences of carbazole, 2-naphthol, pyrazine, benzophenone, and anthraquinone are quenched by pyridine and phenol. In contrast to the latter, triethylamine does not quench the phosphorescence of carbazole and 2-naphthol. In those cases where the system components do not form a hydrogen bond and the functional groups forming a hydrogen bond

with the $\pi$-systems of the aromatic molecules are not conjugated, there is no quenching of the phosphorescence and hence no deactivation of the triplet state.

When processes involving the deactivation of the singlet excited state in proton phototransfer reactions are examined, it is of interest to consider the problem of which process (internal conversion or intercombination transition) is influenced to a greater extent by the acid–base interaction§. It has been stated that proton transfer within 2-naphthol–aliphatic amine complexes [162] increases the degree of internal conversion.

Non-radiative degradation of the electronic excitation energy has also been observed in intramolecular proton transfer reactions in salicylate esters [185]. This is manifested by a sharp increase of the intensity of the fluorescence of the species with proton transfer as the temperature is reduced. The absence of any influence by isotopic substitution on the kinetic characteristics of the deactivation processes is evidence that the latter are not associated with the proton phototransfer reaction. This is the essential difference between the mechanisms of the degradation of the electronic excitation energy in intramolecular and intermolecular proton transfers.

The available data are insufficient to decide whether the deactivation processes in one of the species involved in interconversion play a dominant role or whether deactivation proceeds with a high efficiency in both species.

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§We are not concerned here with the numerous studies devoted to the influence of the formation of hydrogen-bonded complexes on the relative positions of the $n\pi^*$ and $\pi\pi^*$ levels and the associated change in the relative probabilities of the internal and intercombination transitions.

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# The Mechanism of the Adsorption of Sulphur Dioxide on Carbonaceous Adsorbents

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The most important literature data concerning the mechanism of the adsorption of $SO_2$ and the influence of oxygen and water vapour on the latter are described systematically and analysed. The possible types of interaction between the components of the gaseous mixture and the surface of the carbonaceous adsorbent are discussed.
The bibliography includes 112 references.

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## I. INTRODUCTION

During the last 10–15 years, increasing attention has been devoted to active search for new adsorbents in many world scientific centres. The reason for this is, on the one hand, the ease of their preparation as a result of favourable thermodynamic and kinetic factors governing adsorbent–adsorbate systems, and, on the other hand, their importance and the wide variety of their practical applications. The vigorous development of such research is to a large extent associated with the fact that it is directed to the solution of one of the most urgent problems in the development of modern society—the protection of the environment, in particular the elimination of sulphur oxides from gases.

The tendency towards an increase in the amount of waste sulphur oxides is manifested from year to year in connection with the expansion of the manufacture of heavy non-ferrous metals and sulphuric acid, the increase in the output of electric power stations operating on sulphur-containing fuels, etc. Thus the $SO_2$ waste (and the predicted amount of such waste) discharged into the atmosphere in the USA is characterised by the following data (million tonnes)[1]:

| 1966 | 1970 | 1980 | 1990 | 2000 |
|---|---|---|---|---|
| 28.6 | 36.6 | 61.0 | 86.5 | 126.0 |

The development of new methods for the extraction of sulphur dioxide from gases led to the appearance of carbonaceous and silicon-containing adsorbents, adsorbents based on metal compounds, and various ion-exchange resins. Many of these adsorbents have a high thermal stability, chemical resistance, effective characteristics as regards deformation and strength, etc.

The method for the elimination of sulphur dioxide from gaseous mixtures by means of various carbonaceous adsorbents has developed extensively at the present time. The extraction of $SO_2$ by carbonaceous adsorbents has attracted the attention of specialists by its relative simplicity, the ease of preparation of the adsorbents on an industrial scale, and the wide range of particle sizes and types of adsorbents. The elimination of $SO_2$ from gases by carbonaceous adsorbents is one of the procedures undergoing industrial tests. Studies on the applications of carbonaceous adsorbents for the sorption of $SO_2$ have been very numerous; a wide variety of methods and starting materials have been used for their preparation. Nevertheless, despite the different nature and types of these adsorbents, the adsorption of sulphur dioxide on them may involve the same process.

Studies in recent years have been characterised by a growth of interest in the mechanism of the sorption of $SO_2$ on various carbonaceous adsorbents and by a more far-reaching investigation of the properties of the latter. The number of studies on these lines has been increasing every year. However, the published data, scattered throughout numerous articles and journals, have not so far been reviewed systematically and analysed. In the present review, an attempt is made to fill the existing gap.

The review does not claim to cover the available data fully. Attention is concentrated on the mechanism of the adsorption of $SO_2$ and on the influence of various factors on this process.

## II. GENERAL CHARACTERISTICS OF THE SORPTION OF THE COMPONENTS OF THE GASEOUS MIXTURE

The experimental data accumulated hitherto concerning the adsorption of $SO_2$ from gaseous mixtures by carbonaceous adsorbents have shown that the sorption process has many features which depend on the chemical composition of the gas to be purified. However, despite this, it is always possible to isolate a large group of typical primary or secondary reactions occurring when a gaseous mixture is passed through a layer of a carbonaceous adsorbent. One should also note that the general characteristics do not rule out the occurrence of specific individual elementary reactions of the components of the gaseous mixture.

The primary adsorption processes consist mainly in the sorption of the components of the gas stream via fundamental mechanisms[2,3] of the following types:

$$SO_2 \rightleftarrows SO_2^*\ , \qquad (1)$$

$$H_2O \rightleftarrows H_2O^*\ , \qquad (2)$$

$$^1/_2O_2 \rightleftarrows O^*\ , \qquad (3)$$

where an asterisk denotes the sorbed state of the component.

Because of the occurrence of the three fundamental types of the primary interaction of the components of the gaseous mixture with the carbonaceous sorbent, the process involving the elimination of the desired component (sulphur dioxide) proceeds in two ways—via the primary

reaction (1) and via secondary interconversions of the sorption products[4,5]:

$$SO_2^* + H_2O^* \rightleftarrows H_2SO_3^* \quad , \tag{4}$$

$$H_2SO_3^* + O^* \rightleftarrows H_2SO_4^* \quad , \tag{5}$$

$$H_2SO_4^* + n\,H_2O^* \rightleftarrows (H_2SO_4 \cdot nH_2O)^* \quad . \tag{6}$$

It is frequently very difficult to determine the contribution of the adsorption step to the technological process. This is because modern technical procedures permit a reliable and fairly simple identification of only ionised products in the solid state (conductimetric, ESR, infrared spectroscopic, and other methods). As a rule, the role of the adsorbed product in the sorption process must be inferred from indirect data. However, there have been recently many studies where the formation of secondary compounds and their role in various sorption processes were analysed.

The adsorption capacity and catalytic properties of activated charcoals are known to depend not only on the specific surface but also on the nature of the distribution of pores with respect to their effective radii[6-8] and also on the chemical structure of the surface layer[9,10]. Dubinin's studies[11,12] showed that the activated charcoal is a conglomerate of irregularly joined hexagonal graphite prisms. During the preparation and activation of the charcoal, some of the rings are disrupted and ring residues, consisting of one or two carbon atoms, accumulate on the surface. Such atoms have unused valencies and form surface oxides on coming into contact with oxygen. The formation of surface oxides has been observed in numerous investigations[13-16]. It is also noteworthy that many investigators claim the existence of two types of surface oxides—acidic and basic oxides[17-19].

Davtyan and coworkers[20,21] carried out a series of experiments in which they showed that surface oxides are formed on contact with oxygen (and water). They believe that these oxides do not constitute a separate, independent phase but are bound directly to the crystal lattice of the adsorbent. These surface compounds are formed because the energy liberated as a result of oxidation is insufficient for the removal of the oxide molecule from the surface. Reactions (4)–(6) proceed as follows. Sulphur dioxide molecules in the sorbed state interact with the initial adsorbent–oxygen or adsorbent–hydroxyl surface compound, which results in the formation of an activated surface complex having a definite chemical reactivity. If the energy of the system is sufficient for the removal of a species from the surface, the final product of the reaction

$$(H_2SO_4 \cdot n\,H_2O)^* \rightarrow H_2SO_4 + n\,H_2O \tag{7}$$

is formed directly via the activated surface complex. In certain studies, the formation of sulphuric acid is regarded as the primary stage of the gas purification process and it is suggested that the acid is formed before its sorption by the carbonaceous adsorbent[22,23]. We believe that such a process can occur only in the purification of the residual gases in the manufacture of sulphuric acid, containing a sulphuric acid mist[24].

The role of surface oxides in the sorption of $SO_2$ by carbonaceous adsorbents is probably really considerable[25,26]. However, analysis of numerous investigations shows (without going into the details of the mechanism of the primary step involving the sorption of the components of the gaseous mixture and of secondary processes) that the conventional subdivision of the extraction of $SO_2$ from industrial gases by sorption into two groups of processes [reactions (1)–(3) and (4)–(6)] is probably legitimate. One should bear in mind that, under certain conditions, reaction (4) is favoured over reaction (6).

In considering typical reactions of the second group [reactions (4)–(6)], the authors usually distinguish two temperature ranges in each of which a characteristic reaction takes place[27,28]. At low temperatures (up to approximately 200°C), sulphurous acid decomposes to $SO_2$ and water vapour via the reaction

$$H_2SO_3^* \rightarrow SO_2 + H_2O \quad . \tag{8}$$

This reaction is characteristic of the purification of gases which do not contain oxygen. However, under real conditions, an oxygen-free gaseous mixture is hardly ever encountered.

At temperatures above 200°C (approximately 350–450°C), the decomposition of the adsorbed sulphuric acid is most probable:

$$2H_2SO_4^* + C \rightarrow 2SO_2 + 2H_2O + CO_2 \quad , \tag{9}$$

as a result of which the adsorbent reduces the acid to sulphur dioxide with formation of carbon dioxide.

Reactions (8) and (9) were investigated in detail by Dratwa[29]. The experiments were performed using model gases with the following compositions:

I. $SO_2 + N_2$ ,

II. $SO_2 + N_2 + O_2$ ,

III. $SO_2 + N_2 + O_2 + H_2O$ ,

IV. $SO_2 + N_2 + H_2O$ .

The concentration of nitrogen was kept constant and the concentrations of the remaining components of the gaseous mixtures were 5 vol.% $SO_2$, 10 vol.% $O_2$, and 18 vol.% $H_2O$. $SO_2$ was adsorbed at 110–120°C and the regeneration temperature was kept in the range 400–450°C. The results of these studies are presented in Fig. 1.

In the experiments on the $SO_2 + N_2$ (I) model gas, there is only physical adsorption of $SO_2$ by the activated charcoal. In the regeneration of the spent activated charcoal, the presence of $SO_2$ in the desorbed gas is detected over the entire temperature range from 20° to 200°C and the rate of evolution of $SO_2$ increases rapidly after heating the adsorbent above 100°C. The evolution of carbon dioxide is observed only in the temperature range which is not characteristic of the desorption of physically adsorbed $SO_2$.

The results of these experiments with the oxygen-containing model gas (II) are analogous to those analysed above. Here too an increase of temperature during adsorption is insignificant and $SO_2$ is mainly desorbed in the range between room temperature and 200°C. A considerable amount of $CO_2$ is formed together with $SO_2$. It follows from these data that sulphuric acid is not formed in the adsorption of $SO_2$ by carbonaceous adsorbents from an oxygen-containing gas.

In order to investigate the conditions under which $SO_2$ is vigorously oxidised to sulphuric acid, an experiment was performed on the model gas (III), which contains water vapour in addition to $SO_2$ and oxygen. Here an appreciable increase of temperature is observed following the adsorption of $SO_2$. The $SO_2$ content in the desorbed gas increases with increase of regeneration temperature: the evolution of $SO_2$ is initially observed above the adsorption temperature and is accompanied by the formation of a large amount of $CO_2$. These results (the high heat of the phase transition in the adsorption of $SO_2$, the shift of the temperature curve for the desorption of $SO_2$, and the vigorous formation of $CO_2$) can be explained by the fact that the simultaneous presence of oxygen and water vapour promotes the conversion of $SO_2$ into sulphuric acid.

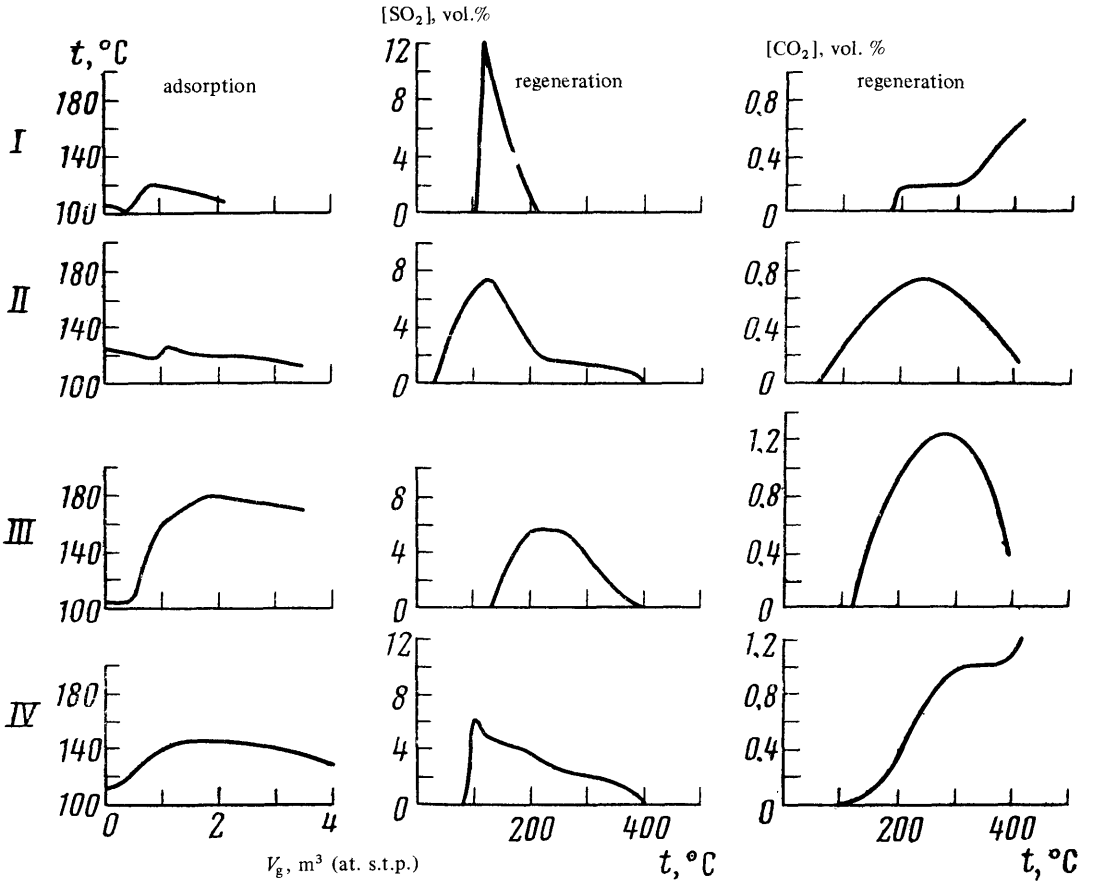



Figure 1. The influence of the composition of the initial gaseous mixture on the adsorption of sulphur dioxide and the regeneration of activated charcoal[29]; $V_g$ ($m^3$ at s.t.p.)—amount of purified gas passed through the layer of adsorbent; $t$ (°C)—regeneration temperature; $[SO_2]$ and $[CO_2]$ (vol.%)—concentrations of the components in the desorbed gas: I)–IV) model gases of different compositions.

In order to discover which reaction takes place in the presence of water vapour but in the absence of oxygen from the gases, the model gas (IV) was used. Here an appreciable increase of temperature was noted in the adsorption process and an extended $SO_2$ desorption curve (Fig. 1). Consequently in this case too there is extensive oxidation of $SO_2$ to sulphuric acid, probably by surface oxides. Similar results were obtained also in later studies[30].

The above classification of the reactions is naturally extremely arbitrary and in specific instances there is a possibility of particular departures from the proposed mechanism. Thus it has been stated[31] that the following reaction is possible in the adsorption of $SO_2$:

$$3SO_2^* \rightarrow S^* + 2SO_3^* \ . \qquad (10)$$

However, its occurrence is extremely doubtful.

One may note that the determination of the exact limits of the temperature ranges corresponding to the occurrence of the adsorption-catalytic processes is not only difficult but also controversial if one is dealing with specified carbonaceous adsorbents. Even for a particular type of activated charcoal, the temperature ranges where given sorption processes occur may be displaced as a function of the nature and amount of various impurities, the history of the active centres, etc.

It is noteworthy that, according to some data[32], free radicals are present on the surface of carbonaceous adsorbents. In the sorption of oxygen by an activated charcoal containing free radicals, the electrons of the latter become localised at oxygen molecules. These electronic states are stable, the corresponding species are rapidly chemisorbed and then activate the oxygen molecules[33,34]. Such a process on the surface of a carbonaceous adsorbent leads to the formation of the radical-ion $O_2$.[35] The occurrence of this stage may be represented by the reaction[36]:

$$R{\equiv}C^- + O_2 \rightarrow RCO_2^- \rightarrow R{\equiv}C \ldots O_2^- \ . \qquad (11)$$

If sulphur dioxide molecules appear on the surface of the charcoal, the following reactions may take place:

$$R{\equiv}C \ldots O_2^- + SO_2 \rightarrow R{\equiv}CO \ldots OSO_2 \ , \qquad (12)$$

$$R{\equiv}CO \ldots OSO_2 \rightarrow R{\equiv}C{-}O{-} + SO_3 \ , \qquad (13)$$

$$R{\equiv}C{-}O^- + SO_2 \rightarrow R{\equiv}C{-}O{-}SO_2 \ . \qquad (14)$$

It is noteworthy that, although the operation of this $SO_2$ sorption mechanism has been questioned by many specialists, the available experimental data are apparently consistent with this interpretation of the primary reactions.

The form of the bond between $SO_2$ and the surface of the carbonaceous material can have a marked influence on the primary $SO_2$ sorption processes. According to the hypotheses put forward by a number of investigators, two types of bond are formed between $SO_2$ and the carbon surface: a weak bond, which dissociates on slight heating in a stream of an inert gas ($a_I$) and a strong bond, the dissociation of which requires an increase of temperature (up to 300°C) as for surface oxides ($a_{II}$). Furthermore, these reactions are considerably influenced by the interaction of the surface with $SO_2$ and water vapour and by the ability of sulphur atoms to form hydrogen bonds[37,38].

We shall now consider the occurrence of the sorption processes from the theoretical standpoint based on the occurrence of reactions (1)–(3). The extent of adsorption of $SO_2$ on the activated charcoal obeys satisfactorily the Langmuir equation[30,31,39]:

$$a = \frac{a_m P}{P + b}, \tag{15}$$

where $a_m$ is the degree of adsorption of $SO_2$ at equilibrium, $P$ the partial pressure of $SO_2$, and $b$ a constant, which depends on temperature and which can be calculated from the Arrhenius equation:

$$b = b_0 e^{-\frac{E^*}{RT}}, \tag{16}$$

where $E^*$ is the heat of adsorption.

If it is assumed that $P \ll o$, Eqn. (16) can be replaced by Henry's law [Eqn. (17)], i.e. the degree of adsorption of $SO_2$ is directly proportional to its partial pressure:

$$a = \frac{a_m}{b} P. \tag{17}$$

$SO_2$ is oxidised to $SO_3$ on the surface of the activated charcoal and sulphuric acid is formed at a rate which is determined by the equation

$$\frac{d[H_2SO_4]}{dt} = k_I [SO_2^*] [O^*]^{0,5} [H_2O^*] - k_{II} [H_2SO_4^*], \tag{18}$$

where $k_I$ and $k_{II}$ are the rate constants for the forward and reverse reactions. The sulphuric acid formed on the surface fills internal pores, which enables the surface of the charcoal to participate in the oxidation process again. Thus the reverse reaction may be neglected in the adsorption of $SO_2$.[29]

We obtain from Eqns. (17) and (18)

$$\frac{d[H_2SO_4]}{dt} = k_I \frac{a_m a_{m_1} \sqrt{a_{m_2}}}{b\ b_1\ \sqrt{b_2}} P\ P_1\ P_2^{0,5}, \tag{19}$$

where the subscripts 1 and 2 refer to water and oxygen respectively.

During sorption, the values of $a_m$, $a_{m_1}$, and $a_{m_2}$ are constant when the partial pressures of sulphur dioxide, water vapour, and oxygen are constant; the rate of formation of sulphuric acid in the catalytic region is likewise constant. The rate constant for the reaction is

$$k_I = k_{0I} e^{-\frac{E_{act}}{RT}}, \tag{20}$$

where $E_{act}$ is the activation energy for the chemical reaction on the surface of the charcoal.

Having substituted in Eqn. (19) the adsorption rate constants defined by Eqn. (16), we obtain

$$\frac{d[H_2SO_4]}{dt} = {}'A e^{-\frac{E^*}{RT}}; \tag{21}$$

and the apparent activation energy $E^*$ for the overall reaction now consists of the activation energy for the entire adsorption process and of the activation energy for the chemical reaction:

$$E^* = E^* + E_1^* + {}^1/_2 E_2^* - E_{act}. \tag{22}$$

When $(E^* + E_1^* + \frac{1}{2}E_2^*) > E_{act}$, the experimental data agree in this case with the calculated results[4] (Fig. 2). Data were obtained for two different types of activated charcoal: BKTs (continuous lines) and BKA (dashed lines). In the former case, the adsorbent particle size was varied for a constant contact time of 12 s and in the latter case the contact time was varied. The logarithm of the rate of adsorption of $SO_2$ ($cm^3\ kg^{-1}\ min^{-1}$) for constant $SO_2$, water vapour, and oxygen concentrations in the gaseous mixture is proportional to the reciprocal of temperature, in agreement with Eqn. (21). The apparent activation energy is 22 kcal $mole^{-1}$ for the BKTs charcoal and 14.6 kcal $mole^{-1}$ for the BKA charcoal. To a first approximation, $E^*$ is comparable to the heat of adsorption.

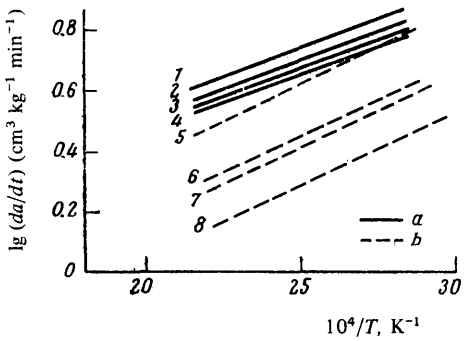



**Figure 2.** Temperature variation of the rate of adsorption of $SO_2$ on different activated charcoals in terms of the Arrhenius equation[4]: *a*) BKTs activated charcoal [particle size (mm): 1) 0.5–1.0; 2) 1–2; 3) 2–3; 4) 4–5]; *b*) BKA activated charcoal (particle size 2–3 mm). Contact time between the solid and gas phases (s): 1)–4) 12; 5) 5.4; 6) 8.6; 7) 13.0; 8) 22.0.

Measurements have been made[40] of the heat of adsorption of $SO_2$ on the "Aussig" coarsely porous charcoal at very low sulphur dioxide concentrations. The authors established that the minimum heat of adsorption is close to the heat of condensation of $SO_2$ (6.32 kcal $mole^{-1}$) and the maximum heat is 8.5 kcal $mole^{-1}$. The heat of adsorption of $SO_2$ on a finely porous activated charcoal reaches 10 kcal $mole^{-1}$.[41] However, the heats of adsorption of $SO_2$ on carbonaceous sorbents (coke, semicoke, and others) are lower than for activated charcoals, amounting to 6.5–8.0 kcal $mole^{-1}$.[42]

It is noteworthy that the heat of sorption of $SO_2$ on activated charcoal from a gaseous mixture containing oxygen and water vapour is much higher, reaching 14–16 kcal $mole^{-1}$.[43]

## III. THE INFLUENCE OF OXYGEN

Real technological and ventilation gases as a rule contain oxygen[44,45]. Studies have shown that sulphur dioxide is in this case oxidised to the trioxide on the surface of carbonaceous adsorbents. In the presence of moisture, sulphur trioxide forms sulphuric acid [reactions (4)–(6)].

Thus the presence of oxygen and moisture must influence the mechanism of the process and hence its equilibrium and kinetic characteristics. The influence of oxygen on the sorption process was observed in the very first experiments designed to investigate the elimination of $SO_2$ from gases by an activated charcoal. However, systematic studies on these lines were undertaken only recently.

In 1956 Davtyan et al.[46] investigated the effect of oxygen in the gas phase in the adsorption of $SO_2$ on surfaces of different chemical types (adsorption from a mixture of $SO_2$ and $O_2$ in proportions of 2 : 1). The adsorbents investigated can be arranged in the following sequence in terms of their catalytic activity at low temperatures:

$$\text{activated charcoal} > V_2O_5 > \text{graphite} > Cr_2O_3 > Fe_2O_3.$$

It follows from Eqn. (19) that the rate of oxidation of $SO_2$ to sulphuric acid is proportional to the square root of the oxygen partial pressure. Under industrial conditions, the addition of oxygen to the gaseous mixture increases the degree of adsorption of $SO_2$[47] and the degree of purification of the gases[29] (Fig. 3). Here too $SO_2$ is apparently oxidised to sulphuric acid.

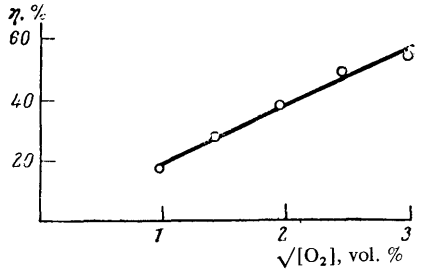



**Figure 3.** Variation of the degree of purification of the gases ($\eta$, %) with the initial concentration of oxygen in the gaseous mixture[29].

At very low (5%) and very high (95%) oxygen partial pressures, a smaller amount of sulphuric acid is obtained than in the case where the oxygen and sulphur dioxide partial pressures are equal (50%) for a given oxidation time[21]. However, the authors note that the amount of oxidised product can reach a limiting value after a specific time interval whatever the oxygen partial pressure. The formation of the limiting amount of the oxidised product on the charcoal is slow, which can be evidently accounted for by the rôle of diffusion in micropores. Only part of the adsorbed sulphur dioxide is then oxidised. On this basis, the authors conclude that "oxides" weakly bound to the charcoal surface and involved in equilibrium with the oxygen in the gas phase take part in the catalytic $SO_2$ oxidation process; these catalytically active "oxides" are readily removed by evacuation for 1 h at 20°C.[48] They consist of chemisorbed oxygen with a low activation energy and occupying about 10% of the entire surface of the charcoal[49,50]. Apart from these "oxides", weakly bound to the activated charcoal surface, Davtyan and Tkach[21] believe that none of the individual surface oxides of the charcoal are involved in the catalytic oxidation of sulphur dioxide.

A similar view has been developed also in other investigations[51,52] in the discussion of the adsorption of $SO_2$ by an activated charcoal from a nitrogen–oxygen–sulphur dioxide mixture. However, in this case the $SO_2$ concentration did not exceed 4 vol.% and the yield of the oxidised product, i.e. sulphur trioxide, was 50% of the adsorbed $SO_2$; the dynamic capacity of the charcoal proved to be 250 mg $g^{-1}$.

The sorption of $SO_2$ from a dry gas on activated SKT charcoal at 26°C consists of two processes: physical adsorption (77%) and chemisorption (23%).[53] With increase of temperature to 150°C, the amount of $SO_2$ chemisorbed from the dry gas hardly changes. This confirms yet again the hypothesis of the presence of a limited and constant number of active centres on the surface of the charcoal.

One should note that the degree of oxidation of $SO_2$ on carbonaceous adsorbents with a low surface activity (semicoke, coke, etc.) is insignificant[5]. The degree of oxidation of $SO_2$ on the semicoke obtained from brown coal at the pyrolysis temperature (650°C) is 10–12, 5–6, 3–4, and 2–3 wt.% of the total amount of adsorbed $SO_2$ at 25°, 75°, 100°, and 150°C respectively. The degree of adsorption of $SO_2$ (its equilibrium concentration in the gas–air mixture is 3 vol.%) is 148, 52, 48, and 26 mg $g^{-1}$ at the temperatures stated.

It is noteworthy that, despite the different surface activities of activated charcoal and semicoke, the rate of acid formation increases in both cases during the first 10 min and is then stabilised[5,46] (Fig. 4). This can probably be explained by the identical mechanism of the interaction of $SO_2$ with the carbon surface.

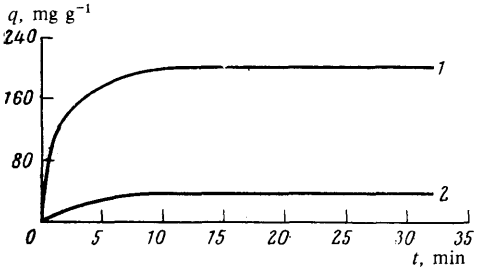



**Figure 4.** Kinetic curves for the increase in the weight of sulphuric acid on activated charcoal (curve *1*) and brown coal semicoke (curve *2*) in the adsorption of $SO_2$ from a gas–air mixture[5,46] at 20°C.

It has been claimed[23,29] that the oxidation of $SO_2$ on a carbon surface, for example on activated coke, is possible only in the presence of water vapour. The reaction

$$SO_2^{\bullet} + {}^1/_2O_2^{\bullet} + H_2O \rightarrow H_2SO_4^{\bullet} \qquad (23)$$

then occurs.

This view is adhered to also in other investigations[54,55], where the adsorption of $SO_2$ on carbonaceous adsorbents with a low surface activity was likewise investigated. The

degree of oxidation of $SO_2$ on semicoke at an adsorption temperature of 100°C for a moist gaseous mixture containing 2, 5, 10, and 15 vol.% of water vapour is 4–5, 5–6, 7–8, and 10–11%.[5] The degree of oxidation is higher in all cases for the moist gas than for the dry gas.

According to some workers[54-59], the oxidation of $SO_2$ on a carbon surface proceeds in the temperature range 20–120°C, while on heating the saturated adsorbent in a stream of inert gas above 220°C, sulphuric acid is reduced by carbon in the adsorbent via reaction (9) with regeneration of $SO_2$ and renewal of the carbon surface. However, this evidence has been disproved by subsequent investigations of the adsorption of $SO_2$ in the temperature range 50–300°C.[60] The spent charcoal was regenerated at temperatures up to 950°C. The authors noted the sorption of $SO_2$ up to 300°C, but physical adsorption of $SO_2$ was not observed at 250° and 300°C (Table 1).

Table 1. Variation of the degree of adsorption of $SO_2$ at different temperatures[60] (charcoal regeneration temperature 950°C).

| Adsorption temp., °C | Degree of sorption of $SO_2$, mg $g^{-1}$ | | |
|---|---|---|---|
| | overall | chemisorption | physical adsorption |
| 150 | 12.4 | 10.4 | 2.0 |
| 150 | 11.1 | 8.3 | 2.3 |
| 150 | 11.8 | 8.2 | 3.6 |
| 150 | 10.8 | 8.2 | 2.6 |
| 150* | 9.3 | 7.2 | 2.1 |
| 150** | 3.6 | 2.9 | 1.0 |
| 300 | 10.8 | 10.8 | nil |
| 250 | 10.5 | 10.5 | nil |
| 100 | 17.8 | 9.9 | 7.9 |
| 50 | 41.3 | 9.3 | 32.0 |

*Regeneration temperature 650°C
**Regeneration temperature 500°C

We may note that the amount of chemisorbed $SO_2$ at temperatures in the range 50–300°C changes insignificantly. In the regeneration of the charcoal in the temperature range 650–950°C, particles of elemental sulphur were observed on the cold surfaces of the column. Hence the authors concluded that, in the adsorption of $SO_2$ at 50–300°C, the chemisorbed sulphur dioxide is converted into elemental sulphur in the regeneration stage.

Chemical analysis of the regenerated charcoal showed that the adsorbent still contains a considerable amount of sulphur (0.68–2.03 wt.%). On this basis, one may conclude that the restoration of the initial adsorption capacity of the charcoal cannot be attributed to its liberation from sulphur. In this case, there is surface migration of sulphur from the initial adsorption centres and the formation of new centres as a result of the evolution of CO and $CO_2$ (observed in the regeneration of the charcoal).

The decrease of the $SO_2$ content in the desorbed gas during the regeneration of the charcoal can be explained by the following reactions[61]:

$$SO_2 + C \rightarrow CO_2 + {}^1/_2S_2 \quad , \tag{24}$$

$$CO_2 + C \rightarrow 2CO \quad . \tag{25}$$

The appearance of CO as a product at 250–300°C (and naturally also up to 700°C, since the adsorbent is sintered above this temperature) cannot be attributed solely to these reactions, since the rate of reaction (25) is insignificant under these conditions[62]. It is more likely that an oxygen-exchange reaction takes place between $SO_2$ and the charcoal, analogous to the well known reaction between $CO_2$ and charcoal[63]. In this case, an intermediate oxygen complex is formed and may be desorbed in the form of CO or converted into a more stable oxygen compound[13,64,65].

The only oxygen compound found at 300°C is CO; $CO_2$ was detected together with CO only at 600–650°C. In contrast to this, when carbon interacts with oxygen, the ratio of CO and $CO_2$ increases with temperature[2,66].

The combustion of carbon is known to yield CO and $CO_2$ from intermediate oxygen complexes with the carbonyl and lactone structures respectively[67,68]. It has been shown by infrared absorption spectroscopy[69,70] that these structures arise when carbon interacts with oxygen at room temperature. During vacuum heat treatment up to a higher temperature, a large amount of $CO_2$ is formed and the concentration of the complexes with the lactone structure decreases faster than that of the complexes with the carbonyl structure. It was observed[69,70] that CO appeared initially at 150°C in the regeneration of the charcoal after the adsorption of $SO_2$; there were no traces of CO up to 500°C. The sulphur content in the charcoal increased with increase of the number of adsorption–desorption cycles. The authors therefore suggested that the presence of sulphur on the surface of charcoal affects either the relative accessibility of peripheral regions, which can give rise to the carbonyl or lactone structures, or the relative thermal stabilities of these complexes after their formation.

Furthermore, $CO_2$ can be evolved also when the reaction

$$SO_2 + 2CO \rightarrow 2CO_2 + {}^1/_2S_2 \tag{26}$$

takes place[61]. Stagy et al.[60] investigated this reaction at 550°, 500°, and 350°C. A gaseous mixture containing 0.5 vol.% $SO_2$ and 2 vol.% CO in a stream of helium passed through a layer of the adsorbent; the experimental results are presented in Table 2.

Table 2. Material balance in the $SO_2$–C (1) and $SO_2$–CO–C (2) systems*.

| Temp., °C | $10^5 c_1$, mole $min^{-1}$ | | Duration of expt., min | $10^5 c_2$, mole $min^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| | $SO_2$ | CO | | $SO_2$ | CO | $CO_2$ | COS |
| 650 | 4.5 | nil | 420 | traces | 1.0 | 8.8 | traces |
| 600 | 4.5 | nil | 130 | traces | 0.5 | 1.8 | traces |
| 550 | 4.5 | 17.0 | 15 | 0.4 | 8.9 | 8.6 | 0.2 |
| 550 | 4.5 | 17.0 | 195 | 0.4 | 8.2 | 7.7 | 0.4 |
| 500 | 4.5 | 17.0 | 240 | traces | 6.6 | 10.6 | 1.2 |
| 350 | 4.5 | 17.0 | 330 | traces | 4.6 | 9.6 | 3.4 |

* $c_1$ and $c_2$ are the $SO_2$, CO, $CO_2$, and COS concentrations in systems (1) and (2) respectively.

Comparison of the results obtained for the above two systems ($SO_2$–activated charcoal and $SO_2$–CO–activated charcoal) shows that the presence of CO appreciably altered the mechanism of the formation of elemental sulphur. It follows from Table 2 that the absence of a loss of carbon from the activated charcoal is characteristic of the $SO_2$–CO–C system. In the $SO_2$–C system at 600°C,

more than 50% of the oxygen bound in $SO_2$ was still retained in the layer of activated charcoal. However, in the $SO_2$–CO–C system at 550°C oxygen was essentially not retained. Evidently the presence of CO fully suppressed the formation of the oxygen complex on the surface of the activated charcoal.

At 550°C, the ratio of CO and $SO_2$ was approximately 2, confirming the occurrence of reaction (26). However, when the temperature was reduced to 350°C, the ratio of CO and $SO_2$ rose to 2.8 and 75% of the total sulphur was detected in the form of carbonyl sulphide. Thus carbon monoxide reacted under these conditions with the sulphur–oxygen surface complex.

Despite the apparent simplicity of the mechanism described above for the reaction of $SO_2$ on a carbon surface during adsorption and desorption, there are data throwing doubt on its validity. There exist different views concerning the details of the process. Some workers observed the oxidation of $SO_2$ during adsorption on a dry adsorbent from a dry gas[38,46], while others assumed that the oxidation is possible only in the presence of water[2,16]. According to one group of investigators[22], all the adsorption centres are catalytically active in the reactions, while others[23] believe that only some are active.

Furthermore, there exist experimental data which cannot be accounted for at all in terms of this mechanism. This applies to the amount of carbon dioxide appearing in the desorption of $SO_2$ via reaction (9). According to Dratwa et al.,[4] its amount is 80–120% relative to the stoichiometric composition based on reaction (9). The increase of the amount of $CO_2$ can be explained by the desorption of part of the surface carbon oxides. On the other hand, the decrease of the amount of $CO_2$ relative to stoichiometry can be attributed only to the fact that not all the chemisorbed $SO_2$ is oxidised to $SO_3$ at a temperature in excess of 220°C, where $SO_2$ is formed from $SO_3$ via reaction (9) according to the mechanism described: in fact ordinary desorption of strongly bound sulphur dioxides takes place to some extent.

The presence of oxygen in the gas causes not only a change in the nature of the process but also leads to a decrease of the overall rate of adsorption. This can be clearly seen in Fig. 5 from a comparison of the kinetic curves characterising the rate of adsorption of $SO_2$ by SKT-2 charcoal grains at an initial concentration of 1 vol. %, at 20°C, and for different amounts of oxygen in the inert gas (nitrogen).[30]

## IV. THE INFLUENCE OF WATER

The influence of water on the sorption properties of activated charcoals can be manifested both in the gas phase and directly in the adsorbent itself. The sorption of water vapour by the activated charcoal or the desorption of water from the latter not only accompany the sorption of other vapours and gases but, as a rule, constitute an important factor, determining the kinetics (and hence also the dynamics) of the adsorption. It has been shown in a number of studies[73–76] that the equilibrium capacity of the activated charcoal with respect to sulphur dioxide depends to a large extent on the moisture content in the system.

The moisture present in the activated charcoal grains constitutes an intermediate diffusion medium in which the volatile component is transferred between the gas phase and the solid substance of the activated charcoal. Consequently the gas–activated charcoal system consists of three phases in the presence of moisture; the equilibrium compositions of the phases and the kinetics of the interphase exchange are determined by the content and nature of the water in the activated charcoal.

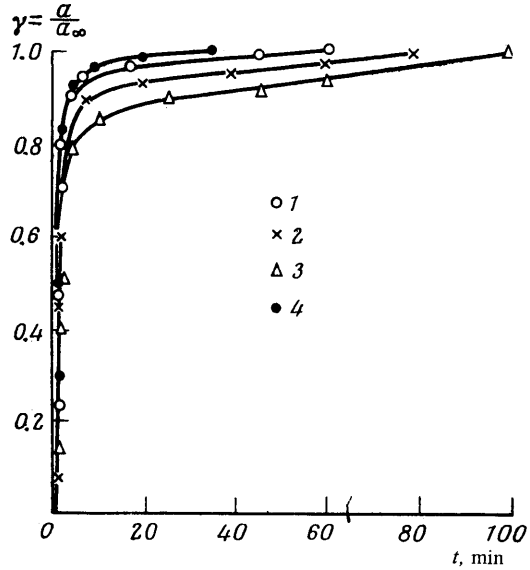



**Figure 5.** The influence of the oxygen content on the kinetics of the adsorption of $SO_2$ by SKT-2 charcoal[30]; initial $SO_2$ concentration 1 vol.%; temperature 20°C; oxygen content in the gaseous mixture (vol.%): 1) 3; 2) 5; 3) 15; 4) no oxygen.

The influence of the moisture content in the activated charcoal on the sorption of $SO_2$ was noted for the first time in 1917 in a study of the sorption properties of wood charcoal[77]. It was found that the overall sorption of $SO_2$ by the moist charcoal greatly exceeds the value for the dry charcoal. Somewhat later a similar effect was observed also for activated charcoals obtained from different starting materials, for example coconut, sugar, etc.[78] In the 1950s and 1960s, several patents were issued abroad for a method of synthesis of sulphuric acid using moist charcoal[79–88]. Widely known methods for the elimination of sulphur dioxide from industrial gases, such as the Lurgi[89–92], Hitachi[93,94], and West-Vaco[95,96] methods, are based on this principle.

The influence of charcoal saturated beforehand with moisture on the adsorption of $SO_2$ has been investigated comprehensively. It has been established that moisture has a significant effect on the nature and shape of the isotherm (Fig. 6), particularly at low partial pressures of sulphur dioxide in the gaseous mixture[48]. The degree of adsorption of $SO_2$ increases sharply with increase of the moisture content in the charcoal. Furthermore, it has been found that the amount of sulphuric acid obtained initially increases almost linearly with increase of the moisture content in the charcoal, reaches a maximum only in the presence of a moisture content of 300 mg $g^{-1}$, and then decreases sharply (Fig. 7).[48] The descending branch of the curve corresponds to saturation of the adsorbent

micropores with water. Similar effects were observed also on other activated charcoals for different initial $SO_2$ concentrations[19].

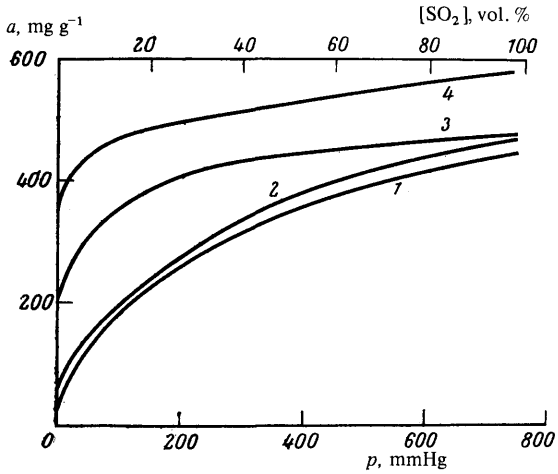



**Figure 6.** $SO_2$ adsorption isotherm at room temperature on activated charcoals with different moisture contents[48] (mg $H_2O$ per gram): 1) 0; 2) 1.98; 3) 13; 4) 19.6.

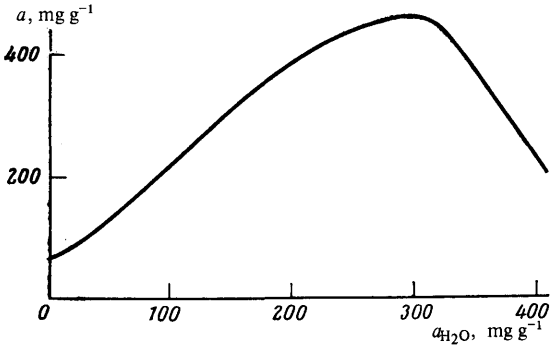



**Figure 7.** Variation of the degree of sorption of $SO_2$ at 20°C on activated charcoal with the amount of moisture adsorbed beforehand[48].

It has been suggested[37] that there are two types of interaction between $SO_2$ molecules and the carbonaceous adsorbent. The first is due to a weak bond between them, which may be broken on heating the adsorbent in a stream of an inert gas up to 100°C. This interaction makes a contribution $a_I$ to the overall degree of adsorption. The second interaction is characterised by a strong bond, which is not dissociated up to 200°C. It makes a contribution $a_{II}$ to the total sorption of $SO_2$. This hypothesis was also confirmed in a study of the adsorption of $SO_2$ on activated charcoal from a moist gas (Fig. 8).[97] With increase of the concentration of water vapour in the gas, $a_I$ diminishes, while $a_{II}$ passes through a maximum. The diametrically opposite effects of water vapour on $a_I$ and $a_{II}$ indicate the presence on the charcoal surface of adsorption centres of two types, involved in different kinds of surface interactions during the adsorption of sulphur dioxide and water vapour.

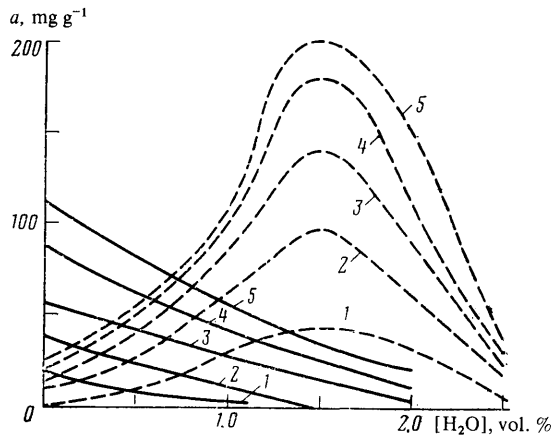



**Figure 8.** Variation of the degree of sorption of $SO_2$ [$a_I$ (continuous lines) and $a_{II}$ (dashed lines)] on SKT-2 charcoal with the concentration of water vapour at 25°C for different $SO_2$ concentrations[97] (vol.%): 1) 0.2; 2) 0.5; 3) 0.8; 4) 1.2; 5) 1.6.

Analysis of the experimental data leads to the following conclusions. The primary active centres in the adsorption of water on carbonaceous adsorbents are known to be oxygen complexes formed on the charcoal as a result of its activation. In the absence of such complexes, there is virtually no adsorption of water on the charcoal[11-16,98]. It is also known that oxygen complexes on the surface of charcoal serve as adsorption centres for sulphur dioxide too[19-23,46,48-53,99]. Under these conditions, the adsorption of $SO_2$ on active oxygen complexes is mainly in the nature of physical adsorption[40,43,100,101].

The water molecules adsorbed on the oxygen centres of the charcoal surface at water vapour pressures close to 0.5 of the saturation pressure are associated with one another via hydrogen bonding, which results in the coverage of the charcoal surface by isolated patches of condensed phase. The hydrogen atoms in the adsorbed water molecule, which are capable of forming hydrogen bonds, then serve as new adsorption centres and fresh portions of water are adsorbed by them. As a result, the number of adsorption centres in the given range of water vapour pressures increases sharply[97]. This mechanism is in fact used to account for the characteristic concave form of the water vapour adsorption isotherms on carbonaceous adsorbents with a sharp rise in the region of vapour pressures greater than 0.5 of the saturation pressure[98,102].

Sulphur is one of the elements capable of association via hydrogen bonding[103-105]. Thus the addition of $SO_2$ to the charcoal surface may proceed via the hydrogen of the adsorbed water. Since both water and sulphur dioxide molecules have strong dipoles, the strength of the bond formed may be greater than in the adsorption of $SO_2$ on silica gel via hydrogen bonding with the surface hydroxyls[106-109].

Thus the adsorption centres of the first type in the adsorption of $SO_2$ on charcoal from moist air are the oxygen complexes on the adsorbent surface. The adsorption centres of the second type in the adsorption of $SO_2$ from a moist gas are the protons of the adsorbed water molecules (hydrogen bonds). The above mechanism has been recently confirmed[97,110,111].

In the industrial synthesis of sulphuric acid, it is important to achieve the complete oxidation of $SO_2$ on carbonaceous adsorbents. Thus it has been stated[55] that, in order to attain the required degree of oxidation of $SO_2$ to $SO_3$, the contact time between the gas and the charcoal must be 10–20 s if the adsorbent temperature is maintained at the same time in the range 65–80°C; below 60°C, the reaction is strongly retarded. The concentration of the sulphuric acid obtained does not exceed 20% when the purified gas and water flow directly through the layer of adsorbent.

In a recently published study[112], carried out on a semi-industrial scale with the aim of purifying the residual gases in the manufacture of sulphuric acid, the influence of the regeneration time of the activated SKT-2 charcoal and of the amount of wash liquid on the concentration of the sulphuric acid formed was investigated (Fig. 9). In these experiments, the charcoal was wetted with the sulphuric acid solution obtained as a result of the adsorption of $SO_2$ before each adsorption–desorption cycle (apart from the first cycle, where the charcoal was wetted with water). The maximum concentration of sulphuric acid was 17% ($SO_2$ content in the gaseous mixture 0.2 vol.%, temperature 30–40°C).

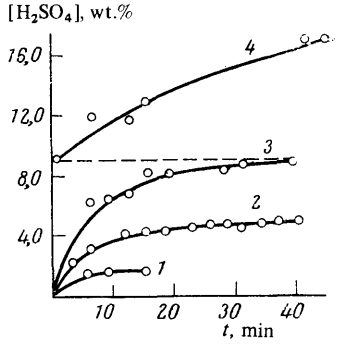



**Figure 9.** Variation of the concentration of the sulphuric acid formed with the regeneration time for dry charcoal (curve *1*), charcoal saturated with moisture after a single cycle (curve *2*), after two cycles (curve *3*), and after four cycles (curve *4*)[112]; SKT-2 charcoal; temperature 30–38°C.

There are data showing that, in the adsorption of $SO_2$, it is possible to obtain a 40% concentration of the acid[20]. However, in this case the gaseous mixture must contain 20 vol.% $SO_2$ and 80 vol.% $O_2$.

Thus the results presented above show that the sorption of sulphur dioxide by carbonaceous adsorbents is a complex physicochemical process, the rate of which and the absolute degree of adsorption of $SO_2$ depend not only on the composition of the gaseous mixture and the specific surface of the adsorbent, but also on its catalytic activity in relation to the oxidation of $SO_2$ to $SO_3$. The latter is in its turn determined by the specific properties of the adsorbent, for example, by the coverage of its surface by surface oxides, by the presence of the appropriate catalysts, and other factors.

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# The Electrochemistry of the π-Complexes and Organometallic Compounds of Transition Metals

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The results of electrochemical studies on the oxidation-reduction reactions of the π-complexes and organometallic compounds of transition metals are surveyed and described systematically. They are compared with other physicochemical properties of compounds of this class.
The bibliography includes 272 references.

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VI. Electrochemical synthesis of π-complexes of transition metals and of complex organometallic catalysts

## I. INTRODUCTION

The application of electrochemical methods (classical polarography, potentiometry, voltamperometry, chronopotentiometry, etc.) in the study of the oxidation-reduction reactions of the π-complexes and organometallic compounds of transition metals yields quantitative information about one of the most important properties of these compounds—their capacity to give up and accept electrons. The undoubted advantage of electrochemical methods is that they make it possible to investigate the distribution of electron density in the molecule and the relative positions of the highest occupied and lowest vacant orbitals for a number of compounds with similar structures. Such information is important for the complicated molecules of the π-complexes and organometallic compounds of transition metals with their unusual type of bonding, for which quantum-chemical calculations are still very laborious and require considerable computer time. It is useful to survey data obtained in electrochemical studies on compounds of this class, since the above properties of the complexes may be of interest for many electrochemists and chemists working on organometallic compounds. The results of the electrochemical study of the π-complexes are particularly significant for the chemistry of these compounds, since they characterise the state and behaviour of the molecules in solutions, i.e. under the conditions where the majority of chemical reactions are carried out.

The results of electrochemical studies are grouped in the present review in terms of types of complexes investigated, since the electrochemical reactions of complexes of the same type as a rule proceed via the same mechanism. Particular attention has been devoted to the problem of the location of the electronic changes in the electrochemical reactions of the complexes. Depending on the relative contribution of the ligand molecular orbital and the metal atomic orbital to the molecular orbital of the complex, it is useful to distinguish three types of location of the electronic changes in the π-complexes and organometallic compounds of transition metals: (1) in the molecular orbital of the complex to which the atomic orbital of the metal makes the main contribution; (2) in the molecular orbital of the complex to which the molecular orbital of the ligand makes the main contribution; (3) in the antibonding orbital of the localised metal–ligand σ-bond. The principal procedures used to solve the problem of the location of the electronic changes in the complexes have already been formulated in a review[1]. In many cases the properties of charged species (radical-cations and radical-anions), formed as a result of the electrochemical reactions of the complexes, have also been discussed.

Brief information concerning the electrochemical behaviour of individual representatives of the π-complexes and organometallic compounds of transition metals may be found in a number of reviews[2-4]. However, a full discussion of studies on the electrochemistry of such π-complexes and organometallic compounds has not so far been published. The present review does not include the results of electrochemical studies on the coordination compounds of transition metals and transition metal complexes with donor–acceptor ligands without at least one metal–carbon bond [for example $M(PR_3)_n$]; however, in these cases, references are given wherever necessary to the most important studies in this field. The review covers the literature up to 1975 inclusive.

## II. ELECTROCHEMICAL BEHAVIOUR OF SANDWICH COMPLEXES

A characteristic feature of neutral complexes of this type is that the metal is enclosed in a stable hydrocarbon shell and that its direct contact with solvent molecules or the electrode is hindered.

### 1. Dicyclopentadienyl and Bisarene Complexes

Reactions involving a change in the formal oxidation state of the metal atom are characteristic of π-complexes of the sandwich type (dicyclopentadienyl and bisarene complexes). The neutral compounds $(\pi\text{-}C_5H_5)_2M$ and $(\pi\text{-}C_6H_6)_2M$ as a rule undergo reversible one-electron oxidation at the electrode with formation of the corresponding cations $[(\pi\text{-}C_5H_5)_2M]^+$ and $[(\pi\text{-}C_6H_6)_2M]^+$. These reactions have been investigated in greatest detail in relation to dicyclo-

pentadienyl compounds and, particularly, ferrocene†. The ferrocene–ferrocenium cation pair is one of the most reversible oxidation-reduction systems under homogeneous conditions. Electron exchange between the oxidised and reduced forms in this system is of the outer-sphere type and proceeds at a high rate, greatly exceeding the rate of electron exchange in rapidly exchanging systems such as, for example, $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$.[7] This means that[8,9], in the transition from the reduced to the oxidised form, there should be no significant changes in the coordination spheres and in the geometry of the complex. Indeed, X-ray diffraction studies have shown that the ferrocenium cation, like ferrocene itself, has a sandwich structure with analogous bond lengths and valence angles. Quantum-chemical calculations on ferrocene[10] and the ferrocenium cation[11,12] as well as experimental data obtained from the photoelectronic spectra of ferrocene[13,14], from magnetic susceptibility measurements[14], and from the ESR spectra of the ferrocenium cation[16,17] have shown that the highest occupied molecular orbital of ferrocene, from which an electron is removed on oxidation, is the weakly bound orbital of the $e_{2g}$ type formed mainly by the $3d$ orbitals of iron ($d_{xy}$, $d_{x^2-y^2}$).

It has been shown by classical polarography at platinum[18–23] and dropping mercury electrodes[21–25] (in aprotic[22,23,26] and protic[21,25,27] media), chronopotentiometry[28–30], oscillographic and a.c. polarography[31–33], and potentiometry[34,35], using for each method standard criteria of the reversibility of the electrochemical reactions, that the electrode reactions involving the oxidation of ferrocene and the reduction of ferrocenium consist in the reversible transfer of a single electron‡. However, it has been observed that the electrode reaction of ferrocene in many organic solvents may be complicated by the subsequent chemical reaction (overall *EC* mechanism) due to the instability of the resulting ferrocenium cation in these solvents[37,39].

The electrochemical behaviour of heavier ferrocene analogues—ruthenocene and osmocene—differs by a number of characteristic features. Ruthenocene undergoes irreversible electrochemical oxidation at a platinum electrode[23,29,40] with abstraction of two electrons. The most probable product is $[(C_5H_5)_2Ru]^{2+}$; however, it has not been possible to isolate salts of this cation owing to their instability§. The oxidation of osmocene at a platinum electrode involves the stepwise abstraction of two electrons[23,29]. The electrochemically irreversible removal of the first electron leads to the formation of a singly-charged cation, which has been isolated in the form of the salt $(C_5H_5)_2OsBF_4$. The observed differences in the behaviour of ferrocene ruthenocene, and osmocene are probably caused by the differences in their electronic structures¶. In conformity with the higher Lewis basicity of ruthenocene and osmocene compared with ferrocene[23], the former two compounds give rise to waves at the dropping mercury electrode (DME) due to the reactions of these metallocenes with the mercury anode[23,41]†:

$$2(C_5H_5)_2M + Hg \rightleftarrows [(C_5H_5)_2M]_2Hg^{2+} + 2e \quad ;$$
$$M = Ru, Os .$$

The electronic changes at the metal atom take place also in the oxidation-reduction reactions of cobaltocene ($d^9$) and nickelocene ($d^{10}$). The reversible ($k_S = 0.98$ cm $s^{-1}$)[43] one-electron oxidation of cobaltocene[25,43–45] and its derivatives[46,47] to the cobaltocenium cation proceeds very readily. Because of this, it is more convenient to employ as the depolariser in electrochemical studies the stable cobaltocenium cation rather than the neutral cobaltocene. The cation gives rise to a cathodic wave, whose half-wave potential $E_{1/2}$ coincides with $E_{1/2}$ for its anodic wave. It has been found that the bisindenylcobalt cation is reduced much more readily[44,48] than the cobaltocenium cation, as has been observed for bisindenyliron complexes[49].

The one-electron reversible oxidation of nickelocene in aprotic[50] and protic[21,51,52] media leads to the formation of the nickelocenium cation. It has been observed by voltamperometry that the cation undergoes further oxidation to $[(C_5H_5)_2Ni]^{2+}$, which reacts extremely readily with nucleophiles[53,54].

The available information about the electrochemical behaviour of the dicyclopentadienyl complexes of other metals is limited. It has been shown that[55,56] $[(C_5H_5)_2V]^{2+}$ combines with a single electron and is reversibly reduced to $[(C_5H_5)_2V]^+$, which has two unpaired electrons. Two reduction waves were obtained on the polarogram of $[(C_5H_5)_2Nb]^+$, while $[(C_5H_5)_2Ta]^{3+}$ does not undergo polarographic reduction. In an aqueous alcoholic medium, $[(C_5H_5)_2Rh]^+$ gives rise to a cathodic wave, while $[(C_5H_5)_2.Ir]^+$ is not reduced under these conditions[51,52]. The electrochemical reduction of the dicyclopentadienylvanadium complexes with chelating ligands L of different types has been investigated in greater detail. It has been shown[57–59] that the reduction at a mercury electrode proceeds via the *EC* mechanism:

$$[(C_5H_5)_2V^{IV}L]^+ + e \rightleftarrows [(C_5H_5)_2V^{III}L]^0 \quad ;$$
$$[(C_5H_5)_2V^{III}L]^0 \xrightarrow{k} [(C_5H_5)_2V^{III}] + L \quad .$$

The electrochemical behaviour of sandwich bisarene complexes has been studied in relation to bisbenzenechromium ($d^6$). It has been shown[26,60–62] that it is readily oxidised to the cation $[(\pi\text{-}C_6H_6)_2Cr]^+$ ($d^5$). The electrode reaction is reversible under all the conditions investigated (aprotic medium[26,44,60,63,64] or protic medium[61,62,65–73]). There is a possibility of further oxidation of $[(\pi\text{-}C_6H_6)_2Cr]^+$ at a platinum electrode[74]:

$$[(\pi\text{-}C_6H_6)_2Cr]^+ - 2e \rightarrow Cr^{3+} + 2C_6H_6 \quad .$$

† A brief description of the electrochemical properties of the ferrocene–ferrocenium cation system as well as other biscyclopentadienyl compounds can be found in a number of reviews on the chemistry of metallocenes[5,6].

‡ However, there is a brief communication[36], unsupported by sound evidence, concerning the equilibrium $[(C_5H_5)_2Fe]_2^+ \rightleftharpoons (C_5H_5)_2Fe + [(C_5H_5)_2Fe]^+$ and the electrochemical irreversibility of the $(C_5H_5)_2Fe/[(C_5H_5)_2Fe]^+$ system.

§ The chemical oxidation of ruthenocene by $FeCl_3$ or $Br_2$ leads to the formation of the stable salts $[(C_5H_5)_2RuCl].FeCl_4$ and $[(C_5H_5)_2RuBr]Br_3$. The introduction of halogens into the inner coordination sphere apparently stabilises the +4 formal oxidation state of ruthenocene[23].

¶ It has been stated[13] that the ionisation energies of the highest occupied orbitals of ruthenocene and osmocene are similar (7.25 and 7.23 eV) and that the energies of the orbitals of the $e_{2g}$ and $a_{1g}$ types in ruthenocene are much smaller (0.18 eV) than in ferrocene (0.35 eV). The highest occupied orbital in osmocene is apparently the $a_{1g}$ orbital (and not $e_{2g}$ as in ferrocene).

† It was suggested initially[42] that ruthenocene and osmocene are oxidised to the corresponding cations at the DME.

Polarograms of $[(\pi\text{-}C_6H_6)_2Cr]^+$ at the dropping mercury electrode in aqueous solutions frequently exhibit adsorption prewaves associated with the low solubility of the reduced form of the complex, namely $(C_6H_6)_2Cr$.[66,70-73] Measurements of the electrocapillary curves for the cation $[(\pi\text{-}C_6H_6)_2Cr]^+$ showed that the reduction proceeds in the adsorbed layer[71]. The area occupied by a single cation $[(C_2H_5C_6H_5)_2Cr]^+$ is 19.2 Å$^2$.[72] The diffusion coefficients of $[(C_6H_6)_2Cr]^+I^-$ have been measured in various media[44,61]. The differences between the half-wave potentials $E_{1/2}$ for the reduction of two structurally similar non-coordinated ligands ($C_6H_6$ and $C_6H_5-C_6H_5$) and their complexes with a chromium atom have been used to estimate the relative contribution of the atomic orbital of the metal and the molecular orbitals of the ligands to the molecular orbital of the bisarene complex, where electronic changes occur during the oxidation-reduction reaction[65]. The coefficient $C_2^2$ for the mixing of the atomic orbital of the metal and the molecular orbital of the ligand in the molecular orbital of the complex in which electronic changes take place during the oxidation-reduction process was calculated from the formula

$$(E^1_{1/2} - E^2_{1/2})_{\text{complex}} = C_2^2 (E^2_{1/2} - E^1_{1/2})_{\text{ligand}} .$$

It was found to be 0.15, which implies that the contribution of the ligand orbital to the molecular orbital of the complex where electronic changes take place during the oxidation of bisbenzenechromium is not more than 15% and this orbital is therefore mainly the atomic orbital of chromium.

The electrochemical properties of the bisarene complexes of other Group VIB metals have been inadequately investigated owing to their low stability. It has been noted that the reversible oxidation of $(\pi\text{-}C_6H_6)_2Mo$ proceeds with somewhat greater difficulty ($E_{1/2} = -0.71$ V) than that of $(\pi\text{-}C_6H_6)_2Cr$ ($E_{1/2} = -0.80$ V).[62] Although the available data are clearly insufficient, they nevertheless indicate that the abstraction of an electron from sandwich compounds of transition metals becomes more difficult on going from downwards in isostructural and isoelectronic series of the Periodic System.

It has been shown that the bisareneiron complexes, which exist in the form of dications, and their heteroanalogue bisthiopheniron are reduced in two stages[75]:

$$[\pi\text{-}L_2Fe]^{2+} + e \rightleftarrows [\pi\text{-}L_2Fe]^+ \rightarrow [\pi\text{-}L_2Fe] .$$

(L = tetramethylthiophen, mesitylene, and hexamethylbenzene).

Sandwich compounds with two different ligands possess electrochemical properties similar to those of their homoligand analogues. Reversible one-electron reactions at the electrode, proceeding with a change in electron density mainly in the metal atom, are also characteristic of these substances. A study of the polarographic behaviour of the cations $[\pi\text{-}C_5H_5Fe\text{-}\pi\text{-arene}]^+$ (arene = $C_6H_6$, biphenyl, naphthalene, anthracene, or phenanthrene) in an aprotic medium has shown[76,78] that the product of the reversible one-electron reduction is a neutral complex of formally univalent iron. The complexes of other metals have been little investigated. It is known only that the reduction of $[\pi\text{-}C_5H_5CrC_7H_7]^+$ in an aprotic medium also proceeds reversibly with addition of one electron[79], while the reversible one-electron oxidation of $\pi\text{-}C_5H_5VC_7H_7\text{-}\pi$ leads to the formation of the unstable cation $[\pi\text{-}C_5H_5.VC_7H_7]^+$.[80,81]

## 2. Sandwich π-Complexes and Their Cations as Standard Oxidation-reduction Systems

The $(C_5H_5)_2Fe/[(C_5H_5)_2Fe]^+$ and $(C_5H_5)_2Co/[(C_5H_5)_2Co]^+$ systems have been suggested[82-87] and widely used (see the relevant references in the papers by Duschek and Gutmann[88] and Coetzee and Campion[89]) as standards to which the potentials measured in various media are referred. Their use as standard systems is based on Strehlow's hypothesis that the free energies of solvation of the above metallocenes and their cations are the same in different solvents. The above redox pairs have considerable advantages over familiar systems such as $Rb/Rb^+$ and $Cs/Cs^+$. Metallocenium cations are even larger than heavy alkali metal ions and the charged atom is located between two cyclopentadienyl rings, which hinders their solvation. However, subsequent studied showed[31,38,89] that the wide-scale employment of the $(C_5H_5)_2Fe/[(C_5H_5)_2.Fe]^+$ system as a standard is hindered by a number of limitations. It has been found that, owing to the specific interaction of $[(C_5H_5)_2Fe]^+$ with water, the hypothesis that $\Delta G_{(C_5H_5)_2Fe} = \Delta G_{(C_5H_5)_2Fe^+}$ does not hold in water and water-organic solvent mixtures as well as formamide. Furthermore, owing to the instability of $[(C_5H_5)_2Fe]^+$ in organic solvents, the $(C_5H_5)_2Fe/[(C_5H_5)_2Fe]^+$ system does not yield satisfactory results in potentiometric measurements in the majority of organic solvents. Thus the ferrocene–ferrocenium cation system is not an ideal standard system and its employment is possible only in relatively similar organic solvents in polarographic and voltamperometric measurements. The $(C_5H_5)_2Co/[(C_5H_5)_2.Co]^+$ system is probably likewise not ideal owing to its negative standard potential (for example, −0.98 V in acetonitrile). According to Gutmann and coworkers[90,91] the larger radius of $[(C_6H_6)_2Cr]^+$ compared with that of $[(C_5H_5)_2M]^+$ and the absence of specific interactions with water make the $(C_6H_6)_2Cr/[(C_6H_6)_2Cr]^+$ system more promising for these purposes than the two previous ones.

## 3. An Electrode Reversible with Respect to the Ferrocenium Cation

The high rate of electron exchange between the oxidised and reduced forms of the ferrocene–ferrocenium cation system as well as the virtual insolubility of ferrocene and its derivatives in aqueous solutions made it possible to devise an electrode reversible with respect to ferrocenium cations[92] derived from both unsubstituted ferrocene and its derivatives[93]. In the study of the properties of the ferrocene–ferrocenium electrode, the following galvanic cells were used:

$$\text{Pt} \mid \underline{\text{Fe}(C_5H_5)(C_5H_4R)}, \ \text{Fe}(C_5H_4R)(C_5H_5)^+X^- \mid \underline{\text{KCl}}, \ \underline{Hg_2Cl_2} \mid \text{Hg}.$$

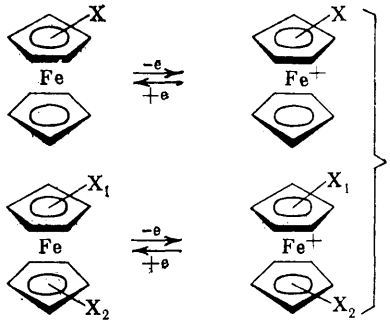
The ferrocene–ferrocenium electrode has been employed to investigate the properties of the ferrocenium cation in solutions: thermodynamic stability in aqueous solutions[94], hydrolytic decomposition[95], complex formation[96,97], and determination of the heat of hydration[98,99].

A perchlorate electrode[100], retaining the perchlorate response in solutions containing oxidants and reductants, has been devised on the basis of alkylferrocenes and the corresponding alkylferrocenium perchlorates.

4. The Electronic Effects of Substituents in the Oxidation-reduction Reactions of $\pi$-Complexes of the Sandwich Type

Electrochemical methods have been used successfully to investigate the nature of the electronic influence of substituents on the reaction centre (the transition metal atom) in oxidation-reduction reactions [29,34,35,101-108]. This problem has been investigated in greatest detail in the following reaction series: monosubstituted ferrocenes [108], heteroannular disubstituted ferrocenes [108], arenecyclopentadienyliron cations with substituents in the arene or cyclopentadienyl ring [76], and bisbenzenechromium derivatives [109]. In all cases, systematic correlation analysis with different sets of substituent constants $\sigma$ showed that the best linear relation is observed when Taft's $\sigma_\pi^0$ constants are used. Furthermore, the additivity of the influence of substituents, located in different rings of the molecule, on the oxidation potential of the metal atom was demonstrated for heteroannular disubstituted ferrocenes [108] and alkyl derivatives of bisbenzene chromium [109].

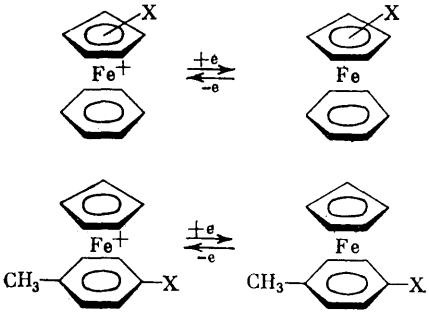
The results obtained led to the hypothesis that the nature of the influence of substituents in the above reaction series‡ differs from the influence of substituents in classical aromatic systems by the fact that there is no direct polar conjugation of the substituent with the reaction centre and that mainly the overall inductive component of the total polar influence of substituents is transmitted to both the metal atom and to the other ring. If the substituent is separated from the ferrocenyl nucleus by a methylene group ($\pi$-$C_5H_5Fe$-$\pi$-$C_5H_4$-$CH_2$-X), preventing the conjugation of X with the five-membered ring, a satisfactory linear relation is observed between $E_f^0$ and the inductive constants $\sigma_i$ of the corresponding substituents. The observed relation has been used successfully to determine the $\sigma_i$ for metallocenyl groups and other polyatomic groups [X = $\pi$-$C_5H_5FeC_5H_4$, $\pi$-$C_5H_5Fe^+$-$\pi$-$C_5H_4$, $\pi$-$C_5H_5Ru$-$\pi$-$C_5H_4$, $\pi$-$C_6H_5Cr(CO)_3$, or $\pi$-$C_6H_5Cr(CO)_3$] [1§].




$E_f^0 = (+0.50\sigma_n^0 - 0.272)$v;

‡ A similar type of influence of substituents has been found in "non-electrochemical" reaction series [110] and reflects a general property of the metal-$\pi$-ligand bond, namely its ability to transmit mainly the inductive component of the total polar influence of substituents in the direction of the metal atom and other ligands.

§ The oxidation-reduction potentials of the ferrocene-ferrocenium cation system have been correlated with other physicochemical parameters of ferrocene derivatives (absorption maxima in ultraviolet spectra [111], $S_N1$ solvolysis rate constants [112], etc.




$E_{1/2} = (+0.52\sigma_n^0 - 1.39)$v;

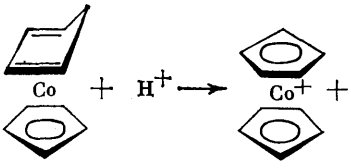
$E_{1/2} = (+0.515\sigma_n^0 - 1.42)$v.

5. Electrochemical Properties of Biferrocenyls

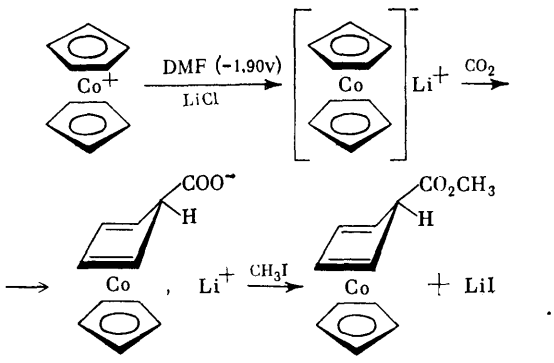
The electrochemical oxidation of biferrocenyl ($\pi$-$C_5H_5Fe$-$\pi$-$C_5H_4$)$_2$ and biferrocenylene ($\pi$-$C_5H_4Fe$-$\pi$-$C_5H_4$)$_2$ proceeds in two one-electron stages [30,113-116]. The first oxidation stage is reversible [30] and leads to a mixed valence Fe(III)-Fe(II) compound [117]. The electron transfer reaction Fe(II)*-Fe(III) $\rightleftharpoons$ Fe(III)*-Fe(II) takes place in the resulting monocation between the oxidised and neutral ferrocenyl nuclei [114,115]. The second electron is apparently abstracted irreversibly [30], which corresponds to the oxidation of the second ferrocenyl nucleus with formation of the Fe(III)-Fe(III) dication. The introduction of a bridge group between the two ferrocenyl nuclei of biferrocenyl and biferrocenylene leads to an appreciable decrease of the difference between the potentials of the first and second oxidation stages. When X = $-CH_2-CH_2-$, $-Hg-$, $-(CH_3)_2C-C(CH_3)_2-$, or $-CH=CHC_6H_4CH=CH-$, biferrocenyl is oxidised in a single two-electron stage [114]. When X = $-C\equiv C-$, the oxidation proceeds in two stages with similar values of $E_{1/2}$. [118] It has been shown that compounds with metal atoms in different oxidation states can be formed when $\pi$-arenebis-($\pi$-cyclopentadienyliron) dications are reduced at the dropping mercury electrode [119].

6. Electrochemical Reduction of Neutral $\pi$-Complexes of the Sandwich Type

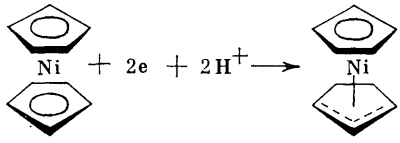
Together with oxidation, electrochemical reduction reactions have been observed for neutral metallocenes (cobaltocene and nickelocene) [22]. In an aprotic medium (1,2-dimethoxyethane) [43] or in an alkaline medium at pH > 11, [47] cobaltocene undergoes reversible electrochemical reduction ($k_S$ = 0.3 cm s$^{-1}$, $E_{1/2}$ = -1.89 V) ($n$ = 1) to the previously unknown anion ($\pi$-$C_5H_5$)$_2$Co$^-$ containing the cobalt atom in the formal +1 oxidation state. In a more acidic medium (pH < 8) or acetonitrile, the anion formed reacts with a proton of the solvent, forming $\pi$-$C_5H_5Co$-$\pi$-$C_5H_6$. [120] A decrease of pH to 0-1 results in an increase of the height of the reduction wave owing to the catalytic evolution of hydrogen [120]:



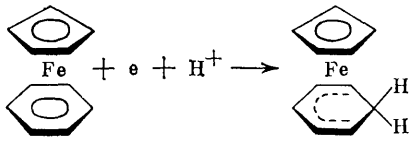
The high reactivity of $(\pi\text{-}C_5H_5)_2Co^-$ has been used in electrochemical syntheses [121]:




The anion $[(C_5H_5)_2Co]^-$ completes the series of cobalt complex $[(C_5H_5)_2Co]^+$ $(d^8)$, $(C_5H_5)_2Co$ $(d^9)$, and $[(C_5H_5)_2Co]^-$ $(d^{10})$ isoelectronic with the analogous nickel compounds: $[(C_5H_5)_2Ni]^{2+}$ $(d^8)$, $[(C_5H_5)_2Ni]^+$ $(d^9)$, and $(C_5H_5)_2Ni$ $(d^{10})$. A cathodic wave is also observed on the polarogram of neutral nickelocene. By analogy with chemical reduction, it is suggested [22] that in this case the reduction proceeds via the ligand in accordance with the following mechanism:




A reaction via the ligand has also been suggested in the reduction of neutral $\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_6H_6$: [76]




## 7. Electrochemical Properties of Dicarbollyl $\pi$-Complexes

Like the dicyclopentadienyl compounds, the dicarbollyl complexes of transition metals, having the general formulae $(\pi\text{-}B_9C_2H_{11})_2M$ and $(\pi\text{-}B_9C_2H_{11})M(\pi\text{-}C_5H_5)$ [122] and the sandwich structure, undergo oxidation-reduction reactions, which lead to a change in the formal oxidation state of the metal atom. The study of the electrochemical behaviour of the dicarbollyl complexes of iron [123], cobalt [123-125], nickel [53,123,124,126,127], palladium [126,128], gold, and copper [128] showed that, in contrast to the $\pi$-cyclopentadienyl ligand, the $\pi$-dicarbollyl ligand stabilises the metal in both the highest and lowest oxidation states. Thus a series of electrochemically reversible one-electron transitions have been observed for the dicarbollyl complexes of cobalt, nickel, and palladium:

$$Co^{IV} \underset{+1.57\ V}{\rightleftharpoons} Co^{III} \underset{-1.36\ V}{\rightleftharpoons} Co^{II} \underset{-2.24\ V}{\rightleftharpoons} Co^{I} \quad ;$$

$$Ni^{IV} \underset{+0.18\ V}{\rightleftharpoons} Ni^{III} \underset{-0.56\ V}{\rightleftharpoons} Ni^{II} \underset{-2.10\ V}{\rightleftharpoons} Ni^{I} \quad ;$$

$$Pd^{IV} \underset{-0.47\ V}{\rightleftharpoons} Pd^{III} \underset{-0.71\ V}{\rightleftharpoons} Pd^{II} \quad .$$

It is interesting that isomeric dicarbollyl complexes, differing in the positions of the carbon atoms in the plane with the metal atom, have half-wave potentials $E_{1/2}$ differing by a very large amount (up to 0.5 V).

As for the ferrocene–ferrocenium cation system, the rate constants for electron transfer between the oxidised and reduced forms, namely $[(B_9C_2H_{11})_2Fe]^{2-}$ and $[(B_9C_2H_{11}).Fe(C_5H_5)]^-$, are high [129]. Owing to the large bulk of the dicarbollyl ligand, an arrangement of molecules in the transition states of these compounds of the "sitting on top" type is unlikely. One can therefore assume that, in both dicarbollyl complexes and in the ferrocene–ferrocenium system, the molecules in the transition state are arranged "side by side". It is useful to express the data described in Section II in terms of a scheme (see Table below) including only electrochemically reversible oxidation-reduction systems.

## III. ELECTROCHEMICAL REACTIONS OF THE FUNCTIONAL GROUPS OF THE LIGAND BOUND IN THE $\pi$-COMPLEX

Apart from the electrochemical reactions involving the metal atom, fairly numerous reactions with participation of the functional groups of the ligand bound in the $\pi$-complex are known. The study of these reactions proved fruitful from the standpoint of the quantitative estimation of the electronic influence of metallocenes as substituents and in the study of the problem of the influence of coordination on the reactivity of ligands bound in $\pi$-complexes.

The numbers of electrons around the metal atom.

| 16e | | 17e | | 18e | | 19e | | 20e |
|---|---|---|---|---|---|---|---|---|
| $[CpVC_7H_7]^+$ | $\underset{}{\overset{+0.18V}{\rightleftharpoons}}$ | $CpVC_7H_7$ | | | | | | |
| | | $[CpCrC_7H_7]$ | $\underset{}{\overset{-0.70V}{\rightleftharpoons}}$ | $CpCrC_7H_7$ | | | | |
| | | $[(C_6H_6)_2Cr]^+$ | $\underset{}{\overset{-0.80V}{\rightleftharpoons}}$ | $(C_6H_6)_2Cr$ | | | | |
| | | $[Cp_2Fe]^+$ | $\underset{}{\overset{+0.31V}{\rightleftharpoons}}$ | $Cp_2Fe$ | | | | |
| | | | | $[CpFeC_6H_6]^+$ | $\underset{}{\overset{-1.46V}{\rightleftharpoons}}$ | $CpFeC_6H_6$ | | |
| | | | | $[(C_6H_6)_2Fe]^{2+}$ | $\underset{}{\overset{-0.30V}{\rightleftharpoons}}$ | $[(C_6H_6)_2Fe]^+$ | | |
| | | | | $[Cp_2Co]^+$ | $\underset{}{\overset{-0.80V}{\rightleftharpoons}}$ | $Cp_2Co$ | $\underset{}{\overset{-1.90V}{\rightleftharpoons}}$ | $[Cp_2Co]^-$ |
| | | | | $[Cp_2Ni]^{2+}$ | $\underset{}{\overset{+0.75V}{\rightleftharpoons}}$ | $[Cp_2Ni]^+$ | $\underset{}{\overset{+0.01V}{\rightleftharpoons}}$ | $Cp_2Ni$ |

Cp = cyclopentadienyl

The electrochemical reactions of the functional groups in the coordinated ligand proceed mainly via mechanisms similar to those which have been established for the analogous substituents in aromatic rings. In accordance with its electronic properties, the metal-containing group alters only the potential of the electrochemical reaction of the substituent, which permits conclusions concerning the electronic effects of the metal-containing group. The polarographic reduction of acyl derivatives of $\pi$-complexes has been investigated in greatest detail. It has been demonstrated [130-132] that the mechanism of the polarographic reduction of the acetyl derivatives of ferrocene [$(\pi$-$C_5H_5)Mn(CO)_3$ and $\pi$-$C_6H_6Cr(CO)_3$] and benzene in a protic medium are identical. The results led to the conclusion that the ferrocenyl group is more electropositive than $C_6H_5$ and is close to pyrrole on the electron affinity scale, while $(CO)_3MnC_5H_4$- and $(CO)_3CrC_6H_5$- are more electronegative than phenyl. The results of the polarographic reduction of $(CO)_3Cr(C_6H_5COCH_3)$ in an aprotic medium lead to the analogous conclusion about the electronic properties of the $C_6H_5Cr(CO)_3$ groups [133].

The $\sigma$ constants ($\sigma_p$, $\sigma_m$, $\sigma_p^0$, and $\sigma_m^0$), characterising quantitatively the electronic influence of ferrocenyl as a substituent, have been calculated [134] on the basis of the correlation between the half-wave potentials $E_{1/2}$ for the reversible one-electron reduction of the C=C bond in the chalcones $C_5H_5FeC_5H_4CH{=}CHCOC_6H_4X$ (*m*, *p*), $C_5H_5FeC_5H_4$.$COCH{=}CHC_6H_4X$ (*m*, *p*), $C_6H_5CH{=}CHCOC_6H_4X$ (*m*, *p*), and $C_6H_5COCH{=}CHC_6H_4X$ (X = $OCH_3$, $CH_3$, F, Cl, Br, or $CNC_5H_4FeC_6H_5$). It was first shown [130,135-139] that ferrocenyl-containing chalcones are reduced in the same way as aromatic chalcones. The polarographic reduction of ferrocenyl aldehydes [139,140] and of nitrogen-containing derivatives of acetylferrocenes of the type $C_5H_5FeC_5H_4CR{=}NA$ [135] also proceed analogously to the reduction of the corresponding benzene derivatives. In conformity with the electron-donating properties of the ferrocenyl group, the half-wave potentials $E_{1/2}$ for these derivatives are displaced towards negative potentials.

It has been established for the quinone complexes of rhodium and iridium [141] that the polarographic reduction of the coordinated quinones proceeds with greater difficulty than that of the free quinones. The half-wave potentials $E_{1/2}$ for the first reversible one-electron quinone waves are displaced towards more negative values by 0.9, 1.1, 0.6, and 0.3 V as a result of the coordination to the $RhC_5H_5$-$\pi$, $IrC_5H_5$-$\pi$, $RhC_9H_7$-$\pi$-indenyl, and Rh(acac) groups respectively. The ligands combined with the metal atom have been arranged in a series in terms of their donating capacity on the basis of the results obtained: $\pi$-$C_5H_5 > \pi$-$C_9H_7 >$ acac.

In a few instances, the application of electrochemical methods made it possible to demonstrate the formation of previously unknown functional derivatives of $\pi$-complexes. Thus the use of cyclic voltamperometry and of a rotating disc electrode with a ring showed [132-144] that the reduction of $C_5H_5FeC_5H_4NO_2$ at an amalgamated gold electrode in an alkaline medium proceeds via the intermediate formation of radical-anions. The reduction of the radical anion leads to the formation of previously unknown ferrocenylhydroxylamine:

$$C_5H_5FeC_5H_4NO_2 + e \rightleftarrows C_5H_5FeC_5H_4NO_2^{\cdot-} \quad ;$$

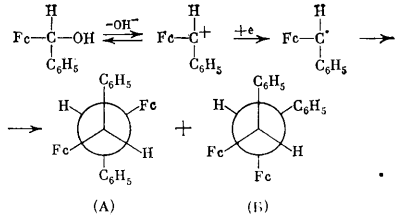
$$C_5H_5FeC_5H_4NO^{\cdot-} + 3e + 3H_2O \rightarrow C_5H_5FeC_5H_4NHOH + 4OH^- \quad .$$

In contrast to $C_6H_5NHOH$, ferrocenylhydroxylamine is extremely unstable and disappears as a result of a disproportionation reaction:

$$C_5H_5FeC_5H_4NHOH + [C_5H_5FeC_5H_4NH_2OH]^+ \rightarrow$$
$$\rightarrow C_5H_5FeC_5H_4NH_2 + Fe^{2+} + C_5H_5^{\cdot} + C_5H_4NO^- + H_2O + H^+ \quad .$$

Electrochemical methods are used fairly widely for the generation of radical-anions. It has been shown that the electrolysis of a number of ferrocene derivatives (benzoyl, *p*-nitrophenyl, cyano-, nitro-, and other derivatives) [145] and of the benzoyl derivative of cyclopentadienylmanganese tricarbonyl [146] leads to radical-anions, which give rise to ESR signals. The study of the distribution of the unpaired spin density in these species showed [145] that, when both the $C_6H_5$ group and the ferrocenyl group are present in the same molecule, the unpaired spin density is delocalised to a larger extent over the $C_6H_5$ group than over the ferrocenyl group.

The electrochemical reduction of a number of other ferrocene derivatives has also been investigated [147,148]. Thus electrolysis of ferrocenylmethanol, which is involved in an equilibrium with the ferrocenylcarbonium ion in an acid medium, proceeds via a one-electron mechanism with formation of a free radical (Fc = ferrocenyl):



The radical then dimerises with formation of the stereoisomers (A) and (B). [147] In this section, it is also appropriate to quote data on the polarographic studies of the mercury derivatives $R_2Hg$ and RHgX [R = ferrocenyl, $(CO)_3MnC_5H_4$, or $(CO)_3ReC_5H_4$], which are reduced similarly to the compounds $R_2^1Hg$ and R'HgX (R' = alkyl or aryl) [149]:

$$\left.\begin{array}{l} R_2Hg + 2e \rightarrow Hg^0 + 2R^- \xrightarrow{+2H^+} 2RH\ (R = C_5H_5FeC_5H_4)\ ; \\ RHgX + e \rightarrow RHg^{\cdot} \\ RHg^{\cdot} + e \rightarrow Hg^0 + R^- \xrightarrow{H^+} RH \end{array}\right\} (R = C_5H_5FeC_5H_4-,\ \text{or}\ (CO)_5MC_5H_4;\ M = Mn \text{ or } Re)$$

A linear correlation is observed between $E_{1/2}$ and $pK_a$(RH): $E_{1/2} = (-0.07pK_a + 0.16)$ (V); $r = 0.966$. The $pK_a$ values for ferrocene ($pK_a = 39$) and $(CO)_3MC_5H_5$ ($pK_a = 31$ for M = Mn and $pK_a = 30$ for M = Re) as CH acids were estimated from this relation [149-151].

## IV. ELECTROCHEMICAL REACTIONS OF METAL CARBONYLS AND THEIR DERIVATIVES

The electrochemical behaviour of metal carbonyl complexes containing n-donor ligands bound in $\pi$- and $\sigma$-complexes is extremely varied, primarily due to the differences between their electronic structures.

### 1. Metal Carbonyls

In contrast to chemical reduction, which has been investigated in fair detail (see, for example, Kaska [152]), the electrochemistry of metal carbonyls has been inadequately studied. It has been shown [26] that in dimethoxyethane singly-charged metal carbonyls $M(CO)_n$ (M = Fe, $n = 5$; M = V, $n = 6$; M = Ni, $n = 4$) combine as a rule with one electron and the process is electrochemically irreversible. $Fe(CO)_5$ and $Ni(CO)_4$ form short-lived paramagnetic species giving rise to ESR signals; however, the nature of these species is obscure. In a protic medium ($C_2H_5OH-H_2O$), $Fe(CO_5)$ is reduced with addition

of two electrons and the dissociation of the M–CO bond[153]. As in the initial compound, in the product $Fe(CO)_4^{2-}$ an 18-electron shell is formed around the metal atom. The polarographic reduction of $M(CO)_6$ (M = Cr, Mo, or W) in aprotic solvents proceeds via the following irreversible electrochemical mechanism[26,154,155]:

$$M(CO)_6 + e \rightarrow [M(CO)_6]^{\mp} \xrightarrow{-CO} [M(CO)_5]^{\mp} \rightarrow \frac{1}{2}[M_2(CO)_{10}]^{2-} .$$

The one-electron reversible voltamperometric oxidation of $Cr(CO)_6$ at platinum and gold electrodes ($E_{a.p.}$ = +1.44 V relative to the $Ag/Ag^+$ electrode) leads to the formation of the 17-electron cation $Cr(CO)_6^+$, which gives rise to a broad signal in the ESR spectrum[154,156]. At higher anodic potentials, a further electron is removed with formation of the unstable species $Cr(CO)_6^{2+}$. The oxidation of $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$ is electrochemically irreversible and involves the abstraction of two electrons. Dinuclear carbonyls containing the M–M bond are reduced at dropping mercury[26,157,158] and platinum electrodes[159,160] with dissociation of the M–M bond and the formation of 18-electron anions of the metal carbonyls (see below for further details).

The reduction of trinuclear $Fe_3(CO)_{12}$ proceeds with addition of one electron[26]; the reaction products are unknown.

## 2. Metal Carbonyl Complexes with n-Donor Ligands

(a) Oxidation. Compounds having the general formula $L_nM(CO)_m$ (L = amines, phosphines, isonitriles, or carbenes¶ and M = Cr, Mo, or W) are oxidised at a platinum electrode in methylene chloride with the loss of one electron and the formation of the corresponding cations[161–164]; the process is electrochemically reversible. The cations $[Mn(CO)_6 - n(CNR)_n]^+$ and $[Cr(NO)_2(CNR)_5]^+$ are oxidised to the dications, which are capable of further oxidation[165–167]. The half-wave potentials $E_{1/2}$ depend on the electronic properties of the ligand L, the number of CO groups, and the nature of the metal atom. The successive weakening of the $\pi$-acceptor properties of L, accompanied by the corresponding increase of the $\sigma$-donor capacity, leads to a shift of $E_{1/2}$ towards lower positive potentials. A similar result is obtained when $n$ in $[(RNC)_nM(CO)_{6-n}]$ is diminished, which is associated with the gradual substitution of the strong $\pi$-acceptor ligand CO by the less effective CNR. It has been shown for $Cr(CO)_5L$ (the L species are different phosphines) that there is a linear correlation between the values of $E_{1/2}$ for the oxidation of the complex and the ionisation potential of the free ligand L. It has been established[162] that the ease of abstraction of the electron from $[(RNC)_nM(CO)_{6-n}]$ diminishes in the sequence Cr > W > Mo.

The observed relations lead to the conclusion that both the atomic orbital of the metal and the molecular orbital of the ligand L contribute to the molecular orbital from which the electron is removed on oxidation. Studies on the ESR and Mössbauer spectra of the radical-cations generated on oxidation of the complexes CoL(CO)(NO), where L = $o$-phenanthroline or 2,2′-bipyridyl, in dimethoxyethane at a mercury electrode[168] have confirmed this view and have shown that the spin density is located in the molecular orbital to which predominantly $s$-type metal orbitals contribute together with the ligand orbitals. However, quantum-chemical calculations on molecules of the type $Cr(CO)_5L$ (L = $NH_3$, $PH_3$, or $PMe_3$) have shown, in contrast to electrochemical data, that the ligand orbitals do not contribute significantly to the highest occupied orbital of the complex, comprising mainly the $3d$(Cr), $2p$(C), and $2s$(O) orbitals. According to Lloyd et al.[163], this contradiction can be resolved if it is supposed that L has a long-range or indirect influence on the energy of the highest occupied orbital of the complex without a change in the relative contributions of the atomic orbitals.

The electrochemical oxidation of complexes with chelating diphosphine ligands, namely $M(CO)_2(DPE)_2$ and $M(CO)_2(DPM)_2$, where M = Mn, Cr, Mo, or W, DPE = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$, proceeds with the successive elimination of two electrons and the formation of cations and dications respectively; the stereochemistry of the electrochemical reactions has been investigated[169,170]. The available information concerning the oxidation of other complexes with $n$-donor ligands is limited. It has been shown, for example, that the oxidation of $M(CO)_3$(triarsine)† in a $C_2H_5OH-C_6H_6$ mixture at mercury and platinum electrodes proceeds with the elimination of two electrons and the formation of a dication[171]. In this section, it is also appropriate to mention the oxidation of the carbonyl hydride complexes $M(H)(CO)L_3$ (M = Rh or Ir and L = $PPh_3$).[172] The reversible oxidation of $Ir(H)(CO)L_3$ in acetonitrile at a platinum electrode leads to the formation of a fairly stable cation containing the metal in the unusual +2 oxidation state:

$$Ir(H)(CO)L_3 \rightleftarrows Ir(H)(CO)L_3^+ .$$

The oxidation of $Rh(H)(CO)L_3$ is irreversible. Owing to the instability of the Rh–H bond, the cation formed reacts further via the following mechanism:

$$Rh(H)(CO)L_3^+ \rightarrow M(CO)L_3^+ + {}^1/_2H_2 .$$

(b) Reduction. Octahedral chromium, molybdenum, and tungsten complexes $L_1M(CO)_5$ ($L_1$ = pyridine or quinoline) and $L_2M(CO)_4$ ($L_2$ = ethylenediamine or 2,2′-bipyridyl) and the tetrahedral cobalt and iron complexes $L_2Co(CO)(NO)$ and $L_2Fe(NO)_2$ ($L_2$ = $o$-phenanthroline or 2,2′-bipyridyl) are as a rule reduced in two electrochemically reversible one-electron stages with formation of radical-anions and dianions[60,168,173]. The reduction proceeds at less negative potentials than the reduction of the non-coordinated ligand L and in the case of the chromium, molybdenum, and tungsten complexes also at less negative potentials than the corresponding unsubstituted metal carbonyl. The radical-anions formed give rise to an ESR signal and exhibit an enhanced chemical stability compared with the radical-anions of the non-coordinated ligand. It has been concluded[168,173] on the basis of the similarity of the hyperfine splitting constants for the ESR spectra of the radical-anions of the complexes and the non-coordinated ligands that the electron occupies on reduction the antibonding $\pi$-orbital of the ligand L; the infrared spectra of the radical-anions showed that the addition of the electron does not lead to a change in the symmetry of the molecule. The absence of an ESR signal from the spectrum of the dianion showed that it exists in the singlet state. Analysis of the ESR, infrared, Mössbauer, and NMR spectra of the radical-anions and dianions led to a conclusion concerning the distribution of spin and charge densities in these species (for a more detailed treatment, see below).

¶ The M–C bond is present in carbenes.

† Triarsine = methylbis-(3-propyldimethyl)arsine.

The reduction of cobalt carbonyl nitrosyl complexes $Co(NO)(CO)L_{n-3}$ ($L = EPh_3$; E = P, As, or Sb) and iron carbonyl nitrosyl complexes $Fe(NO)_2(CO)_nL_{n-2}$ ($L = PPh_3$) (the formal degree of oxidation of the metal in the complexes is −1) in acetonitrile at the DME has been investigated[174-177]. Brief information concerning the electrochemical behaviour of other substituted carbonyl compounds can be found in a number of reports[26,60,179,180]. The reduction proceeds as a rule irreversibly and the reaction products have not been identified. The reduction of metal carbonyl compounds with an M—M bond and bridging phosphorus- and sulphur-containing ligands is discussed below.

## 3. Complexes Containing Hydrocarbon Ligands Bound in π-Complexes

(a) Complexes with two-electron ligands. The reduction reactions of the bipyramidal complexes (olefin)$Fe(CO)_4$ and carbonyl complexes with *n*-donor ligands (see the previous section) have much in common. The electrochemically reversible addition of one-electron to (olefin)$Fe(CO)_4$ leads to fairly stable radical-anions, where the unpaired electron is located in the antibonding π*-orbital of the olefin ligand[26,60,178]; the distribution of spin and charge densities in the radical-anions formed has been investigated by ESR, infrared spectroscopy, and Mössbauer spectroscopy (see below).

The cationic olefin complexes of platinum $[Pt(NH_3)_2.(RCH{=}CH_2)Cl]ClO_4$ (R = H, $CH_3$, $CH_2OH$, or $C_6H_5$) have been reduced at the dropping mercury electrode[181]. It was found that these complexes are reduced more readily than the initial amine complex $[Pt(NH_3)_3Cl]^+$.

(b) Complexes with three-electron π-allyl ligands. The electrochemical behaviour of π-allyl complexes $(\pi\text{-}C_3H_5MX)_2$ of platinum group metals, where the formal oxidation state of the metal is +2, is determined by the well known ease of reduction of these metal ions $M^{2+}$ and of their chloride complexes. $Pd^{2+}$ and $Pt^{2+}$ ions ions are reduced even with metallic mercury without the application of a potential difference[182,183]. The study of the reduction of $(\pi\text{-}C_3H_5PdX)_2$ (X = halogen) at the DME showed[183-186] that these compounds react with the mercury of the electrode:

$$(\pi\text{-}C_3H_5PdX)_2 + Hg \rightarrow Pd^0 + 2C_3H_5HgX \quad .$$

The waves observed on the polarogram correspond to the reduction of $C_3H_5HgX$. The diffusional nature of the waves shows that the preceding chemical reaction of the π-allyl complexes of palladium with mercury proceeds so fast that its rate does not affect the electrode reduction of $C_3H_5HgX$. The results suggest that the coordination of $Pd^{2+}$ to the π-allyl ligand has little influence on the capacity of $Pd^{2+}$ for reduction.

The electrochemical reduction of $\pi\text{-}(C_3H_5M)(CO)_3X$ (M = Fe or Ru) leads to the dissociation of the M—X bond (see Section V). $\pi\text{-}C_3H_5Fe(CO)_2NO$ and $\pi\text{-}C_3H_5Co(CO)_3$, which do not contain π-bonds, behave differently. The addition of two electrons leads to the dissociation of the π-bond between the allyl ligand and the metal atom[187,188]:

$$\pi\text{-}C_3H_5Fe(CO)_2NO + 2e \rightarrow [Fe(CO)_2NO]^- + C_3H_5^- \xrightarrow{+H^+} CH_2{=}CH{-}CH_3 \quad ;$$

$$\pi\text{-}C_3H_5Co(CO)_3 + 2e \rightarrow Co(CO)_3^- + C_3H_5^- \xrightarrow{H^+} C_3H_6 \quad .$$

(c) Complexes with four-electron ligands. The polarographic reduction of $(\pi\text{-diene})Fe(CO)_3$ at the dropping mercury electrode in aprotic media proceeds via the successive addition of two electrons, as was observed for the free diene ligand[189]. The first electrochemically reversible stage leads to the formation of a radical-anion, which gives rise to an ESR signal in the case of complexes with cyclic dienes[190]. In view of the identity of the polarographic characteristics of $(\pi\text{-diene})Fe(CO)_3$ and the free dienes, it was concluded that the electronic changes occurring on reduction of the complexes are localised in the antibonding π*-orbital of the diene ligand.

(d) Complexes with five-electron ligands. The electrochemical properties of monocyclopentadienylmetal carbonyls have been inadequately investigated. It has been shown[26,60,149] that $\pi\text{-}C_5H_5M(CO)_3$ (M = Mn or Re) and some of their derivatives are reduced at the DME, but the number of electrons added and the reaction products are unknown. The complexes $\pi\text{-}C_5H_5V(CO)_4$, $\pi\text{-}C_5H_5Co(CO)_2$, $\pi\text{-}C_5H_5W(CO)_2NO$, and $\pi\text{-}C_5H_5NiNO$ are reduced with addition of one electron, but the formation of a short-lived anion has been demonstrated only for the last two compounds[191].

The addition of one electron to the cationic complexes $[\pi\text{-}C_5H_5Fe(CO)_2L]^+$ ($L = CO$ or $PPh_3$) apparently leads to the formation of the dimer $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, the reduction of which gives rise to the second wave on the polarograms[60].

The one-electron oxidation of cyclopentadienylmanganese and cyclopentadienylrhenium tricarbonyls at a platinum electrode proceeds with much greater difficulty than, for example, the reduction of ferrocene under analogous conditions; cyclopentadienylrhenium tricarbonyl is oxidised at more positive potentials than cyclopentadienylmanganese tricarbonyl[192]. The replacement of carbonyl groups by the more strongly electron-donating phosphine ligands leads to a significant cathodic shift of the oxidation potentials and to an increase of the stability of the cation formed[193]:

$$\pi\text{-}C_5H_5M(CO)_2L \underset{+e}{\overset{-e}{\rightleftarrows}} [\pi\text{-}C_5H_5M(CO)_2L]^+ (M{=}Mn \text{ or } Re;\ L{=}PR_3) \quad .$$

The cationic nitrosyl complexes $[\pi\text{-}C_5H_5Mn(NO)LL']^+$ (L and L′ are Lewis bases such as $PR_3$ and amines) are oxidised to the dications[194]. The change in $E_{1/2}$ reflects the change in the π-acceptor properties of the Lewis bases as ligands.

The polarographic behaviour of π-cyclopentadienylmetal complexes with chelating ligands has been investigated in greater detail. It has been found that π-cyclopentadienyldithiolenemetal complexes are as a rule reduced reversibly in dimethoxyethane (with the addition of one electron and the formation of radical-anions, which give rise to an ESR signal[26,60,179]. The half-wave potentials $E_{1/2}$ of $\pi\text{-}C_5H_5MS_2C_4F_6$ depend on the nature of the metal atom and increase in the sequence Fe < Co < Ni (from left to right in Mendeleev's Table) and in the cobalt subgroup Co < Rh < Ir (from above downwards (see also McCleverty[195]). The anionic complexes $[\pi\text{-}C_5H_5MS_4C_4(CN)_4]^-$ (M = Ti, Mo, or W) are oxidised to neutral species at a platinum electrode in $CH_2Cl_2$ solution[196].

A detailed study of π-cyclopentadienylnitrosyldithiolenemanganese complexes showed that those with 1,2-dithiolenes are capable of reversible oxidation and reduction to radical-cations and radical-anions respectively. The complexes of 1,1-dithiolenes are capable of one-electron reduction only, while dithiocarbamates and thioxanthates

are capable of one-electron oxidation [194,196-198]. The paramagnetic species have been characterised by their ESR spectra.

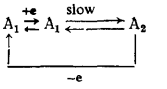
(e) Arenemetal carbonyl complexes. It follows from chemical data‡ that ($\pi$-arene)$Cr(CO)_3$ complexes are oxidised with greater difficulty than ($\pi$-arene)$_2$.Cr. Indeed, the complexes ($\pi$-$C_6H_5X$)$Cr(CO)_3$ are oxidised at a platinum electrode in $CH_2Cl_2$ in two electrochemically reversible stages at fairly considerable positive potentials [199,200]. The values of $E_{1/2}$ for the first waves are sensitive to the nature of the substituent in the benzene ring (X = alkyl or $NR_2$). A linear relation has been observed between $E_{1/2}$ for the first wave of ($\pi$-$C_6H_5X$)Cr.$(CO)_3$, on the one hand, and the $E_{1/2}$ and the ionisation potentials of the non-coordinated ligand $C_6H_5X$, on the other, the half-wave potentials $E_{1/2}$ of the complexes being less sensitive to structural changes in the arene bound in the complex than the $E_{1/2}$ of the free ligand. There is also a linear relation between $E_{1/2}$ for the first wave and the ionisation potentials of the complexes. The observed relations indicate the involvement of the orbitals of the arene ligand in the highest occupied molecular orbital from which the electron is removed on oxidation. The problem of the degree of involvement of the metal orbitals in this molecular orbital remains obscure [cf. the above discussion of the oxidation of $LM(CO)_5$].

The half-wave potential $E_{1/2}$ for the oxidation of the $\pi$-cycloheptatriene complex ($\pi$-$C_7H_8$)$Cr(CO)_3$ is close to $E_{1/2}$ for its isomer ($\pi$-$C_6H_5CH_3$)$Cr(CO)_3$. It has been found that the *exo*- and *endo*-isomers of $RC_7H_7Cr(CO)_3$ (R = Ph or CN) differ significantly (by approximately 70 mV) in their capacities for oxidation [200]. The reversible one-electron oxidation of ($\pi$-$C_6Me_{6-n}H$)$Cr(CO)_2$(PhC≡CPh) to the corresponding cations proceeds at potentials lower by 0.8 V than for ($\pi$-arene)$Cr(CO)_3$, which reflects the more pronounced $\sigma$-donor and weaker $\pi$-acceptor properties of the acetylene ligand compared with CO. [201]

The polarographic reduction of ($\pi$-$C_6H_6$)$Cr(CO)_3$ proceeds in a single two-electron stage with formation of a dianion [26,202]. The intermediate formation of the radical-anion has been demonstrated by electrolysis at a controlled potential. The polarograms of ($\pi$-arene)$Cr(CO)_3$ (arene = diphenyl or naphthalene) as well as those of the non-coordinated aromatic hydrocarbons show one-electron reversible waves corresponding to the reduction to the radical-anions. As in the reduction of metal carbonyl complexes with $\pi$-olefinic and $n$-donor ligands, the electron apparently occupies in this case the antibonding $\pi^*$-orbital of the aromatic hydrocarbon ligand. The observed shift of the $E_{1/2}$ for the complexes relative to the $E_{1/2}$ for the free ligands towards more positive potentials by 600–700 mV is consistent with the available data [199] showing a decrease of electron density in the aromatic ring on coordination to the $Cr(CO)_3$ group.

It has been noted that the reduction of the cationic arene complexes $[1,3,5\text{-}(CH_3)_3C_6H_3Mn(CO)_3]^+$ and the cycloheptatrienyl complexes $[\pi\text{-}C_7H_7Cr(CO)_3]^+$ and $[(\pi\text{-}C_7H_6OMe)Cr.(CO)_3]^+$ proceeds readily [26,200], but the nature of the process and the reaction products have not been investigated in detail.

(f) Complexes obtained on interaction of acetylenes with metal carbonyls. The complexes obtained when acetylenes react with metal carbonyls contain $\pi$-linked organic ligands of various types; cyclobutadiene, cyclopentadiene, quinone, tropone, and other ligands, containing as a rule several metal atoms and carbonyl groups. Many of these compounds undergo reversible electrochemical reduction at the dropping mercury electrode with formation of radical-anions and then dianions [190]. The stability of the radical-anions varies within wide limits. Studies of the individual radical-anions showed that, despite the electrochemical reversibility of the process demonstrated by triangular voltamperometry, the half-wave potentials $E_{1/2}$ for their oxidation do not agree with the half-wave potentials for the reduction of the initial complex. The electrochemical oxidation of the radical-anions nevertheless restores the initial state. The authors believe that the discrepancy between $E_{1/2}$(ox) and $E_{1/2}$(red) is due to the slow change in the structure of the radical-anion§:




The foregoing data are of interest from the standpoint of the investigation of the properties of organometallic radical-anions.

## 4. General Conclusions Concerning the Electrochemical Reactions of Metal Carbonyls and Their Derivatives

The results of electrochemical studies on the majority of metal carbonyl complexes with $\pi$-linked or $n$-donor ligands have shown that these undergo both oxidation and reduction reactions. The reduction processes have been investigated in greater detail. The reversible stepwise addition of two electrons leads to the formation of radical-anions and then dianions. The agreement of the hyperfine splitting constants for the radical-anions of the complexes and the non-coordinated ligands shows that the electron is located in the antibonding $\pi^*$-orbital of the ligand. The absence of splitting by the nitrogen of the NO group in the radical-anions $L_2Co(NO)CO$ and $L_2Fe(NO)_2$ (see subsection 2 above) shows that the spin density of the unpaired electrons belonging to $L_2$ is not transmitted via the metal atom to the other ligands. The infrared spectra of the radical-anions confirmed this conclusion and, together with the NMR spectra of the dianions, showed that a major proportion of the charge density in the radical-anion and the dianion is concentrated in the $M(CO)_n$ group. Thus, in contrast to organic compounds, the distribution of spin and charge densities in the radical-anions of the complexes may not be the same. While the spin density is concentrated at the ligand L, the charge density is largely concentrated at the metal atom and the carbonyl groups. The study of the Mössbauer spectra of the radical-anions of iron-containing complexes showed that charge transfer proceeds via $\sigma$-bonds [203].

It is noteworthy that, compared with their reduction, the electrochemical oxidation of the complexes has been inadequately investigated. There are virtually no data for the kinetics of the electrochemical processes.

## V. ELECTROCHEMICAL REACTIONS OF COMPLEXES CONTAINING $\sigma$-BONDS

Together with the complexes examined in the previous sections, studies have been made on a large number of compounds containing $\sigma$-bonds of different types: M–M,

‡ See A.R. Siedle, J.Amer.Chem.Soc., 97, 5931 (1975).

§ The nature of the rearrangement is so far obscure.

M–halogen, and M–C. It has been shown that, as a rule, these compounds are reduced or oxidised with participation of the σ-bond, while π- and donor–acceptor bonds are electrochemically inactive.

## 1. METAL COMPLEXES WITH AN M–M σ-BOND

Compared with compounds containing M–X and M–C σ-bonds, complexes with an M–M bond have a wide variety of structures, as a result of which various types of electrochemical reactions are characteristic of these substances.

### Electrochemical Reactions Involving the Dissociation of the M–M σ-Bond

(a) Homodimetallic compounds. Complexes of this type are reduced polarographically in a single irreversible two-electron stage with dissociation of the M–M σ-bond and formation of an 18-electron metal carbonyl anion [157,158,204,205]:

$$L_nM{-}ML_n + 2e \rightarrow 2[L_nM]^- \quad ;$$

$L_nM = C_5H_5M(CO)_3$, (M = Cr, Mo or W), $(CO)_5M$, (M = Mn or Re); $C_5H_5M(CO)_2$, (M = Fe or Ru), $(CO)_4Co$ or $C_5H_5NiCO$ .

It has been shown [206] that the anions $M(CO)_5^-$ (M = Mn or Re) enter into the following chemical reaction under the conditions of electrolysis:

$$M(CO)_5^- + M_2(CO)_{10} \rightarrow [M_3(CO)_{14}]^- + CO \ .$$

The reduction of complexes of Group VI–VIII metals becomes more difficult on moving from above downwards in the Periodic Table. For $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, this is satisfactorily consistent with the higher Re–Re bond energy ($\Delta H$ = 2.22 eV) compared with the Mn–Mn bond energy ($\Delta H$ = 0.96 eV). [207] It has been stated [157] that in the remaining compounds the bond energy also increases with increasing atomic number down the Group in the Periodic System. In those cases where the M–M bond energy is low, as happens for $[\pi\text{-}C_3H_5Fe(CO)_3]_2$, dissociation with formation of a monomeric radical takes place at room temperature when the solution is diluted [208] and the polarographed solution contains radical species, which are reduced at the electrode [209]. For other homodimetallic compounds, the dissociation energy is not sufficiently small to enable the detection of paramagnetic species in the solution, but it has been shown for $Mn_2(CO)_{10}$ [210] that many reactions may proceed via the initial homolytic dissociation of the M–M bond. One can therefore suppose that, in the polarographic reduction of compounds with an M–M bond, there is also homolytic dissociation of the reduced bond with formation of a pair of radicals having a half-filled orbital to which the electron is transferred.

The electrochemically irreversible oxidation of homodimetallic compounds at a platinum electrode also proceeds with the dissociation of the M–M bond [156,211,212]

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 - 2e \xrightarrow{L} [\pi\text{-}C_5H_5Fe(CO)_2L]^+ \quad ;$$

L = $CH_3CN$, acetone, $Cl^-$, or S$(C_2H_5)_2$ .

$$Mn_2(CO)_{10} - 2e \rightarrow 2Mn(CO)_5^+ \xrightarrow{CH_3CN} 2(CO)_5Mn{-}N{\equiv}\overset{+}{C}{-}CH_3 \ .$$

(b) Heterodimetallic compounds ($L_nM{-}M'R_3$). The majority of compounds of this class [$L_nM$ = $C_5H_5M(CO)_3$ (M = Cr, Mo, or W), $(CO)_5M$ (M = Mn or Re), $C_5H_5Fe(CO)_2$, or $(CO)_4Co$; M′ = Sn or Pb; R = $CH_3$ or $C_6H_5$] are reduced polarographically with addition of one electron at potentials intermediate between the reduction potentials of the related homodimetallic compounds [157]. The addition of one electron results in the formation of an anion of the homodimetallic compound, which is reduced at less negative potentials to a radical, which dimerises at the limiting current potentials for the first wave with formation of a homodimetallic compound, identifiable by the appearance of the corresponding wave on the polarogram. The polarographic reduction of $\pi\text{-}C_5H_5FeCO.(SiCl_3)H$ and $\pi\text{-}C_5H_5Fe(CO)_2SiCl_3$ has also been investigated [213].

(c) Polymetallic compounds. Symmetrical mercury derivatives containing two M–Hg bonds are reduced polarographically in a single two-electron irreversible stage with dissociation of the M–Hg bonds and formation of a pair of metal carbonyl anions [157,158,204,205]:

$$L_nM{-}Hg{-}ML_n + 2e \rightarrow 2[L_nM]^- + Hg \quad ;$$

$L_nM = C_5H_5M(CO)_3$, (M = Cr, Mo, or W), $C_5H_5Fe(CO)_2$; or $(CO)_5Mn$ .

The reduction proceeds at more positive potentials than the reduction of the corresponding $(L_nM)_2$. Owing to the non-equivalence of the Hg–Cl and M–Hg bonds, the asymmetric mercury derivatives M–Hg–Cl are reduced in two stages. The first wave is of the one-electron type and corresponds to the dissociation of the Hg–Cl bond. The mercury radical formed dimerises at the limiting current potentials for the first wave with formation of the compound $(L_nM)_2Hg$, which is reduced in the second stage.

The trimetallic complexes $[\pi\text{-}C_5H_5(CO)_3Mo]_2Sn(CH_3)_2$ and $[\pi\text{-}C_5H_5(CO)_2Fe]_2Sn(CH_3)_2$ are reduced in a single two-electron irreversible stage with dissociation of the Mo–Sn and Fe–Sn bonds and formation of the metal carbonyl anion [157]. The complexes $[\pi\text{-}C_5H_5Mo(CO)_3]_2Sn[Fe(CO)_2.C_5H_5\text{-}\pi]_2$, containing four metal–metal bonds, are reduced in several stages, each of which corresponds to the rupture of one of the M–M bonds [157].

(d) The nucleophilic properties of the metal-containing anions $[L_nM]^-$. It follows from the foregoing that the reduction of homo-, hetero-, and poly-metallic compounds results as a rule in the formation of the metal carbonyl anions $[L_nM]^-$. The nucleophilicity of the $[L_nM]^-$ anion is a parameter which determines quantitatively its reactivity in relation to electrophiles. The study of the electrochemical behaviour of these anions permitted the determination of their nucleophilic properties [214]. It has been found that the anions $[L_nM]^-$ give rise to distinct oxidation waves at a platinum electrode; the variation of the current with the $[L_nM]^-$ concentration is linear. Polarographic study of the kinetics of the reaction of $[L_nM]^-$ with alkyl halides RX showed that the reaction is described by the equation for second-order kinetics. The rate constants $k_2'$, adjusted to conform to $k_2$ for the anion $[(CO)_4CO]^-$, have been adopted as a measure of the nucleophilicity of $[L_nM]^-$.

It has been established that the nucleophilicity of $[L_nM]^-$ varies in parallel with $E_{1/2}$ for its oxidation. Thus the possibility of one-electron transfer from $[L_nM]^-$ to the substrate (Sub),

$$[L_nM]^- + Sub \rightarrow [L_nM]^{\cdot} + Sub^{\cdot -}$$
$$\downarrow$$
$$^1/_2L_nM{-}ML_n \ ,$$

is related to $E_{1/2}$ for the oxidation of $[L_nM]^-$ and hence to its nucleophilicity. The problem of the relation between

$E_{1/2}$ for the oxidation of $[L_nM]^-$ and $E_{1/2}$ for the reduction of the substrate and of the possibility of one-electron transfer reactions between them has been examined[215].

The determination of $E_{1/2}$ for the reduction of compounds with an M–M bond and for the oxidation of $[L_nM]^-$ and the quantitative determination of the nucleophilicity of the latter made it possible to establish the fundamental characteristics of the formation of complexes with an M–M bond in the following reactions[216,217]:

$$[L_nM]^- + L_nM'-X \rightarrow L_nM-M'L_n + X^- \quad ;$$
$$[L_nM]^- + L_nM-M'L_n \rightarrow L_nM-ML_n + [L_nM']^- \quad .$$

A linear correlation has also been observed between $E_{1/2}$ for the oxidation of $[L_nM]^-$ and $E_{1/2}$ for the reduction of the hydrides $L_nM-H$ formed when proton donors are added to $[L_nM]^-$.[218]

Electrochemical Reactions Occurring Without the Dissociation of the M–M Bond

(a) Clusters. Clusters containing triangular or polyhedral fragments made up of the metal atoms and the M–M bond are capable of electrochemical oxidation and reduction, the structure of the cluster being retained. The reduction proceeds in a single reversible one-electron stage with formation of paramagnetic radical-anions[60,157]. The stepwise oxidation of $[\pi\text{-}C_5H_5FeCO]_4$ and $[\pi\text{-}C_5H_5FeS]_4$ in acetonitrile at a platinum electrode leads to a series of oxidation states[219,220]. The complex monocations are paramagnetic:

$$[Fe_4]^{2+} \overset{+1.08V}{\rightleftarrows} [Fe_4]^{+} \overset{+0.32V}{\rightleftarrows} [Fe_4]^{0} \overset{-1.30V}{\rightleftarrows} [Fe_4]^{-} \quad .$$

(b) Metal carbonyl complexes with phosphorus- and sulphur-containing bridge ligands. The compounds $[(CO)_4ME(CH_3)_2]_2$ (M = Cr, Mo, or W; E = P or As) and $[Mn(CO)_3SPh]_2$ and $[(CO)_3.ME(CH_3)_2]_2$ (M = Fe or Ru; E = As or P) are reduced to the dianions in a single electrochemically reversible stage[157,179]. The interaction of solutions of the dianions with the initial compounds as a rule leads to the formation of coloured solutions of the radical-anions, which give rise to an ESR signal. A detailed study of $[(CO)_3MP.(CH_3)_2]_2$ (M = Fe or Ru) showed[180] that, on passing from the neutral compound to the radical-anion, the molecular structure is retained, but, on further conversion into the dianion, the molecular geometry is altered. It is assumed[180] that the addition of two electrons to the molecular orbital incorporating the metal orbitals leads to an increase of the charge on the metal and hence to the repulsion of the metal atoms from one another and to an increase of the Fe–Fe distance. This in its turn leads to a decrease of the P–P distance. It has been shown by NMR that, compared with the initial molecule, the frequency of the inversion of the bridge groups in the dianion increases.

The oxidation of the diphosphineiron carbonyl complex $\{[\pi\text{-}C_5H_5Fe(CO)_2]_2Ph_2P(CH_3)_nPPh_2\}$ ($n$ = 2 or 3) also does not lead to the dissociation of the M–M bond[221,222]. The elimination of the first electron proceeds reversibly both electrochemically and chemically and leads to the formation of a cation containing a one-electron M–M bond. The removal of the second electron is electrochemically irreversible and results in the formation of a short-lived dication, which then reacts via the following mechanism:

$$\{[(\pi\text{-}C_5H_5)\,Fe\,(CO)I_2\,Ph_2PCH_2CH_2PPh_2\}^{2+} \longrightarrow$$
$$\xrightarrow{k_1} [(\pi\text{-}C_5H_5)\,Fe\,(CO)_2\,Ph_2PCH_2CH_2PPh_2]^{+} + Fe^{2+}$$
$$\xrightarrow[(Solv\,=\,solvent)]{k_2,\ 2Solv} \{[(\pi\text{-}C_5H_5)\,Fe\,(CO)\,Solv]_2\,Ph_2PCH_2CH_2PPh_2\}^{2+} \quad .$$

In contrast to the complexes examined, in neutral compounds with sulphur-containing bridge ligands $[\pi\text{-}C_5H_5.MLSR]_2$ (M = Mn or Mo and L = NO; M = Fe and L = CO) and $[\pi\text{-}C_5H_5MSR]_2$ (M = Co or Ni), there is no M–M bond. However, in the cation formed after reversible one-electron oxidation, the formation of a one-electron M–M bond is postulated[194,223]. The considerable decrease of the M–M distance in the cation (the Fe–Fe distance is 2.93 Å) compared with the neutral compound (3.39 Å) leads to the same conclusion. It is believed that oxidation to the dication can result in a further contraction of the molecule and the formation of a two-electron M–M bond.

2. METAL COMPLEXES WITH A METAL–HALOGEN σ-BOND

Depending on the structure of the complexes, the reduction proceeds in one two-electron or one-electron stage. The irreversible addition of one electron results in the dissociation of the metal–halogen bond and the formation of 17-electron organometallic radicals, the stability of which varies within wide limits[60,173,204,205,209,224]:

$$L_nM-Hal + e \rightarrow [L_nM]^{\cdot} + Hal^- \quad .$$

The gradual transition from one- to two-electron reduction of the M–X bond has been observed in $\pi\text{-}C_5H_5W(CO)_3X$. While the first wave for the iodide is of the one-electron type, the polarograms of the bromide and chloride showed a single two-electron wave[205]:

$$L_nM-Hal + 2e \rightarrow [L_nM]^- + Hal^- \quad .$$

The compounds $(CO)_5M-Hal$ (M = Mn or Re) are reduced via a similar mechanism[158]. The appearance of a two-electron wave in the reduction of the M–Hal bond is associated with the fact that the potential at which there is a possibility of the transfer of the first electron from the electrode is displaced to an increasing extent towards negative values and approaches the reduction potential of the dimers of the symmetrical mercury compounds, which are the products of the stabilisation of the unstable organometallic radicals formed on transfer of the first electron.

The observed sequence based on the decrease in the ease of reduction of the metal–halogen σ bond in both one-electron and two-electron reduction is the opposite of the sequence of the electronegativities of the halogens, which determine the polarity of this bond. The increase of the polarity of the Fe–Hal bond in $\pi\text{-}C_3H_5Fe(CO)_3Hal$ on passing from the iodide to the chloride has been confirmed by Mössbauer spectra[225]. The observed sequence based on the decrease of the ease of reduction of the metal–halogen bond agrees with the sequence based on the variation of the halfwave potentials $E_{1/2}$ for the reduction of the C–Hal bond[226] in alkyl halides. A radical reduction mechanism is postulated in this case and the decrease of the ease of reduction in the sequence C–I > C–Br > C–Cl is explained by the increase of the strength of the C–Hal bond. Presumably, a similar explanation is applicable

also to the reduction of the transition metal–halogen bond. Thus, in contrast to the simplest inorganic halides, the metal–halogen bond in the carbonyl complexes of transition metals is distinctly covalent and exhibits a tendency towards a predominantly homolytic rather than heterolytic dissociation.

The electrochemical oxidation of complexes with a metal–halogen σ bond has been hardly investigated. It is only known that the voltamperometric oxidation of the halogenopentacarbonylmetallate anions $[(CO)_5MHal]^-$ (M = Cr, Mo or W) takes place in two one-electron reversible stages with formation of an uncharged complex and a cation respectively [227].

## Electrochemical Behaviour of Cyclopentadienyl Complexes of Titanium and Zirconium Containing Metal–Halogen σ-Bonds

The enhanced interest in the electrochemical reduction of dicyclopentadienyl compounds of titanium is due to the fact that the system incorporating $(\pi\text{-}C_5H_5)_2TiCl_2$ and reducing agents are catalysts of the Ziegler type and are also capable of the active fixation of molecular nitrogen.

It has been shown that, in an aprotic medium (dimethylformamide, acetonitrile, dimethoxyethane, and tetrahydrofuran), $(\pi\text{-}C_5H_5)_2TiCl_5$ is reduced at the dropping mercury electrode in two stages with subsequent cleavage of the Ti–Cl bonds [60,228,233]. The first wave on the polarogram corresponds to the reversible transfer of a single electron with formation of a titanium(III) compound:

$$(\pi\text{-}C_5H_5)_2TiCl_2 + e \rightleftarrows (\pi\text{-}C_5H_5)_2TiCl + Cl^- \quad .$$

The compound $(\pi\text{-}C_5H_5)_2TiCl$ gives rise to an ESR signal [60, 229]; its subsequent reduction proceeds irreversibly with the apparent formation of titanocene:

$$(\pi\text{-}C_5H_5)_2TiCl + e \rightarrow [(\pi\text{-}C_5H_5)_2Ti]_n + Cl^- \quad .$$

The reduction of $(\pi\text{-}C_5H_5)_2TiX_2$ (X = F, Br, or I) proceeds via analogous mechanisms. The difference between $E_{1/2}$ for the first X = Cl, Br, or I waves is small, while $(\pi\text{-}C_5H_5)_2TiF_2$ is reduced at much more negative potentials [229]. The reduction of $(\pi\text{-}C_5H_5)_2Ti(R)Cl$ [R = $CH_3$, $C_6H_5$, $C_5F_5$, or $OTiCl(C_5H_5\text{-}\pi)$] also begins with the one-electron cleavage of the TiCl bond and the formation of $(\pi\text{-}C_5H_5)_2TiR$. [232] A study [229] has shown that the reduction of $\pi\text{-}C_5H_5TiCl_3$ proceeds in three stages with successive dissociation of Ti–Cl σ-bonds.

In a protic medium, $(\pi\text{-}C_5H_5)_2TiCl_2$ is readily hydrolysed to $(\pi\text{-}C_5H_5)_2TiOH^+$, which is then reduced at the dropping mercury electrode:

$$(\pi\text{-}C_5H_5)_2TiOH^+ + e + H^+ \rightarrow [(\pi\text{-}C_5H_5)_2Ti]^+ + H_2O \quad .$$

The half-wave potentials have also been found for the reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ in other solvents (ethylenediamine [234], morpholine [235], phenylphosphonic dichloride [236], and dimethyl sulphoxide [237]) and for the reduction of $(\pi\text{-}C_5H_5)_2TiBr_2$ in formamide [44].

The reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ in an aprotic medium likewise proceeds in two stages, but has more negative potentials. The product of the addition of the first electron does not give rise to an ESR signal, evidently because of dimerisation and the formation of the M–M bond [60]:

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + e \rightarrow (\pi\text{-}C_5H_5)_2\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Zr}}\!\!-\!\!\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Zr}}(C_5H_5\text{-}\pi)_2 \quad .$$

In an aqueous medium with $NaClO_4$ as the supporting electrolyte, the reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ is not observed, because its reduction potential lies outside the limits of the discharge of the supporting electrolyte [51,55].

## Transition Metal Complexes with a Metal–Carbon σ-Bond

Transition metal compounds with a metal–carbon σ-bond are as a rule reduced at more negative potentials than the complexes with metal–halogen and metal–metal σ-bonds. Depending on the structure of the complex, the reduction proceeds via different mechanisms. Octahedral iron, tungsten, manganese, and rhenium complexes are reduced irreversibly at the dropping mercury electrode in an aprotic medium (acetonitrile) in a single two-electron stage with dissociation of the metal–carbon σ-bond [158,205, 238].

$$\pi\text{-}C_5H_5(CO)_2Fe\text{—}R + 2e \rightarrow [\pi\text{-}C_5H_5(CO)_2Fe]^- + R^- \xrightarrow{H^+} RH \quad .$$

The reaction products are the metal carbonyl anion and the carbanion $R^-$. The latter is stabilised with formation of RH, evidently on interaction with the solvent or with the traces of water in the solvent¶. The structure of the group R has a significant influence on the values of $E_{1/2}$, displacing them towards more negative potentials with increase of the basicity of $R^-$. A satisfactory linear correlation is observed between the $E_{1/2}$ for the reduction of the Fe–C bond and the values of $pK_a(RH)$ in the series of compounds $\pi\text{-}C_5H_5(CO)_2FeR$: $E_{1/2} = -0.03\ pK_a - 0.81$ (V); $r = 0.994$†. It has been suggested that the observed correlation be used for the determination of new values of $pK_a$ [151] for C–H acids whose acidity is unknown.

The replacement of one carbonyl group in $\pi\text{-}C_5H_5(CO)_2\text{.}FeC_6H_4X$ by a phosphorus-containing ligand L leads to a change in the reduction mechanism [238,240]. In this case, the first stage involves the addition of one electron. Simultaneously with electron transfer, the M–C bond is dissociated. The values of $E_{1/2}$ for the first wave were used to estimate the influence of substituents on the transition state in the electrode reaction [238]. The best linear correlation is observed between $E_{1/2}$ and the values of $\sigma_n^0$ for the substituents X ($r = 0.873$; $\rho = +0.19$ V). Consequently, the polar influence of substituents is slight, in good agreement with the hypothesis of the homolytic dissociation of the M–C bond during reduction.

The reduction of the organometallic derivative $(\pi\text{-}C_5H_5)_2\text{.}TiR_2$ (R = $CH_2\text{–}C\text{–}CH$, with $B_{10}H_{10}$) proceeds in two irreversible one-electron stages with subsequent dissociation of Ti–C σ-bonds. When R = $CH_3$ or $C_6H_5$, a single one-electron wave is observed on the polarogram [241].

The polarographic reduction of $RCOM(CO)_5$—the acyl derivatives of manganese and rhenium carbonyls—has also been investigated [158].

¶ According to Vlček [239], a proton is split off from the solvent in the solvation shell of the depolariser molecule and the R–H bond is formed in the activated complex.

† A similar relation has also been observed in the polarographic reduction of symmetrical organomercury compounds and organomercury salts (see, for example, Denisovich and Gubin [149,150]).

Organometallic Derivatives of Planar Chelate Complexes of Cobalt

The oxidation-reduction reactions of σ-organocobalt derivatives of corrin complexes (natural organometallic compounds related to the vitamin $B_{12}$ series) and of their simpler analogues are of considerable interest. Electrochemical studies have shown that, under certain conditions, the cleavage of the Co–C bond during their reduction or oxidation is preceded by rapid electron transfer. This is also important for the understanding of biochemical processes involving vitamin $B_{12}$. The availability of a series of model organocobalt chelates makes it possible to determine the role of chelating ligands and of the organic group in the mechanism of the reductive cleavage of the Co–C σ-bond. The polarographic behaviour of the organometallic complexes of cobalt having the general formula $[RCo^{III}(chel)L]$ and $\{RCo^{III}[(do)(doh)pn]L\}^+$, where R is a hydrocarbon group, L a Lewis base (in the simplest case a solvent molecule), and chel and [(do)(doh)pn] are the equatorial chelating dianion and the monoanion respectively‡, has been investigated in greatest detail [242–245]. The reduction of these complexes proceeds with greater difficulty than that of the corresponding chelates without Co–C bonds [244], but much more easily than, for example, the reduction of organomercury compounds with the same groups R. Polarographic cyclic voltamperometric and electrolytic studies at a controlled potential have shown that the reduction at the dropping mercury electrode proceeds in accordance with the following mechanisms:

$$[RCo^{III}(chel)L] \underset{-e}{\overset{+e}{\rightleftarrows}} [RCo^{II}(chel)L]^- \underset{-e}{\overset{+e}{\rightleftarrows}} [RCo^{I}(chel)L]^{2-} ;$$

$$\{RCo^{III}[(do)(doh)ph]L\}^+ \underset{-e}{\overset{+e}{\rightleftarrows}} \{RCo^{II}[(do)(doh)ph]L\}^0 \underset{-e}{\overset{+e}{\rightleftarrows}} \{RCo^{I}[(do)(doh)ph]L\}^- .$$

The above mechanisms show that the reduction is electrochemically reversible and does not therefore require an appreciable activation energy for electron transfer. The values of $E_{1/2}$ for the first reduction stage ($Co^{III} \rightarrow Co^{II}$) of complexes of the same type depend on R. It has been found [243–246] that the values of $E_{1/2}$ vary linearly with the $pK_a$ for the corresponding RH, i.e. the electron affinity of the organometallic chelate depends on the stability of $R^-$, and the orbital to which the electron is transferred on reduction is therefore the antibonding orbital of the Co–C bond. The electron-donating capacity of the equatorial ligands influences the electron affinity of the complexes investigated [243–246]. The dependence of $E_{1/2}$ on the nature of the equatorial ligand shows that the energy of the antibonding orbital of the Co–C bond increases in the sequence from [(do)(doh)pn] to salen and bae. The stability of the intermediate and final products depends to a large extent on the nature of R. Thus the one-electron reduction of $[C_6H_5Co^{III}(salen)L]$ leads to the formation of a potential carbanion, while the products of the reductive cleavage of $[CH_3Co(salen)L]^-$ are a cobalt(I) complex and $CH_3^{\cdot}$: [246]

$$[C_6H_5Co^{II}(salen)L]^- \xrightarrow{H^+} C_6H_6 + [Co^{II}(salen)L] ;$$

$$[CH_3Co^{II}(salen)L]^- \rightarrow CH_3^{\cdot} + [Co^{I}(salen)L]^- .$$

The differences in the behaviour of these complexes are explained by the changes in the lowest vacant molecular orbital of the complex where the electron is accepted on transition from $[C_6H_5Co(salen)L]$ to $[CH_3Co(salen)L]$, namely in the case of powerful donors (R = $CH_3$) the lowest free orbital may be a metal orbital of the $d_{xy}$ type.

The ability of organometallic chelates to behave as donors of the methyl group is greatly enhanced on their reduction. Thus $\{CH_3Co^{I}[(do)(doh)pn]L\}^-$ behaves as a methylating agent in relation to the initial compound even under electrolysis conditions:

$$RCo^{I}[(do)(doh)pn]\}^- + \{RCo^{III}[(do)(doh)pn]\}^+ \rightarrow$$
$$\rightarrow \{R_2Co^{III}[(do)(doh)pn]\} + \{Co^{I}[(do)(doh)pn]\} .$$

The reversible one-electron oxidation of cobalt(III) organic chelates in the series [RCo(salen)] and $[RCo(Dh)_2]$ (Dh is the dianion of a 1,2-dioxime) has also been observed at a platinum electrode in acetonitrile with formation of labile cobalt(IV) compounds which readily transfer the σ-linked organic group to nucleophiles [247].

The polarographic behaviour of alkylcobalamins, glucopyranosylcobalamin, and 5′-deoxynucleoside analogues of the cobamide coenzyme in an aqueous medium has been investigated [248]. The great complexity of the polarographic reduction of $RCo(Dh)_2$ compared with organocobalt chelates of other series is also noteworthy [248–250].

## VI. ELECTROCHEMICAL SYNTHESIS OF π-COMPLEXES OF TRANSITION METALS AND OF COMPLEX ORGANOMETALLIC CATALYSTS

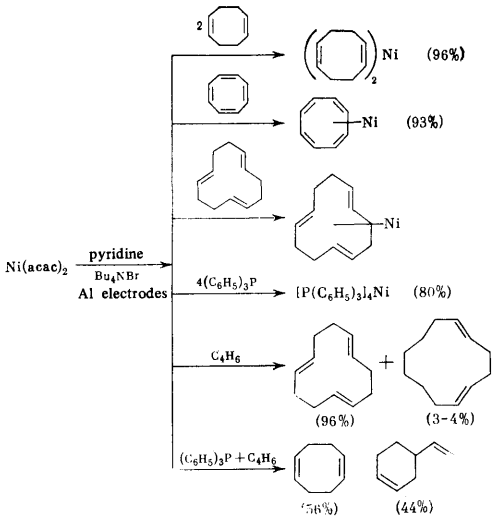
The polarographic study of the behaviour of transition metal π-complexes and of the corresponding non-coordinated ligands at electrodes leads to the possibility of selecting conditions for the electrochemical synthesis of transition metal π-complexes [251,252]. As a rule, the starting compounds for the electrochemical synthesis of transition metal complexes are chelate complexes of the same metals or their salts. Electrolysis is carried out using an organic compound, which subsequently behaves as the π-ligand for the complex to be formed, in the presence of electron-donating molecules [pyridine, DMF, $P(C_6H_5)_3$, etc.] capable of stabilising a low oxidation state of the metal. Thus, transition metal carbonyls have been synthesised from acetylacetonates and carbon monoxide [253, 254]. The electrolysis was carried out at a stainless steel cathode in anhydrous pyridine containing 1–5% $Bu_4NBr$; the anode was metallic aluminium. The carbon monoxide pressure was varied within wide limits, whereupon the following processes take place at the electrodes:

$$\text{Cathode: } M(acac)_n + XCO + ne \rightarrow M(CO)_x ;$$
$$\text{Anode: } Al \rightarrow Al^{3+} + 3e .$$

The carbonylation of $CrCl_3(Py)_3$ in pyridine at 85 °C and a carbon monoxide pressure of 60 atm leads to the formation of $Cr(CO)_6$ in 85% yield [255]. The reduction of $Fe(acac)_3$ at a mercury cathode in the presence of $P(C_6H_5)_3$ and 1,3-dienes leads to the formation of $FeP(C_6H_5)_3$ (diene)

‡ The following notation has been adopted for various chelating dianions: salen = *NN′*-ethylenebis(7,7′-dimethylsalicylideneaminate); bae = *NN′*-ethylene bis(acetylacetone iminate) [*NN′*-ethylenebis(1-methylethylideaminate)]; saloph = *NN′*-*o*-phenylenebis(salicylideneaminate); [(do)(doh)pn] = monoanion of 1,3-diacetylmonoxime-iminodiacetylmonoximatoiminopropane.

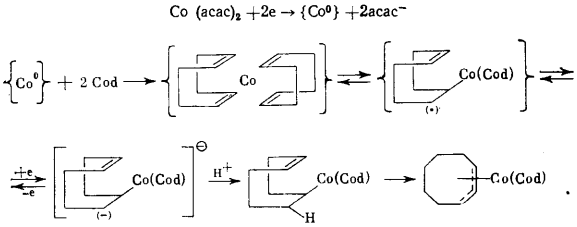
(diene = buta-1,3-diene or isoprene)[256]. Olefin complexes of nickel have also been obtained by a similar procedure[257]:



The last two rows of the above scheme show that the complexes of zero-valent nickel synthesised electrochemically catalyse the oligomerisation of butadiene. The electrochemical preparation of butadiene oligomerisation and polymerisation catalysts containing zero-valent nickel and cobalt has been investigated in greater detail in other studies[258-262]. It has been shown that the conversion of butadiene and the composition of the products formed are influenced by the nature of the initial nickel and cobalt compounds, the nature of the solvent, and the potential at which the electrolysis is carried out. Similarly electrolysis at a platinum electrode of a solution containing $Py_4Ni(ClO_4)_2$ or $NiCl_2$ and butadiene involves the tetramerisation of butadiene[263], but this reaction is not catalytic. The electrochemical synthesis of previously unknown $(Ph_3P)_4Rh(O)$ has also been described[264].

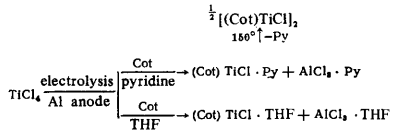
The following mechanism has been proposed for the electrochemical synthesis of cobalt complexes of cyclo-octa-1,5-diene (Cod) at aluminium electrodes[265]:

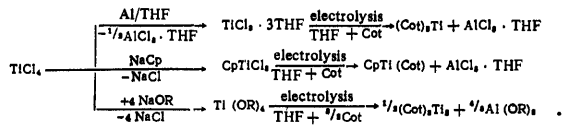
$$Co(acac)_2 + 2e \rightarrow \{Co^0\} + 2acac^-$$



The intermediate biscyclo-octa-1,5-dienecobalt is subsequently reduced to an anionic complex, which reacts with a proton, forming $\pi$-cyclo-octenylcyclo-octadienecobalt.

The electrochemical preparation of cobalt complexes of acyclic 1,3-dienes $(\pi\text{-}C_4H_6)Co(\pi\text{-}C_4H_6R)L$, where L = $P(C_6H_5)_3$ or $P(C_4H_9)_3$, by the reduction of $CoCl_2$ at a mercury cathode in the presence of buta-1,3-diene and L has been described[266].





Another approach to the electrochemical synthesis of $\pi$-complexes is based on the involvement of the electrode material in the electrode reaction. Ferrocene has been obtained in this way from $C_5H_5Tl$ at an iron anode in 94.6% yield[268]:

$$\text{Anode: } 2C_5H_5Tl + Fe \rightarrow (C_5H_5)_2Fe + 2Tl^+ + 2e \ ;$$

$$\text{Cathode: } 2C_5H_5Tl + 2e \rightarrow 2Tl^0 + 2C_5H_5^- \ .$$

A method for the preparation of cyclopentadienylmanganese carbonyl compounds, based on the anodic dissolution of manganese, has been patented[269,270]. Similarly, in the electrolysis of solutions of indenylsodium and fluorenylsodium in THF or diglyme, the manganese anode dissolves with formation of di-indenylmanganese and difluorenylmanganese[271]. When a current is passed between two copper electrodes in a methanol solution of $Cu(BF_4)_2$ and cyclo-octa-1,5-diene, the copper undergoes anodic dissolution with formation of bis(cyclo-octa-1,5-diene)copper tetrafluoroborate:

$$Cu + n\,(Cod) + BF_4^- \rightarrow Cu\,(Cod)_n\,BF_4 + e \ .$$

At the same time copper(II) is reduced at the cathode to copper(I) and the subsequent reaction of copper(I) with Cod likewise leads to the formation of $Cu(Cod)_nBF_4$:[272]

$$Cu^{2+} + n\,(Cod) + BF_4^- + e \rightarrow Cu\,(Cod)_n\,BF_4 \ .$$

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In conclusion, one should note that, together with the undoubted advances in electrochemical research on transition metal $\pi$-complexes, there are a number of branches of this field which have so far been inadequately investigated and whose study is likely to be rewarding: (1) investigation of the mechanisms of electrode processes involving $\pi$-complexes; (2) investigation of the properties of the intermediate species and the final products of the electrochemical reactions of $\pi$-complexes; (3) the study of the relation between electrochemical data and the chemical and physical properties of $\pi$-complexes (acid–base properties, reactivity in relation to electrophiles and nucleophiles, ionisation potentials, electron affinities, quantum-chemical data, etc.); (4) electrochemical synthesis of $\pi$-complexes and complex organometallic catalysts.

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# Rearrangements in Sulphoxides and Sulphones Induced by Electron Impact

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The survey covers processes involving the isomerisation of molecular ions and the rearrangement of ionic fragments during the initial stages of the dissociative ionisation of sulphoxides and sulphones on electron bombardment. Characteristic ions are formed by skeletal rearrangements, in particular by migration of an alkyl or an aryl group from the sulphur to an oxygen atom. The relative statistical weight of a particular structure of a molecular ion is the main factor determining subsequent competitive decomposition paths of the primary ionic fragments. A list of 82 references is included.

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## I. INTRODUCTION

Migrations of groups on electron impact, with the formation of new bonds—so called skeletal rearrangements—make the interpretation of mass spectra substantially more difficult, since they cannot be predicted *a priori* with sufficient certainty. On the other hand, the rearranged ions, whose activation energy of formation is low, often corresponds to the most intense peaks in the mass spectra, and can therefore be most effectively used to identify compounds and establish their structure.

Several reviews have appeared on rearrangements involving aliphatic and aromatic sulphoxides and sulphones[1-5]. They reflect the variety of such processes characterising the behaviour of sulphur-containing organic compounds under electron bombardment—migration of an alkyl or an aryl group from the sulphur atom to an oxygen atom in aliphatic or aromatic sulphoxides and sulphones to form a sulphenic or a sulphinic ester, migration of a hydrogen atom to an oxygen atom in aliphatic sulphoxides and sulphones, and finally reactions involving formation of new bonds accompanied by detachment of neutral molecules, of the type $(ABC)^+ \rightarrow (AC)^+ + B$.

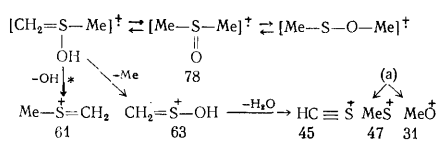
In the present Review we shall summarise the large amount of new work that has appeared on skeletal rearrangements in aliphatic and aromatic sulphoxides and sulphones. Discussion of the mechanisms is based on the application of high-resolution mass spectrometry and isotopic labelling.

## II. ALIPHATIC SULPHOXIDES

The breakdown of aliphatic sulphoxides involves the formation of weak peaks of rearranged ions due to loss by the molecular ion of a hydroxy-group or a neutral alkene. These processes are accompanied by migration of hydrogen to the oxygen atom.

Several studies have been made of the behaviour of symmetrical dialkyl sulphoxides[6-11]. The first member of the series—dimethyl sulphoxide—is unable, of course, to eliminate an alkene on electron impact, but its mass spectrum reveals the occurrence of other rearrangements: together with the formation of $[M - OH]^+$ and $[M - CH_3]^+$ ions (where $M$ is the molecular ion), due to successive or simultaneous cleavage of the sulphur–oxygen or a sulphur–carbon bond accompanied by migration of an alkyl hydrogen atom to the oxygen atom, approximately equally intense peaks of $CH_3S^+$ and $CH_3O^+$ ions are observed[9] in the mass spectrum of dimethyl sulphoxide. From this it was concluded that the molecular ion isomerised into the structure (a)†, and this was followed by cleavage of the sulphur–oxygen bond (Scheme 1)†. Detachment of a methyl radical leads to formation of the maximum peak (of mass 63) in the spectrum. The high probability of elimination of a hydroxyl from the molecular ion of dimethyl sulphoxide is due to formation of sulphonium ions $R\overset{+}{S}=C\langle$.[10] The spectrum of dimethyl sulphoxide contains also weak peaks corresponding to rearranged hydrocarbon ions $[M - SOH]_n^+$, where $n = 0-3$.

Scheme 1




The dissociative ionisation of higher dialkyl sulphoxides

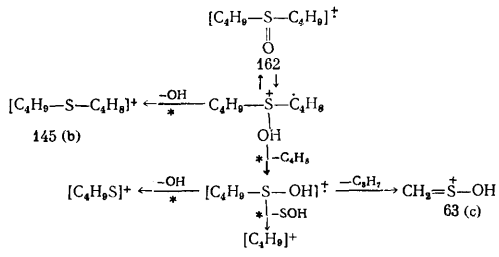


($R$ = n-$C_3H_7$, n-$C_4H_9$, iso-$C_4H_9$) is accompanied by elimination of R associated with migration of a hydrogen atom to the charged fragment. This process corresponds formally to detachment of a neutral alkene. Detailed study of deuterated di-n-butyl sulphoxide has shown[11] that the migration of hydrogen is non-specific. The location of

†Here and subsequently the numerals accompanying ionic formulae indicate $m/e$ values, and asterisks denote metastable ions.

the migrating hydrogen atom probably determines the probability of successive or simultaneous loss of hydroxyl, cleavage of a carbon–sulphur bond, or other process (e.g. McLafferty rearrangement). Indeed, fission of a carbon–sulphur bond in an aliphatic sulphoxide hardly takes place without migration of hydrogen. Even in dimethyl sulphoxide such migration is probably involved in removal of a methyl group[11]. Formation of the new carbon–hydrogen bond is accompanied by single-stage detachment of a hydroxy-radical with formation of fragment (b) of mass 145 (Scheme 2).

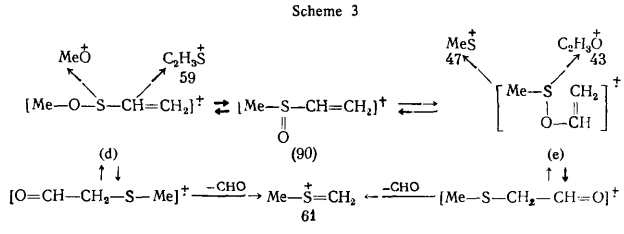
Scheme 2



Another common feature of the mass spectra of these compounds is a characteristic peak due to ions of mass 63 (ion c). Study of deuterated compounds indicates that this fragment contains an $\alpha$-methylene group and a hydrogen atom that has migrated[11]. The dissociative ionisation of dibutyl sulphoxide exhibits all the characteristic modes of breakdown of dialkyl sulphoxides (Scheme 2). It is interesting that migration to oxygen of a hydrogen atom more remote from the oxygen atom may occur partly also through a McLafferty rearrangement. Randomisation of hydrogen is then completely absent from these compounds[11].

It was suggested[1] that an unsaturated migrating group in an unsymmetrical sulphoxide should facilitate rearrangement, resulting in relatively intense ion peaks due to $[M - SO]^+$, $[M - SOH]^+$ and $[M - SOH_3]^+$.[6] The peaks in the mass spectrum of methyl vinyl sulphoxide[12] due to ionic fragments of masses 31, 43, 47, and 59—$[CH_3O]^+$, $[C_2H_3O]^+$, $[CH_3S]^+$, and $[C_2H_3S]^+$ respectively—also indicate isomerisation of molecular ions of the sulphoxide into the sulphenates (d) and (e) followed by cleavage of the sulphur–oxygen bond. The maximum peak in the spectrum, corresponding to ions of mass 61, however, results from rearrangement of the isomerised molecular ion. This may involve either migration of two methyl hydrogen atoms to the vinyl group of the ion (d) followed by rupture of the sulphur–oxygen bond, or rearrangement of the ion (e) (Scheme 3).

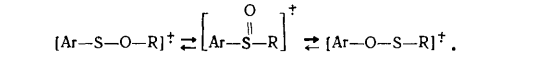
Scheme 3



The spectra of unsymmetrical compounds, such as n-butyl methyl, ethyl, propyl, and isopropyl sulphoxides, show that, when unbranched alkyl groups are present, a small alkyl is eliminated preferentially, with migration of a hydrogen atom to the oxygen; in $\alpha$-branched systems this effect is ill defined[11].

## III. AROMATIC SULPHOXIDES

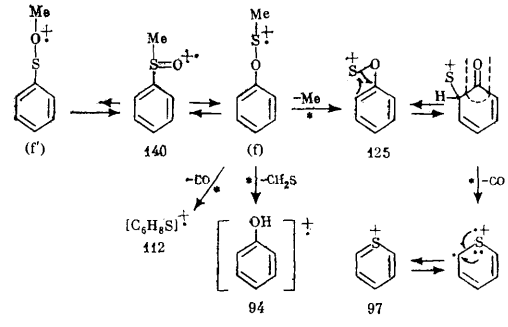
The mass spectra of aromatic sulphoxides, in contrast to those of the aliphatic compounds, containing weak peaks of rearranged ions, are characterised by intense peaks due to ions that may result from isomerisation of the molecular ion. Alternative migration of one of the groups from the sulphur atom to oxygen is observed in the dissociative ionisation of alkyl aryl or unsymmetrical diaryl sulphoxides. This indicates that the molecular ion can exist in at least three forms[1]:



Reversible O → S migration of allyl and benzyl with formation of a sulphoxide has been demonstrated[13] on heat-treatment of the sulphenate. However, phenyl sulphoxides probably do not undergo S → O migration on thermolysis[14].

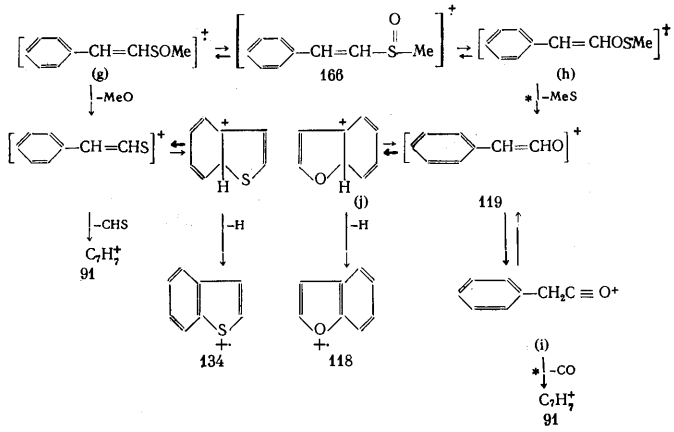
The elimination of carbon monoxide in the dissociative ionisation of aromatic sulphoxides[8] indicates unambiguously formation of a carbon–oxygen bond by isomerisation of the molecular ion or of ionic fragments appearing in the first stage of breakdown. Thus the mass spectrum of methyl phenyl sulphoxide shows that the molecular ion and the ion $[M - CH_3]^+$ of mass 125 lose carbon monoxide. In addition, the molecular ion eliminates a $CH_2S$ group with formation of an ion of mass 94 $[C_6H_6O]^+$ (perhaps having the phenol structure), a process which is confirmed by a metastable peak. The molecular ion of methyl phenyl sulphoxide can be regarded as represented mainly by structure (f) (Scheme 4).

Scheme 4



However, these workers[8] do not detect the $CH_3O^+$ ion, which would have indicated isomerisation of the molecular ion involving migration of the alkyl group from the sulphur to the oxygen atom (f′). Such isomerisation has been observed with methyl styryl and phenethynyl sulphoxides[15–17], when alternative formation of the intermediate structures (g) and (h) takes place (Scheme 5) with preferential migration of the styryl or the alkyl group from the sulphur to the oxygen atom. Decomposition of these ions (g) and (h) yields the characteristic ionic fragments. Thus the mass spectrum of methyl styryl sulphoxide indicates elimination of a methoxy-group from the former ion, although no metastable ions were observed for this purpose. Study of deuterated derivatives of methyl styryl sulphoxide confirmed the above observation[15].

Scheme 5

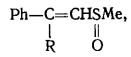


Migration of the styryl group from sulphur to oxygen can be traced by the detachment of a methylthio-radical from the isomerised molecular ion of structure (h) and the appearance of the peak of the corresponding metastable ion. One of the main pathways along which the resulting ion of mass 119 breaks down involves migration of a hydrogen atom to the $\alpha$-carbon atom relative to the ring with formation of the phenylacylium ion (i) followed by elimination of carbon monoxide (Scheme 5).

Another mode of breakdown of the ion of mass 119 involves [15-17] electrophilic attack on the benzene ring by the positively charged oxygen atom to form the protonated benzofuran ion (j), from which the hydrogen atom splits off to give the pseudomolecular benzofuran ion of mass 118. Electrophilic attack induced by electron impact is made not only by oxygen [18] but also by sulphur [7], as shown by formation of a pseudomolecular benzothiophen ion of mass 134 when structure (g) breaks down.

Appearance of the tropylium ion of mass 91 probably has a lower activation energy [4] than that of the benzofuran ion. With ionising electrons of low energy the process $119^+ \rightarrow 91^+$ still occurs, but the ion of mass 118 disappears.

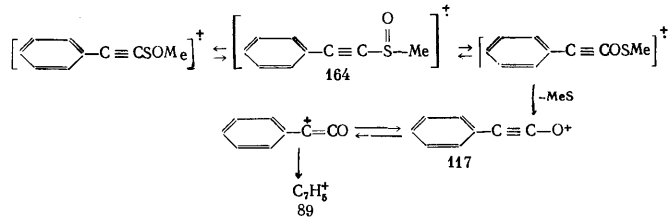
The molecular ion of methyl styryl sulphoxide also loses carbonyl (and/or formyl) and hydroxyl. Examination of deuterium-labelled compounds has established that the carbon atom present in the formyl radical had probably been attached to the sulphinyl group, whereas the hydroxyl hydrogen atom may have belonged either to the phenyl ring or to the alkyl group, which is confirmed by the mass spectra of the compounds



where R = $CH_3$, $C_2H_5$, $C_6H_5$.

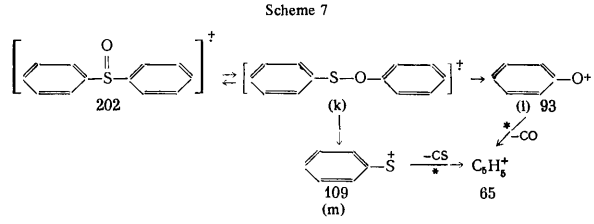
The presence of a second phenyl group in the styryl system greatly facilitates the sulphoxide–sulphenate rearrangement. High-resolution mass-spectrometric data and results for labelled compounds showed that elimination of the sulphinyl group from the molecular ions occurred neither with methyl styryl nor with methyl phenethynyl sulphoxide (Scheme 6), the latter of which is characterised by preferential migration of the acetylenic group with its *sp*-hybridised carbon atom from sulphur to oxygen. Successive detachment of a methylthio-group and of carbonyl gives the $[C_7H_5]^+$ ion of mass 89.

Scheme 6



Formation of a carbon–oxygen bond and elimination of carbon monoxide do not occur on electron bombardment of alkyl aryl sulphoxides having a long alkyl chain [19] and of $\beta$-keto-sulphoxides [20], owing to sulphenate isomerisation of the molecular ion. These compounds are characterised not only by rupture of $\alpha$- and $\beta$-bonds relative to the aromatic ring but also by the McLafferty rearrangement, which involves a six-membered transition state. This specific rearrangement occurs even with ionising electrons of very low energy. Elimination of the sulphinyl group from the molecular ion, which takes place with diphenyl [7], dibenzyl [21,22], and di-*p*-tolyl [8] sulphoxides, was not observed.

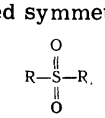
Scheme 7



Some evidence of the isomerisation of molecular ions of diphenyl sulphoxides into sulphenates (k) can be obtained from an examination of the mass spectra of diphenyl sulphoxide. Cleavage of the sulphur–oxygen bond causes the appearance of ions of mass 93 and 109—$[C_6H_5O]^+$ (*l*) and $[C_6H_5S]^+$ (*m*)—(Scheme 7). The metastable peaks indicate that elimination of carbonyl and thiocarbonyl groups leads in each case to an ion of mass 65 $[C_6H_5]^+$. In the mass spectra of higher homologues the fragments (*l*) and (*m*) are formed directly from the molecular ion (Scheme 7). The elementary composition of the fragments is confirmed by the high-resolution spectra [7]. Another feature of the above diaryl sulphoxides is the elimination of carbon monoxide and a hydrogen atom from the molecular ion, as well as the presence of the intense rearranged ion $[M - SO]^+$.

## IV. ALIPHATIC SULPHONES

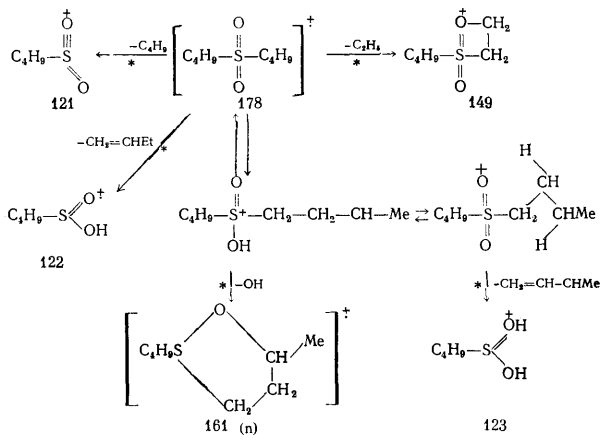
Aliphatic sulphones behave like the sulphoxides towards electrons. With the exception of dimethyl sulphone the mass spectra of saturated symmetrical dialkyl sulphones



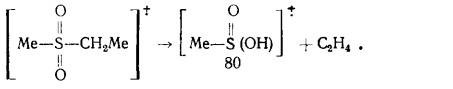
(R = $C_2H_5$, n-$C_3H_7$, n-$C_4H_9$, n-$C_5H_{11}$, n-$C_6H_{13}$, n-$C_7H_{15}$) contain intense peaks of hydrocarbon ions. Formation of rearranged ionic fragments $[RSO_2H_n]^+$, where $n = 0-2$, is characteristic of aliphatic sulphones [7,8,11,23]. The dissociative ionisation of dibutyl sulphone exhibits all the typical features of the breakdown of saturated dialkyl

sulphones due not only to rupture of a carbon–sulphur bond but also to $\gamma$-cleavage with migration of one or two hydrogen atoms to the oxygen atoms. The use of deuterium-labelled compounds has shown[11] that oxygen, together with the $\gamma$-hydrogen atom migrating to it, is detached from the molecular ion as a result of a McLafferty rearrangement with formation of the cyclic ionic fragment (n) of mass 161 (Scheme 8). It is interesting that the probability that an alkyl group will split off, with double migration of hydrogen to the charged ionic fragment, increases with the length of the alkyl chain[8].

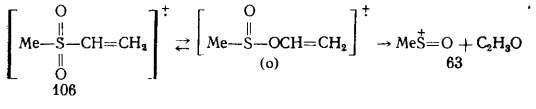
Scheme 8



Study of the mass spectra of unsymmetrical aliphatic sulphones—e.g. ethyl methyl and butyl methyl, ethyl, n-propyl, and isopropyl—shows[11] that the larger group is more easily removed from unbranched compounds, whereas cleavage of the secondary carbon–sulphur bond predominates in $\alpha$-branched systems. Furthermore, hydrocarbon fragments do not appear from the breakdown of ethyl methyl sulphone, as with dimethyl sulphone. In this case the rearrangement caused by migration of a hydrogen atom to oxygen leads to formation of an ion of mass 80:



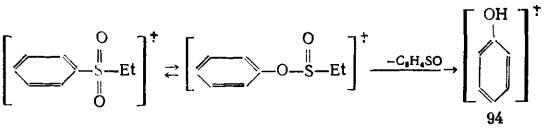
An unsaturated group present in an unsymmetrical sulphone migrates from the sulphur atom to oxygen. Thus the mass spectrum of methyl vinyl sulphone contains an intense peak of the $CH_3SO^+$ ion formed as a result of S → O migration of the vinyl group followed by fission of the sulphur–oxygen bond in the intermediate structure (o):



## V. AROMATIC SULPHONES

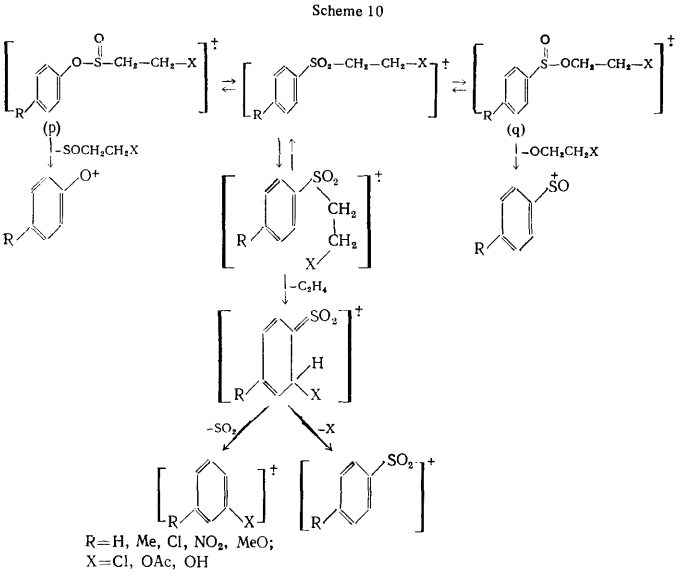
The spectra of mixed alkyl aryl sulphones $C_6H_5.SO_2.R$ (where R = $CH_3$, $C_2H_5$, iso-$C_3H_7$, cyclo-$C_3H_7$, n-$C_4H_9$, n-$C_6H_{13}$) exhibit the S → O migration of phenyl also observed with sulphoxides[8,24–26]. For example, the molecular ion of ethyl phenyl sulphone eliminates $C_2H_4SO$ in a single stage with formation of the $[C_6H_6O]^+$ ion of mass 94. This mode of decomposition has been proved by high-resolution mass spectrometry and by the study of deuterium-labelled specimens (Scheme 9).

Scheme 9



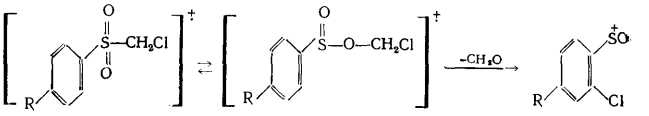
A $\beta$-substituent X present in an aryl ethyl sulphone may migrate to the aromatic ring[27–31]. However, the ions $[M - C_2H_4.X]^+$ and $[M - C_2H_4.SO_2]^+$, formed by the McLafferty arrangement, do not represent the chief mode of decomposition. The most intense peaks in the mass spectra of substituted aryl ethyl sulphones correspond to the ions $[M - OCH_2CH_2X]^+$ and $[M - SOCH_2CH_2X]^+$, which can be formed only by isomerisation of the molecular ion followed by rupture of the sulphur–oxygen bond in the intermediate structures (p) and (q) (Scheme 10).

Scheme 10



Furthermore, a substituent in the aromatic ring may influence migration of the aryl group from the sulphur atom to oxygen[25–32]. Thus the electron-accepting *p*-nitro-group hinders S → O migration of the aryl in the dissociative ionisation of 2-chloroethyl *p*-nitrophenyl sulphone, whereas the electron-donating methoxy-group (in 2-chloroethyl *p*-methoxyphenyl sulphone) facilitates such migration.

Although unsaturation in the migrating group is regarded as a factor increasing the probability of rearrangement, investigation of substituted aryl chloromethyl sulphones shows[28] that migration of the alkyl competes successfully with that of the aryl. The appearance of $[RC_6H_4SO]^+$ ions in the mass spectra of these compounds is due to formation of an alkyl–oxygen bond in the transition state with subsequent elimination of the neutral species $CH_2O$ and migration of the chlorine atom to an *ortho*-position relative to the sulphur atom:



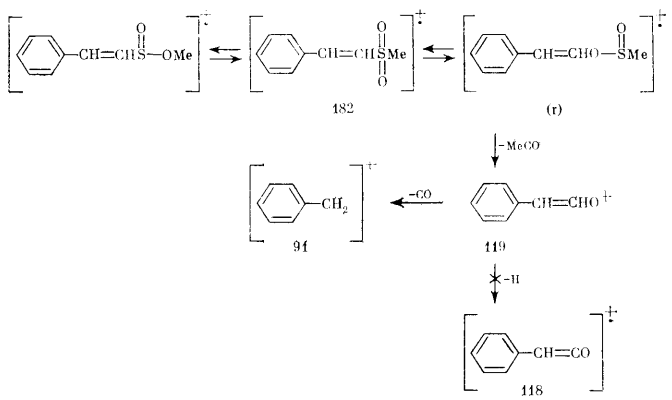
where R = $CH_3O$, $CH_3$, H, Cl, Br, $NO_2$. When the chlorine atom is replaced by hydrogen, such rearrangement is not observed, but an $SOCH_2$ group is eliminated with formation of an ion having the structure of the corresponding phenol.

Evidence of S → O migration of the aryl is lacking for benzenesulphonyl chlorides and their derivatives[27,33,34]. These compounds undergo rearrangement with formation of the $[M - SO_2Cl]^+$ ion. The *ortho*-effect is responsible for the absence of this ion peak in *o*-nitrobenzenesulphonyl chloride, which undergoes initial abstraction of a nitroso-group from the molecular ion followed by elimination of a chlorine radical.

Aryl vinyl sulphones behave similarly to aryl ethyl sulphones. Isomerisation of their molecular ions involves migration of the vinyl in preference to the phenyl group[30]. The peak due to $[M - OCH:CH_2]^+$ ions produced by rupture of the sulphur–oxygen bond is the most intense in the mass spectra of these compounds.

A substituent in the aromatic ring influences not only the migrating power of the phenyl group but also the less significant mode of decomposition involving detachment of a neutral sulphonyl group from the molecular ion. Thus, although the $[M - SO_2]^+$ ion peak is absent from the spectrum of *p*-nitrophenyl vinyl sulphone, it becomes the most intense in the spectrum of the methoxy-derivative, which is evidence of the influence of the electron-donating power of a ring substituent on the probability of elimination.

Scheme 11



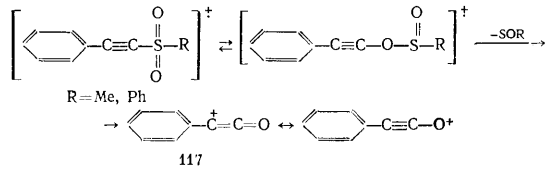
Styryl sulphones show similar competition between the S → O migration of alkyl or styryl[17]. Thus in the decomposition of methyl styryl sulphone on interaction with electrons the preferential migration of styryl from sulphur to oxygen followed by abstraction of a $CH_3SO$ radical from the intermediate structure (r) promotes formation of a carbon–oxygen bond and elimination of carbon monoxide from the fragment of mass 119 (Scheme 11). The loss of hydrogen by the ionic fragment of mass 119 observed with methyl styryl sulphoxides is completely absent from the mass spectrum of the sulphone. The process $119^+ \rightarrow 118^+$ probably requires more energy than does $119^+ \rightarrow 91^+$ (Scheme 11). Elimination of hydrogen from the $[M - CH_3SO]^+$ ion and removal of carbonyl or formyl from the molecular ion are absent also from the mass spectra of higher homologues of methyl styryl sulphone.

In view of the above, the lack of competition between the S → O migration of the groups in phenyl styryl sulphone is extremely curious. The mass spectrum indicates unambiguously migration of the styryl group and absence of migration of phenyl[17].

Loss of the sulphonyl group as a result of a rearrangement of the type $[ABC]^+ \rightarrow [AC]^+ + B$ also exhibits a lower probability than the removal of sulphinyl from methyl styryl sulphoxide.

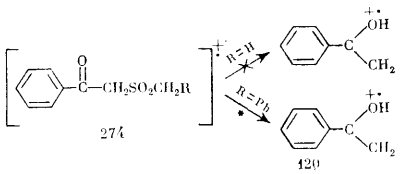
The dissociative ionisation of methyl or phenyl phenethynyl sulphone reveals peculiar behaviour of the acetylenic group, which alone migrates from sulphur to oxygen, while the methyl or phenyl group plays almost no part in the process (Scheme 12).

Scheme 12

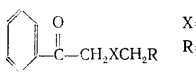


The stability of the neutral species expelled from the molecular ion is responsible for the McLafferty rearrangement[20,22], which has an important role in the formation of the characteristic ions. Indeed, with a keto-sulphone [20] such rearrangement is not followed by elimination of a simple sulphine. In the case of the phenyl derivative, however, such a sulphine may be stabilised, since the spectrum contains a peak at mass 120 corresponding to the $[M - SO_2CHR]^+$ ion, which is confirmed by a metastable transition (Scheme 13).

Scheme 13



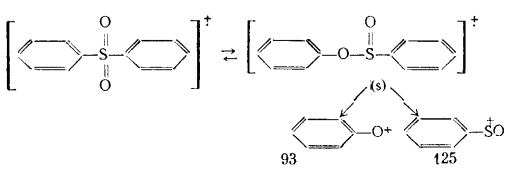
Investigation of the series of compounds [20]



revealed that increase in the stability of the neutral fragment XCHR with R = $C_6H_5$ is accompanied by intensification of the peak of the rearranged ion $[M - XCHR]^+$ in comparison with that obtained with R = H.

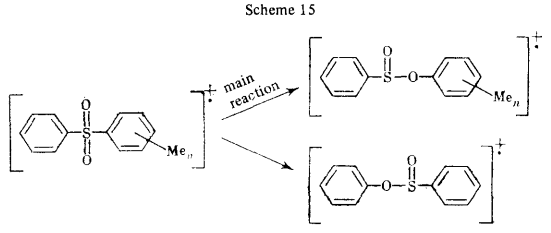
A peculiarity of the dissociative ionisation of diphenyl sulphones is the equally probable S → O migration of aryl with formation of an intermediate aryl arenesulphinate (s). Whereas benzophenone and diphenylmethane are characterised by the formation of ions undergoing rearrangement with detachment of the bridging group, together with one or two hydrogen atoms that have migrated, resulting in formation of an ion of biphenylene structure[35], this process is less strongly developed with diphenyl sulphone, for which the main reaction involves cleavage of the sulphur–oxygen bond in (s) with formation of an intense peak of mass 125 [22] (Scheme 14).

Scheme 14



The introduction of different substituents into the aromatic rings leads to competition in migration of the aryl groups with preferential formation of ionic fragments containing a substituted or an unsubstituted phenyl. The tendency to migrate increases with the number of electron-donating methyl groups [26]. It was suggested [26] that the electron deficit is localised mainly in the non-bonded orbital of the oxygen, so that the phenyl ring better able to function as an electron donor would be more likely to migrate [26,36] (Scheme 15).

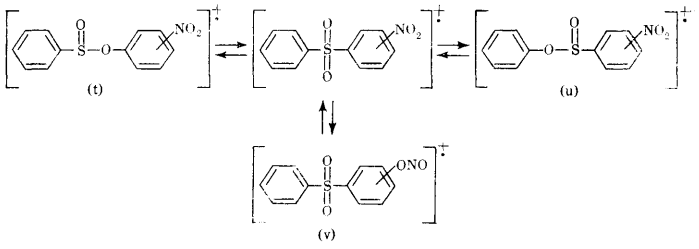
Scheme 15




However, study of a series of *para*-substituted diphenyl sulphones has shown that both electron-donating and electron-accepting substituents are able to increase the migratory power of an aromatic ring [37]. Since an electron-donating group has a considerably stronger stabilising influence on $[ArO]^+$ than on $[ArSO]^+$ ions, the increased migratory power of such a group can be attributed to the stability of the resulting ion. On the other hand, electron-accepting substituents obviously facilitate bond rupture, since they diminish the stability of the positively charged species. If the change in energy of bond rupture exceeds the change in stability of the resulting ion, the migratory power of the aromatic ring containing the electron-accepting group may exhibit an apparent increase [37].

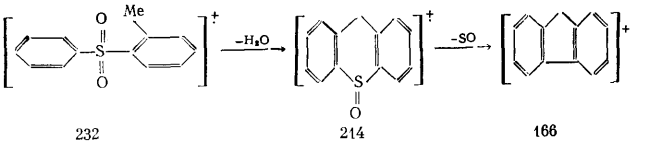
The intensity ratio of the $[ArSO]^+$ and $[ArO]^+$ ion peaks varies within wide limits depending on the type and position of a substituent in the aromatic ring, which indicates competition in formation of intermediate sulphinate structures by migration of a ring from sulphur to oxygen. Thus for the isomeric nitrophenyl phenyl sulphones the probability of formation of the intermediate structure (t) decreases in the sequence *para* > *meta* > *ortho*, whereas the structure (u) is most characteristic of the *ortho*-isomer and less typical of the *para*- and *meta*-compounds [38] (Scheme 16).

Scheme 16



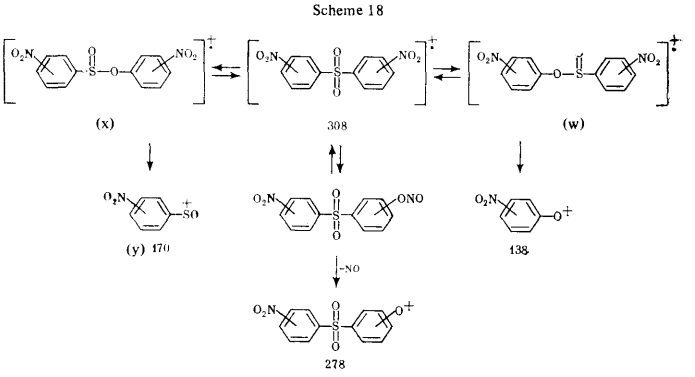
The possibility of nitro-nitrate isomerisation of the molecular ions must be taken into account when considering the dissociative ionisation of nitro-substituted aromatic sulphones [39]. In the case of nitrodiphenyl sulphones it leads to the formation of ions (v) whose subsequent breakdown with elimination of a nitroso-group results in the appearance of characteristic $[M - NO]^+$ ions. The probability of nitro-nitrate isomerisation is doubled in the case of the *ortho*-isomer, owing to the presence of an *ortho*-effect. Such an effect is apparent also in the decomposition of phenyl *o*-tolyl sulphone, where it causes the formation of characteristic $[M - H_2O]^+$ and $[M - OH]^+$ ions, which then eliminate the sulphinyl group [26] (Scheme 17). Elimination of hydrogen atoms from the *o*-methyl group was confirmed by a study of deuterated compounds. The relative intensities of the ion peaks formed by the detachment of $SO_2$, $SO_2H$, and $SO_2CH_3$ from the molecular ion also depend on the position of the substituent in the aromatic ring [26].

Scheme 17




With 2,4-dinitrophenyl phenyl sulphone migration of the unsubstituted aromatic ring from sulphur to oxygen is preferred [38]. The probability of such isomerisation increases with decrease in the energy of the ionising electrons, and the $[ArO]^+$ ion becomes the main peak in the spectrum.

Scheme 18



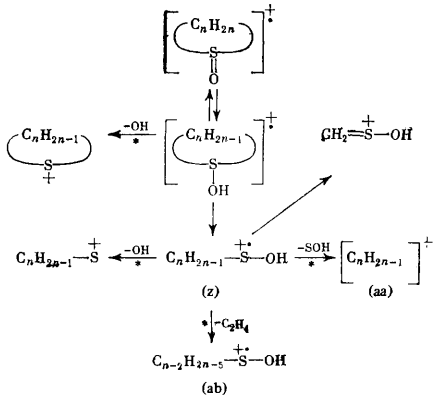

When both rings in a diphenyl sulphone are substituted [40], cleavage of the sulphur–oxygen bond in the ions (w) and (x) formed by migration of either aromatic ring from sulphur to oxygen leads to preferential formation of $[Ar'SO]^+$ ions of mass 170 (y) in relation to $[Ar'O]^+$ ions [40] (Scheme 18). Depending on the positions of substituents in the aromatic ring relative to the sulphonyl group the ion (y), corresponding to the maximum peak in the spectrum of all the isomers other than 2,4'-dinitrodiphenyl sulphone, increases in intensity relative to the total ion current in the sequence of isomers *ortho* < *meta* < *para*.

## VI. CYCLIC SULPHOXIDES

The mass spectra of sulphoxides and sulphones containing the sulphur atom in a saturated or partly saturated ring system had not been studied in such great detail as those of the aliphatic and aromatic compounds. The behaviour of saturated cyclic compounds such as thietan, thiolan, thian, and thiepan *S*-oxides is similar to that of aliphatic sulphoxides subjected to electron bombardment [11]. The general pattern is shown in Scheme 19. Migration of a hydrogen atom to the oxygen atom followed by cleavage of a carbon–sulphur bond is responsible for the appearance of the ion $[R-S-OH]^+$ (z). The fact that this bond forms part of the ring impedes direct detection of the migration of hydrogen atoms involved in the process. The character

of the migration can be determined only after loss of the SOH group, i.e. after the process (z) → (aa). Rupture of the carbon–sulphur bond may be followed by removal of ethylene comprising $\alpha$- and $\beta$-methylene groups—process (z) → (ab)—which increases the difficulty of establishing the mechanism of decomposition.

Scheme 19

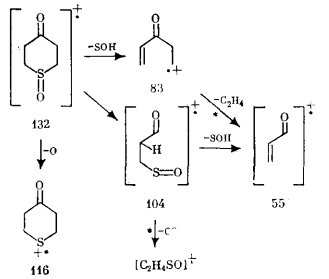


The mass spectra of deuterated sulphoxides [11] indicate that the migration of hydrogen involved in the cleavage of a carbon–sulphur bond (loss of SOH) is effected by a McLafferty rearrangement. The elimination of a hydroxyl is less important than thietan, thiolan, and thian-1-oxides, but leads to intense peaks in the mass spectrum of thiepan 1-oxide, whereas the probability of elimination of the SOH group increases as the ring becomes smaller. This effect is attributed [41] to the difference in the distance of closest approach of the sulphinyl oxygen atom to $\beta$- and $\gamma$-hydrogen atoms.

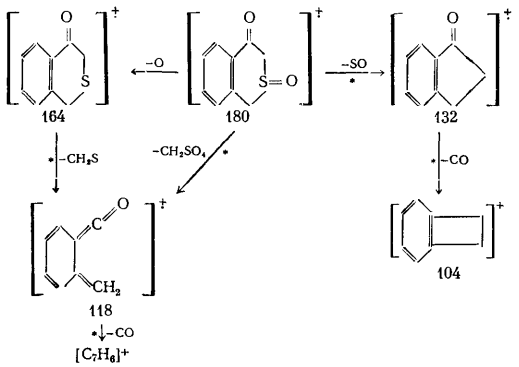
The pattern of decomposition is greatly changed by introduction of a 4-keto-group into thian 1-oxide [42], when it involved mainly loss of ethylene as a result of a retrodiene reaction. This indicates that the presence of an $sp^2$-hybridised carbon atom attached to sulphur in the cyclic sulphoxides promotes rearrangement, whereas a specifically introduced carbonyl group causes retrodiene decomposition. For example, application of the concept of charge localisation to the dissociative ionisation of 4-oxothian 1-oxide suggests preferential elimination of an alkene from the molecular ion, which is evident in formation of the corresponding metastable ion. Subsequent detachment of the group SOH from the $[M - \text{Alkene}]^+$ ion tends to produce the maximum peak in the spectrum at mass 55 [Scheme 20]. From the low intensity of the $[M - \text{SOH}]^+$ ion peak it may be supposed that this mode of decomposition is less favourable, while the weak ion peak at mass 116, formed as a result of removal of an oxygen atom from the molecular ion, indicates the improbability of this process. The elimination of hydroxyl from the molecular ion, observed with aliphatic and caromatic sulphoxides [8], is found also in the spectrum of the present compound.

Competition between retrodiene decomposition and elimination of a sulphinyl or sulphonyl group has been detected among compounds of the thiachromanone series [43]. Accompanying elimination of an oxygen atom, a hydroxy-group, or a water molecule from the molecular ion, the chief mode of breakdown of 4-oxothiaisochroman 2-oxide involves initial loss with formation of the maximum ion $[M - \text{SO}]^+$. Subsequent detachment of carbon monoxide yields an ion of mass 104 having a benzocyclobutene structure. Scheme 21 is confirmed by the metastable peaks observed in the mass spectrum. Retrodiene decomposition, which is less probable in this case, involves abstraction of a $CH_2SO$ group and is also accompanied by a metastable transition.

Scheme 20

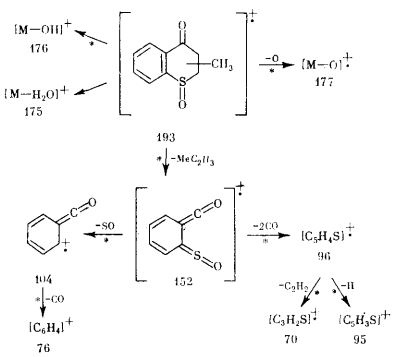


Scheme 21



Thiachromanone and its methyl derivatives undergo breakdown mainly by a retrodiene reaction involving loss of $CH_3C_2H_3$ with formation of a maximum ion peak at mass 152. The ion then loses sulphur monoxide to give an ion peak at mass 104 (Scheme 22). Direct detachment of a sulphinyl group from the molecular ion is secondary in character.

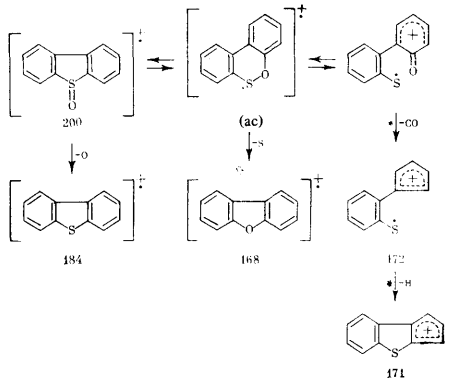
Scheme 22



It is noteworthy that, although sulphur is attached to two $sp^2$-hybridised carbon atoms in oxothiachroman oxides, rearrangement of the molecular ion into a sulphenate on electron bombardment, which is characteristic of unsaturated cyclic compounds, could not be demonstrated [43]. Thus dibenzothiophen S-oxide breaks down [44] with formation of the dibenzothiophen cation of

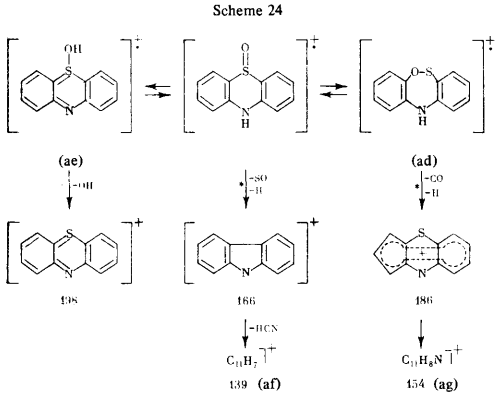
mass 184. This is accompanied by detachment of CO or CO + H from the molecular ion. This can be explained by the rearrangement noted with open-chain sulphoxides[8]. Appearance of the intermediate ion (ac) as a consequence of the rearrangement is confirmed by a weak peak of mass 168, corresponding to the dibenzofuran cation (Scheme 23).

Scheme 23



Detachment of a sulphinyl group in a single stage is not observed with compounds containing two heteroatoms in the middle ring[44], where the sulphoxide oxygen is involved in formation of the $[M - CO - H]^+$ ion, but the ring oxygen atom is involved in a subsequent stage of fragmentation. The dissociative ionisation of phenothiazine 5-oxide is remarkable in a mode of decomposition, accompanying those mentioned above, in which the middle ring expands to seven members (ad).[45] It is also noteworthy that hydroxyl is removed from the molecular ion (ae) following transannular redistribution of hydrogen (Scheme 24). The ions (af) and (ag) are extremely stable: the former is met in almost all mass spectra of dibenzo-derivatives of heterocyclic compounds; and the latter is always present when one or two heteroatoms in a six-membered ring are attached to hydrogen.

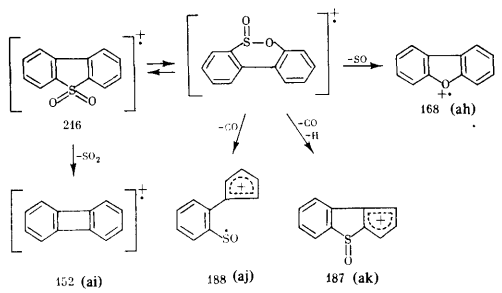
Scheme 24



## VII. CYCLIC SULPHONES

Cyclic sulphones are characterised by rearrangements involving isomerisation of the molecular ion. For example, the main processes in the initial breakdown of dibenzothiophen [*S*-dioxide] include the loss of sulphinyl and carbonyl groups[8,46,47], probably as a result of isomerisation of the molecular ion into a sulphinic ester similarly to alkyl aryl and diaryl sulphones[26]. The dibenzofuran ring system (ah) is formed considerably more readily than is the four-membered cyclobutadiene ring of biphenylene (ai). Elimination of carbonyl and formyl groups from the molecular ion produces the ions (aj) and (ak) respectively (Scheme 25).

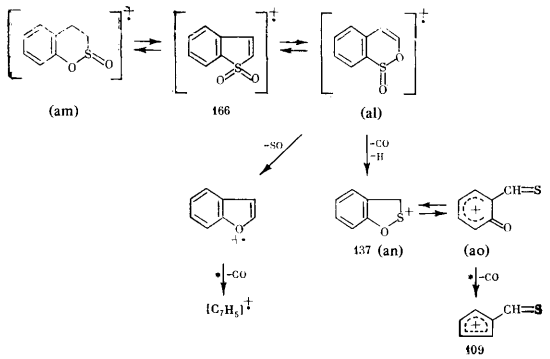
Scheme 25



When a heteroatom has been introduced into the ring—thiaxanthen, oxothiaxanthen, phenothiazine, thianthren, and phenoxathiin *S*-dioxides—decomposition involves preferential elimination of sulphur dioxide[44,45,48]. In the ensuing stages carbon monoxide is removed, which is evidence of formation of a carbon–oxygen bond by isomerisation of the molecular ion into a cyclic sulphinate.

The mode of decomposition is greatly affected by change in the structure of the cyclic sulphone. In this respect the mass spectrum of dihydronaphthobenzothiophen *S*-dioxide is quite remarkable[49], containing an intense peak of $[M - SO_2]^+$ ions but without the elimination of carbonyl and sulphinyl groups resulting from isomerisation of the molecular ion into a sulphinic ester. Yet benzothiophen 1-dioxide[44,50,51] isomerises with preferential formation of the intermediate structure (al), not (am). Subsequent elimination of SO and CO + H groups from the ion (al) leads to the formation of characteristic ions, the latter of which can be represented by the two tautomers (an) and (ao) (Scheme 26). Investigation of deuterated compounds established the initial elimination of CO + D, which was confirmed by the corresponding metastable peak: i.e. the rearrangement involves a hydrogen atom in an $\alpha$-position with respect to the sulphur atom[50].

Scheme 26

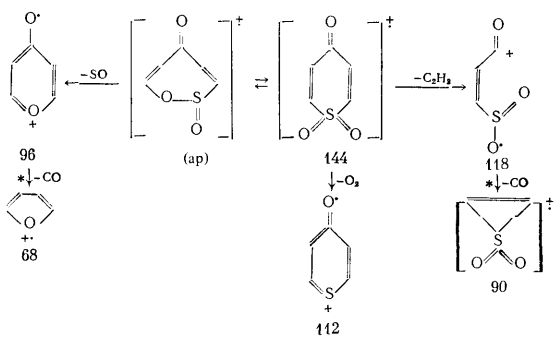


The most probable process with phenylated and chlorinated benzothiophen 1,1-dioxides is the elimination of $COC_6H_5$ and COCl from the isomerised molecular ion[52]. Nevertheless, dihydrobenzothiophen 1,1-dioxide after isomerisation breaks down in a different way, with elimination of sulphinyl and hydroxymethyl groups from the molecular ion.

The saturated cyclic compounds rearrange and decompose[45] similarly to aliphatic sulphones[8]. The dissociative ionisation of thiolan, thian, and thiepan 1,1-dioxides is accompanied by migration of a hydrogen atom with preferential detachment of sulphonyl and sulphino-groups as a result of rupture of a carbon–sulphur bond[11]. If a carbonyl groups is introduced into the six-membered ring, e.g. at position 4, the pattern of dissociative ionisation changes fundamentally[45], to resemble the scheme of decomposition of substituted five- and six-membered sultams[53]. A characteristic reaction in the decomposition of the above compounds is the detachment of sulphur dioxide not from the molecular ion but from the ionic fragments $[M - C_2H_4]^+$ and $[M - CO]^+$ respectively.

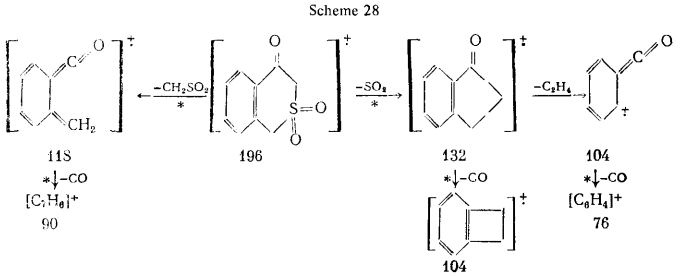
If the ring contains unsaturated bonds, the molecular ions of cyclic sulphones isomerise similarly to aryl sulphones[29]. Thus the dissociative ionisation of thiapyrone 1,1-dioxide [42] involves the intermediate ion (ap), from which sulphinyl is removed. However, the principal mode of decomposition includes preferential elimination of acetylene from the molecular ion. This takes place by a mechanism of retrodiene breakdown with subsequent formation of a carbon–oxygen bond and loss of carbon monoxide (Scheme 27).

Scheme 27



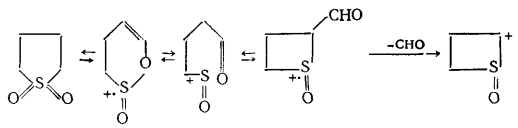

Change in the size of ring in a cyclic sulphone does not affect the mode of decomposition. This was revealed in a study of thiepin 1,1-dioxide and its dihydro-derivative[44,54]. The characteristic $[M - CHO]^+$ ion peak indicates sulphone–sulphinate rearrangement of these compounds.

Scheme 28



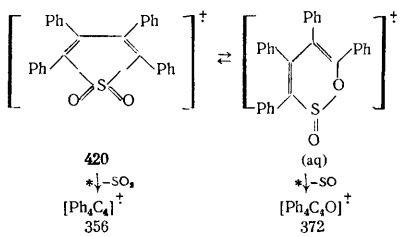

Nevertheless, although sulphur is combined with an $sp^2$-hybridised carbon atom in such compounds as thiachromanone dioxide, the molecular ion does not isomerise into a sulphinic ester[43] before decomposition begins. For example, 4-oxothiaisochroman 2,2-dioxide breaks down mainly with elimination of sulphur dioxide from the molecular ion. Retrodiene decomposition with the detachment of $CH_2SO_2$ is of secondary importance (Scheme 28). The most probable process for 4-oxothiachroman 1,1-dioxide, however, involves detachment of ethylene with subsequent elimination of sulphur dioxide. Direct removal of a sulphonyl group from the molecular ion is far less probable. Introduction of a methyl substituent into a thiachromanone does not in principle change the mode of decomposition, which involves a retrodiene reaction resulting in elimination of a $C_3H_6$ group.

Scheme 29




It is interesting that the mass spectrum of sulpholan contains peaks due to ions formed by direct detachment of SO, $HSO_2$, and $CH_3SO_2$ groups from the molecular ion. Cleavage of a carbon–sulphur bond with retention of charge on the carbon fragment is highly probable in the decomposition of this compound[55]. Nevertheless, the presence of unsaturated bonds promotes isomerisation of the molecular ion of sulpholan into a sulphinic ester with subsequent elimination of a COH group (Scheme 29). The molecular ions of mono- and di-substituted sulpholans do not undergo sulphone–sulphite isomerisation on decomposition[55], whereas tetraphenylthiophen 1,1-dioxide readily loses a sulphinyl group from the isomerised molecular ion[56,57] formed as a result of sulphur–oxygen migration of a ring carbon atom (Scheme 30).

Scheme 30



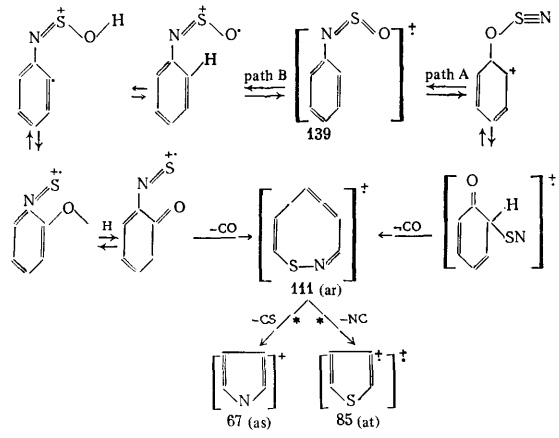

It must be added that complicated cyclic keto-sulphones, which readily lose sulphur dioxide from the molecular ion, do not undergo sulphone–sulphite isomerisation[58,59].

## VIII. NITROGEN-CONTAINING SULPHOXIDES AND SULPHONES

### Sulphinylanilines

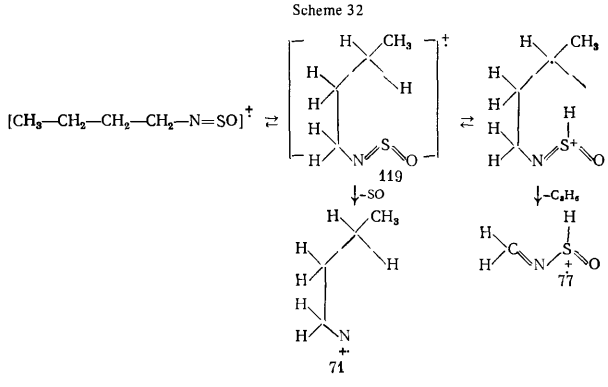
The chief modes of decomposition of arylsulphinylanilines result in formation of a carbon–oxygen bond, and ions are formed even with ionising electrons of low energies. Such rearrangement should take place either with migration of the aromatic ring to the oxygen atom followed by movement of the SN group to position 2 (path A) [60] or with migration of an *ortho*-hydrogen atom from the ring to the oxygen atom followed by regrouping of the hydroxy-group in the aromatic ring (path B)[61]. In the former case the $C_{(1)}$ atom is lost, and the latter case the $C_{(2)}$ atom (Scheme 31). Study of a 1-$^{13}$C-sulphinylaniline has shown[65] that the $C_{(2)}$ atom, not $C_{(1)}$, is lost when carbon dioxide is eliminated. The $[M - CO]^+$ ion (ar) may be a cyclic ion, which then breaks down with removal of CS and HCN groups to form structures (as) and (at) respectively[62].

Scheme 31

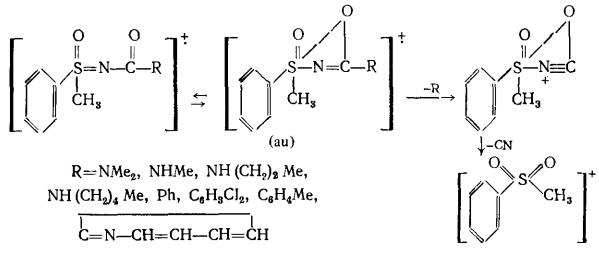


Substituted sulphinylanilines may also undergo rearrangement. The spectrum of *m*-methoxy-sulphinylaniline, for example, reveals well defined rearranged ions, whereas the mass spectra of the *ortho*- and *para*-isomers are devoid of corresponding peaks[63].

Scheme 32



Scheme 33



The decomposition of alkylsulphinylanilines[63-65], however, involves a McLafferty rearrangement, in which the hydrogen atom attached to the $\gamma$-carbon atom migrates to the sulphur atom, after which an ionic fragment of mass 77 is formed (Scheme 32). A second important mode of dissociative ionisation is formation of the $[M - SO]^+$ ion. When the $\alpha$- or $\beta$-carbon atom is substituted, however, simple rupture of a carbon–carbon or carbon–nitrogen bond is correspondingly more probable than a McLafferty rearrangement.

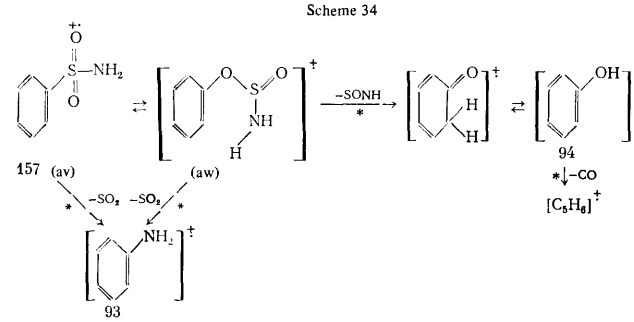
## Sulphoximines

The principal decomposition pathway of *N*-substituted sulphoximines is characterised by the appearance of $[M - R]^+$ and $[M - CH_3]^+$ ion peaks. The observed formation of a sulphone ion $[C_6H_5SO_2CH_3]^+$ is due to breakdown of the $[M - R]^+$ ion and is responsible for establishment of a bond between the carbonyl oxygen atoms and the sulphur atom in the transition state[66] (Scheme 33).

## Sulphonamides

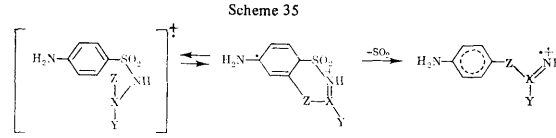
Available data on the decomposition of sulphonamides reveal a tendency to rearrangement with removal of sulphur dioxide. Thus the mass spectrum of benzenesulphonamide and its derivatives shows well defined skeletally rearranged ions resulting from the formation of carbon–oxygen and carbon–nitrogen bonds. Two rearrangements of $(M - SO_2)$ and $(M - SONH)$ take place[36,37,67,68]. The migration of phenyl from the sulphur to an oxygen atom promotes formation of an intermediate structure (aw), from which an ion of phenolic type can then be formed (Scheme 34). The ion of the aniline radical $[M - SO_2]^+$ can probably be formed from (av) or (aw). It is noteworthy that elimination of carbon monoxide from the molecular ion is not observed in the case of sulphonamides[69].

Scheme 34



The nature of the alkyl substituent in secondary sulphonamides affects the behaviour of the compounds on electron impact. The main process is $\beta$-rupture relative to the nitrogen atom; skeletally rearranged ions are absent. When alkyl is replaced by amino the main process becomes formation of $[M - NH_2 - O_2]^+$ ions, whereas sulphonamides containing two substituents undergo fission at the nitrogen–sulphur bond with the charge retained on the nitrogen-containing fragment. Skeletally rearranged ions are represented by weak peaks. The mass spectrum contains no ion corresponding to formation of a carbon–oxygen bond.

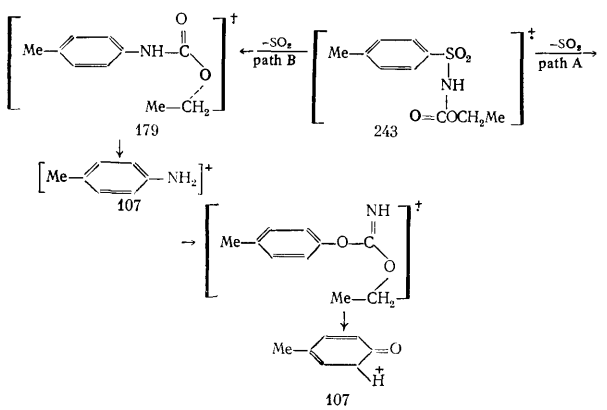
Scheme 35



The probability of the loss of sulphur dioxide increases considerably with the basicity of the substituting group in sulphonamides. With steric factors taken into account, the general direction of decomposition can be represented by Scheme 35. The behaviour of sulphonamide derivatives is explained by the influence of strongly electrophilic substituents, which create a partial positive charge and favour rearrangement with elimination of sulphur dioxide[70,71].

Evident skeletal rearrangements, associated with the appearance of $[M - SO_2]^+$ ions, are in turn characteristic also of sulphonylureas [72,73] and sulphonylcarbamates [74] containing primary, secondary, and tertiary alkyl substituents. The combination of high-resolution mass spectrometry with use of labelled compounds has established the occurrence of two decomposition processes involving rearrangement with elimination of sulphur dioxide from the molecular ion. With both groups of compounds the main process includes preferential formation of an aryl–oxygen bond (path A) and to a lesser extent an aryl–nitrogen bond (path B) followed by breakdown of the $[M - SO_2]^+$ ion with a McLafferty rearrangement. An example is the decomposition of an alkyl *N*-toluenesulphonylcarbamate (Scheme 36). The probability of decomposition of a sulphonylcarbamate by path B can be increased by strengthening the nucleophilic character of the *N*-methylated derivative or by the steric effect of the methyl substituent.

Scheme 36

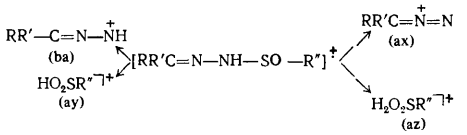


It is interesting that the spectrum of t-butyl *N*-*p*-methoxybenzenesulphonylcarbamate does not contain the $[M - SO_2]^+$ ion. The most probable decomposition involves elimination of carbon dioxide accompanied by a methyl radical. This was explained [74] by the influence on the relative stability of the aryl–sulphur and alkyl–oxygen bonds of the factors responsible for the direction of decomposition. In primary and secondary alkyl derivatives of sulphonylcarbamates the aryl–sulphur bond is weakest, so that decomposition along path B (Scheme 36) predominates. Introduction of a t-alkyl group results in some strengthening of the alkyl–oxygen bond. Yet introduction of an *N*-methyl substituent lowers the strength of the aryl–sulphur bond. This unusual change in stability of the two types of bond on the introduction of a methyl substituent is difficult to interpret in terms of the inductive effect alone, since steric factors cannot be ignored. Interaction of methyl with the sulphonyl group and the aromatic ring lengthens the aryl–sulphur bond sufficiently to neutralise the effect of the t-alkyl on the alkyl–oxygen bond. The relative stability of the former bond can be changed also by introducing various *para*-substituents into the benzene ring: electron-donating substituents will strengthen the aryl–sulphur bond in comparison with unsubstituted rings, whereas electron-accepting substituents will tend to weaken the bond [71].

## Sulphonylhydrazones, Sulphonylhydrazines, and Sulphonyl Azides

Elimination of relatively stable neutral species from ions $[ABC]^+ \rightarrow [A-C]^+ + B$ is most characteristic of sulphonylhydrazones [74]. Four ionic species are produced when the molecular ion decomposes with rupture of the nitrogen–sulphur bond. Fragments (ay) and (az) are formed with migration of hydrogen. The ion (az), into which two hydrogen atoms have migrated, is converted into (ay) when the compound contains an alkyl group with hydrogen attached to the $\alpha$-carbon atom (Scheme 37).

Scheme 37

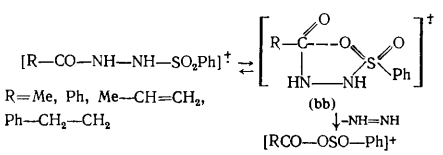


Aromatic sulphonylhydrazones (R = $C_6H_5$, R′ = H) decompose with elimination of molecular nitrogen from the ion (ax), whereas the ion (ba) rearranges with removal of a nitrile molecule from the middle of the chain.

The mass spectra of aliphatic sulphonylhydrazones indicate formation of (ba) in preference to (ax), (ay), and (az). The decomposition sequence is greatly dependent on the type and size of the aliphatic groups.

The decomposition of *N*-acyl-*N*′-*p*-toluenesulphonylhydrazines [74,75] also involves a rearrangement $[ABC]^+ \rightarrow [AC]^+ \rightarrow B^2$ with elimination of a di-imide molecule from the molecular ion, perhaps via an intermediate cyclic structure (bb) (Scheme 38).

Scheme 38

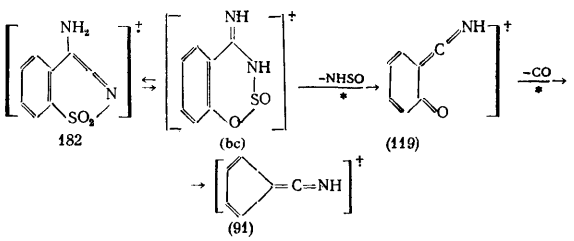


Skeletal rearrangements with elimination of sulphur dioxide from the molecular ion do not occur with sulphonyl azides [76,77]. Detachment of an azide radical is inconsistent with the photochemical behaviour, which involved elimination of nitrogen [75].

## Benzisothiazoles and Thiazolidines

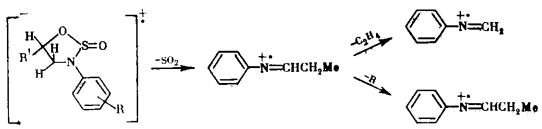
Benzisothiazole derivatives [78] on dissociative ionisation undergo rearrangement with formation of an intermediate structure (bc). For example, an investigation of 3-aminobenzisothiazole 1,1-dioxide labelled with deuterium in the amino-group confirmed the occurrence of decomposition in conformity with Scheme 39.

Scheme 39



*ortho*-Alkylated derivatives undergo rupture with migration of two hydrogen atoms and loss of an alkyl group followed by elimination of sulphur dioxide from the ionic fragment.

Scheme 40



Higher homologues are characterised by decomposition with McLafferty rearrangement, but *N*-substituted compounds by elimination of an alkylamine from the molecular ion. Direct detachment of sulphur dioxide is improbable. Yet various oxathiazolidines [79,80] undergo rearrangement with removal of sulphur dioxide (Scheme 40). The probability of formation of an $[M - SO_2]^+$ ion varies with the nature and the position of the substituent. Thus with chloro-derivatives this is the most intense peak in the mass spectrum of the *ortho*-isomer, whereas with the methyl derivatives the $[M - SO_2]^+$ ion peak has approximately the same intensity for all the isomers. Its subsequent decomposition can take place in two ways, with elimination of ethylene or of the ring substituent.

The chief mode of decomposition of oxothiazolidine having a t-butyl substituent in the ring [81] involves loss of a methyl radical preceding elimination of sulphur dioxide, whereas introduction of a chloromethyl substituent into the oxathiazolidine ring [82] suppresses the rearrangement associated with the elimination. With such a compound sulphur dioxide and a chlorine radical are detached in a single stage.

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# Mono- and Bis-α-diketones and Related Polymers

E.S.Krongauz

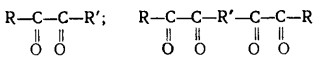
Published information on the methods of preparation and the reactions of mono- and bis-α-diketone is reviewed. Special attention is paid to use of the latter to obtain heat-resistant and thermostable polymers, in particular polyphenylquinoxalines. A list of 201 references is included.

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III. Reactions of α-dicarbonyl compounds 64
IV. Bis-α-dicarbonyl compounds in the preparation of heterocyclic polymers 67

## I. INTRODUCTION

The past decade has witnessed appreciable heightening of interest in mono- and bis-α-dicarbonyl compounds of general types



(where R and R′ represent aliphatic or aromatic groups), which are finding ever wider application in organic synthesis in virtue of their high reactivity. Such compounds provide a basis for obtaining aliphatic, aromatic, and heterocyclic products, whether of low or high molecular weight, possessing several valuable properties. Previous reviews[1-3] have paid insufficient attention to methods for the preparation of α-diketones, and have completely disregarded their chemical reactions and practical application. The present Review aims to fill this gap, paying special attention to methods of preparation that have already found or may find application in obtaining bis-α-dicarbonyl compounds, and also to the use of the latter in the synthesis of thermostable high polymers. Although compounds containing α-diketone groupings are mainly considered, methods of obtaining α-keto-aldehydes and polymers based on them are also included.

## II. METHODS OF PREPARATION OF α-DIKETONES

Existing methods for preparing α-diketones can be separated into the following main groups—(1) oxidation of acyloins, (2) oxidation of α-methylene-carbonyl compounds, (3) oxidation of compounds containing carbon–carbon multiple bonds, and (4) other methods.

### 1. Oxidation of Acyloins

The first observations indicating that benzoin could be oxidised by nitric acid to benzil were made more than a century ago by Zinin[4]. Since then the reaction conditions and the oxidising agents have been varied. The most widely used oxidants have been copper(II) salts, applied in the presence of regenerating agents (air, ammonium nitrate): e.g.[5]

$$RCH(OH)COR' + 2\,Cu(OAc)_2 \rightarrow RCOCOR' + 2\,CuOAc + 2\,AcOH\ ,$$
$$2\,CuOAc + NH_4NO_3 + AcOH \rightarrow 2\,Cu(OAc)_2 + NH_4NO_2 + H_2O\ ,$$
$$NH_4NO_2 \xrightarrow{H^+} N_2 + 2H_2O\ .$$

Acetic acid not only acts as solvent but also favours decomposition of the ammonium nitrite formed in the regeneration of copper(II). The yield of α-diketones is often nearly theoretical. This reaction is specific to acyloins, for benzaldehyde, benzhydrol, and mandelic acid are not oxidised under these conditions[5].

Table 1. Characteristics of α-diketones from acyloins.

| α-Diketone | Yield, % | M.p., °C | Ref. |
|---|---|---|---|
| (*a*) Oxidation by $Cu^{II}$ sulphate in pyridine | | | |
| Benzil | 86-97 | 94.5 | 6 |
| *o*-Methoxybenzil | 60 | 71-72 | 7 |
| *p*-Methoxybenzil | 68 | 64-65 | 7 |
| *o*-Ethoxybenzil | 60 | 101-102 | 7 |
| *oo*′-Diethoxybenzil | 50 | 157-158 | 7 |
| *pp*′-Diphenylbenzil | 95 | 141-142 | 8,9 |
| (*b*) Oxidation by $Cu^{II}$ acetate in acetic acid* | | | |
| Hexane-3,4-dione | 70 | 32-35 (10) | 10 |
| 2,7-Dimethyloctane-4,5-dione | 70 | 67-70 (12) | 11 |
| Cyclodecane-1,2-dione | 89 | 104-106 (10) | 12 |
| Cyclononane-1,2-dione | 67-72 | 80-82 (3) | 13 |
| (*c*) Oxidation by $Cu^{II}$ salts with $NH_4NO_3$ in acetic acid | | | |
| Benzil | 100 | 95 | 5 |
| *pp*′-Dimethoxybenzil | 97 | 132 | 5 |
| 2,2′,3,3′-Tetramethoxybenzil | 98 | 146 | 5 |
| 2,2′-Furil | 91 | 165 | 5 |
| *oo*′-Dichlorobenzil | 55 | 132 | 14 |
| Diphenanthr-9-yl diketone | 90 | 283 | 15 |
| Phenyl thien-2-yl diketone | 93 | 59-69 | 16 |
| *p*-Dimethylaminophenyl pyrid-3-yl diketone | 40 | 132-133 | 17 |
| *p*-Hydroxyphenyl pyrid-3-yl diketone | 66 | 178 | 17 |

*Boiling points given (*p*, mmHg).

Table 1 gives some data on α-diketones obtained by oxidising acyloins with salts of bivalent copper[5-17]. Salts of tervalent iron can also be used for this purpose[10,18-20].

## 2. Oxidation of α-Methylene-carbonyl Compounds

In 1932 Riley et al.[21] first showed that selenium dioxide is a specific reagent for oxidising a methylene-carbonyl group to dicarbonyl. Since then the dioxide has been widely used for obtaining α-dicarbonyl compounds from aliphatic or aliphatic–aromatic aldehydes and ketones under mild conditions. In contrast to chromic acid, potassium permanganate, and other reagents that oxidise primarily the carbonyl group, selenium dioxide acts on a methyl or methylene group attached to various activating groups—alkene, alkyne, aldehyde, ketone, carboxyl, ester, amide, anhydride, nitrile, or an aromatic ring—where the degree of activation varies within wide limits[22-28]. Oxidation can be accomplished either in the absence of a solvent or in various organic solvents not oxidised by selenium dioxide—in alcohol, acetic anhydride or acid, or dioxan[29].

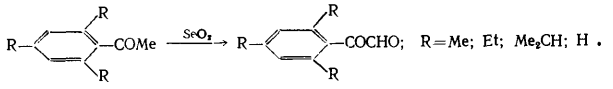
Oxidation occurs most simply with carbonyl compounds $RCH_2COR'$ having one active position, when high yields of α-dicarbonyl products are obtained. For example, acetaldehyde gives a 90% yield of glyoxal[21,29]:

$$CH_3CHO \xrightarrow{SeO_2} CHOCHO .$$

Propionaldehyde and butyraldehyde form methyl- and ethyl-glyoxal respectively; phenylacetaldehyde is converted into phenylglyoxal; etc.[29] The rate of oxidation of aliphatic aldehydes decreases with increase in their molecular weight[30]. α-Keto-aldehydes or α-diketones are the main products of the oxidation of ketones by selenium dioxide[21,22,30-46]. Thus acetone is converted into methylglyoxal in 60% yield[21], and acetophenone into phenylglyoxal in 50% yield[21,47]. α-Diketones are obtained in high yields when various substituted benzyl phenyl ketones are oxidised with selenium dioxide; for example, deoxybenzoin and its derivatives containing various unoxidisable substituents in the ring are converted into theoretical yields of benzils[29,48]:

$$ArCCH_2Ar' \xrightarrow[96-100\%]{SeO_2} Ar{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Ar' .$$

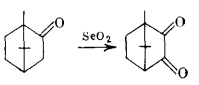
Here the methylene group is doubly activated, and the steric conditions do not favour secondary aldol condensation. 2,4,6-Trialkylacetophenones are oxidised without steric hindrance to the corresponding glyoxals[49-51]:



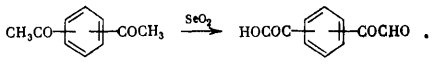

It is interesting that a higher yield of phenylglyoxal is obtained by the oxidation of acetophenone than by that of phenylacetaldehyde, which is probably due to the liability of the latter to undergo aldol condensation[3]. The oxidation of ω-bromoacetophenone in methanol gives an 80% yield of methyl phenylglyoxylate[52]:

$$PhCOCH_2Br \xrightarrow[MeOH]{SeO_2} PhC(O)C(O)OMe .$$

Non-aromatic systems, having only one position open to attack, give high yields of α-diketones when oxidised. For example, camphor is converted into camphorquinone in 90% yield[53], and α-santene forms the corresponding dione in quantitative yield[55]. Several bicyclic compounds containing a methylene-carbonyl grouping also give α-diketones[53,56]:




Nor does the presence of two equivalent α-methylene-carbonyl functions in the molecule present special difficulties in oxidation. Thus *p*- and *m*-diacetylbenzene are oxidised to the corresponding diglyoxals[57,58]:

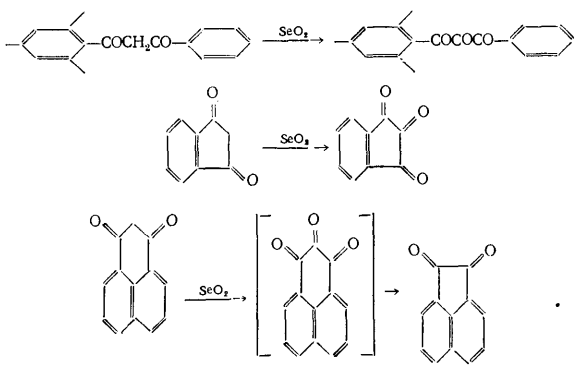



This reaction formed the basis for the later development of general methods for preparing diglyoxals of type $CHOCOArCOCHO.2H_2O$ [59-64] (Table 2) and bis-α-diketones of general formula $Ar'COCOArCOCOAr'$ [65-80] (Table 3, No. 1–9 and 15–25).

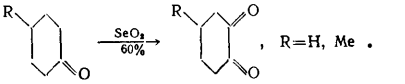
Table 2. Aromatic bisglyoxals[59-64].

| No. | Compound | M.p., °C (decomp.) |
|---|---|---|
| 1 | HOCOC–Ar–COCOH·2H₂O | 162—164 |
| 2 | HOCOC–Ar–Ar–COCOH·2H₂O | 162—166 |
| 3 | HOCOH–(Ar)₃–COCOH·2H₂O | 211—214 |
| 4 | HOCOC–Ar–O–Ar–COCOH·2H₂O | 141—143 |
| 5 | HOCOC–(Ar–O–)₂Ar–COCOH·2H₂O | 157—160 |
| 6 | HOCOC–(Ar–O–)₃Ar–COCOH·2H₂O | 154—156.5 |
| 7 | (H₂O·HOCOC–Ar–O–Ar–)ₓ | 178—180 |
| 8 | HOCOC–Ar–SO₂–Ar–COCOH·2H₂O | 138—139 |
| 9 | HOCOH–Ar–S–Ar–COCOH·2H₂O | 100—100.5 |
| 10 | HOCOC–Ar–COCOH·2H₂O | 110—111 |

Several systems containing β-diketone groups can be oxidised to 1,2,3-triones[54,56]:

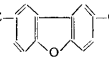
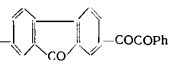
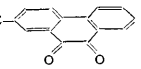
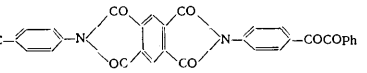
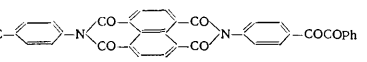
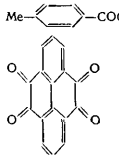
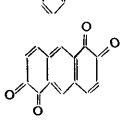



Oxidation by means of selenium dioxide presents no difficulties also with symmetrical systems containing two equivalent groups separated by an activating centre. For example, cyclohexanone and 4-methylcyclohexanone are oxidised to cyclohexane-1,2-dione and 4-methylcyclohexane-1,2-dione respectively[21,81]:




1,2-Diones are formed more slowly from cyclopentanone and cycloheptanone than from cyclohexanones, and cyclooctanone does not give diones at all[42]. Alicyclic ketones

**Table 3.** Aromatic bis-α-diketones.

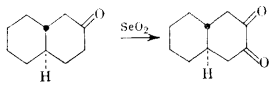
| No. | Compound | M.p., °C | Ref. |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 1 | PhOCOC-$(CH_2)_6$-COCOPh | 63—64 | 71,72 |
| 2 | PhOCOC-C$_6$H$_4$-COCOPh | 98—99.5 | 66,72,74 |
| 3 | PhOCOC-C$_6$H$_4$-COCOPh | 123—124.5 | 66,67, 72,88 |
| 4 | PhCCOC-C$_6$H$_4$-C$_6$H$_4$-COCOPh | 205—206 | 68,72, 73,76 |
| 5 | PhOCOC-C$_6$H$_4$-$CH_2$-C$_6$H$_4$-COCOPh | 144—144.5 | 72,73,88 |
| 6 | PhOCOC-C$_6$H$_4$-O-C$_6$H$_4$-COCOPh | 107—108.0 | 68,72, 73,76 |
| 7 | PhOCOC-C$_6$H$_4$-CO-C$_6$H$_4$-COCOPh | 128—130 | 72,76 |
| 8 | PhOCOC-C$_6$H$_4$-S-C$_6$H$_4$-COCOPh | 90—91.6 | 72,73 |
| 9 | PhOCOC-C$_6$H$_4$-$SO_2$-C$_6$H$_4$-COCOPh | 164—166 | 72 |
| 10 | PhOCOC-  -COCOPh | 193—194 | 76 |
| 11 | PhOCOC-  -COCOPh | 239—241 | 76,77 |
| 12 | PhOCOC-  | 230—232 | 76 |
| 13 | PhOCOC-  -COCOPh | 365—367 | 70 |
| 14 | PhOCOC-  -COCOPh | 358—360 | 106 |
| 15 | Et-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Et | 53.5—54.5 | 75 |
| 16 | MeO-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-OMe | 116.5—117.5 | 75 |
| 17 | PhO-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-OPh | 131.5—132.5 | 75 |
| 18 | Ph-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Ph | 136—137.5 | 75 |
| 19 | CN-C$_6$H$_4$-O-C$_6$H$_4$-OCOC-C$_6$H$_4$-COCO-C$_6$H$_4$-O-C$_6$H$_4$-CN | 139.5—141.5 | 75 |
| 20 | OH-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-OH | 204—205 | 75 |
| 21 | Br-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Br | 192—193 | 75 |
| 22 | CN-C$_6$H$_4$-COCO-C$_6$H$_4$-O-C$_6$H$_4$-COCO-C$_6$H$_4$-CN | 194—196 | 75 |
| 23 | MeCOCO-C$_6$H$_4$-O-C$_6$H$_4$-COCOMe | 80.5—81.5 | 75 |
| 24 | Ph-(-O-C$_6$H$_4$-)$_2$-COCO-C$_6$H$_4$-COCO-(-C$_6$H$_4$-O-)$_2$-Ph | 170—172 | 157 |
| 25 | Ph-(-O-C$_6$H$_4$-)$_3$-COCO-C$_6$H$_4$-COCO-(-C$_6$H$_4$-O-)$_3$-Ph | 153—154.5 | 157 |
| 26 | Me-C$_6$H$_4$-COCO-C$_6$H$_4$-COCO-C$_6$H$_4$-Me | 167—168 | 99 |
| 27 |  | 365—370 | 107 |
| 28 |  | 305—306 | 108,109 |

(cyclohexanone and the isomeric methylcyclohexanones) are oxidised by selenium dioxide more rapidly than are aromatic and aliphatic ketones containing the same number of carbon atoms. 4-Methylcyclohexanone is oxidised most rapidly, and the 2-methyl isomer the most slowly[42,81].

It is often observed that only one of two or more oxidisable groups is predominantly oxidised. Thus the doubly activated methylene group in pentane-2,4-dione is oxidised to give a 29% yield of the final product, which indicates the simultaneous occurrence of side-reactions:

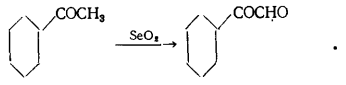
$$CH_3COCH_2COCH_2 \xrightarrow{SeO_2} CH_3COCOCOCH_3 .$$

*trans*-2-Decalone (which enolises at the 3 position) forms the 2,3-dione in 60–65% yield[46]:



3-Keto-steroids are oxidised by selenium dioxide to the corresponding 2,3-diones[46].

Under comparable conditions the oxidation of α-methyl groups by selenium dioxide is more vigorous than that of α-methylene. Thus cyclohexyl methyl ketone gives a 59% yield of cyclohexylglyoxal:



More butane-1,2-dione than butane-2,3-dione is formed by the oxidation of butan-2-one[21]:

$$CH_3COCH_2CH_3 \xrightarrow{SeO_2} \underset{(17\%)}{CH_3CH_2COCHO} + \underset{(1\%)}{CH_3COCOCH_3} .$$

The reason for such behaviour is still obscure. It may be supposed that steric factors play an important part, as well as secondary processes involving further oxidation, polymerisation, etc. of the products. The rates of oxidation of aldehydes and ketones by selenium dioxide depend on their structure and the reaction conditions. The rate falls with increase in the molecular weight of aldehydes and of straight-chain alkyl methyl, dialkyl, and alkyl phenyl ketones, as well as in the presence of secondary and tertiary groups in the α-position with respect to the carbonyl[82]. Alkyl methyl ketones are oxidised more rapidly than are straight-chain aldehydes containing the same number of carbon atoms[30]. Ketones of general formula $C_6H_5[CH_2]_nCOCH_3$ with $n$ and even number are oxidised more slowly by selenium dioxide than are ketones containing an odd number of methylene groups[3]. The nature of the substituent influences the rate of oxidation of substituted acetophenones: thus the rate constants for oxidation by selenium dioxide of the compounds $RC_6H_4COCH_3$ in 75% acetic acid decrease according as R represents[3]

$$p\text{-I} > p\text{-M} > \text{H} > p\text{-MO} > p\text{-Cl} > p\text{-Br} > m\text{-}NO_2 .$$

The rate constant of the oxidation of ketones by selenium dioxide depends also on the solvent: it is lower in alcohols than in acetic acid, which is related to the formation of complexes between ketones and alcohols. The oxidation of ketones by selenium dioxide is catalysed by acids[3].

## MECHANISM OF OXIDATION BY SELENIUM DIOXIDE

Although the oxidation of aldehydes and ketones by selenium dioxide has been the subject of many detailed studies, its mechanism cannot be regarded as fully established.

The first kinetic data on this reaction in 75% acetic acid, obtained from gravimetric determinations of the precipitate of colloidal selenium, were published by

Mel'nikov et al.[3] These workers stablished the second order, and noted that the reaction was controlled by enolisation of the ketonic group by means of a hydrogen atom from the $\alpha$-carbon atom, since ketones incapable of enolisation are not oxidised by selenium dioxide.

Later Duke[83] suggested the third order for this reaction, regarding formation of an intermediate reactive complex as the rate-determining stage:

$$RCOCH_2R' + SeO_2 - H^+ \xrightarrow{\text{slow}} \left[ \begin{matrix} R-C-CH_2R' \\ \| \\ O \rightarrow SeO \\ \quad\quad \backslash OH \end{matrix} \right]^+ .$$

The most careful investigation was made by Corey and Schaefer[29], although doubt was cast on their results by Waters et al.[84] Deoxybenzoin was chosen for investigation, having only one possible oxidisable position and forming benzil in theoretical yield:

$$PhCOCH_2Ph \xrightarrow{SeO_2} PhCOCOPh + Se + H_2O.$$

The introduction of various substituents into the aryl groups revealed their electronic influence on the oxidation. Kinetic measurements were made by titrating the unchanged selenous acid in 70% acetic acid over a wide range of substrate and selenium dioxide concentrations. The results indicated the third order in conformity with the equation

$$-d[SeO_2]/dt = k[SeO_2] \cdot [PhCOCH_2Ph] \cdot [H^+] .$$

Electron-donating groups in the benzyl component and electron-accepting substituents in the benzoyl group increased the reaction velocity. The easier oxidation of benzyl methyl ketone than of acetone indicated that the course of the reaction was not affected by steric hindrance at the carbonyl group. On the other hand, steric hindrance at the $\alpha$-methylene group explains why the rate of oxidation of phenyl 2,4,6-trimethylbenzyl ketone is around 10% of that of benzyl methyl ketone. Benzoin is not an intermediate product, since it is oxidised at one-twentieth of the rate of oxidation of deoxybenzoin. The reaction is initiated by bases (alkali-metal acetates), is insensitive to radical initiators and inhibitors, and hence cannot be described in terms of a radical-chain mechanism.

On the basis of the above results the following mechanism was suggested[29] for the oxidation of deoxybenzoin by selenium dioxide:

$$ArCOCH_2Ar' + HSeO_3^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\quad\quad | \\ \quad OSeO_2H}{ArC=CHAr'} + H_2O + H_3O^+ \rightarrow$$

$$\rightarrow ArCO-\underset{\quad\quad | \\ \quad OSeOH}{CH}-Ar' \rightarrow ArCOCOAr' .$$

This is analogous to acid-catalysed enolisation, and has closely similar Hammett constants. According to the above mechanism unsymmetrical ketones should be oxidised on the side on which they are enolised in an acid. Thus *trans*-2-decalone will be enolised and oxidised at the 3 position. However, there are exceptions: as remarked earlier, the oxidation of ethyl methyl ketone yields 17% of ethylglyoxal and only 1% of biacetyl, although enolisation should take place at the methylene group[21]. The low yield of butane-2,3-dione can be attributed to its degradation by secondary reactions after it has been formed. The selenous ester of the enol may be assumed to rearrange more rapidly than biacetyl is formed from it.

Since benzoin is not an intermediate product in the oxidation of deoxybenzoin, it may be concluded that the formation of benzil is more rapid than is solvolysis of the intermediate product to benzoin. This conclusion is not entirely consistent with results obtained by Schaefer and Horvath[85] in a study of the behaviour of analogous intermediate products in the oxidation of alkenes. However, the difference can be attributed to the circumstance that, whereas solvolysis of intermediate products in the oxidation of alkenes yields resonance-stabilised cations, solvolysis of intermediate products in the oxidation of deoxybenzoins is always accompanied by the appearance of a positive charge on the carbon atom adjacent to the positive end of the carbonyl dipole. The $\alpha$-hydrogen atom is then acidic owing to the contiguity of the carbonyl, and is more liable to direct abstraction under the influence of bases:

$$Ar-\underset{\quad\quad \| \\ \quad O}{C}-\underset{H}{C}(-O-Se-OH)-Ar' \xrightarrow{B^-} ArCOCOAr' + H_2O + Se .$$

Formation of the selenous ester of the enol was regarded[29] as the rate-determining stage. An attempt was made to use the suggested mechanism to explain the formation from certain ketonic systems of $\alpha\beta$-unsaturated compounds instead of the expected $\alpha$-diketones, as well as the greater rapidity of the oxidation of aldehydes and ketones than of the aldol condensation, but the latter is still not entirely clear.

### 3. Oxidation of Compounds containing Carbon–Carbon Multiple Bonds

Compounds of transition metals, because of their stability and adequate selectivity towards different functional groups and also unsaturated bonds, occupy an important place among the oxidising agents used in organic chemistry[86]. The principal oxidant used for a triple bond C≡C is potassium permanganate in neutral or weakly acid medium, when the main undegraded products of the oxidation of alkynes are $\alpha$-diketones and $\alpha\beta$-unsaturated alcohols[87]. The oxidation of acetylenic bonds by potassium permanganate has recently been successfully applied to the preparation of bis-$\alpha$-diketones, previously obtained by oxidising the corresponding deoxybenzoins with selenium dioxide (Table 3, No. 3–7 and 10–12):[76,88,89]

$$Ph{\equiv}C-Ar-C{\equiv}CPh \xrightarrow{KMnO_4} PhC(=O)-C(=O)-Ar-C(=O)-C(=O)-Ph$$

(Ar = arylene). Potassium permanganate in acetic anhydride has been used to obtain $\alpha$-diketones from cycloalkenes of the type[90]

$$(CH_2)_{10}\begin{matrix} CH \\ \| \\ CH \end{matrix} \rightarrow (CH_2)_{10}\begin{matrix} C=O \\ | \\ C=O \end{matrix} + (CH_2)_{10}\begin{matrix} C=O \\ | \\ CHOAc \end{matrix} + (CH_2)_{10}\begin{matrix} COOH \\ | \\ COOH \end{matrix} .$$

However, this method was unsuitable for the preparation of $\alpha$-diketones from small rings (below cyclo-octene). The explanation proffered was that reaction takes place only when the carbonyl groups in the expected $\alpha$-diketone are incapable of cisoid orientation. This oxidising system is advantageous because many organic compounds dissolve in acetic anhydride. In several cases, however, dimethoxyethane alone or added to acetic anhydride is recommended as solvent[90].

Numerous attempts have been made to use other oxidants, but convenient preparations of $\alpha$-diketones have not resulted. Oxidation by organic peroxy-acids yields various products depending on the conditions and the acid

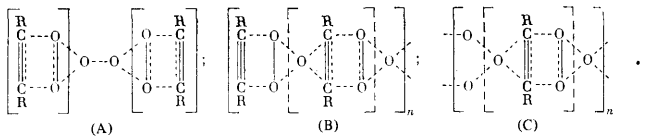
used[91]. Thus trifluoroperacetic acid converts diphenylacetylene into benzil and benzoic acid, the latter obviously a product of further oxidation of the benzil:

$$PhC{\equiv}CPh \xrightarrow[Na_2HPO_4,\ CH_2Cl_2]{2CF_3CO_3H} \underset{(76\%)}{PhCOCOPh} + \underset{(17\%)}{PhCOOH}\ .$$

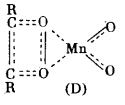
More highly oxidised products—finally a mixture of carboxylic acids or their esters—are obtained by the action of perbenzoic, peracetic, and trifluoroperacetic acids on penylacetylene, involving cleavage of the triple bond[92]. One reason suggested was the intermediate formation of [1,3-dioxabicyclo[1,1,0]butanes:]

$$R{-}C{\equiv}C{-}R' \rightarrow \left[R{-}C\begin{matrix}O\\ \diagup\\ \diagdown\\ O\end{matrix}C{-}R'\right] \rightarrow RC{-}C{-}R' + RCOOH + R'COOH\ .$$

Oxidation of a carbon–carbon triple bond has been accomplished by means of selenium dioxide in the presence of catalytic quantities of sulphuric acid[93], thallium trinitrate[94], ozone[95,96], tetracarbonylnickel in the presence of alkyl halides[97], bromosuccinimide in anhydrous dimethyl sulphoxide (e.g. No. 26 in Table 3), [98,99] oxides of nitrogen[100], and ruthenium tetraoxide[101]. In spite of good yields of α-diketones, however, these oxidants have not found wide application for preparative purposes.




Molecular aspects of mechanisms of the oxidation of acetylenic compounds to α-diketones by singlet oxygen, ozone, and potassium permanganate in neutral or weakly alkaline media have been discussed[102]. The oxidation is assumed to involve intermediate formation of dioxetans without the involvement of "ene", free-radical, or ionic processes, since traces of peroxides or products of an "ene" reaction are not detected when singlet oxygen is used. Ozonisation also involves formation and decomposition of a dioxetan as molecular intermediate transition complex (A), whose breakdown is accompanied by rapid evolution of singlet oxygen. The complex (A) may undergo rearrangement into the thermodynamically more stable complexes (B) and (C), which also decompose into monomeric ozonides and singlet oxygen. Oxidation by potassium permanganate (pH 7) involves intermediate formation of the complex




which then breaks down into the α-diketone, singlet oxygen, and manganese dioxide.

## 4. Other Methods of Preparation of α-Diketones

To complete the account mention must be made of a few other methods of obtaining α-diketones, which have not become widely used. Thus they can be obtained from monoximes or isonitroso-ketones, formed by the action of nitrous acid on ketones $RCOCH_2R'$; as well as via dioximes, which are produced by replacing the nitrous acid by an alkyl nitrite, hydroxylamine, or an aromatic nitroso-compound[103]. Condensation of isonitroso-ketones with diazo-compounds has been used to obtain several aryl methyl α-diketones[1]:

$$MeCOC\begin{matrix}H\\ \diagdown\\ NOH\end{matrix} \xrightarrow{ArN_2Cl} \left[MeCOC\begin{matrix}N:N\cdot Ar\\ \diagdown\\ NOH\end{matrix}\right] \rightarrow MeCOC\begin{matrix}Ar\\ \diagdown\\ NOH\end{matrix} \rightarrow MeCOCOAr\ .$$

α-Diketones can be prepared by the action of organomagnesium compounds on vinylidenoxanilide[1]:

$$\begin{matrix}O{=}C{-}N\\ |\\ O{=}C{-}N\end{matrix}\begin{matrix}Ph\\ \diagdown\\ C{=}CH_2\\ \diagup\\ Ph\end{matrix} \xrightarrow{2\,MeMgI} MeCOCOMe\ .$$

αβ-Unsaturated monoketones (e.g. vinyl ketones) will yield α-diketones by the series of reactions[1]

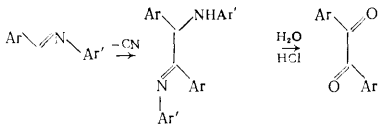
$$RCOCH{=}CHR' \xrightarrow{Br_2} RCOCHBrCHBrR' \xrightarrow{-HBr} RCOCBr{=}CHR' \xrightarrow{+\text{piperidine}} \rightarrow RCOCBr(NC_5H_{10})CH_2R' \xrightarrow{-HBr} RCOC(NC_5H_{10}){=}CHR' \xrightarrow{+H_2O} RCOC(OH){=}CHR' \xrightarrow{-H_2O} RCOCOR'.$$

Several α-diketones can be obtained by the Friedel–Crafts condensation of phenyl ethers, e.g. anisole, with oxalyl chloride[104]:

$$2\,MeOC_6H_5 + ClOC{-}COCl \xrightarrow[CS_2]{AlCl_3} \underset{(90\%)}{4\text{-}MeOC_6H_4COCOC_6H_4OMe\text{-}4'}\ .$$

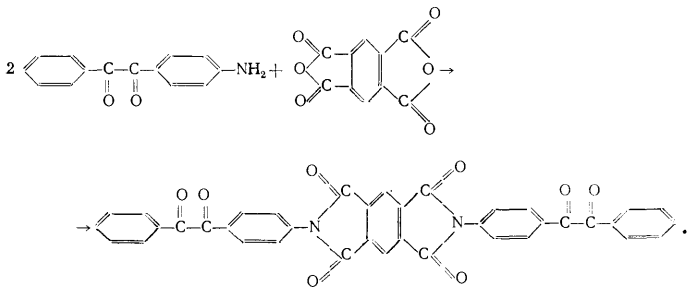
In most cases, however, the ethers are insufficiently reactive, and the oxalyl chloride decomposes under the influence of the aluminium chloride before it can react with the ether.

A convenient method published recently involves oxidative dimerisation of several aromatic aldimines in the presence of the cyanide ion, followed by hydrolysis of the α-diketimines formed as intermediates[105]:

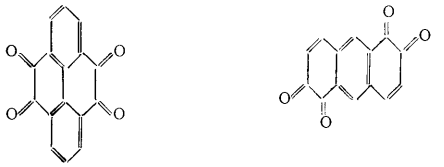


The reaction is usually conducted in dimethyl sulphoxide or dimethylformamide at room temperature, when the yield of α-diketones reaches 85–95%.

Bis-α-diketones containing imide rings (Table 3, No.13 and 14) have been prepared by an original route consisting in the action of *p*-aminobenzil on the dianhydride of a tetracarboxylic acid[70,106]. In the case of pyromellitic dianhydride the reaction can be written



The di-*o*-quinones used in the synthesis of ladder polyphenylquinoxalines—4,5,9,10-tetrahydro-4,5,9,10-tetraoxopyrene (I) and 1,2,5,6-tetrahydro-1,2,5,6-tetraoxoanthracene (II)

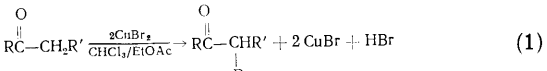


I II

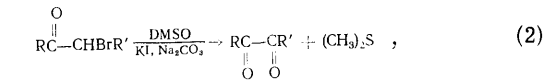
(Table 3, No. 27 and 28)—are obtained by special methods. The first step in the preparation of (I) is oxidation by ozone of pyrene to 5-formylphenanthrene-4-carboxylic acid, which on treatment with phenylhydrazine followed by reduction is converted into 4-amino-5-hydroxypyrene, and this is oxidised to the 4,5-quinone. The most difficult step is the further oxidation of this diketone to the diquinone, conducted in acetic acid by means of aqueous chromium trioxide. After crystallisation from nitrobenzene the total yield of (I) does not exceed 15%.[107]

The second di-*o*-quinone (II) is obtained by treating anthracene-2,6-diol with a solution of zinc chloride and sodium nitrite. Subsequent reduction of the resulting 1,5-dioxime with sodium dithionite forms 1,5-diaminoanthracene-2,6-diol, whose oxidation with sodium dichromate in dilute sulphuric acid gives the 1,2,5,6-tetraketone (II) in a total yield of 3% (after crystallisation from dioxan)[108].

A two-stage preparation of α-diketones from α-methylene-ketones involves intermediate formation of α-bromoketones, which are then oxidised with dimethyl sulphoxide in the presence of iodide ions[109]:



(1)



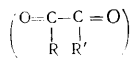
(2)

where R and R′ = Alk or Ar. The total yield of α-diketones reaches 65–92%.

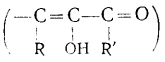
## III. REACTIONS OF α-DICARBONYL COMPOUNDS

The simultaneous presence of two carbonyl groups ensures that α-diones are able to undergo not only all the reactions of simple aldehydes and ketones but also reactions leading to the formation of heterocyclic systems. Either one or both carbonyl groups may react depending on the conditions[110].

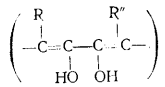
The contiguity of the two carbonyl groups is responsible for the colour of α-diketones. These compounds may exist either in the diketonic form



in the monoenolic form



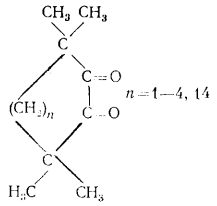
or in the dienolic form



depending on several factors, primarily the nature of substituents adjacent to the carbonyl groups. Thus acyclic α-diketones (e.g. butane-2,3-dione) are true diketones and possess a yellow colour: cyclic α-diketones are usually colourless and react typically tautomerically, forming both monoximes and dioximes[111]. When enolisation is sterically hindered, as e.g. in camphorquinone, cyclic diketones also have a yellow colour.

Investigation on a series of α-substituted diketones have shown that the ultraviolet spectra of all the compounds contain two maxima, at 219–269 and 391–421 nm, which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transitions respectively. The position of the second maximum depends on the nature of the substituent governing the spatial arrangement of the carbonyl groups. The same factors determine absorption by the carbonyl groups in the infrared spectra[112].

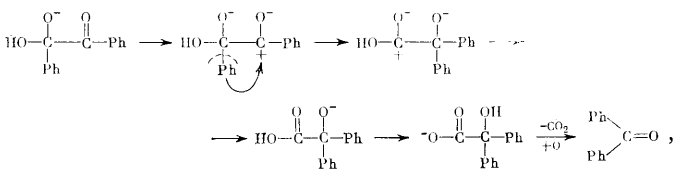
Study of the influence of steric configuration on the ultraviolet spectra of α-diketones of the type



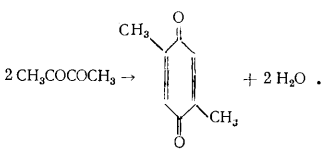
has shown that the position of absorption bands at the longer wavelengths correlates with the relative steric orientation of the carbonyl groups, which is supported by inspection of molecular models. The position of the bands varies with the angle between the planes of the carbonyl groups: a band moves to shorter wavelengths with increase in the angle from 0 to 90°, and moves back to longer wavelengths with further increase in the angle (>90°).[113]

### 1. Action of Alkalis

Under the influence of alkalis α-diketones tend to undergo a so called benzil rearrangement. This has been studied in greatest detail on and named after benzil itself. The benzil rearrangment compares formally with the pinacol rearrangement

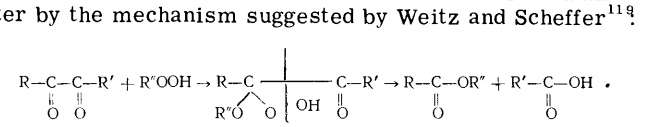


where the benzil molecule is written in hydrated form. Butane-2,3-dione is characterised by condensation, in the presence of an alkali, to a cyclic xyloquinone[37]:

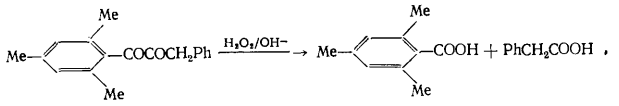


### 2. Action of Acids and Peroxides

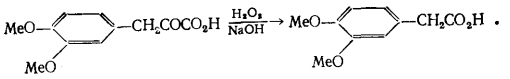
The carbonyl–carbonyl bond undergoes cleavage when α-dicarbonyl compounds are treated with peroxy-acids or peroxides[116–118]. The first stage probably involves 1,2- or 1,4-addition of hydroxy-groups to the system with formation of an unsymmetrical product, subsequent cleavage of which (e.g. in the case of ethyl hydroperoxide) yields either two acid molecules or a mixture of an acid and an ester by the mechanism suggested by Weitz and Scheffer[119].



Alkaline hydrogen peroxide also splits α-dicarbonyl compounds to give high yields of the corresponding carboxylic acids[120,121]:

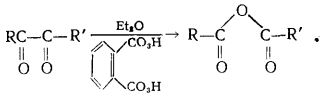


α-Keto-acids are readily decarbonylated under these conditions[122]:



Complicated mixtures are obtained by the action of a hydroxamic acid in the presence of concentrated sulphuric acid. The example of benzil shows that this reaction also involves bond rupture between the two carbonyls. The main product, N-benzoyl-N'-phenylurea, is then accompanied by 5-anilinotetrazole, 5-amino-1-phenyltetrazole, 5-benzamido-1-phenyltetrazole, and minute quantities of benzoic acid, aniline, and other products[123].

α-Dicarbonyl compounds react rapidly with peroxyacids. The structure of the anhydrides isolated from the reaction was regarded[124] as indicating migration of an acyl group:



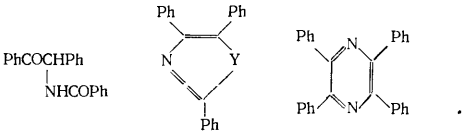
## 3. Hydrogenation

The selectivity of the hydrogenation of α-diketones is determined by the nature of the catalyst and the conditions of the reaction[125-128]. Thus reduction at a copper cathode in aqueous medium converts benzil into benzoin[125]. 1,2-Diphenylethane is formed when zinc amalgam is used as cathode in an aqueous–alcoholic solution of an acid (sulphuric) at 70–90°C.[125] The use of relatively inactive catalysts—platinum on carbon, Raney nickel, palladium on poly(methyl methacrylate)—enables hydrogenation to be arrested after 80 min, at the *meso*-1,2-diphenylethane-1,2-diol stage. Further saturation with hydrogen (for 30 h) also yields 1,2-diphenylethane[125].

When benzil is heated with sodium tetrahydroborate or lithium tetrahydroaluminate in methanol at 60°C, *meso*-1,2-diphenylethane-1,2-diol is formed[126]. Heating benzil with potassium iodide, red phosphorus, and concentrated hydrochloric acid for 15 h enabled deoxybenzoin to be isolated, together with minute quantities of 1,2,3,4-tetraphenylbutane-2,3-diol[127].

## 4. Action of Ammonia and Amines

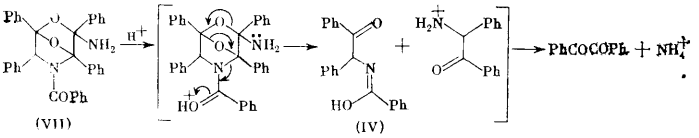
The action of ammonia on benzil has led to the isolation of various products depending on the solvent, the temperature, and the duration of the reaction—ethyl benzoate, benzamide, N-desylbenzamide (IV), and three aromatic heterocycles—2,4,5-triphenyloxazole (Va), 2,4,5-triphenylimidazole (Vb), and tetraphenylpyrazine (VI)[129]



(IV) (V) (VI)

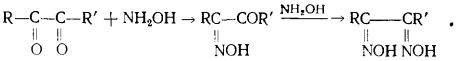
a) Y=O;
b) Y=NH

Later another product (VII), of high molecular weight and empirical formula $C_{35}H_{28}O_3N_2$, was isolated. It was regarded as formed via an intermediate complex containing three benzyl groups per ammonia molecule, whose disproportionation gave compounds (IV) and (VII). The latter was assumed to be labile, readily decomposing in the presence of acids and alkalis to form (IV), benzil, and other products[130,131]:

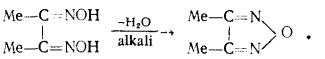


(VII) (IV)

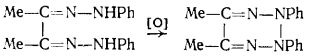
α-Dicarbonyl compounds react vigorously with hydroxylamine at one or both carbonyl groups to form monoximes and dioximes[132,133]:



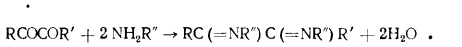
Alkalis abstract a water molecule from dioximes and convert them into furazans[134]:



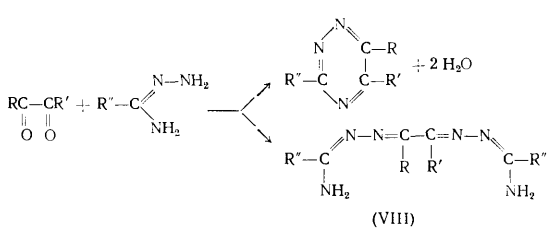
The action of semicarbazide on α-diketones is similar: mono- or di-semicarbazones or cyclic condensation products are formed depending on the reaction conditions. With phenylhydrazine mono- or bis-phenylhydrazones are obtained also depending on the conditions[135-138]. Oxidation of the latter products (osazones) can be represented as



Several reports have appeared of the formation of Schiff bases by the action of amines on glyoxal and biacetyl[139,140]:



The reaction between α-dicarbonyl compounds and amidrazones, yielding either 1,2,4-triazines or acyclic products such as (VIII)



(VIII)

has been discussed in a review by Rusanov[141].

**Table 4.** Data on bisquinoxalines[64,67,68].

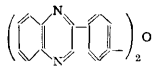
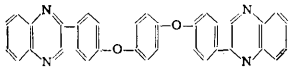
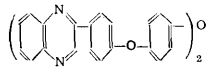
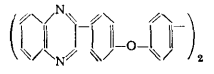
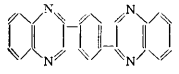
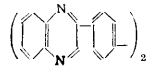
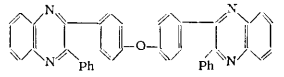
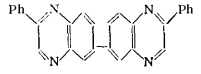
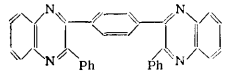
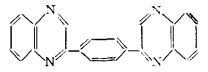
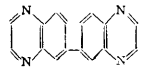
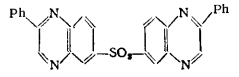
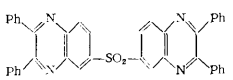
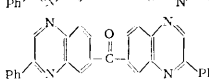
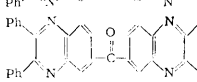
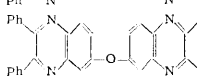
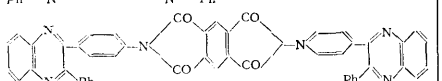
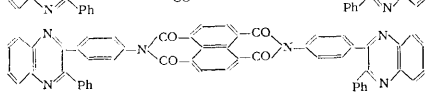
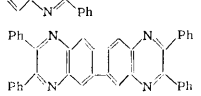
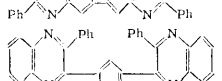
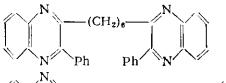
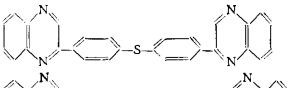
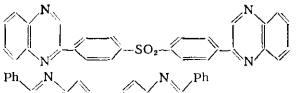
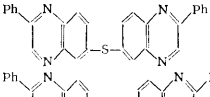
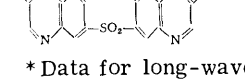
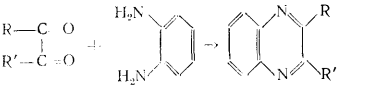
| No. | Compound | M.p., °C | Ultraviolet spectra* $\lambda_{max}$, nm | Ultraviolet spectra* $10^3\epsilon$ |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 1 |  | 171—173 | 315 | 38.0 |
| 2 |  | 222—224 | 315 | 46.9 |
| 3 |  | 190—191 | 315 | 56.8 |
| 4 |  | 229—231 | 310 | 50.5 |
| 5 |  | 266—267 | 276 | 39.0 |
| 6 |  | 261—262 | 312 | 39.8 |
| 7 |  | 292—294 | 350 | 45.2 |
| 8 |  | 226—227 | 280 | 32.0 |
| 9 |  | 314—315 | 303 | 68.0 |
| 10 |  | 260—260.5 | 323 | 85.0 |
| 11 |  | 272—274 | 280 | 101.0 |
| 12 |  | 257—258.5 | 381 | 29.0 |
| 13 |  | 295—304 | 295 | 40.3 |
| 14 |  | 247—247.5 | 323 | 85.3 |
| 15 |  | 260—260.5 | 268 | 66.5 |
| 16 |  | 266—267 | 292 | 28.4 |
| 17 |  | 264—265.5 | — | — |
| 18 |  | 436—437 | — | — |
| 19 |  | 460—462 | — | — |
| 20 |  | 309—310 | — | — |
| 21 |  | 224—225 | — | — |

**Table 4 contd.**

| No. | Compound | T. пл., °C | Ultraviolet spectra* $\lambda_{max}$, nm | Ultraviolet spectra* $10^3\epsilon$ |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 22 |  | 151.5—152.5 | 355 | 22.7 |
| 23 |  | 194—195 | 264 | 29.8 |
| 24 |  | 297—298 | 261 | 34.0 |
| 25 |  | 306—307 | 368 | 17.6 |
| 26 |  | 274—275 | 345 | 12.0 |

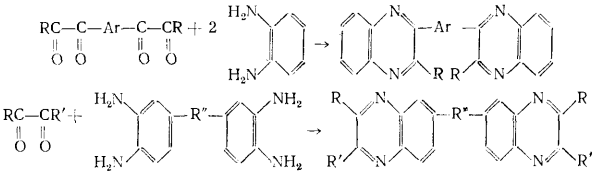
*Data for long-wavelength absorption maximum.

The reaction of greatest interest and practical importance is the quantitative cyclocondensation of $\alpha$-dicarbonyl compounds with aromatic $o$-diamines, which led to the discovery in 1884 of a new class of heterocyclic compounds—the quinoxalines[142,143]:



The chemistry of quinoxaline has been actively developed since then: diverse derivatives have been prepared, their physical and chemical properties have been studied, and possible practical applications have been examined[144].

The reaction of bis-$\alpha$-dicarbonyl compounds with aromatic $o$-diamines or of $\alpha$-dicarbonyl compounds with bis-$o$-diamines yields bisquinoxalines of diverse structure (Table 4):

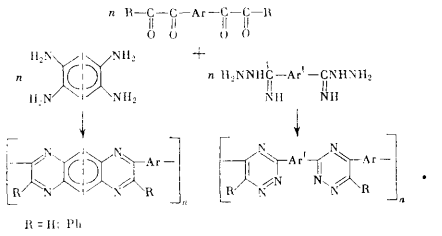


R=R′=H, Ph; R″=$CH_2$; O; $SO_2$; CO; S; —; Ar = arylene

Spectral investigations show that wavelengths $\lambda_{max}$ are the same for compounds containing $p$-diphenylene ether units between unsubstituted quinoxaline rings. Replacement of these bridges by $p$-phenylene units produces a bathochromic shift in $\lambda_{max}$, which increases on passing from $p$-phenylene to $p$-biphenylylene and to $p$-terphenylylene, which is evidence of the presence of conjugation in the system. Introduction of phenyl substituents into the pyrazine ring has an analogous effect[65], which indicates that the quinoxaline and phenyl units are coplanar.

## IV. BIS-$\alpha$-DICARBONYL COMPOUNDS IN THE PREPARATION OF HETEROCYCLIC POLYMERS

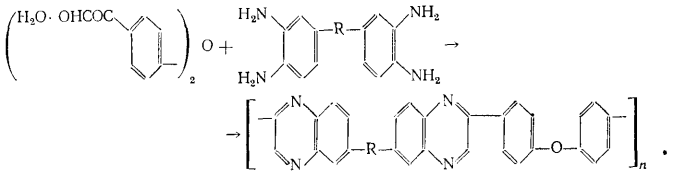
Whereas $\alpha$-dicarbonyl compounds have as yet found limited practical application only for obtaining certain quinoxaline derivatives exhibiting pharmacological activity[144], bis-$\alpha$-dicarbonyl compounds are acquiring increasing value as monomers for the synthesis of thermostable heterocyclic polymers, in particular polyquinoxalines and poly-1,2,4-triazines[145-153]:



R = H; Ph

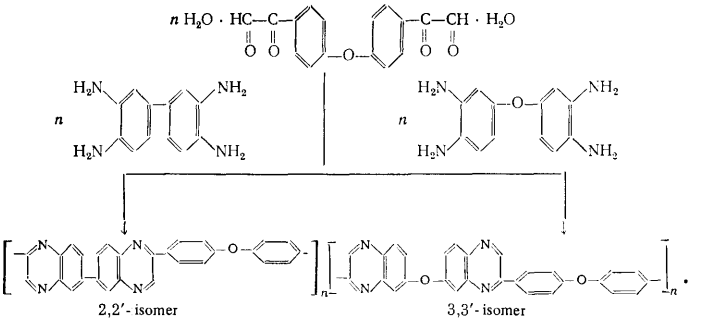
In the opinion of Hergenrother[146] phenylated quinoxalines are among the most promising heterocyclic systems known at the present time, whose structure has the potentiality for high thermal, thermo-oxidative, and hydrolytic stability.

The route to the synthesis of polyquinoxalines was mapped out by Sorenson[147] in 1961, since when the reaction of bis-$\alpha$-dicarbonyl compounds with bis-$o$-diamines has been widely used to obtain polymers containing quinoxaline rings. To this period belong papers by Stille[59-61] and a patent[148] on the method of obtaining polyquinoxalines by the reaction of bis-$o$-phenylenediamines with aromatic bisglyoxals or their hydrates:



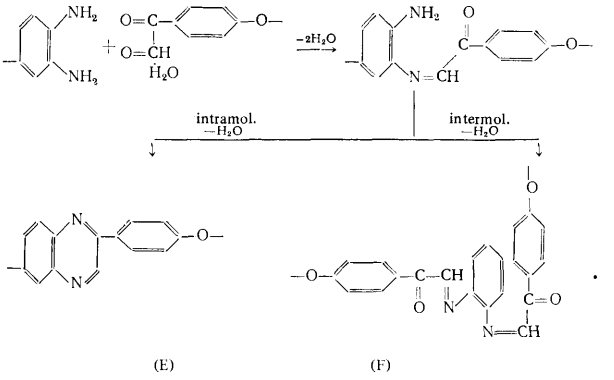
The same process for synthesising polyquinoxalines was suggested simultaneously by some French chemists[62,63,149].

The reaction of aromatic bisglyoxals with aromatic bis-$o$-diamines can obviously yield a mixture of position isomers (2,2'-, 2, 3'-, and 3,3'-polyquinoxalines), a possibility investigated by Stille et al.[59-61]. From the ultraviolet spectra of model compounds and X-ray examination of polyquinoxalines obtained from 3,3'-diaminobenzidine and $p$-diglyoxyloylbenzene dihydrate these workers concluded that the 2,2'-isomer predominated in the mixture. They considered that preferential formation of a particular isomer could be predicted from the relative nucleophilicity of the $o$-amino-groups and the relative reactivity of the aldehydic and ketonic carbonyls in the aromatic bisglyoxals. For example, the $p$-amino-groups in bis-3,4-diaminophenyl ether should be more nucleophilic than those in 3,3'-diaminobenzidine (owing to the electron-donating effect of the ethereal oxygen), which would lead to predominant formation of the 3,3'-isomer, whereas mainly the 2,2'-isomer should be formed from 3,3'-diaminobenzidine[72]. However, it seems more probable that the formation of isomers is governed by the difference in nucleophilicity of the $o$-amino-groups within the tetramine itself:



2,2'-isomer 3,3'-isomer

Intermolecular interaction of the more reactive aldehydic part of the bisglyoxal with the unreactive amino-group often leads to the formation of branched and cross-linked polyquinoxalines, having diminished resistance to oxidation owing to incompleteness of cyclisation:

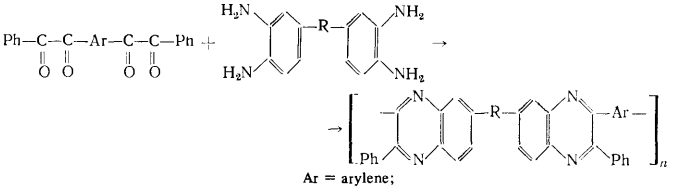


(E) (F)

When the reaction between the starting materials is conducted in suspension (not in solution), the less reactive keto-group of the intermediate product is able to react intramolecularly to give the required product (E).[64,72]

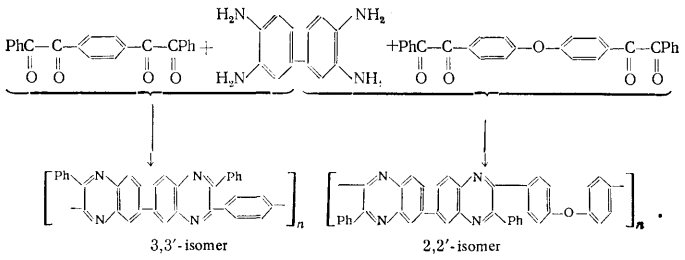
Table 5 shows that increasing the number of $p$-phenylene ether units in the polymer lowers both the softening temperature and the glass point of the polyphenylquinoxalines. The decomposition temperatures determined by dynamic thermogravimetric analysis exhibit no definite trend, but a sharp difference is evident under isothermal conditions in air at 400°C: polyquinoxalines containing $p$-phenylene links were more resistant to oxidation than those containing $p$-phenylene ether links. The former, as was to be expected, had higher softening temperatures and were less soluble in organic solvents[65].

In order to improve the thermo-oxidative stability of the pyrazine ring, which is readily oxidised at a methine group, phenylated polyquinoxalines were synthesised[69] from bis-$\alpha$-diketones instead of bisglyoxals:



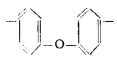
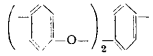
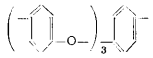
Ar = arylene;
R=—, O, CO, $SO_2$, $CH_2$, S, etc.

The possibility of isomeric structures is even greater with polyphenylquinoxalines than with polyquinoxalines. The relative reactivity of the adjacent carbonyl groups in bis-$\alpha$-diketones (Table 3) is independent of steric factors, in contrast to glyoxals, but inductive and electromeric effects are more significant. For example, the reaction of 3,3′-diaminobenzidine with *p*-bisphenylglyoxyloylbenzene or with dibenzyl ether may be expected to yield the isomers[72]




The influence of isomerism on the properties of polyphenylquinoxalines will be discussed later.

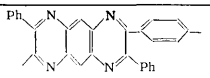
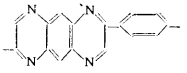
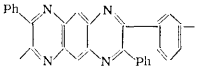
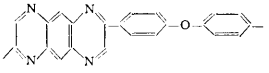
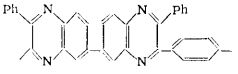
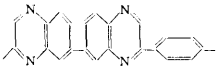
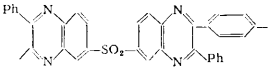
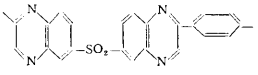
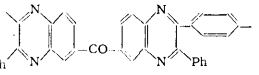
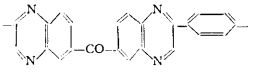
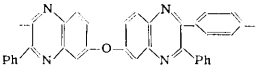
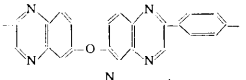
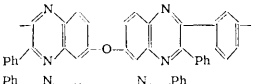
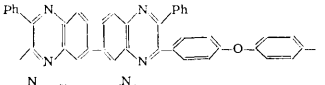
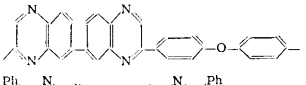
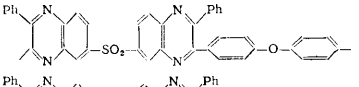
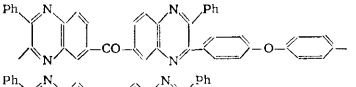
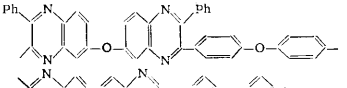
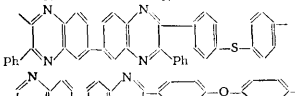
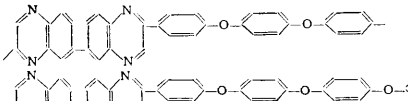
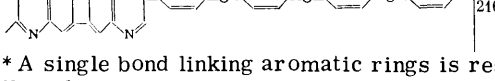
Table 5. Data on polyquinoxalines[65].

| No. | Ar | $\eta_{log}$,* dl g$^{-1}$ | $T_{gl}$,** °C | $T_{soft}$,*** °C | $T_{decomp}$, °C in**** $N_2$ | $T_{decomp}$, °C in**** air | Ultraviolet spectra***** $\lambda_{max}$, nm | Ultraviolet spectra***** $10^3\epsilon$ |
|---|---|---|---|---|---|---|---|---|
| 1 |  | 1.62 | 280 | 315 | 550 | 530 | 280;331 | 22.0;35.2 |
| 2 |  | 1.21 | 195 | 262 | 530 | 510 | 283;333 | 29.9;42.3 |
| 3 |  | 1.27 | 133 | 240 | 520 | 510 | 286;337 | 30.0;46.0 |
| 4 |  | 0.82 | 213 | 253 | 560 | 535 | 280;327 | 34.0;78.5 |
| 5 |  | 1.07 | 350 | >350 | 575 | 535 | 292 | 29.0 |
| 6 |  | 1.03 | 305 | 330 | 565 | 515 | 275;330 | 20.0;34.0 |
| 7 |  | 0.91 | — | 340 | 600 | 525 | 284;365 | 24.0;36.0 |

* Viscosity of 0.5% solution in sulphuric acid at 25°C.
** Glass point determined from dielectric losses.
*** Softening temperature determined by means of a Fisher–John apparatus.
**** Decomposition points determined from thermogravimetric analysis ($\Delta T$ = 5 deg min$^{-1}$).
***** Measured in sulphuric acid.

The thermo-oxidative stability of phenylated polyquinoxalines was indeed considerably greater than that of their non-phenylated analogues. This is made especially clearly apparent by comparing the behaviour of the polymers under isothermal conditions. Thus the polyphenylquinoxaline obtained by the reaction of *p*-bisphenylglyoxylbenzene with 3,3′-diaminobenzidine (Table 6, No. 5) has lost only 6% of its original weight after being heated

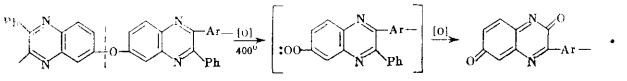
Table 6. Values of $\Delta C_p$ for quinoxaline polymers.

| No. | Structure | $T_{gl}$, °C | Flexible bonds* | $\Delta C_p$, cal deg$^{-1}$ | $\Delta C_p$, cal deg$^{-1}$ mole$^{-1}$ | $\Delta C_p$, cal deg$^{-1}$ bond |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 |  | 395 | 4 | 0.063 | 25.9 | 6.48 |
| 2 |  | 392 | 2 | 0.050 | 12.7 | 6.67 |
| 3 |  | 365 | 4 | 0.065 | 26.7 | 6.32 |
| 4 |  | 353 | 4 | 0.059 | 20.6 | 5.18 |
| 5 |  | 372 | 5 | 0.060 | 28.4 | 5.78 |
| 6 |  | 376 | 3 | 0.56 | 18.5 | 6.15 |
| 7 |  | 345 | 6 | 0.058 | 31.8 | 5.33 |
| 8 |  | 242 | 4 | 0.059 | 22.1 | 5.52 |
| 9 |  | 325 | 6 | 0.063 | 32.1 | 5.37 |
| 10 |  | 318 | 4 | 0.067 | 23.9 | 6.00 |
| 11 |  | 304 | 6 | 0.066 | 33.3 | 5.56 |
| 12 |  | 306 | 4 | 0.061 | 39.8 | 5.43 |
| 13 |  | 270 | 6 | 0.067 | 33.6 | 5.56 |
| 14 |  | 300 | 7 | 0.074 | 42.7 | 6.11 |
| 15 |  | 305 | 5 | 0.070 | 29.6 | 5.94 |
| 16 |  | 290 | 8 | 0.070 | 45.0 | 5.63 |
| 17 |  | 271 | 8 | 0.077 | 46.5 | 5.85 |
| 18 |  | 258 | 8 | 0.071 | 41.6 | 5.23 |
| 19 |  | 283 | 7 | 0.067 | 39.4 | 5.67 |
| 20 |  | 235 | 8 | 0.081 | 42.0 | 6.00 |
| 21 |  | 216 | 9 | 0.089 | 54.4 | 6.00 |

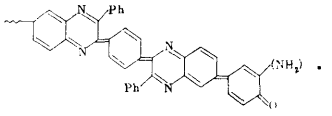
* A single bond linking aromatic rings is regarded as flexible.

in air at 400°C for 200 h, whereas the loss of weight of its unsubstituted analogue (No. 6) under the same conditions is 50%. In differential thermogravimetric analysis phenylated and non-phenylated polyquinoxalines show the same behaviour: they begin to decompose above 500°C. Polyphenylquinoxalines have the advantages of easier preparation of initial monomers and of the polymers themselves, better solubility, and ability to be converted into articles in the cyclised form. Great attention has been paid during recent years to research on the preparation and properties of polyphenylquinoxalines[66-72,150,151].

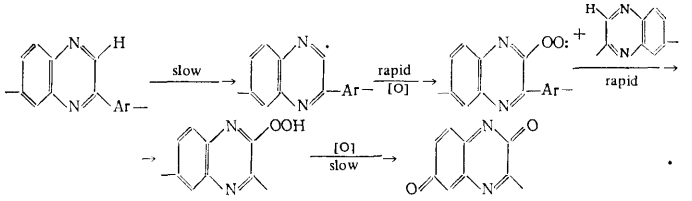
As would be expected, the introduction of ethereal oxygen into the main polymer chain produces a considerable decrease in the resistance to oxidation of polyphenylquinoxalines, accelerates the formation of volatile products, and increases their yield[150,151]. Wrasidlo[150] suggested a mechanism for the action of oxygen in which oxidation is initiated by radicals formed slowly by rupture of a carbon–oxygen bond:



The appearance of radicals is accompanied by degradation of the main chain, resulting ultimately in loss of film flexibility and strength. The phenoxy-radicals formed are rapidly converted by molecular oxygen into peroxy-radicals, whose decomposition and isomerisation liberate phenyl side-groups and yield quinonoid structures[151]

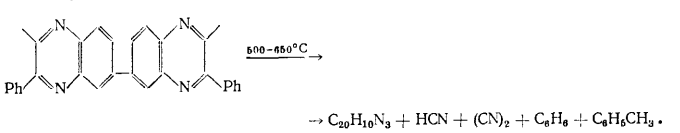


Oxidative degradation of unsubstituted polyquinoxalines proceeds differently: oxidation is initiated in the heterocycle by the action of molecular oxygen, and leads to formation of peroxy-radicals of the type[150]



These peroxy-radicals interact with a hydrogen atom of the heterocycle, to form a more stable hydroperoxy-radical. This is followed by a slow stage, which determines the rate of decomposition of the hydroperoxide and produces a resonance-stabilised quinonoid structure.

Thermo-oxidative degradation is influenced by the nature of the terminal groups[150,151,163]. In the absence of air both types of polyquinoxalines decompose between 500 and 640°C by a mechanism involving cleavage of the heterocycle[150]:



These polymers have potential uses as highly thermostable adhesives[152,153].

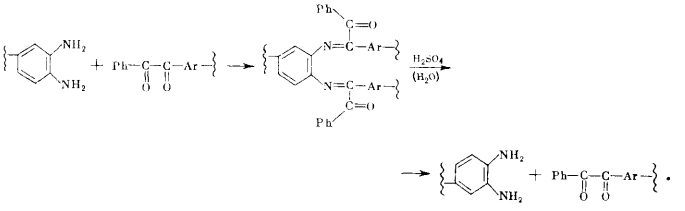
The ease of formation of polyphenylquinoxalines is extraordinary: in contrast to methods used to obtain other polyheteroarylenes, it takes place only in a single stage even at room temperature and yields completely cyclised final polymers. In no case have uncyclised intermediate products, including fragments like Schiff bases, been isolated, which evidently indicates a high degree of completeness of cyclisation. This is obviously promoted by the relatively similar nucleophilic reactivity of the *o*-amino-groups of bis-*o*-phenylenediamines and electrophilicity of the bis-$\alpha$-diketones used, and also by thermodynamic and kinetic factors favouring closure of the six-membered pyrazine ring.

Polyphenylquinoxalines have been obtained in quantitative yield both in the melt and in solution. In the former case equimolecular quantities of the tetramine and the bis-$\alpha$-diketone were heated in an inert atmosphere to 180–280°C, with the evolution of volatile products and the formation of polymers of relatively low molecular weight ($\eta_{log}$ = 0.46 dl g$^{-1}$). Polycondensation in solution involves the use of various solvents (dimethylformamide, dimethylacetamide, and *m*-cresol) over the range 10–202°C. However, polymers of high molecular weight ($\eta_{log} > 1$ dl g$^{-1}$ in sulphuric acid at 25°C) could not be obtained by boiling the initial compounds directly in dimethylformamide or in dimethylacetamide, owing to the sparing solubility of the polymers formed, which separated from the reaction mixture in the initial stages[68].

The most suitable solvent for this reaction proved to be *m*-cresol, in which polyphenylquinoxalines of high molecular weight were readily formed at room temperature (within 2–3 h); subsequent heating (boiling for 72 h) produced hardly any increase in viscosity or molecular mass of the polymers. With $\eta_{log}$ = 2.16 dl g$^{-1}$ the scattering of light gave the molecular mass $M_n$ = 247 000. *m*-Cresol probably not only is a good solvent for polyphenylquinoxalines but also catalyses their formation. This conclusion forms the basis of a method for synthesising these polymers in a cresol-free medium, e.g. a chlorinated hydrocarbon, with proton-donating compounds—methanol, acetic acid, phenols—as catalysts[154]. Reaction takes place readily and rapidly in solution at room temperature to give polymers of high molecular weight ($\eta_{log}$ = 1.5 dl g$^{-1}$).

Kinetic investigation of the formation of polyphenylquinoxalines in dilute media indicates[155] the second order for the reaction catalysed by *m*-cresol; similar results have been obtained by other workers[156]. From a study of the molecular-weight distribution and the hydrodynamic properties of dilute solutions of the polymers it was concluded that one branch point was present in ~180 ± 10 chain units[155].

Analogous conclusions were reached by Hergenrother[157], who observed gel formation during synthesis of the polymers in concentrated solutions, as well as a decrease in the viscosity of their solutions in concentrated sulphuric acid. He related this to the possibility of the formation of side-chains containing azomethine bonds, which are easily broken by the action of an acid:

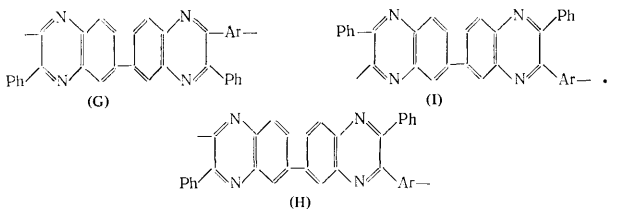


Such an explanation appears unconvincing, however, since it contradicts the good solubility of the polymers, as well

as the formation of Schiff bases usually at high temperatures[158]. It is quite possible that the branching, gel formation, and fall in viscosity mentioned by several investigators[155,157] may be due to contamination of the initial tetraketone by small amounts of impurities of functionality ≳4. This seems likely, as the method used to prepare the bis-α-diketones involved a stage of acylation in the presence of aluminium chloride, leading to formation of the required product with difficulty separable products of incomplete or excessive acetylation. Furthermore, the oxidation of deoxybenzoins by selenium dioxide may be incomplete. When bis-α-diketones obtained via diethynyl compounds are used to prepare the polymers, gel formation and the fall in viscosity of solutions in sulphuric acid are not observed[76,88,159].

Polyphenylquinoxalines are distinguished from other polyheteroarylenes in being true thermoplasts. However, their plastic properties become undesirable when the polymers are used at high temperatures (above 300°C). Numerous and varied attempts have therefore been made to overcome this defect by raising the glass point $T_{gl}$ of polyphenylquinoxalines, which usually lies below 300°C and prevents realisation of the high thermal stability inherent in the polymers.

Three main factors—molecular flexibility (mobility) of the chains, molecular symmetry, and intermolecular interaction, i.e. polar interactions and hydrogen bonds—determine the glass points of polymers. This is clearly evident from results obtained by Wrasidlo[160] and by other workers[161], who studied the molecular mobility of phenylated and non-phenylated polyquinoxalines. Position isomerism is possible with these polymers:

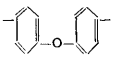
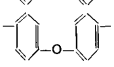
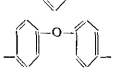



The probability of formation of these isomers decreases from (G) to (I), owing to the reactivity of the active groups in the initial reactants (i.e. the inductive and electromeric effects); they are all randomly distributed in the polymer chain. As a result, configurational disorder is observed, intensified by the introduction of flexible groups— O, CO, and $SO_2$— into the chain, with loss of crystallinity.

It is noteworthy that structurally similar phenylated and non-phenylated polyquinoxalines have almost the same glass points (Table 6). Wrasidlo[160] considers that the mobility responsible for the second-order transition in these polymers corresponds to movement of the main chain, since the barrier to internal rotation in them (measured by $\Delta C_p$) is extremely high owing to the effects of *ortho*-substitution and resonance, while depending little on the structure of the monomer unit. Table 6 shows that increasing the number of single bonds in the unit from two to nine (No. 1 and 21) results in a fall in the glass point from 395 to 216°C, caused mainly by the introduction of hinge groups—ether bonds, carbonyl and sulphonyl groups.

The influence of the above factors on the glass points can be traced in polyphenylquinoxalines containing various polar groups in the *para*-position of the phenyl substituent.

**Table 7.** Properties of ordinary and cross-linked polyphenylquinoxalines[75].

| No. | R | Ar | X | $\eta_{log}$, gl g$^{-1}$ | $T_{gl}$, °C | |
|---|---|---|---|---|---|---|
| | | | | | initial | after * heating |
| 1 | — |  | OH | 1.10 | 375 | 370 |
| 2 | — |  | OCN | 1.17 | ⩽450 | none |
| 3 | — |  | — | 1.19 | 280 | 284 |
| 4 | — |  | CN | 1.62 | 340 | 371 |
| 5 | >C=O |  | OPh | 0.72 | 215 | 219 |
| 6 | >C=O |  | 4-O-$C_6H_4$CN | 0.51 | 227 | 327 |
| 7 | — |  | Me | 0.63 | 165 | 210 |
| 8 | — |  | Et | 0.64 | 286 | — |
| 9 | — |  | OMe | 0.64 | 305 | — |
| 10 | — |  | OPh | 0.45 | 245 | — |
| 11 | — |  | Ph | 0.81 | 326 | — |

* In nitrogen at 400°C for 0.5 h.

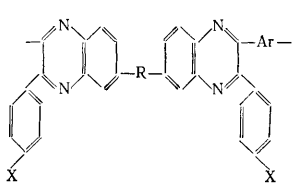
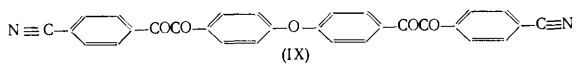


Table 7 [75] shows that such substitution has a significant effect on the glass point in comparison with polymers not containing polar groups (No. 3 and 4). With Ar = *m*-$C_6H_4$, R representing a singly bonded group, and X = $C_2H_5$, $OCH_3$, and $OC_6H_5$—i.e. groups conferring flexibility on the molecule—the glass point of the polymers falls (286, 305, and 245°C respectively—No. 8–10); with X = $C_6H_5$ (No. 11) the glass temperature rises to 326°C, but the introduction of hydroxyl (X = OH, No. 1) is accompanied by a rise to 375°C, obviously owing to the strengthening of interchain interaction by hydrogen bonding. The rise to 340°C when X = CN (No. 4) is probably due both to strengthening of polar interaction and to greater molecular symmetry, i.e. a more regular configuration of the chains and hence a more perfect conformation.

Position isomerism in polyphenylquinoxalines provides a good explanation of their solubility, amorphism, and ability to be processed in the cyclised form. However, the carbonyl groups of bis-α-diketones may differ appreciably in electrophilicity owing to non-equivalence of the inductive effects of substituents, which can in principle

lead to preferential formation of one isomer[75]. Thus in the case of the bis-$\alpha$-diketone

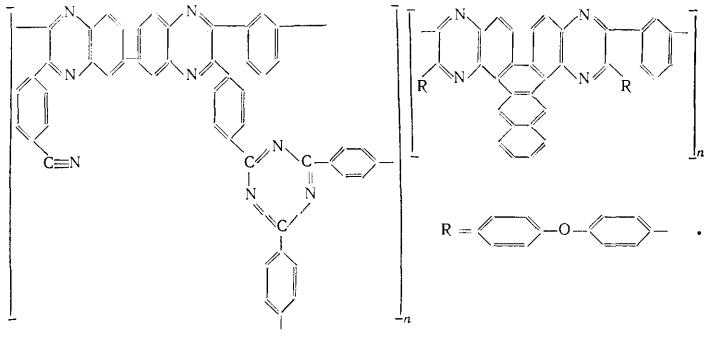


(IX)

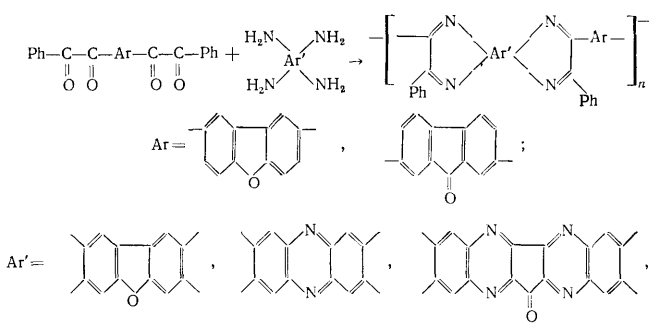
the electron-accepting effect of the cyano-group should increase the reactivity of the nearer carbonyl, whereas the ethereal oxygen atom—an electron donor with respect to the second carbonyl—would lower its reactivity, which should ultimately cause the predominance of one isomer in the polymer chain and increase the molecular symmetry[75].

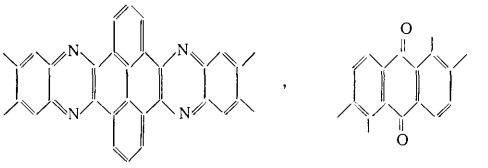
The thermal plasticity of polyphenylquinoxalines can be diminished by heat-treatment above the glass point, which is accompanied by a rise in the temperature at which the mechanical properties of the polymers are maintained. Thus heating films in helium at 400°C for 1, 4, 6, and 8 h gradually moves the temperature dependence of the modulus of elasticity to higher temperatures (the modulus begins to decrease at 316, 347, 375, and 387°C respectively). An analogous effect is achieved by heat-treatment in air, but in a shorter time, The effects are obviously due to pyrolytic cross-linking combined with oxidising processes[162,163].

Another method is available for raising the glass temperature, e.g. by introducing into the polymer functional groups—cyanato, cyano, carbonyl, phenethynyl, etc.—that on subsequent heat-treatment at moderate temperatures or treatment with simple compounds form cross-linked structures. The thermal plasticity and the solubility of the polymers are thereby lowered, and the glass point is raised considerably. In polymers containing nitrile, cyanate, and phenethynyl groups heat-treatment is accompanied by intermolecular trimerisation and formation of 1,3,5-triazine and other rings, yielding highly thermostable rigid systems of the type[75,164]



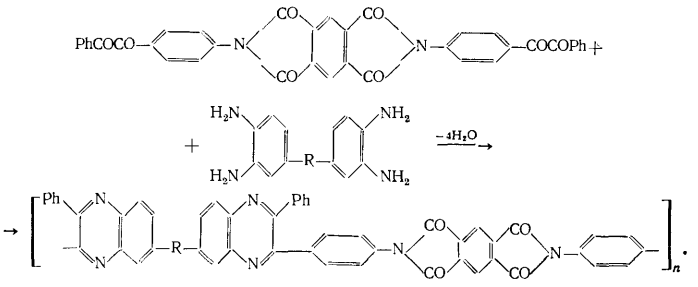
The glass point of polyphenylquinoxalines can be raised also by introducing fused rings into the amine[165] or ketone[166] component:





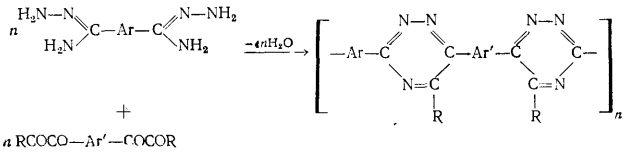
The polymers obtained from tetramines or tetraketones having high melting points possessed glass points of ~400°C and above, but exhibited loss of solubility and workability, as well as considerable impairment of their mechanical properties[165-167].

A more promising approach was the synthesis of polyphenylquinoxaline copolymers[70,168-172], in particular of polyimido-phenylquinoxalines, obtained by Augl et al.[169,170] from $\Lambda\Lambda'$-di-$p$-benzilylpyromellitimide and aromatic tetramines:

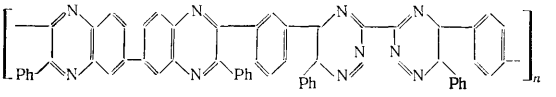


The thermal and other characteristics of the copolymers usually lie between those of the corresponding homopolymers. Table 8 lists glass points and temperatures of maximum mechanical and dielectric losses $E''$ and $\epsilon''$ for five different compositions, three of which are copolymers obtained from 3,3'-diaminobenzidine and different mixtures of $p$-bisphenylglyoxyloylbenzene and $pp'$-bisphenylglyoxyloylbenzophene.

Poly-1,2,4-triazines have been obtained by reaction between bis-$\alpha$-dicarbonyl compounds and bisamidrazones of dicarboxylic acids[75,174-176]:



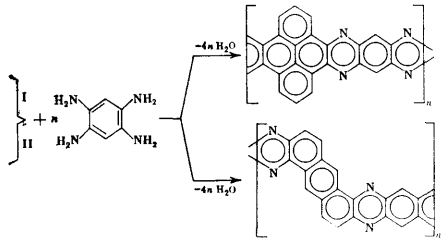
(where R = $C_6H_5$ and Ar, Ar' represent arylene groups). Copolymers containing quinoxaline and 1,2,4-triazine rings in the macromolecules



have also been prepared[157,177]. The phenylated polytriazines possess better solubility and thermal properties than do their non-phenylated analogues, but both are inferior to polyphenylquinoxalines in thermal and thermo-oxidative stability. Thus phenylated poly-2,2,4-triazines exhibit good stability in air at 260°C, whereas polyphenylquinoxalines retain their properties at 316°C for a long time (1000 h).[157]

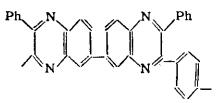
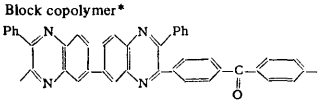
The highest heat resistance and thermal stability are found with "ladder" polyquinoxalines, which have been obtained by the reaction of pyrene-4,5:9,10-diquinone (I)

or anthracene-1,2:5,6-diquinone (II) with benzene-1,2,4,5-tetramine, naphthalene-1,2,5,6-tetramine, anthracene-1,2,5,6-tetramine, or dibenzo-5,10-dioxin-2,3,7,8-tetramine[178,179]. Completely aromatic polymers have been synthesised by the reaction of (I) or (II) with benzene-1,2,4,5-tetramine in hexamethylphosphoramide (or *m*-cresol or polyphosphoric acid) at 180°C for 120 h:



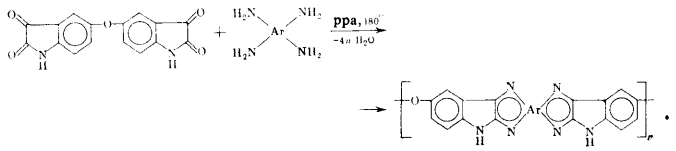
They are readily soluble in the hydrate of dichlorotetrafluoroacetone and possess viscosities $\eta_{log} \leq 2.1$ dl g$^{-1}$. Thermogravimetric analysis indicates that their degradation begins at 550°C in air and at 700°C in an inert atmosphere; they are regarded as some of the most thermostable heterocyclic polymers known at the present time[178,179].

**Table 8.** Influence of structure of copolymers on transition temperatures and relaxation maxima[173].

| Polymer | Comp., %/% | $T(\Delta C_p)$, °C | $T(E''_{max})$, °C | $T(\varepsilon''_{max})$, °C |
|---|---|---|---|---|
|  | 100/0 | 372 | 385 | 435 |
| Block copolymer* | 72/25 | 352 | 369 | 415 |
| Block copolymer* | 70/50 | 344 | 352 | 408 |
| Block copolymer* | 25/75 | 330 | 346 | 391 |
|  | 0/100 | 325 | 340 | 378 |

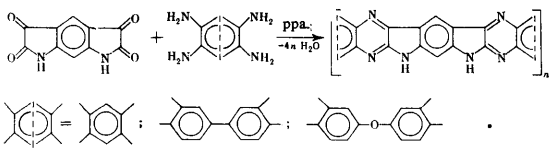
* Mean length of block determined viscosimetrically is 10–20 units[173].

A peculiar variety of this type of polymer comprises polyindoloquinoxalines, obtained by the interaction of tetramines and bi-isatins (e.g. of 5,5′-di-isatinyl ether with 3,3′-diaminobenzidine and bis-3,4-diaminophenyl ether in polyphosphoric acid at 180°C):[180–184]



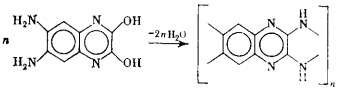
These polymers begin to decompose in air at 420–500°C, dissolve in sulphuric and methanesulphonic acids, and possess comparatively low viscosities ($\eta_{log}$ = 0.1–0.4 dl g$^{-1}$).

Ladder polymers of similar structure but higher molecular weight, with $\eta_{log}$ = 0.86–0.96 dl g$^{-1}$, have been obtained by the reaction between aromatic tetramines and tetrahydro-2,3,5,6-tetraoxodipyrrolobenzene in polyphosphoric acid[185,186]:

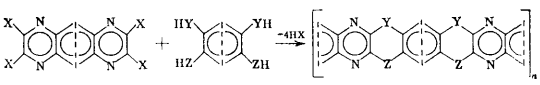


Decomposition of these polymers began in air at 460°C, and in nitrogen at 700°C.

Marvel and his coworkers[187,188] have described ladder polymers formed from tetrasubstituted quinoxalines containing activated functional groups and polymers of graphitic structure based on tetra-aminoanthraquinone and naphthalene-1,8:4,5-bisindanedione. Thus the homocondensation of diaminodihydroxyquinoxaline in polyphosphoric acid gave a ladder polymer containing quinoxaline and dihydrophenazine rings:



Similar polymers have been synthesised by condensing tetrasubstituted bisquinoxalines or anthracenes containing like functional groups with tetramines, diamino-diols, diamino-dithiols, and tetrahydric phenols[189–197]:



X=Cl, OH, OPh; Y=Z=NH; O; Y=S, O; Z=NH

Such polymers are obtained in the melt, in a solvent of high boiling point, or in polyphosphoric acid. They contain alternating quinoxaline and dihydrophenazine, oxazine, triazine, and dioxin rings, and have comparatively good thermal characteristics (they decompose in air at ~450–550°C), but are very sparingly soluble in the usual solvents and have poor workability.

In conclusion it must be remarked that α-dicarbonyl compounds are of undoubted interest as convenient subjects for the study of molecular configuration by conformational analysis[113], electron spectroscopy[198], and photochemical methods[199]. In virtue of their great reactivity they have found application for a wide range of chemical reactions[144,200] yielding in several cases valuable products[201].

The above phenylquinoxaline polymers obtained from bis-α-diketones possess a set of valuable properties, such as ease of formation, solubility, and ability to be processed by the usual technical methods into articles having great heat resistance, theremal stability, and strength against distortion, which makes then extremely promising from practical utilisation.

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# Three-stage Synthesis of "Ladder" Polyheteroarylenes

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Discussion of the fundamental principles of a general method for synthesising polyheteroarylenes, based on the three-stage reaction of tetrafunctional nucleophiles with tetracarboxylic acids, their derivatives, and analogues, is followed by detailed analysis of optimum procedures, principal characteristics, and fields of practical application of the main classes of "ladder" polymers—polyaroylenebenzimidazoles and related systems, polyisoindoloquinazolinediones, polyaroylene-1,2,4-triazoles, etc. A list of 280 references is included.

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## I. INTRODUCTION

In the chemistry of synthetic polymers great attention has been paid to aromatic heterochain polymers, in particular polyheteroarylenes—polymers containing aromatic heterocycles in the main chains of the macromolecules—during the past twenty years [1-5]. The demands of new technology, requiring synthetic materials of ever increasing thermal stability, have caused the development during the past decade of an extremely interesting and peculiar field in the chemistry of polyheteroarylenes—research on "ladder" or "double-chain" polymers possessing, according to calculations by Tessler [6,7], enhanced resistance to the action of high temperatures. A completely or partly "ladder" structure is conferred on polyheteroarylenes by introducing fused aromatic heterocycles into main chains of the macromolecules [8-17].

Research in this field has yielded many polymers containing fused heterocycles in the main chains [8-17], the large majority of them obtained by one of the main methods for synthesising "ladder" structures—polyfunctional polycondensation, primarily its chief variant—polyheterocyclisation [15]. According to the Reviewers' proposed classification [18,19] the reactions involved in the synthesis of most ladder polyheteroarylenes by polyheterocyclisation can be divided into three main groups—(1) two-stage homo- or co-polymerisation of tetrafunctional monomers containing pairs in mutually *ortho*, $\alpha$, or *peri* positions; (2) two-stage reactions of aromatic dicarboxylic acids of their derivatives with aromatic diamines containing *ortho* to the amino-groups aromatic heterocycles containing labile hydrogen atoms; and (3) three-stage reactions of aromatic tetracarboxylic acids, their derivatives, or analogues with tetrafunctional nucleophilic reagents containing four amino-groups as such or as carbamoyl, hydrazide, and other residues. The last process is the most widely used for synthesising ladder polyheteroarylenes, and can be regarded as a logical extension and development of two-stage polyheterocyclisation, which is very commonly applied in the synthesis of several thermostable polyheteroarylenes [1] and is in turn a complicated variant of the synthesis of linear condensation polymers, e.g. aromatic polyamides.

The transition from the synthesis of aromatic polyamides to that of polyheteroarylenes such as polyimides [20] or polybenzimidazoles [21] in fact requires the use of one potentially tetrafunctional monomer and also an additional stage in the process, actual polycyclisation. Similarly, the transition from the synthesis of polyheteroarylenes by two-stage polyheterocyclisation to that of ladder polyheteroarylenes by three-stage polyheterocyclisation demands that both the initial compounds should be potentially tetrafunctional, as well as an additional stage in the cyclisation process [22].

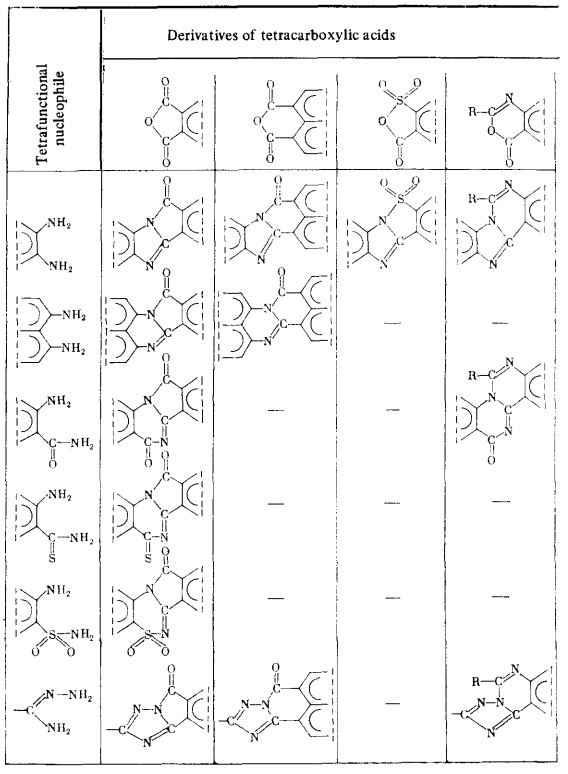
Being a more complicated variant of two-stage polyheterocyclisation, the three-stage synthesis of ladder polyheteroarylenes exhibits all the features of polycyclocondensation processes—the difficulty of selective difunctional polycondensation of potentially tetrafunctional monomers in the first stage, the complication of achieving 100% cyclisation, etc.—with the problems considerably greater than in two-stage polyheterocyclisation. The first stage in the three-stage synthesis actually involves selective polyamidation, which is more successful the greater the difference in nucleophilic reactivity between adjacent reaction centres in the tetrafunctional nucleophilic compound used, the lower the electrophilic reactivity of the acylating agent, and the lower the reaction temperature [23,24]. The nature of the solvent also has a considerable influence on the course of the process.

The tetrafunctional character of both monomers creates in several cases not only difficulties in achieving high selectivity of polyamidation but also the possibility of the formation in the first stage of polymers containing isomeric groups and thus essentially "heterounit" polymers [25]. The problem of such heterogeneity in ladder polyheteroarylenes is still more clearly evident in the second stage—polycyclisation giving polymers containing comparatively simple heterocycles *ortho* to functional substituents in aromatic rings—when the "heterounit" character of the polymers is due not only to incomplete cyclisation but also to the participation of different kinds of *ortho*-substituents, with the possible formation of at least two kinds of *ortho*-substituted polyheteroarylenes. In the third stage, finally, which usually requires more severe conditions, increase in the number and types of "foreign" units may be due to incomplete cyclisation and to secondary reactions of the heterocycles formed.

These considerations demand the most careful choice of method for the synthesis of each class of ladder polyheteroarylenes, so that in each individual case the polymers may correspond as closely as possible to the specified structure and so that their inherent properties may

be most fully realised. The three-stage synthesis of ladder polyheteroarylenes can be accomplished in different ways—(i) multistage polycyclocondensation with isolation of soluble products of the first stage, their processing into articles, and subsequent cyclisation as finished articles by gradually raising the temperature; (ii) polycyclocondensation in the melt under the conditions of the so called "Marvel reaction"[26]; or (iii) high-temperature polycyclocondensation (without isolation of intermediate polymeric structures) in solvents of high boiling point, in particular acids[27-30]. Many compounds of various classes can be used as tetrafunctional monomers in the three-stage synthesis, which is responsible for the structural diversity of the heterocycles present in the main chains of the required ladder polyheteroarylenes (see Table).

Typical monomer units and "ladder" polyheteroarylenes based on them.

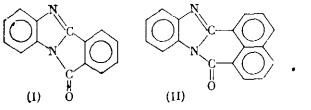



## II. POLYAROYLENEBENZIMIDAZOLES

Among the ladder polyheteroarylenes whose structural units are shown in the Table the first to attract the attention of research workers were products of the reaction of aromatic bis-*o*-diamines—also termed bis-*o*-phenylenediamines—and aromatic tetramines with aromatic tetracarboxylic acids or their derivatives.

These polymers are macromolecular compounds of the polyaroylenebenzimidazole type. The main achievements in the synthesis, processing, and application of the polymers have been summarised not only in monographs[1-5] and reviews concerned with ladder polymers as a whole[8-17] but also in several specialist reviews[31-36]. Nevertheless, many aspects of the chemistry of polyaroylenebenzimidazoles continue to be extremely controversial.

Although polyaroylenebenzimidazoles are often regarded as a single class of polyheteroarylenes, whose properties vary within narrow limits, they can be quite validly divided into two large classes—polybenzoylene- and polynaphthoylene-benzimidazoles—differing both in methods of synthesis and in properties, whose units are modelled by the compounds



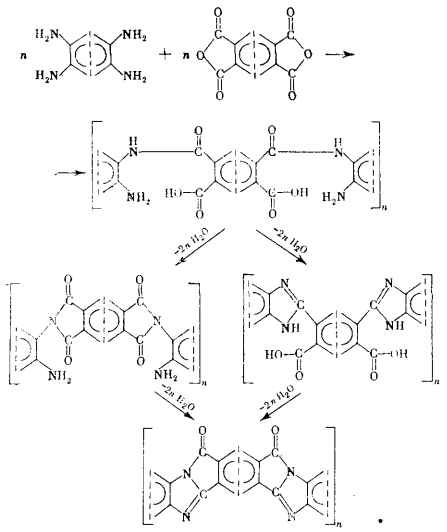

An equally valid classification distinguishes polymers obtained from tetracarboxylic acids or their derivatives of high or low electrophilic reactivity. Such differences in the initial tetracarboxylic acids, connected primarily with the charges on the carbonyl carbon atoms, are responsible for significant differences not only in the course of their acylation of bis-*o*-diamines but also in the electron densities on the carbonyl carbon atoms in the terminal heterocycles, influencing the resistance to hydrolysis of the latter, the action of nucleophilic reagents, etc. The two proposed classifications coincide in considerable measure, since in general bisphthalic acids and their derivatives are considerably more strongly electrophilic than are bisnaphthalic acids and derivatives. In several cases, however, departures from the above general principles are encountered.

### 1. Polybenzoylenebenzimidazoles

The first polyaroylenebenzimidazoles to attract the attention of investigators were polybenzoylenebenzimidazoles, known also as polyimidazopyrrolones, polybenzimidazopyrrolones, or "pyrrones"[41]. Since the initial publicity[37] attributed to these polymers extraordinarily high thermal stability, high resistance to deformation, and the ability to be processed into articles, they attracted the attention of a considerable number of research workers.

Polybenzoylenebenzimidazoles can be prepared by the interaction of aromatic bis-*o*-diamines or their salts with diesters[38-40], tetraesters[42], and also dichlorides of diesters of tetracarboxylic acids[43-45], but bisphthalic dianhydrides have found the greatest application. This reaction was conducted under conditions of "hot reactive extrusion" of the monomers[46,47], by melting the initial compounds together[48], under conditions of high-temperature polycondensation in solution in an organic solvent—nitrobenzene[49], phenol[50], or an amide solvent[49-51]—or in polyphosphoric acid[50,52-59], and also under conditions of low-temperature polycondensation at the interface[60] and in solution followed by cyclisation of the resulting initial polymers. In most cases dipolar aprotic solvents are used in the reactions of aromatic bis-*o*-diamines with

tetracarboxylic dianhydrides, when the poly-*N*-*o*′-aminophenylphthalamic acids obtained in the first stage undergo cyclodehydration to the polybenzoylenebenzimidazoles:



Considerable numbers of patents [61-98] and papers [38,43,44,50-55,99-122] have dealt with the synthesis by this scheme of completely aromatic polybenzoylenebenzimidazoles containing also various aromatic carbocyclic and/or heterocyclic rings. Polybenzoylenebenzimidazoles have been obtained also by the use of dianhydrides or cycloaliphatic tetracarboxylic acids [123-128]. Furthermore, polyesterbenzoylenebenzimidazoles [129] and polyamidobenzoylenebenzimidazoles [130-134] have been synthesised from bis-*o*-diamines and bisphthalic dianhydrides containing ester and amide groups respectively.

The first stage in the preparation—the synthesis of poly-*o*-amino-*o*′-carboxyamides—is usually conducted under conditions of low-temperature polycondensation in a dipolar aprotic solvent, such as dimethylformamide, dimethylacetamide, *N*-methylpyrrolid-2-one, hexamethylphosphoramide, dimethyl sulphoxide, etc. Thermochemical investigations indicate that the interaction of the most widely used bis-*o*-diamines and bisphthalic dianhydrides [135-137] is characterised by considerable exothermic effects, which are responsible in all cases for the high equilibrium constants (owing to the insignificant contribution by the entropy component to the Gibbs free energy) and hence potentially high degrees of polymerisation [138].

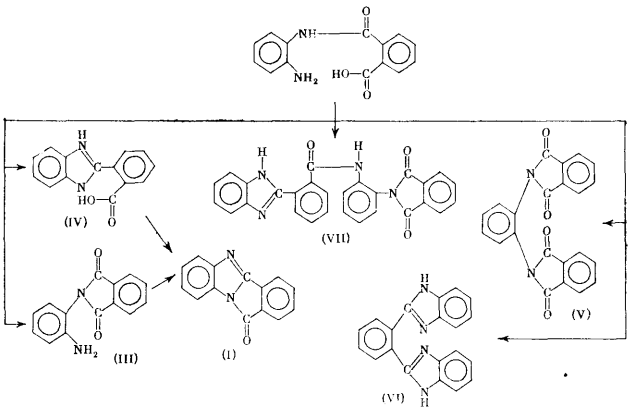
The only problem complicating synthesis of the poly-*o*-amino-*o*′-carboxyamides is the possibility of gel formation, since bis-*o*-diamines in particular are nucleophiles with neighbouring amino-groups of closely similar nucleophilic reactivities, while bisphthalic dianhydrides are the most active of the acylating agents shown in the Table. Therefore, although quantum-chemical calculations [23,24] and thermochemical investigations [137] indicate that, after the first amino-group has undergone acylation, the amino-group *ortho* to the acylated amino-group is the most strongly deactivated, the latter remains sufficiently reactive to react with dianhydrides, forming initially branches and then intermolecular "cross-links". The possibility of gel formation increases in the concluding stage, when the number of *o*-amino-groups exceeds considerably the number of amino-groups at the ends of the macromolecules.

In conformity with the above principles [23,24] success in selective polyamidation depends significantly on the temperature of the reaction and the nature of the solvent. Selectivity is actually increased by cooling from room temperature to −20°C and on passing from dimethyl sulphoxide to dimethylacetamide and thence to dimethylformamide, but gel formation cannot be completely suppressed even by conducting the reaction in dimethylformamide at −20°C. Success therefore requires a continual deficiency of the acylating agent, at least in the last stage: i.e. the last 5–10% of the dianhydride should be added as a solution to the reaction mix.

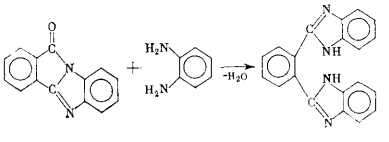
Nevertheless, such addition lowers the viscosity characteristics [139] of poly-*o*-carboxyamides, and this probably applies also to poly-*o*-amino-*o*′-carboxyamides. An alternative procedure for selective polyamidation would be somehow to increase the difference in nucleophilic reactivity between neighbouring reaction centres in the bis-*o*-diamines. With this aim use was made as initial compounds of 5,5′-dichlorobiphenyl-3,3′,4,4′-tetramine [106] and also bis-*o*-diamines in which two amino-groups had been protected by preliminary acetylation or ethoxycarbonylation [140-142], and also by "blocking" with hydrogen chloride [70,109]. However, such deactivation of two amino-groups has an adverse effect on the nucleophilic reactivity of the two remaining amino-groups, since bis-*o*-diamines are monomers with interdependent functional groups. This makes it impossible to obtain *ortho*-substituted polyamides of high molecular weight, and also complicates appreciably the process of cyclisation. Hence the preferred method for preparing initial polymers of polybenzoylenebenzimidazoles is the above interaction of unprotected bis-*o*-diamines and bisphthalic dianhydrides in dimethylformamide; the reaction goes especially smoothly in the presence of triethylamine or other base [62,142] that stabilises solutions of poly-*o*-amino-*o*′-carboxyamides against gelation. Workable polymers of high molecular weight, possessing great resistance to deformation, have been obtained by this method from most of the bis-*o*-diamines and bisphthalic dianhydrides used.

The most common method of cyclising poly-*o*-amino-*o*′-carboxyamides to polybenzoylenebenzimidazoles is thermal solid-phase cyclodehydration of the polymers in a vacuum while the temperature is gradually raised to 350°C. Investigation of the thermodynamics [49,143,144], kinetics [111,112], and mechanism [99,101,111,112] of this process has shown that, although formation of both intermediate polymeric structures—poly-*o*-aminoimides and poly-*o*-carboxyphenylbenzimidazoles—is allowed thermodynamically under the temperature conditions of the first stage of cyclisation (up to 200°C), poly-*o*-aminoimides are formed predominantly. Since both *N*-*o*-aminophenylphthalimide (III) and *o*-benzimidazol-2′-ylbenzoic acid (IV) [49,120,145] were found among the products of the model cyclisation of *N*-*o*′-aminophenylphthalamic acid occurring in the melt under the same temperature conditions, it was suggested [146] that (IV) was formed as a result of the isomerisation of (III), which involved a mutual rotation of the moieties of the molecule. Such rotation is difficult in the case of a solid-phase polymer reaction, so that the cyclisation of poly-*o*-amino-*o*′-carboxyamides to polybenzoylenebenzimidazoles occurs predominantly via poly-*o*-aminoimides. Furthermore, investigation of the cyclisation of poly-*o*-amino-*o*′-carboxyamides has shown [111,112] that imidisation and formation of the benzoylenebenzimidazole ring are superimposed on one another: i.e. the second stage of cyclisation begins before completion of its first stage.

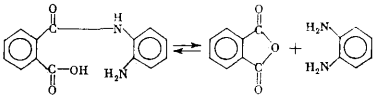
In contrast to earlier results[50] it has now been established that, with few exceptions[56,57], the polymers lose their solubility during cyclisation, and the final polybenzoylenebenzimidazoles in most cases do not dissolve in any of the solvents tested. This is explained not only and not so much by the rigidity of the macromolecular chains as by the three-dimensional structure of the final polymers resulting from a series of secondary processes. Indeed, among the products of the model cyclisation of *N*-*o*'-aminophenylphthalamic acid were detected, together with compounds (III), (II), and (I), respectively intermediate and final products of cyclisation, also *o*-phenylene-*NN*'-diphthalimide (V), *o*-phenylene-2,2'-bisbenzimidazole (VI),[49,120,145], and *o*-benzimidazol-2"-yl-*o*-phthalimidobenzanilide (VII):[145]



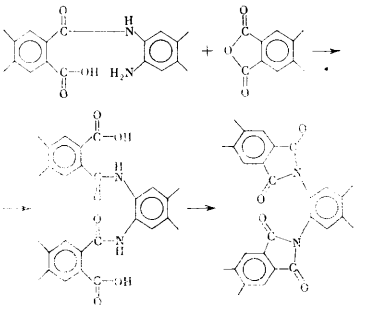
The structure of the last three products gives an idea of the nature of the intermolecular "cross-links" in the final polybenzoylenebenzimidazole structures, while the reactions involved in their formation indicate the processes occurring on the heat-treatment of poly-*o*-amino-*o*'-carboxyamides. The most important of the reactions governing the formation of "side" model compounds are most closely connected with the nature of the initial dianhydrides and occur more easily the greater the electrophilic reactivity of these compounds. Thus the product (VII) is formed from (III) and (IV) more readily the larger the positive charge on the carboxyl carbon atom. Formation of *o*-phenylene-2,2'-dibenzimidazole from *o*-phenylenediamine and 1,2-benzoylenebenzimidazole[147-149]



proceeds more easily the higher the positive charge on the carbonyl carbon of the second reactant. Finally, in the formation of (V) the strongly exothermic character of the reaction of bis-*o*-diamines with dianhydrides (becoming stronger with increase in the reactivity of the latter) is responsible for shifting the equilibrium towards the monomers with rise in temperature (also more marked the more reactive the dianhydride):

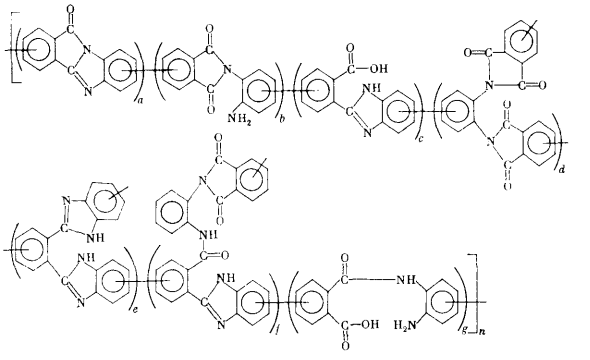


The regenerated anhydride groups react preferentially with regenerated *o*-phenylenediamine groups but, because of the relatively high temperature and hence diminished selectivity of reaction, some of them interact with amino-groups of the *N*-*o*'-aminophenylphthalamic acid:



This reaction also, of course, occurs more readily the more reactive is the initial dianhydride. Subsequent dehydration of the resulting *o*-phenylene-*NN*'-bisphthalamic acid yields (V).

According to these results polybenzoylenebenzimidazoles obtained from the most common bisphthalic dianhydrides would be more correctly represented as "heterounit" polymers having a random distribution along the chain of such units as



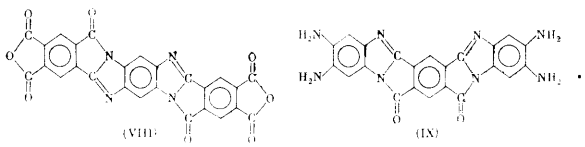
This by no means complete set of structural units present in polybenzoylenebenzimidazoles obtained by the solid-phase polycyclodehydration of poly-*o*-amino-*o*'-carboxyamides indicates the high proportion of defects in these systems. Such polymers obtained by polycyclocondensation in polyphosphoric acid would have been less defective, but this method is suitable only for obtaining polymers from dianhydrides of low reactivity[56-59], whereas syntheses using the most common anhydrides terminate in gel formation[49,107,122], caused primarily by interaction of terminal *o*-phenylenediamine groups of some macromolecules with benzoylenebenzimidazole rings of other macromolecules, a process which is especially intense in polyphosphoric acid[147-149].

Owing to their "three-dimensional" structure polybenzoylenebenzimidazoles—products of the solid-phase cyclodehydration of poly-*o*-amino-*o*'-carboxyamides—are infusible and insoluble, and can therefore be worked into articles, mainly at the poly-*o*-amino-*o*'-carboxyamide stage, the subsequent cyclodehydration being conducted on the ready made articles. This procedure has been used to obtain polybenzoylenebenzimidazole films[44,100,150-153] possessing high radiation resistance and photoconductivity, able to compete successfully with cellulose acetate films in the preparation of membranes for the deionisation of

water by reverse osmosis. Such films possess comparatively high tensile strength (up to 1500 kg $cm^{-1}$) but fairly low elongation (up to 10%) at break. The same method has been used to obtain polybenzoylenebenzimidazole fibres [61], extruded and cast articles, adhesives for glass plastics [140,141,154-161], and also foams [162-164] possessing high radiation stability. These and other possible fields of application of the polymers have been surveyed [164].

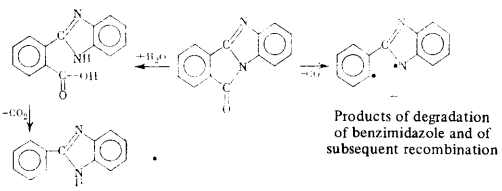
Polybenzoylenebenzimidazoles can thus be used to obtain the most diverse goods, but they differ little in thermal stability from the usual "single-chain" polyheteroarylenes: under the standard conditions of dynamic thermogravimetric analysis in air most of the former polymers already lose weight at 450°C, and under the corresponding isothermal conditions appreciable losses in weight are observed at 350°C even after a short period (up to 10 h). Most investigators link the relatively poor thermal stability [43,44,111,113,165-175] with the comparatively low degree of cyclisation of these polymers, roughly 70% according to thermochemical [143,176] and mass-spectrometric [169] results (this must be regarded as an approximate value, since in both cases only contributions by the main structural units of the polymers were taken into account).

Attempts have therefore been made to raise the degree of cyclisation by "chemical plasticisation" of the macromolecules by saturating them with ether bonds [90,95,112-114], as well as by using as initial compounds oligomers already containing 1,2-benzoylenebenzimidazole rings and possessing degrees of polymerisation of 1.5–5.5, [66] e.g.



However, neither method produced any considerable increase in thermal stability of the polymers.

The question that arises naturally from these results, whether it is fundamentally possible to produce highly thermostable polymers containing 1,2-benzoylenebenzimidazole rings, can be solved only by examining the degradation of model compounds free from the influence of "defective" units, end groups, etc. Investigation of the hydrolytic [177] and thermal [178] stability of the simplest model compound (I) has shown that hydrolysis to (IV) with decarboxylation of the latter begins at 400°C, and homolytic decomposition of the heterocycle with evolution of carbon monoxide at 435°C:



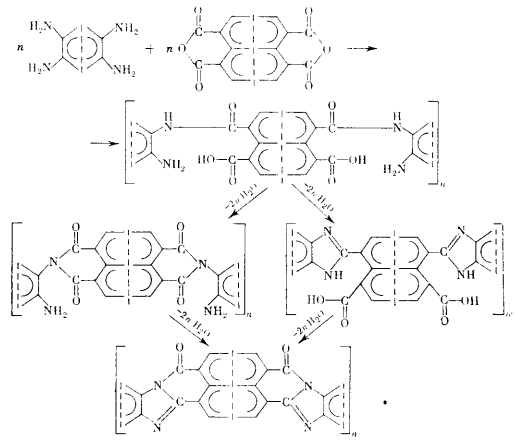

Such mechanisms of hydrolytic and homolytic degradation of (I), which are consistent with several other results [101,165,166,169], indicate that the C–CO and N–CO bonds are the least stable in this compound, a conclusion consistent also with calculation of the molecular diagram of (I) by the Hückel $\pi$-electron approximation in the LCAO–MO method [178]. The comparatively low temperatures of the start of hydrolytic and homolytic decomposition of (I) are evidence that the limited thermal stability of polybenzoylenebenzimidazole is due both to the marked "heterounit" character of the polymers and to the chemical nature of the heterocylic system itself.

## 2. Polynaphthoylenebenzimidazoles

1,2-Naphthoylenebenzimidazole (II) is considerably more thermostable than I. [178] Quantum-chemical calculations by the LCAO-MO method to the Hückel $\pi$-electron approximation indicate that the C–CO and N–CO bonds are the weakest in (II) as in (I), but their bond orders are considerably higher in (II) than in (I), while the positive charge on the carbonyl carbon atom is lower in (II) than in (I). [178] Hydrolytic degradation of (II) therefore begins at 475°C, and homolytic degradation at 525°C. [178]

A considerable amount of research, the main results of which have appeared in several patents [70-75,179-186], and papers [52,53,108,109,187-214], has been done on the synthesis of polymers modelled by (II)—polynaphthoylenebenzimidazoles, also termed polybisbenzimidazobenzophenanthrolines and polybenzobisbenzimidazophenanthrolinediones.

Two main methods—multistage polycyclocondensation [181,203-205,208-214] and single-stage high-temperature polycyclocondensation in an acid solvent [52-58,70-75,108,109,179,180,182,204-209,212,214]—are used to obtain these polymers. The multistage polycyclocondensation of bis-*o*-diamines with bisnaphthalic dianhydrides is conducted in dimethyl sulphoxide containing an inorganic salt (e.g. lithium chloride) to increase the polarity of the solvent, and is followed by solid-phase heat-treatment of the initial polymers:

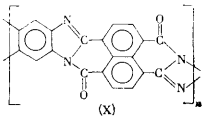


Because of the low reactivity of bisnaphthalic dianhydrides the first stage—the production of film-forming poly-*o*-amino-*peri*-carboxyamides—is accomplished at 80°C or above. In the second stage the thermodynamically advantageous six-membered imide ring is formed preferentially, according to infrared spectroscopy [214]; cyclisation is completed when the temperature is raised to 300°C. Polynaphthoylenebenzimidazoles obtained by multistage polycyclocondensation, owing to the rigidity of their macromolecular chains, which prevents effective solid-phase polycyclisation, probably contain a considerable proportion of incompletely cyclised groups. However, processes leading to three-dimensional structures, similar to those considered above for polybenzoylenebenzimidazoles, do not take place in the present case, so that the

present polymers dissolve in sulphuric acid, methyl hydrogen sulphate, and polyphosphoric acid. The most thermostable polynaphthoylenebenzimidazoles obtained by multistage polycyclocondensation retained 90% and 50% of their initial weight after isothermal heat-treatment in air at 316°C for 140 and 210 h respectively.

High-temperature polycyclocondensation in acid solvents, according to the above scheme but without isolation of initial or intermediate polymer structures, has found considerably wider use. Both bis-*o*-diamines and their salts can be used as monomers, and the acid components can be bisnaphthalic acids and their dianhydrides. The most convenient acid solvents have proved to be polyphosphoric acid alone [52,58,70-75,108,109,179,180,182,183,187-195,198-200,202,204-209,212,214] or mixed with sulphuric acid [201] or a Lewis acid [184], as well as various Lewis acids [30,75,185,186,196,197]. The absence of gel formation is attributed to the lower reactivity of bisnaphthalic than of bisphthalic dianhydrides, the ease of formation of a six-membered heterocycle, and the greater stability of the 1,2-naphthoylbenzimidazole than of the 1,2-benzoylenebenzimidazole ring towards nucleophilic reagents [178].

Naphthalene-1,4,5,8-tetracarboxylic acid and its dianhydride are the most generally used acid components; and 3,3′-diaminobenzidine, bis-3,4-diaminophenyl ether, and benzene-1,2,4,5-tetramine are the bis-*o*-diamines. Reaction between the last compound and the dianhydride gave the completely "ladder" polymer

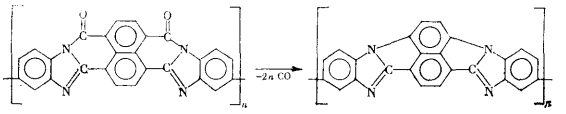


(X)

of high molecular weight, soluble in sulphuric acid, methyl hydrogen sulphate, and polyphosphoric acid, and beginning to lose weight appreciably at ~550°C according to the results of dynamic thermogravimetric analysis [190]. However, the polymer of partly ladder structure based on the more readily available 3,3′-diaminobenzidine has become more common. This polymer is also completely soluble in the three acid solvents, can be obtained with an intrinsic viscosity exceeding 6 dl $g^{-1}$, and is closely similar to the completely ladder polymer in thermal characteristics [190]. Because of the complexity of the nomenclature of these polymers, the polynaphthoylenebenzimidazole obtained from benzene-1,2,4,5-tetramine is usually denoted as BBL, and that based on 3,3′-diaminobenzidine as BBB.

Detailed investigations of the thermal characteristics of polynaphthoylenebenzimidazoles have shown that they surpass the corresponding polybenzoylenebenzimidazoles not only under conditions of dynamic thermogravimetric analysis but also under isothermal conditions both in a vacuum and in an inert environment [109,169-172,202-205,214-218]. Thus after isothermal ageing in air at 316°C for 500 h the polymers BBB and BBL retained 58% and 87% respectively of their initial weight. The higher thermal stability of polynaphthoylenebenzimidazoles is explained both by the greater thermal and chemical stability of the 1,2-naphthoylenebenzimidazole than of the 1,2-benzoylenebenzimidazole ring [178] and by the higher degree of cyclisation of the naphthoylene polymers obtained by high-temperature polycyclocondensation in acid solvents, primarily in polyphosphoric acid. Thus several workers have found that the degree of cyclisation of the polymers obtained in this acid is close to 100% [169,183,190]. Such a high value is not surprising, for the polymers are synthesised in solution, so that increase in the rigidity of the macromolecular chains is not so significant as in solid-phase polycyclisation [219-221], and furthermore polyphosphoric acid is not only a solvent but also a dehydrating agent, catalysing cyclisation.

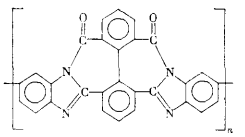
Several methods are now planned for further improving the thermal stability of polymers of this type. In particular, great interest attaches to the use of 1,2,5,6-tetraaminoanthraquinone [195] and 2,3,5,6-tetra-aminopyridine trihydrochloride [109] as initial bis-*o*-diamines. In the latter case the polymers contain only one weak carbon–hydrogen bond, which excludes a quinoid mechanism [222] of thermo-oxidative degradation. As a consequence, polymers obtained from this trihydrochloride and naphthalene-1,4,5,8-tetracarboxylic dianhydride retain 97% of their initial weight when aged at 316°C for 500 h. Another extremely interesting method for improving the thermal stability of polynaphthoylenebenzimidazoles by 40–100 deg consists in removing their weak bonds (C–CO and N–CO) by brief (<50 ms) insertion into the flame of a propane burner at 1000–1300°C. [223,224] Decarbonylation entails the formation of new polymeric structures, which are assumed to have a ladder structure:



After such pyrolytic treatment the polymers have lost their solubility, but the treatment can be applied directly to ready made articles [223,224].

The excellent thermal properties of polynaphthoylenebenzimidazoles and the comparative simplicity of their synthesis have also attracted great practical interest. In particular, the production of thermostable films [191] and ablation-resistant materials [225-227] has been reported, but the use of these polymers for the production of fibres has attracted the greatest interest [228-232]. Spinning BBB polymer from sulphuric-acid solutions into a precipitating bath of 70% sulphuric acid gave fibres which, after being drawn 1.8–2.2-fold at 525–600°C, possessed a tensile strength of 5 g $denier^{-1}$ at room temperature with an extension of 5% at break. The fibres retained 55–60% of their strength after remaining in air at 600°C for 1 min, or at 360°C for 30 h; they were resistant to moisture and ultraviolet radiation [232]. At the present time these are the most thermostable organic fibres and open up a most promising field for the practical application of ladder polyheteroarylenes.

The attention of research workers has been attracted not only to polymers containing heterocycles representing a combination of two five-membered rings or of a five-membered and a six-membered ring but also to those containing combinations of five- and seven-membered heterocyclic systems. In particular, an attempt was made to synthesis a partly ladder polymer, corresponding to the structural formula

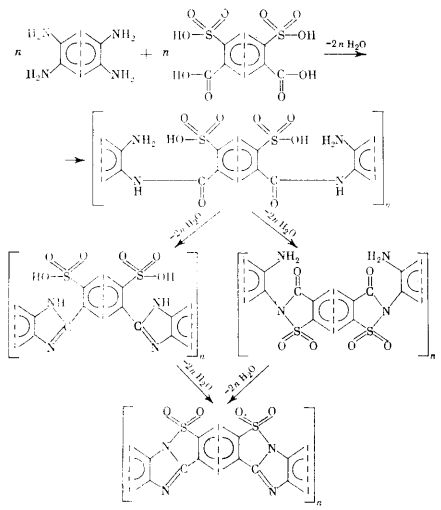


from biphenyl-2,2′,6,6′-tetracarboxylic dianhydride and 3,3′-diaminobenzidine [233]. The reaction was accomplished in polyphosphoric acid, when the dianhydride underwent

decarboxylation to the monoanhydride of fluorenedicarboxylic acid. Only polymers of low molecular weight with a low degree of cyclisation were obtained, which began to degrade at low temperatures.

## III. SYSTEMS RELATED TO POLYAROYLENEBENZIMIDAZOLES

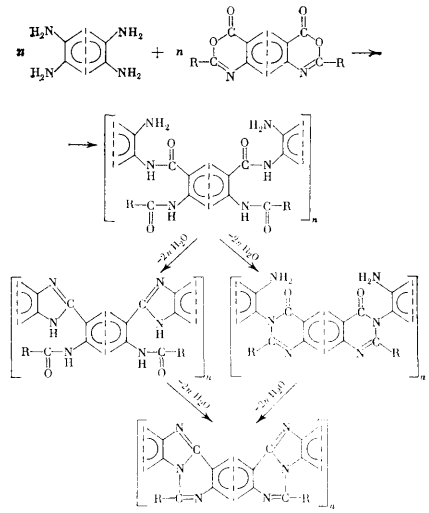
No significant advances have been made by research workers in synthesising sulphimide analogues of polyaroylenebenzimidazoles, containing bisbenzimidazobenzodi-isothiazole tetroxide rings and termed "polythiazones"[234-236]. These polymers were obtained by the polycyclocondensation of bis-*o*-diamines with disulphodicarboxylic acids or their derivatives in the melt, in solution in polyphosphoric acid, or as a multistage process:



The first stage was conducted in dimethylacetamide, and gave polymers—*oo'*-disubstituted polyamides—possessing reduced viscosities up to 1.45 dl $g^{-1}$ when dissolved in sulphuric acid. On heat-treatment these polymers underwent desulphurisation, and the final polymers exhibited comparatively low thermal stability (they began to lose weight below 400°C).

Cyclisation at 420°C of the initial polymers in the presence of triethylamine, i.e. of the triethylammonium salts of the polymers, yielded "polythiazones" that began to degrade above 450°C. Analogous polymers were obtained by conducting the reaction in the presence of triethylamine in the melt[237]. Insoluble "polythiazones" synthesised in polyphosphoric acid began to decompose in air above 450°C.[234-236]. Considerably better thermal characteristics are exhibited by "polythiazones" in an inert atmosphere. Thus the polymer obtained from 3,3'-diaminobenzidine and 4,6-disulphoisophthalic acid does not lose weight when heated in nitrogen to 520°C, and the losses on being heated to 600 and 1000°C are respectively 2.7% and 38.0% of the initial weight.

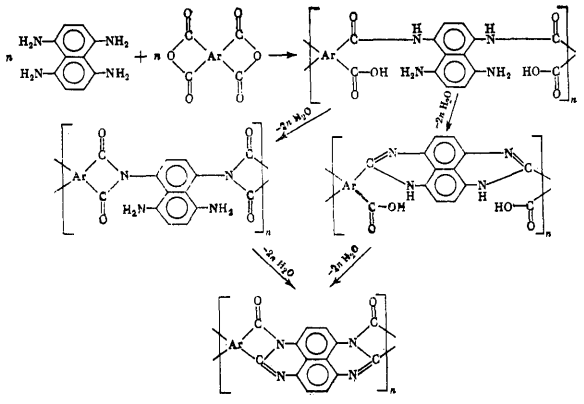
During recent years the attention of research workers has been attracted to polyheteroarylenes and in particular to "ladder" polymers based on "latent" dianhydrides, bisbenzoxazines. Reaction of the latter with bis-*o*-diamines, yielding polymers of completely or partly ladder structure—so called polybenzimidazoloquinazolines—and represented by the scheme



were accomplished by several investigators as a multistage process and as single-stage polycyclocondensation in polyphosphoric acid[238-242]. Multistage polycyclocondensation was achieved by the interaction of bisbenzoxazinones and bis-*o*-diamines in ambipolar aprotic solvents, the most suitable of which was *N*-methylpyrrolid-2-one, followed by solid-phase cyclodehydration of the resulting initial polymers. The low electrophilic reactivity of bisbenzoxazinones—even in comparison with bisnaphthalic dianhydrides—is responsible for the occurrence of this process even at higher temperatures (up to 150°C) without any signs of gel formation, but the same factor makes it difficult to obtain high molecular weights. Attempts to catalyse the process were unsuccessful, and at the present time only initial polymers of polybenzimidazoloquinazolines of comparatively low molecular weight have been obtained. According to spectral data the solid-phase cyclodehydration of these initial polymers involves intermediate formation of poly-*o*-aminoquinazolones, which cyclise to polybenzimidazoloquinazolines with difficulty (owing to the low positive charge on the carbonyl carbon atom of the quinazolone). As a consequence, the polymers formed are shown by spectral data to have a "heterounit" structure determined by the incompleteness of cyclisation, which prevents realisation of the potentially high thermal stability inherent in the benzimidazoloquinazoline ring.

It might have been expected that the problems consequent on the low reactivities of the benzoxazinone and quinazolone rings could be solved by conducting the polycyclocondensation in polyphosphoric acid, but polybenzimidazoloquinazolines of low molecular weight were then obtained, containing according to spectral data other structural residues. Since quantum-chemical calculations and the degradation of model compounds indicate that these rings surpass in thermal stability both 1,2-benzoylene- and 1,2-naphthoylene-benzimidazole rings[243], the search must be continued for methods of synthesising polybenzimidazoloquinazolines of high molecular weight, approaching the idealised structure as closely as possible.

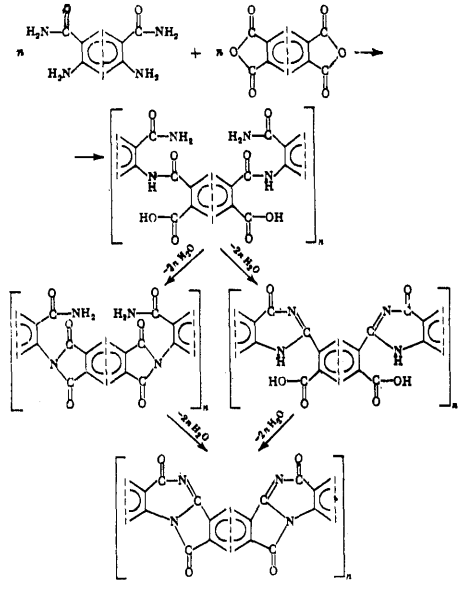
Ladder polyheteroarylenes based on bis-*peri*-diamines are considerably less common than those based on bis-*o*-diamines owing to the relative inaccessibility and very ready oxidisability of the initial compounds, in particular of naphthalene-1,4,5,8-tetramine. Investigations on the interaction of this tetramine with bisphthalic and bisnaphthalic dianhydrides



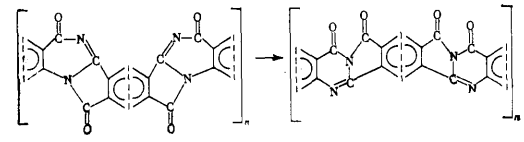
have shown[50,179,244] the theoretical possibility of synthesising such polymers, but workable polymers of high molecular weight could not be obtained.

## IV. POLYISOINDOLOQUINAZOLINEDIONES AND RELATED SYSTEMS

Syntheses of polymers of ladder structure from various bis-*o*-amino-amides as tetrafunctional nucleophiles have become quite common. These compounds react with derivatives of bisphthalic acids to form polyisoindoloquinazolinediones[245-256]. The acid derivatives may be either the dianhydrides[245-255] or the dichlorides of diesters[256]. The dianhydrides have been the most widely used:



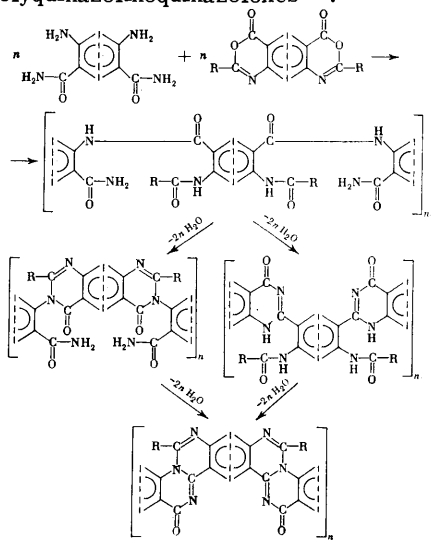
According to Kurihara[246] the final system isomerises into a thermodynamically more advantageous isomer:



Polyisoindoloquinazolinediones have been synthesised by a multistage process[245-250,256,257] and by single-stage high-temperature polycyclocondensation in polyphosphoric acid[251-255]. Multistage polycyclocondensation is effected by low-temperature interaction of the initial compounds in polar solvents followed by solid-phase polycyclodehydration of the resulting poly-*o*-carbamoyl-*o'*-carboxyamides. This process possesses several advantages and disadvantages in comparison with the multistage synthesis of polybenzoylenebenzimidazoles. Its chief merit is that bis-*o*-aminoamides are tetrafunctional nucleophiles whose reactive centres possess markedly different nucleophilic reactivities. As a consequence, the less reactive carbamoyl groups do not undergo acylation, and the first stage is not complicated by the possibility of gel formation[23,24]. On the other hand, the amino-groups are less basic and less strongly nucleophilic than those in bis-*o*-diamines, which in several cases creates difficulties in obtaining initial polymers of high molecular weight. Furthermore, since most investigators find that cyclisation of the polymers involves intermediate formation of poly-*o*-carbamoylimides, the low nucleophilicity of the carbamoyl groups may hinder the formation of isoindoloquinazolinedione rings in the concluding stage. Nevertheless, it has proved possible in several cases to obtain high polymers giving films of strength characteristics approaching those of polybenzoylenebenzimidazole films.

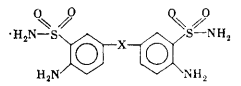
Synthesis in polyphosphoric acid is in considerable measure free from the disadvantage of the multistage process, and can be successfully used to obtain polyisoindoloquinazolinediones of high molecular weight. These polymer structures contain two pairs of weak bonds, N–CO and C–CO, and therefore with few exceptions exhibit limited thermal stability: they begin to lose weight in air at 380–400°C, and in argon above 400°C. In this connection it is somewhat surprising that due attention has not yet been paid to ladder polyheteroarylenes from bis-*o*-aminoamides and bisnaphthalic acids or their derivatives, from which greater themal stability might have been expected than from the polyisoindoloquinazolinediones examined. However, Japanese workers have accomplished the reaction of bis-*o*-aminoamides with

bisbenzoxazinones in polyphosphoric acid, and hence obtained polyquinazolinoquinazolones [258]:

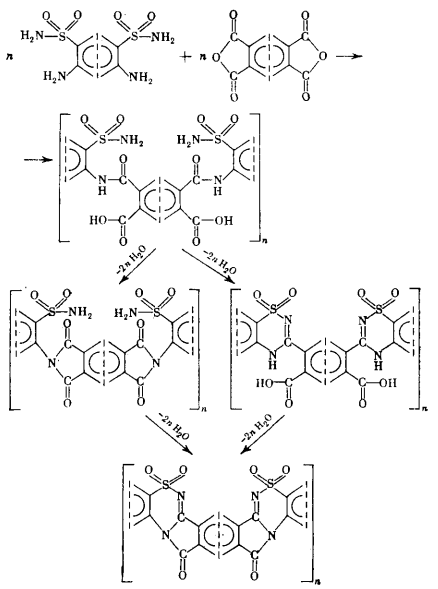


According to the results of dynamic thermogravimetric analysis (in nitrogen with $\Delta T$ = 6 deg min$^{-1}$) the loss of the initial weight at 600°C is 8–13% depending on the structure of the polymers, but it is quite clear that this line of research requires further development.

The possibilities of using bis-*o*-aminothioamides [259] and bis-*o*-aminosulphonamides [260,261] for the synthesis of ladder polyheteroarylenes have been studied still less. The patent literature contains in particular information [261] on a synthesis of such polymers from dianhydrides of aromatic tetracarboxylic acids and bisaminosulphonamides of general formula



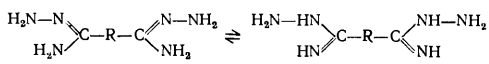
(X = O, CO, $CH_2$, $SO_2$, or S), indicating mild interaction of the starting materials in ambipolar aprotic solvents—*N*-methylpyrrolid-2-one, dimethylacetamide, dimethylformamide, dimethyl sulphoxide, hexamethylphosphoramide, etc.—followed by heat-treatment of the resulting poly-*o*-carboxy-*o*′-sulphamoylamides at 200–400°C:



The first stage of this process, like the synthesis of poly-*o*-carbamoyl-*o*′-carboxyamides, is not complicated by gel formation, since the initial nucleophilic monomers contain neighbouring centres differing markedly in reactivity. Furthermore, the amino-groups in the initial bisamino-sulphonamides are relatively strongly nucleophilic, so that in almost all cases poly-*o*-carboxy-*o*′-sulphamoylamides of high molecular weight were obtained, from whose solutions ($\eta_{red}$ = 0.4–1.2 dl g$^{-1}$) films having tensile strengths up to 1500 kg cm$^{-2}$ and extensions at break up to 10% were formed. The cyclisation of poly-*o*-carboxy-*o*′-sulphamoylamides, like that of poly-*o*-carbamoyl-*o*′-carboxyamides, occurs predominantly via *ortho*-substituted polyimides. As a consequence, the second stage—the formation of benzoylenebenzothiadiazine dioxide residues by interaction of imide carbonyls with sulphonamide units—is hindered by the diminished nucleophilicity of the *o*-sulphamoyl substituents. The final products of cyclisation are probably "heterounit" polymers containing in the macromolecules all four kinds of residues shown in the fundamental scheme of the reaction, with *o*-sulphamoylimide and benzoylenebenzothiadiazine dioxide groups predominating. Indeed, in several cases these polymers already lose weight at 400–450°C, according to dynamic thermogravimetric analysis in air, with $\Delta T$ = 5 deg min$^{-1}$. The most completely cyclised polymers do not lose weight under similar conditions up to 500°C. Poly(benzoylenebenzothiadiazine dioxide) films possess tensile strengths up to 2500 kg cm$^{-2}$ and elongations at break up to 30%.

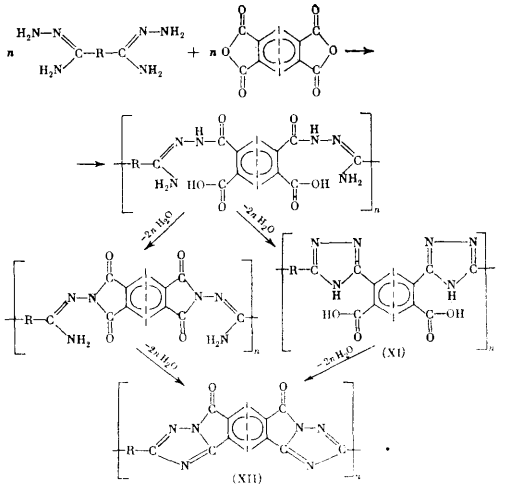
## V. POLYAROYLENE-1,2,4-TRIAZOLES

Among tetrafunctional monomers that during recent years have found considerable application for the synthesis of ladder polyheteroarylenes are bisamidrazones of dicarboxylic acids corresponding to the general formula



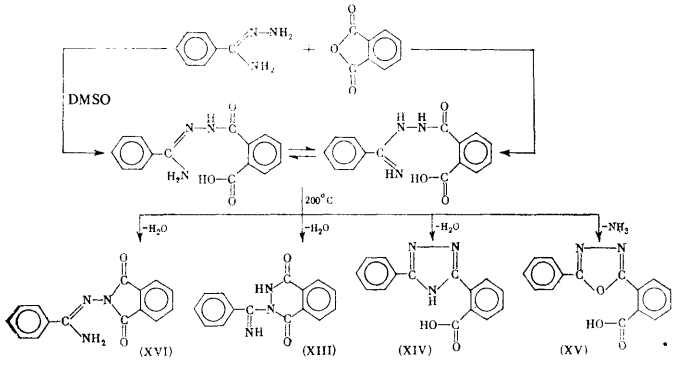
which are relatively easily available, stable compounds [262]. Polymers obtained from bisamidrazones and bisphthalic dianhydrides have been studied in the greatest detail. By 1970 extremely contradictory information had been published on the nature of these products. Thus results obtained by different investigators indicated that the first stage gave poly-*o*-carboxybenzoylamidrazones [263–266], but various structures were ascribed to the final product of

cyclisation, in particular poly-*o*-carboxyphenyl-1,2,4-triazole (XI) [263] and polybenzoylene-1,2,4-triazole (XII): [265, 266]:



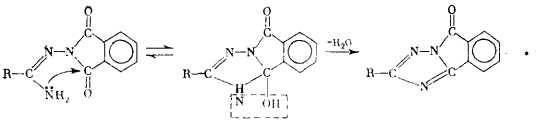
More recent results based on model reactions have shown [19,267-271] that the final products of these reactions are polybenzoylene-1,2,4-triazoles (XII), but these polymers are typical "heterounit" macromolecular compounds, which often hinders unambiguous establishment of their structure.

Several factors are responsible for the "heterounit" character of the polybenzoylenetriazoles. Firstly, although cyclisation of the products of the action of phthalic anhydride on amidrazones, *o*-carboxybenzoylamidrazones, occurs predominantly through the formation of amidino-imides, at least three other modes of cyclisation are possible, with formation of a six-membered cyclic hydrazide (XIII) [272] or of products of cyclisation of the acyl-amidrazone residue—the 3,5-disubstituted 1,2,4-triazole (XIV) and the 2,5-disubstituted 1,3,4-oxadiazole (XV): [273-275]



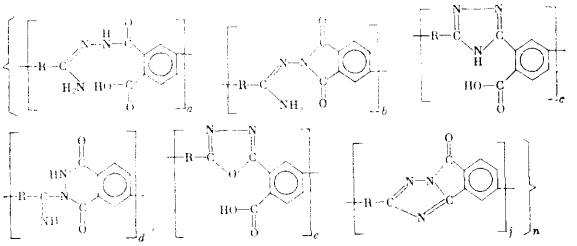
Only two of the four possible intermediate products of cyclisation—(XVI) and the *N*-amidinophthalimide (XIV)—are able to undergo a further stage of cyclisation, whereas the other two products—(XIII) and (XV)—cannot be converted into the final benzoylene-1,2,4-triazole, which is responsible for appearance of the "heterounit" character during synthesis of the polymers. The formation of structures other than (XVI) can be suppressed by treating the reaction mixture with the complex of pyridine and acetic anhydride [267], which acts as an imidisation catalyst [20], but this procedure complicates the synthesis and processing of the polymers.

Another factor contributing to the "heterounit" character of the polybenzoylenetriazoles (even when the *N*-amidinophthalimide is the sole intermediate product in the cyclisation) is the low nucleophilic reactivity of the amino-group in this intermediate, since the limiting stage is nucleophilic attack by the amino-group on a carbonyl carbon of the imide:



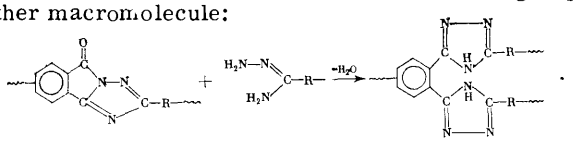
Because of the low nucleophilic strength of the amino-group this reaction is a slow process, but at higher temperatures it may be accompanied both by degradation of the *N*-benzamidinophthalimide at the weak nitrogen–nitrogen bond and by thermal and hydrolytic degradation of the benzoylenetriazole rings.

Taking into account all the above considerations, we must represent the structure of polybenzoylene-1,2,4-triazoles by the "heterounit" system



with the benzoylenetriazole units predominating. The thermochemical method of estimating degree of cyclisation developed and applied to a series of polyheteroarylenes by Korshak, Rabinovich, et al. [143,176], which involves determining heats of combustion, indicates that the final polymers contain ~80% of benzoylene-1,2,4-triazole rings. However, it must be borne in mind that estimation of the degree of cyclisation is based on the postulate that only amidino-imide and the benzoylenetriazole units are present in the polymers.

The above formula suggests that the polybenzoylenetriazoles are linear polymers, so that their heterounit character should be apparent in enhanced solubility. Nevertheless, none of the polymers obtained dissolved in any of the solvents tried. There is no doubt that, as with polybenzoylenebenzimidazoles [49], these products are "cross-linked" structures, in which the intermolecular branch points are most probably *o*-phenylenebistriazolyl residues formed by interaction between a benzoylenetriazole ring of one macromolecule and a terminal amidrazone group of another macromolecule:

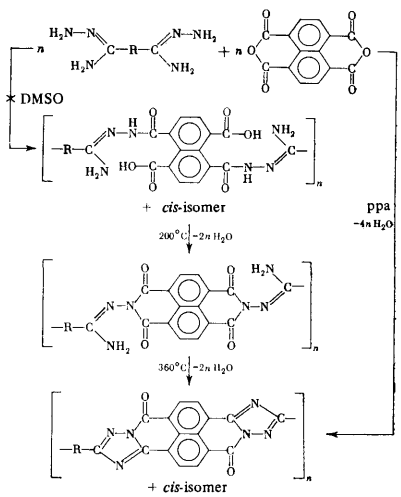


The heterounit character of the polybenzoylenetriazoles has a significant effect on their properties. X-Ray diffraction indicates that they are all amorphous, which is not surprising if they are regarded as copolymers containing various structural units. The effect on the thermal characteristics is very significant: even dynamic thermogravimetric analysis indicates the comparatively low thermal stability of these polymers, which at 350–410

and 400–440°C (rate of heating in air 4.5 deg $min^{-1}$) lose 5% and 10% respectively of their initial weight. It is interesting that polymers based on pyromellitic dianhydride are in most cases thermally less stable than corresponding polymers obtained from dianhydrides of other tetracarboxylic acids. This is probably caused by the lower degree of cyclisation due to the enhanced rigidity of macromolecules based on pyromellitic dianhydride.

Thus polybenzoylene-1,2,4-triazoles, like polybenzoylenebenzimidazoles, are cross-linked heterounit polymers, undergoing degradation at comparatively low temperatures. Yet the synthesis of their initial polymers, poly-*o*-carboxybenzoylamidrazones, owing to the differences in nucleophilic reactivity between hydrazine and amide amino-groups of amidrazones, is not complicated by branching and gel formation, so that this reaction can be conducted under the most favourable conditions to give poly-*o*-carboxybenzoylamidrazones that can easily be worked into the most diverse articles.

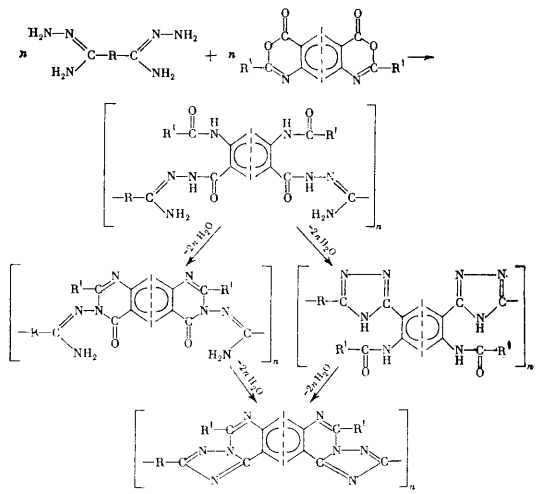
Polynaphthoylene-1,2,4-triazoles—products of the reaction of bisamidrazones with naphthalene-1,4,5,8-tetracarboxylic acid or its dianhydride—differ significantly from the corresponding benzoylene polymers both in methods of preparation and in their main characteristics. Study of model reactions indicates [19,271] that the polynaphthoylenetriazoles can be obtained either by a multistage or by single-stage polycyclocondensation in polyphosphoric acid:




However, attempts to effect polycyclocondensation with any bisamidrazone and the naphthalenetetracarboxylic dianhydride as monomers in a multistage process did not yield macromolecular products, since oligomers having a naphthalimide structure (according to their infrared spectra) separated from the solutions in the early stages. Hence the single-stage polycyclocondensation of bisamidrazones with naphthalene-1,4,5,8-tetracarboxylic dianhydride in polyphosphoric acid was chosen as general method for the synthesis of polynaphthoylene-1,2,4-triazoles [19,271,276–279]. The structure of the products was considerably more nearly perfect than that of the corresponding benzoylene polymers.

The polynaphthoylenetriazoles resemble polynaphthoylenebenzimidazoles in being completely soluble in sulphuric, methanesulphonic, ethanesulphonic, and polyphosphoric acids. Their high viscosities ($\eta_{log} \leq 3.0$ dl $g^{-1}$) are evidence of their high molecular masses. The most thermostable of these polymers lose 10% of their weight at 520–530°C under the conditions of dynamic thermogravimetric analysis, are stable in air at 400°C under conditions of isothermal thermogravimetric analysis, and do not soften up to 500°C. Polymers of this group possess high ablation resistance, and are of considerable interest as potential fibre-forming polymers.

Summarising these results, we note that on the whole polyaroylene-1,2,4-triazoles are closely similar to polyaroylenebenzimidazoles of corresponding structure and somewhat inferior to the latter in thermal stability. Considerable similarity is evident also on comparing products of the interaction of bisbenzoxazinones with bis-*o*-phenylenediamines and with bisamidrazones. The latter products, polytriazoloquinazolines, obtained in conformity with the general reaction scheme [280]



are closely similar to polybenzimidazoloquinazones. With neither structure has it yet been possible to realise the high thermal characteristics potentially inherent in them, owing to incompleteness of cyclisation and the low molecular weights of the polymers.

Critical analysis of all the above results indicates that the best classes of "ladder" polyheteroarylenes, obtained by three-stage polycyclocondensation, e.g. polynaphthoylene benzimidazoles, are significantly superior to the usual polyheteroarylenes in thermal stability and in operating temperatures. The achievement of the same or still higher thermal stability in other structures, e.g. polybenzimidazoloquinazolines, requires further research aimed at finding methods of synthesising polymers having high molecular weights and high degrees of cyclisation. Overall these polymers may make a significant contribution to the further enhancement of the thermal stability and the operating temperatures of polymeric materials on the solution of several problems facing the chemistry and the technology of ladder polyheteroarylenes—problems of the raw materials base, of processing, and of the production of almost perfect structures.

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# Photoinitiation of the Reactions of Quinones

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The primary photochemical reactions of quinones as well as secondary dark or light-induced processes involving either the initial quinones or the products of their primary photochemical reactions are considered and the reaction mechanisms are discussed. The bibliography includes 262 references.

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## I. INTRODUCTION

Under the influence of light, quinones are capable of undergoing numerous reactions. Some of the photochemical reactions (for example photochemical reduction) are components of important processes such as photosynthesis in green plants and photochemical degradation of materials coloured by vat dyes. Other photoinitiated reactions of quinones can also be of considerable theoretical and practical interest, since many of them have no analogues among dark chemical reactions.

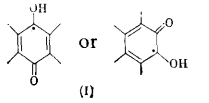
Attempts to survey the light-induced reactions of quinones were made outside the Soviet Union in 1947,[1] 1967,[2] and 1969,[3] the last review dealing with *o*-quinones only. However, since the publication of these reports, a series of new photochemical reactions of quinones have been discovered and those already known have been investigated in greater detail, which has led to the revision of old views and to the appearance of new ones in this field. Bearing in mind these factors and the fact that similar reviews have not been published in the Soviet Union, we attempted to survey the published data (up to 1974 inclusive) and to demonstrate as fully as possible the entire wide variety of the photochemical reactions of quinones. Equal attention has been devoted both to the primary photochemical steps and to the secondary processes leading to the final photolysis products.

## II. PHOTOCHEMICAL REDUCTION

### 1. Primary Photochemical Processes

Photochemical reduction is the simplest photochemical reaction of quinones (Q). It involves the addition of an electron or a hydrogen atom to the oxygen atom of the carbonyl group under conditions where the analogous dark

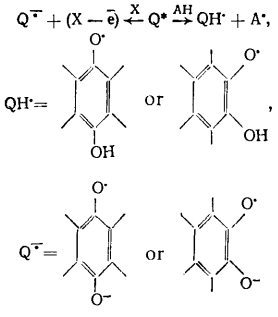
reactions are impossible. The formation of ketyl radicals (I) (or the corresponding anions), the redistribution of electron density in which leads to semiquinones or their dissociated forms, is assumed under these conditions[4]. Ketyl structures, mesomeric with respect to semiquinones, can also make a definite contribution to their resonance hybrid[5]:



(I)

The products of one-electron reduction of quinones can be obtained in two ways. In one of these, which is less frequently encountered and has therefore been less thoroughly studied, the quinone molecule in the ground state behaves as the electron (or hydrogen) acceptor in relation to the photoexcited molecules of certain pigments (chlorophylls, porphyrins, etc.), usually in the triplet state[6]. The process proceeds as a result of the significant decrease, following electronic excitation, of the ionisation potentials of the pigments or the increase of their capacity to donate a hydrogen atom. Mainly 1,4-benzoquinones[7-14] and in a few instances naphtho- and anthra-quinones[6,15-20] have been studied in such photochemical reactions, unrelated to the excitation of the quinone molecule.

Another, more frequently encountered process used in the photochemical reduction of quinones has been studied in much greater detail. It involves the abstraction of an electron by the excited quinone molecule Q* from a molecule (anion) X with conversion of the latter into a radical-cation (radical) $(X - \bar{e})$ or the abstraction of a hydrogen atom from a molecule AH with formation of a radical A· from the latter[1-3,15]:



When the side chain of quinones contains substituents which are potential electron (hydrogen) donors, the photochemical reduction of quinones also proceeds via an intramolecular mechanism. On the other hand, when both photochemical reduction pathways are possible, it is frequently difficult to decide whether the process proceeds intramolecularly or intermolecularly or via both mechanisms simultaneously.

One should note that the possibility of subdividing reagents (or substituents in quinone molecules) into electron and hydrogen donors of the kind discussed above, which seemed an obvious approach, has now given rise to doubts. One cannot rule out the possibility that the semiquinones QH· are not formed in a single-stage step involving the abstraction of a hydrogen atom from a neutral reactant molecule but are produced as a result of the abstraction of an electron from such a molecule with subsequent rapid proton transfer from the resulting radical-cation $AH^{+}$ to the radical-anion $Q^{\bar{\cdot}}$:[21,22]:

$$Q^{*} + AH \rightarrow Q^{\bar{\cdot}} + AH^{+} \rightarrow QH^{\cdot} + A^{\cdot}.$$

In particular, this mechanism has been suggested for the photochemical oxidation of hydrocarbons[2,23] and alcohols[24,25] by quinones in matrices. In view of the lack in the vast majority of instances of rigorous evidence for one- or two-step abstraction of a hydrogen atom by excited quinone molecules, it appears more correct to regard the process as the transfer of $(\bar{e} + H^{+})$ with the possibility of a two-stage mechanism (see, for example, Refs. 2 and 23–25).

The driving force of the photochemical reduction of quinones is the increase in the electron affinity of the quinonoid system on excitation. It is therefore natural that the efficiency of the process should depend primarily on the oxidation–reduction potential of the quinone in the reactive electronically excited state. However, these quantities have so far been determined only in a few instances[15]; attempts to relate the efficiency of photochemical reduction to the polarographic characteristics of quinones in the ground state have been made much more frequently[15]. Because of this, it is at present impossible to resolve adequately the problem of the comparative reactivities of various quinones and of its relation with their structure in photochemical reduction processes; one can only assess their behaviour in photolysis in reducing media, with reference to the nature of the lowest excited states.

It was believed that the reactive excited states of quinones in their photochemical reduction may be both triplet and singlet states; for some quinones (for example duroquinone), the involvement of only the singlet state is postulated[2]. Incidentally, numerous experiments have made it possible to exclude in almost all the known instances the involvement of the $S$ state of quinones (without denying such a possibility in individual cases)[15,26-28] and to give preference in this role to the long-lived biradical[4,29] triplet[15,30,31] state.

Of the two states $T_{n,\pi^*}$ and $T_{\pi,\pi^*}$, the former should be more active despite its shorter lifetime[4,29], because the delocalisation of $\pi$ electrons in the $T_{\pi,\pi^*}$ state leads to a low unpaired electron density at the reaction centre, while the localisation of excitation in the carbonyl group and the radical-like nature of the oxygen atom are characteristic of the $T_{n,\pi^*}$ state[4,15,29]. Indeed, this hypothesis has been found to hold and photoexcited quinones with the lowest $T_{n,\pi^*}$ level are effective oxidants. The transitions to this reactive state from higher energy levels usually proceed with the same probabilities (frequently close to unity), which are manifested by the constancy of the quantum yield of the photochemical reduction of the substrate over the entire wavelength range of its absorption[2,15,25,32]. If the photochemical reduction of quinones of this type is inefficient, which happens rarely, the phenomenon is usually attributed[15] to a low interconversion quantum yield $\Phi_{ST}$—for example, $\Phi_{ST}$ for ubiquinone-30, which is difficult to reduce, amounts to approximately 0.04.[30]

A small change in the ratio of the number of $n$ and $\pi$ orbitals on passing from quinones with a $T_{n,\pi^*}$ lowest excited state to polyquinones does not lead to significant changes in the ordering of the energy levels and in the photochemical properties[33,34]. However, when the solvent is altered, a specific substituent is introduced, etc., there is a possibility of the inversion of the quinone levels and the relatively unreactive $T_{\pi,\pi^*}$ or $T_{c.t.}$ levels can become the lowest†[2,15,22,35]. Anthraquinone (as well as

† The $S_{c.t.}$ or $T_{c.t.}$ levels correspond to the state with charge transfer.

other quinones [33]), with powerful electron-donating groups (OH, $NH_2$, $NR^1R^2$) as ring substituents, can serve as a characteristic example of the considerable decrease of photodehydrogenating capacity under the influence of the substituent [2,15,36,37]. The fact that such quinones do not lose completely their capacity for photochemical reduction is explained either by the involvement in the process of their $T^2_{n,\pi^*}$ state, whose level lies above the $T^1_{\pi,\pi^*}$ (or $T_{c.t.}$) [38] level, or by their reduction in the relatively inactive $T_{\pi,\pi^*}$ (or $T_{c.t.}$) state [35,37]. Nevertheless even compounds of this kind can be reduced photochemically with a fairly high efficiency. For this purpose, one uses as the light absorbing substrate a hydrogen (electron) donor, i.e. a pigment [6] which interacts with the quinone in the ground state (see above) or the photochemical reaction is carried out with the usual reducing agents but in acid media with excitation of the protonated molecules of the quinones, which have the lowest $T_{n,\pi^*}$ state [26,39,40].

Quinones can form fairly stable charge-transfer complexes (CTC) with the other reactant (solvent). If $T_{n,\pi^*}$ remains the lowest state under these conditions, then excitation by light corresponding to their absorption band is accompanied by the reduction of the quinone. The formation of such CTC is assumed for the reaction of 1,4-benzoquinone and its derivatives with ethanol [41], of sulphoanthraquinones with halide anions in aqueous solutions [42], and of quinones with aliphatic amines [2,25] and has been observed for the reactions of 1,4-benzoquinone with certain aliphatic-aromatic hydrocarbons in low-temperature matrices [23] but not solutions [43]. If the CTC energy level is lower than the $T_{n,\pi^*}$ level of the quinone (which is characteristic of powerful electron donors), then, as in the photolysis of quinones with the lowest $T_{\pi,\pi^*}$ (or $T_{c.t.}$) levels (see above), the photochemical reduction of the quinonoid structure is inhibited [23].

Water [15,16,18,19,44] and virtually all organic compounds (hydrocarbons [6,45], alcohols [2,5,15,45-51], aldehydes [1], ketones [52,53], ethers [52], amines [46,54], and amides [55]), which are usually regarded as hydrogen donors, can serve as reductants in the intermolecular photochemical reduction of quinones. Organic anions (for example alkoxide anions [15,32,39,42,56], $CH_3COO^-$, and $CCl_3COO^-$ [15]), inorganic anions ($OH^-$, $SO_4^{2-}$, $SO_3^{2-}$, $SeO_3^{2-}$, $SCN^-$, $CO_3^{2-}$, $PO_4^{3-}$, $NC_3^-$, [15,57,58] and $Hal^-$ [15,59]), and sometimes alcohols [24-26,60], and amines [2,46] are believed to be electron donors. Quinones with side-chain substituents, resembling the above reductants in their capacity to donate an electron (hydrogen), undergo intramolecular photochemical reduction.

The properties of the reductants as well as those of the quinones determine the efficiency of the photochemical reduction. This applies in the first place to the capacity of the reductant to give up an electron or hydrogen. The latter is clearly illustrated by the reactivity series of alcohols in their photochemical dehydrogenation by quinones: t-BuOH $\ll$ MeOH $<$ EtOH $<$ i-PrOH; [47] this series has been explained [2,15] by the increased mobility of hydrogen atoms at the carbinol carbon atoms as a result of the increased positive inductive effect of the alkyl group in the alcohol molecule. The conclusion that a hydrogen atom is abstracted from this position was reached on the basis of the analysis of the products of the photochemical oxidation of alcohols [2,15,47,48]. One must also take into account the steric characteristics of the reacting molecules: in particular, it has been suggested that the bulk and mass of the substituents in the quinone molecule can influence significantly its photodehydrogenating capacity in intermolecular photochemical reduction [2]. The steric factors in the reductant molecules are important in their turn; for example, in ethers the hydrogen atom is abstracted from the carbon atom involved in the ether linkage and an increase in the length and branching of the alkyl groups reduces the reactivity of the ether by shielding [2,15,47]. Steric factors play an even greater role in the intramolecular photochemical reduction of quinones, where the feasibility of the process is determined, apart from other requirements, by the possibility of achieving a cyclic transition state [2].

The photochemical reduction of quinones has been investigated in greatest detail in alcohol matrices [24,25]. It has been shown recently by electronic spectroscopy and ESR that the hydroxy-group of the alcohol $R^1R^2CHOH$ serves in this case as the donor of hydrogen (an electron and then a proton); the $R^1R^2\dot{C}OH$ radicals are formed from the radicals $R^1R^2CHO^\cdot$ in secondary reactions (cf. the interaction of photoionised quinone molecules with alcohols in the gas phase [61]):

$$(R^1R^2CHOH)^{\cdot+} + Q^{\cdot-} \leftarrow Q^* + R^1R^2CHOH \xrightarrow{R^1R^2CHOH} R^1R^2\overset{+}{C}HOH_2 + R^1R^2\dot{C}OH \qquad Q^{\cdot-} + R^1R^2\overset{+}{C}HOH_2 + R^1R^2CHO^\cdot,$$

$$R^1R^2CHO^\cdot \rightarrow R^1R^2\dot{C}OH \quad \text{or}$$

$$R^1R^2CHO^\cdot + R^1R^2CHOH \rightarrow R^1R^2CHOH + R^1R^2\dot{C}OH,$$

$$Q^{\cdot-} + R^1R^2\overset{+}{C}HOH_2 \rightarrow QH^\cdot + R^1R^2CHOH,$$

$$QH^\cdot + R^1R^2CHOH \rightarrow QH_2 + R^1R^2CHO^\cdot, \quad \text{or}$$

$$QH^\cdot + R^1R^2CHOH \rightarrow QH_2 + R^1R^2\dot{C}OH.$$

The above mechanism agrees with the hypothesis that the hydrogen bond between the alcoholic hydroxyl and the carbonyl group of the quinone in the ground state should facilitate the abstraction of a hydrogen atom ($e + H^+$) from the OH group [62-64]. Possibly the above mechanism is also applicable to the photochemical dehydrogenation of alcohols by quinones in solution (see, for example, the studies on the photochemical reduction of tetrachloro-1,4-benzoquinone in alcohols [26,60]); this process is still being discussed [24,25,47]. On the other hand, in the photochemical reduction of certain quinones in solution by acetone and aromatic [65] and acetylenic ($RC \equiv CH$) [25] hydrocarbons, the primary electron transfer in the abstraction of a hydrogen atom from their molecules is believed to have been experimentally demonstrated.

The photochemical reduction of anthraquinone and its derivatives on cellulose [66] and the hydrated surface of silica gel [67] is evidently closely related to the photochemical dehydrogenation of alcohols in matrices as regards mechanism (in the sense that a hydrogen atom is abstracted from the hydroxy-group). On the other hand, in solutions the abstraction of a hydrogen atom by excited quinone molecules from the hydroxy-group of the reductant (other than water) has been observed for certain oximes ($R^1R^2C=NOH$) with formation of iminoxy-radicals ($R^1R^2C=NO^\cdot$) from the latter [68] and for t-butylphenols with formation of the corresponding phenoxy-radicals [69]. In the latter case, the radicals produced from the substrate and the reductant have the same spin polarisations (which has been demonstrated by chemically induced dynamic electron polarisation), in agreement with the theoretical model propoced by the authors [69]. The spin states of the radicals formed in the photochemical reduction of quinones were also considered in other studies [23,70].

Finally, we shall consider the possibility of a type of intermolecular photochemical reduction of quinones where the reductant is the quinone molecule in the ground state. It is suggested, for example, that at fairly high concentrations of 2-sulphoanthraquinone, its excited molecules

react with the unexcited molecules and form the corresponding radical-anion ($Q^{\cdot-}$) and radical-cation ($Q^{\cdot+}$). Their interaction with $H^+$ and $OH^-$ ions (from water) leads to anthrasemiquinonesulphonate ($QH^{\cdot}$) and the $^{\cdot}OH$ radical [71-74]:

$$Q^* + Q \longrightarrow [Q^{\cdot-}\ Q^{\cdot+}] \longrightarrow Q^{\cdot+} + Q^{\cdot-}$$
$$\downarrow H_2O/{}^-OH \qquad\qquad \downarrow H_2O/{}^-OH$$
$$\longrightarrow Q + {}^{\cdot}OH,$$
$$Q^{\cdot-} + H^+ \rightarrow QH^{\cdot}.$$

It is suggested that this mechanism be regarded as a pathway competing with other pathways to the photochemical reduction of 2-sulphoanthraquinone (as well as quinones of other types) under any conditions [72], although its feasibility has frequently aroused doubts [73-76] or has been rejected on energetic grounds [15], the photochemical reduction of 2-sulphoanthraquinone being attributed solely to the interaction of the excited substrate ($Q^*$) and the reductant ($^-OH/H_2O$).

It is assumed that the excited quinone molecule may also be reduced by a quinone molecule in the ground state as a result of the oxidation of a substituent and not the quinonoid ring—for example, such a pathway is possible (but has not been demonstrated rigorously), in the photochemical reduction of alkoxymethyl-1,4-benzoquinones [2].

## 2. Secondary Intermolecular Photochemical Reduction Reactions

Intermolecular photochemical reduction involves numerous secondary reactions in which quinones and their reduced forms, the reductants, and their oxidation products participate in various combinations.

Apart from its formation in the photochemical process, the product of the one-electron reduction of the quinone can be obtained also in a secondary dark reaction of the quinone with the radical (radical-anion) produced from the reductant, as happens, for example, in alcoholic media [2,77]:

$$Q + R\dot{C}HOH \rightarrow QH^{\cdot} + RCHO.$$

The interaction of the product of the one-electron reduction of the quinone and the oxidised substance can lead to the regeneration of the initial compounds. Thus, this type of reaction is fairly rapid in the photochemical reduction of sulphoanthraquinones by the $CO_3^{2-}$ ion [6,15,78]:

$$Q^* + CO_3^{2-} \rightarrow Q^{\cdot-} + CO_3^{\cdot-}, \qquad Q^{\cdot-} + CO_3^{\cdot-} \rightarrow Q + CO_3^{2-}.$$

photochemical (forward) reaction — dark (reverse) reaction

The reverse reaction is frequently comparatively slow and there is then sufficient time for the product of the one-electron reduction of the quinone to undergo other reactions. In particular, regardless of which of the species ($QH^{\cdot}$ or $Q^{\cdot-}$) arises in the primary photochemical step, an equilibrium is established among the photolysis products:

$$QH^{\cdot} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Q^{\cdot-}.$$

Its position is determined by the acid–base properties of these species and the medium [2,15,21,79-81].

In the ground or a high vibrationally excited state, the semiquinone can abstract a hydrogen atom from the reductant, forming the hydroquinone ($QH_2$): [2,82]

$$QH^{\cdot} + AH \rightarrow QH_2 + A^{\cdot}.$$

The study of the photochemical reduction of anthraquinone in alcohols with added alkali led the author to the conclusion that there is also a possibility of the photochemical reaction of the products of the one-electron and two-electron reduction of the quinone [83,84]:

$$(QH^{\cdot})^* \xrightarrow{AH} QH_2 + A^{\cdot}$$
or
$$(Q^{\cdot-})^* \xrightarrow{X} Q^{2-} + (X - \bar{e}).$$

However, hydroquinones are not formed solely in the processes enumerated above. It is believed that the main pathways to their formation is the disproportionation of the semiquinones $QH^{\cdot}$ and the radical-anions $Q^{\cdot-}$ in the reversible process [2,15,72,77,79,82,85-87]; the semiquinones then disproportionate approximately 10 and more times as efficiently as the radical-anions [2,15,79]. All these substances are at the same time involved in an acid–base equilibrium:

$$2\,Q^{\cdot-} \rightleftarrows Q^{2-} + Q \qquad 2\,QH^{\cdot} \rightleftarrows QH_2 + Q$$
$$\uparrow\downarrow \quad \overset{+H^+}{\rightarrow} \quad QH^- \quad \overset{+H^+}{\leftarrow} \quad \uparrow$$
$$-H^+ \qquad\qquad -H^+$$

where $QH^-$ and $Q^{2-}$ are the hydroquinone mono- and di-anions.

In certain cases (see Refs. 88–90), the hydroquinones thus produced can retard the photochemical reduction of the quinone, deactivating its excited state (chemical quenching) via the reaction

$$Q^* + QH_2 \rightarrow 2QH^{\cdot} \rightarrow Q + QH_2$$

or can undergo further photochemical reduction. Thus it has been established that prolonged irradiation of anthrahydroquinone and its derivatives produced photochemically in hydrocarbons [91] and alcohols as well as aqueous alcoholic media [31,40,92-94] leads to the corresponding anthrols, anthrones, and anthracene.

Taking into account the above formation reactions and subsequent transformations of the reduced forms of quinones, a mathematical model has been devised for the intermolecular photochemical reduction of quinones, which describes satisfactorily the process as a whole [95,96].

Semiquinones as well as radical-anions, hydroquinones, and their dissociated forms are produced in deaerated media, since they are all readily oxidised by oxygen (and are capable of being oxidised by other reagents [2,15,97]) with regeneration of the initial quinone [15,47,72]:

$$QH^{\cdot} + O_2 \rightarrow Q + HO_2^{\cdot}; \quad Q^{\cdot-} + O_2 \rightarrow Q + O_2^{\cdot-};$$
$$QH_2 + O_2 \rightarrow Q + H_2O_2.$$

Under aerobic conditions, the overall process appears to involve the photochemical oxidation of the reductant and there is good reason for the term "photochemical oxidation sensitised by quinones" frequently given to it [15]. When the reductant is an alcohol, the overall mechanism is as follows [72]:

$$Q^* + RCH_2OH \rightarrow QH^{\cdot} + R\dot{C}HOH,$$
$$Q + R\dot{C}HOH \rightarrow QH^{\cdot} + RCHO,$$
$$QH^{\cdot} + O_2 \rightarrow Q + HO_2^{\cdot},$$
$$R\dot{C}HOH + O_2 \rightarrow RCH(O_2^{\cdot})OH,$$
$$RCH(O_2^{\cdot})OH + HO_2^{\cdot} \rightarrow RCHO + H_2O_2 + O_2,$$
$$2\,RCH(O_2^{\cdot})OH \rightarrow 2\,RCO_2H + H_2O_2,$$
$$RCH(O_2^{\cdot})OH \rightarrow RCHO + HO_2^{\cdot},$$
$$2\,HO_2^{\cdot} \rightarrow H_2O_2 + O_2.$$

The mechanism does not include hydroquinones $QH_2$, since there is insufficient time for their formation from

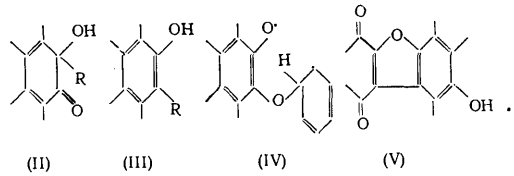
the semiquinones QH$^{\cdot}$ owing to the rapid oxidation of the latter [15]‡. Naturally, such photochemical oxidation of the reductant can be achieved only in those cases where oxygen does not quench or only slightly quenches the reactive state of the quinone. In particular, this happens for anthraquinone and its derivatives owing to the short lifetime of their $T$ states [6,15,75,76,100].

In the light of the foregoing considerations, the photochemical reduction of anthraquinone dyes in matrices in the presence of air as a result of the transfer of a hydrogen atom (or electron) appears fairly probable and is believed to be the main primary process in the theory of the photochemical degradation of materials coloured by such dyes which is most widely held at the present time [15, 38,39,100–105].

The secondary intermolecular photochemical reduction processes, described above in the most general form, are the most typical examples; the specific products of similar and other secondary reactions as well as the pathways leading to their formation are discussed below.

Hydrocarbons. The hydrocarbon radicals arising in the photochemical oxidation of hydrocarbons by *p*-quinones under anaerobic conditions alkylate the quinone (semiquinone) ring and add to the oxygen atom, forming ultimately a hydroquinone ether, or are dehydrogenated by the quinone (semiquinone) to alkenes [1,2]. In the photochemical reduction of *o*-quinones by hydrocarbons, 1,2-addition [compounds (II)] and 1,4-addition [compounds (III)] products are obtained [1–3]. Thus the cyclohexyl radicals generated in the photolysis of 1,4-benzoquinone in cyclohexane give rise to cyclohexyl-1,4-benzoquinone and cyclohexene in the corresponding reactions [2]. By irradiating quinizarin in aliphatic hydrocarbons, alkyl derivatives of its leuco-form were obtained, but the positions of the alkyl groups were not established [106].

Mainly cycloaddition products are formed in the photochemical reactions of *o*-quinones with olefins, but the photolysis of phenanthrenequinone in the presence of isobutene, *cis*- and *trans*-but-2-enes, and tri- and tetramethylethylenes also results in the formation of the compounds (II, R=$CH_2CR^1=CR^2R^3$, $CR^2R^3CR^1=CH_2$) as a result of the capture of the allyl radical by the semiquinone [3]:



(II) (III) (IV) (V)

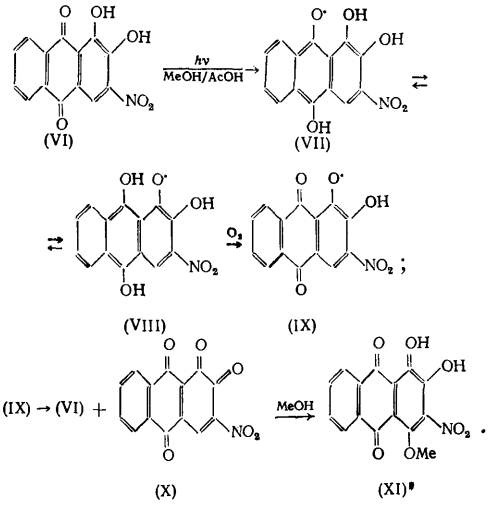
The nature of the secondary products of the photochemical reduction of quinones by alkylbenzenes as a function of the nature of the quinone and the radical formed from the reductant has been more thoroughly investigated than for aliphatic hydrocarbons. The photochemical reduction of *p*-quinones with a relatively high oxidation-reduction potential yields products of the addition of radicals of the type $Ar\dot{C}H_2$ to the oxygen atom and of the dehydrogenation of radicals of the type $Ar\dot{C}H-CH<$. Thus irradiation of tetrachloro-1,4-benzoquinone (but not of 1,4-benzo- and naphthoquinones) in the presence of *p*-xylene, cumene, or tetralin leads respectively to the mono-*p*-methylbenzyl ether of 1,4-dihydroxybenzene, methylstyrene, and 1,2-dihydronaphthalene [2].

The radicals obtained by the abstraction of a benzyl hydrogen atom in the photolysis of the corresponding compounds in the presence of *o*-quinones are sometimes dehydrogenated [107], but 1,2- and 1,4-addition products are normally formed [1,2,5]. The ratio of the products of the 1,2- and 1,4-addition of the *p*-$RC_6H_4\dot{C}H_2$ radicals has been shown [2] to be determined by the nature of the substituent R—the fraction of the 1,2-addition product increase with increase of its electron-donating capacity owing to the electron deficiency at the carbon atom and the electron excess at the oxygen atom of the semiquinone.

By irradiating phenanthrenequinone [3,108] and tetrachloro-1,2-benzoquinone [3] in benzene, the monophenyl ethers of the hydroquinones (III, R = Ph) were obtained together with the corresponding hydroquinones and biphenyl. In the case of phenanthrenequinone, the formation of a 1,4-adduct is assumed to result from the intramolecular abstraction of a hydrogen atom from the biradical (IV) produced photochemically; incidentally, the usual pathway involving the recombination of the semiquinone and phenyl radicals, but without their emergence from the solvent cage, is not excluded either.

One should bear in mind that, apart from the above pathways leading to the stabilisation of hydrocarbon radicals, another pathway, which is not discussed here, frequently occurs, namely their recombination [2,109].

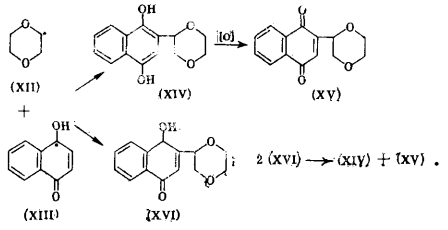
Alcohols. In contrast to hydrocarbon radicals, the $R^1R^2\dot{C}OH$ radicals obtained in the photochemical oxidation of alcohols by quinones do not form adducts with the latter or with their reduced forms. They are stabilised by disproportionation or are dehydrogenated by the quinone or the semiquinone. Semiquinones are stabilised in alcoholic solutions by an intramolecular mechanism or interact (sometimes after conversion into other intermediates) with the solvent. An example of the first pathway is the formation of the cyclic products (V) when 2,2′-biphenyl- and 2,2′-binaphthyl-1,4,1′,4′-diquinones are irradiated in alcohols [2]. The second pathway is illustrated by the conversion of 1,2-dihydroxy-3-nitroanthraquinone (VI) into 1,2-dihydroxy-4-methoxy-3-nitroanthraquinone (XI): [2]



(VI) (VII) (VIII) (IX) (X) (XI)

‡ All the secondary reactions of semiquinones or the corresponding radical-anions discussed above can be suppressed by combining the reactive species into complexes and micelles [98,99].

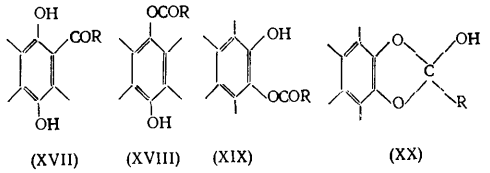
Ethers and related compounds. The radicals generated in the photochemical oxidation of ethers (thioethers) by quinones alkylate *p*-semiquinones in the ring form 1,2- and 1,4-addition products with *o*-semiquinones. For example, the dioxanyl radical (XII) was found to react with the radical (XIII) (obtained from 1,4-naphthoquinone), compound (XV) being the final product [110]. The dioxanyl derivative of 1,4-benzoquinone may be present among the unidentified products of the photolysis of 1,4-benzoquinone in dioxan [2]. Phenoxymethyl-1,4-benzoquinone is obtained similarly by the irradiation of 1,4-benzoquinone in aqueous anisole [2]:




1,4-Addition products are formed by the recombination of radicals generated from *o*-quinones and ethers (thioethers), i.e. by the reactions of tetrachloro-1,2-benzoquinone with dioxan [2] and of phenanthrenequinone with di-isopropyl, dibutyl [110], benzyl phenyl, and dibenzyl ethers as well as the dibenzyl ethers of ethyleneglycol and 1,4-dihydroxybenzene [111], ethyl acetate and propionate, dithian [2], and ethyl vinyl sulphide [3]. In most cases the products are unstable and readily decompose in air, for example as a result of hydrolysis, while on irradiation they can rearrange to 1,2-addition products, as shown for the adducts of phenanthrenequinone with anisole and dioxan [2].

The formation of the 1,2-addition product in the photolysis of acenaphthenequinone in tetrahydrofuran [112] and of 1,4-dihydro-2-hydroxy-1-oxo-4-xanthylnaphthalene on irradiation of 1,2-naphthoquinone or its 3-chloro, 3-bromo-, and 6-bromo-derivatives in the presence of xanthene are rarer examples [113,114].

Aldehydes. The products of the secondary reactions in the photochemical reduction of *p*-quinones by aldehydes are compounds of type (XVII) and (or) (XVIII):

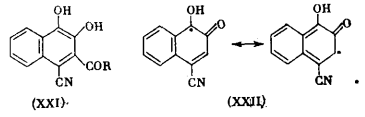



Ring acetylation by the $CH_3\dot{C}O$ radical occurs in the photolysis of 1,4-benzoquinone and its mono-, di-, and tri-methyl, acetyl, and 2,3-dichloro-derivatives, 1,4-naphthoquinone, 2-methylnaphthoquinone [2], 1,4,9,10-anthradiquinone, 1,4,5,8-naphthodiquinone, the anhydride of 1,4-benzoquinone-2,3-dicarboxylic acid, and 2,3-dicyano-1,4-benzoquinone [115,116] in acetaldehyde; the products of the photolysis of anthraquinone in acetaldehyde were not identified [2]. Acyl derivatives of type (XVII) have also been obtained in the photolysis of 1,4-benzoquinone in the presence of trimethylacetaldehyde and acrylaldehyde [2,115]. Diacylhydroquinones are sometimes formed in these processes [2].

The final products of the reactions of tetrasubstituted 1,4-benzoquinones (dichlorodicyano- and tetrachloro-derivatives) are hydroquinone monoethers, which are formed also in the photolysis of quinizarin in the presence of the aldehydes *p*-$XC_6H_4CHO$ (X = H, $NO_2$, or MeO). [2] Irradiation of 1,4-benzoquinone in the presence of cinnamaldehyde yielded only the hydroquinone monoether [3], irradiation of cortonaldehyde gave both possible substances of types (XVII) and (XVIII), [115] and irradiation of the benzaldehydes *p*-$XC_6H_4CHO$ resulted in the formation of benzoylhydroquinones (X = Me, t-Bu, or MeO) and monobenzoates (X = $NO_2$, CHO, CN, or $CF_3$). [115]

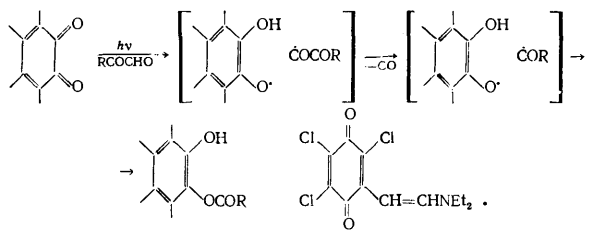
Together with the view that the $R\dot{C}O$ radicals and the semiquinone are involved in the formation of compounds (XVII) and (XVIII), there exists another hypothesis, namely that the $R\dot{C}O$ radical reacts with the quinone [2,115]. It is believed that the nature of the reaction product [(XVII) or (XVIII)] depends on the nucleophilic properties of the $R\dot{C}O$ radical: the more nucleophilic the radical, the greater the probability of attack on the ring (if not all its positions are occupied) and, conversely, a decrease of nucleophilicity leads to an increased yield of the ether. The oxidation-reduction potential of the quinone plays a significant role. Thus, it is assumed that a competitive mechanism involving electron transfer from the $R\dot{C}O$ radical to the quinone Q and the formation of the radical-ion pair $[Q^-RCO^+]$, in which the acylium ion should be localised near one of the oxygen atoms, operates in the case of quinones with high oxidation-reduction potentials (1,4,9,10-anthradiquinone, 1,4,5,8-naphthodiquinone, the anhydride of 1,4-benzoquinone-2,3-dicarboxylic acid, and 2,3-dicyano-1,4-benzoquinone). This also explains the interaction of acyl radicals with the above quinones at the oxygen atom.

The photolysis of *o*-quinones in the presence of aldehydes yields mainly 1,4-addition products—the monoethers of 1,2-enediols (XIX) and (or) the cyclic acetals (XX): [2,3,117]




By irradiating 1,2-naphthoquinone and many of its derivatives in aliphatic (but not aromatic [2]) aldehydes, it was possible to obtain ring-acylation products (XXI) [evidently by the recombination of the radicals (XXII) and $R\dot{C}O$ [2,3,109]], in addition to enediol ethers of type (XIX), and to substitute the halogen atom (if present) in the 3-position in the acyl group.

Compounds of type (XIX) are formed on recombination of the radicals $RCO\dot{C}O$ obtained from glyoxals and semiquinones as a consequence of decarbonylation in the solvent cage [118]:



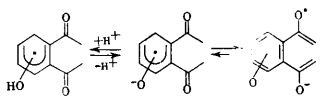

Amines. The excitation of [amine$^+$ quinone$^-$] CTC or the [(amine – H)$^\cdot$ (quinone + H)$^\cdot$] radical pair in quinone

(2,5-dichloro-3,6-dimethoxy- and tetrachloro-1,4-benzoquinones)–tertiary amine (triethylamine and 2-methylpiperidine) systems leads to the hydroquinone monoanion ($QH^-$) and an ion of the type $Et_2\overset{+}{N}=CHCH_3$. When they interact, the chlorine atom is substituted with formation of aminovinylquinones, for example (XXIII).[2]

Water, $H^+$ and $OH^-$ ions, and ammonia. The photolysis of tetramethyl-1,4-benzoquinone in water yields only the corresponding hydroquinone[2,119], while 1,2,4-trihydroxybenzene and (or) 2-hydroxy-1,4-benzoquinone have been obtained from 1,4-benzoquinone in addition to 1,4-dihydroxybenzene[2,119–122]. The formation of these substances has been explained[121] by the interaction of the photochemically generated ·OH radical with the quinone (or semiquinone). The 1,2,4-trihydroxybenzene thus produced reacts with the initial quinone to form 2-hydroxy-1,4-benzoquinone and 1,4-dihydroxybenzene. This oxidation is faster in acid and alkaline solutions and is slow in solutions close to neutrality; consequently the pH of the medium determines the composition of the final products. The alternative mechanism involving the abstraction of the ·OH radical from water by the excited quinone followed by attack by a hydrogen atom on the quinone molecule in the ground state[2] appears much less probable.

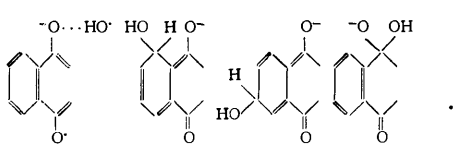
The efficiency of the single-photon process involving the disappearance of 1,4-benzoquinone is independent of its concentration in solution and of the wavelength of the exciting light, remaining constant in the pH range between 0.4 and 8; according to some data, the quantum yield is smaller than unity[2,119–121], while according to others[122] it is greater than unity. The variation of the quantum yield in the photolysis of 1,4-benzoquinone in micellar systems (increased and decreased respectively in the presence of anionic and cationic surfactants) can indicate, according to some workers[119], the involvement of cationic intermediates in the process.

The weakly electrophilic ·OH radicals generated in the photolysis of 2-sulphoanthraquinone in neutral, aqueous alkaline[15,75,123–127], and aqueous alcoholic[2,48,124,128] media hydroxylate sulphoanthraquinone in the range without the sulpho-group[15]. The adduct (XXIV) formed is oxidised by the initial quinone or oxygen to hydroxysulphoanthraquinone[15,123,129,130]:



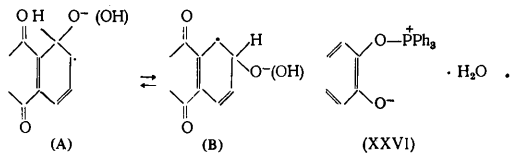
(XXIVa) (XXIVb) (XXIVc)

A hydrogen-bonded complex (XXVa) or an adduct of type (XXVb)–(XXVd) may precede the intermediate (XXIV) and only their interaction with an unexcited sulphoanthraquinone molecule leads to the adduct (XXIV) and the radical-anion $Q^{\cdot-}$:[75]



(XXVa) (XXVb) (XXVc) (XXVd)

The composition of the products of the hydroxylation of 2-sulphoanthraquinone as well as 1,4-benzoquinone depends on the pH of the medium: in highly alkaline solutions (pH ≥ 12), the main products are 6- or 7-hydroxyanthraquinone-2-sulphonates, while in neutral and weakly alkaline solutions (pH ≤ 12), the main products are 6-, 7-, 5-, and 8-hydroxy-derivatives[15,130], this is attributed either to the different natures of the hydroxylating agents (·OH or $O^{\cdot-}$ formed as a result of the $\cdot OH \rightleftharpoons O^{\cdot-} + H^+$ equilibrium)[15,126] or to the reversible interconversion of forms A and B, which depends on the pH of the medium[75]:



(A) (B) (XXVI)

1-Sulphoanthraquinone, which is photochemically reduced with greater difficulty and has therefore been less thoroughly investigated in photochemical hydroxylation reactions, evidently yields hydroxy-1-sulphoanthraquinones by a similar mechanism.

Photochemical hydroxylation yields dihydroxy-derivatives of sulphoanthraquinones in addition to the monohydroxy-derivatives; their formation is promoted by the decrease in the concentration of the substrate and when the photolysis is carried out under aerobic conditions[130]. The selectivity of the hydroxylation reaction and the possibility of introducing the OH group into other aromatic compounds present in the reaction mixture, particularly in a cyclic process using oxidants, can make it useful for the synthesis of aromatic hydroxy-derivatives[15].

Amination of 2-sulphoanthraquinone in its photolysis in aqueous ammonia, hydrazine, and methylamine solutions, resulting in the preferential formation of 6(7)-amino-(methylamino)-2-sulphoanthraquinones[15], is tentatively assumed to involve a mechanism similar to that of photochemical hydroxylation.

In the instances described above, the oxidised form of the reductant interacts with the quinone, but processes are also known where the reduced forms of the quinones interact with the reductants (solvents). For example, the displacement of methoxy-group by the $OH^-$ ion (dark process) on irradiation of 1- and 2-methoxyanthraquinones in alkaline aqueous alcoholic solutions occurs precisely in the way described—in the photochemically generated dissociated methoxyanthrasemiquinones[131]. The semiquinone obtained by the photochemical reduction of phenanthrenequinone in water reacts similarly with triphenylphosphine and then either with water or with the ·CH radical, forming the dipolar hydrate (XXVI), which is unstable in air[132].

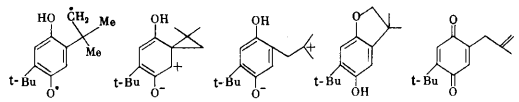
The functional groups in quinones reduced by the two-electron mechanism are also capable of reacting under the influence of the reductant. In particular, it has been established that anthrahydroquinonesulphonic acids dissociated at the alcoholic hydroxyl—the products of the reaction of photochemically generated anthrasemiquinonesulphonates—eliminate the sulpho-group on photoexcitation[15,94,133,134]. The quantum yield of this single-photon process has been shown in the case of 1-sulphoanthrahydroquinone to be higher for the dianion than for the monoanion and to be independent of the concentration of $OH^-$ ions in the region corresponding to the existence of both forms. It is assumed that the highest electronically excited state of the substrate is reactive, since desulphonation proceeds effectively only on excitation with light corresponding to the absorption band at the shortest wavelength. The sulpho-group in the $\beta$-position is eliminated with greater difficulty than that in the $\alpha$-position; halogenoanthrahydroquinonesulphonic acids undergo photochemical dehalogenation together with photochemical

desulphonation[15,94]. The photochemical desulphonation of undissociated anthrahydroquinonesulphonic acids, obtained by the photolysis of sulphoanthraquinones in aqueous alcoholic solutions of inorganic acids proceeds via a different (hydrolytic) mechanism; in this case, light is photochemically active over the entire region corresponding to absorption by sulphoanthrahydroquinones[135,136].

### 3. Secondary Intramolecular Photochemical Reduction Reactions

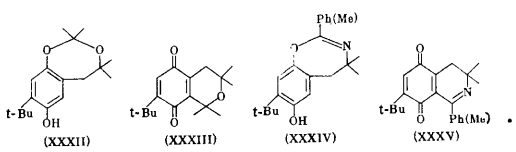
Intramolecular photochemical reduction of quinones almost always involves the abstraction of a hydrogen atom from the 2'-position of the side chain via a readily achieved six-membered cyclic transition state. This determines both the structure of the biradicals generated and the nature of the products formed on their stabilisation (intramolecular or intermolecular) with participation of the solvent.

Quinones with a hydrocarbon side chain. The radicals (XXVII), obtained from t-butyl-1,4-benzoquinones on photolysis of the latter in benzene, dioxan[137], acetone, acetonitrile, and benzonitrile[138], are converted into a zwitter-ionic spirocyclopropane structure (XXVIII), which exhibits a strong tendency towards aromatisation. Because of this, the three-numbered ring is cleaved and converted into the structure (XXIX):



(XXVII) (XXVIII) (XXIX) (XXX) (XXXI)

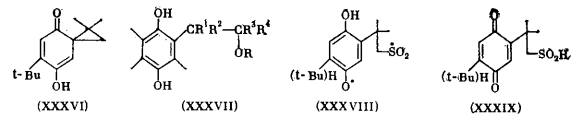
When the latter is subjected to nucleophilic attack, it can give rise to dihydrobenzofuran (XXX), the products of the rearrangement of the side chain (XXXI), and the products (XXXII)–(XXXV) resulting from the 1,4- and 1,5-cycloaddition of solvents (acetone, nitriles)[138,139]:



(XXXII) (XXXIII) (XXXIV) (XXXV)

Incidentally, one cannot rule out the possibility that the spiroketone (XXXVI) is an intermediate, the anomalous Claisen rearrangements of which yields compound (XXXI), while the remaining substances, (XXX) and (XXXII)–(XXXV), are formed as a result of the opening of the cyclopropane ring[138,139]. It is noteworthy that other compounds, in addition to those described, are formed, but their yields are insignificant[140].

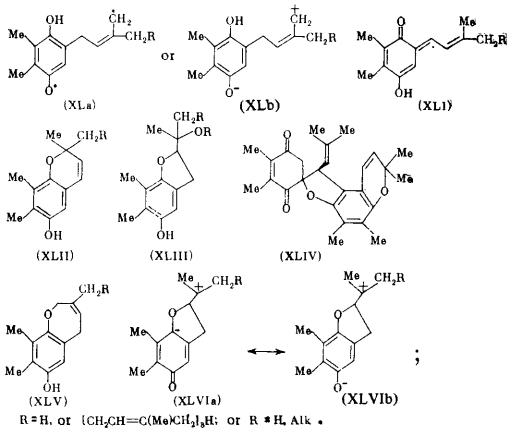
The exclusive formation of dihydrobenzofuran derivatives of type (XXX) was noted in the photolysis of 2-(2-phenylethyl)- and 2-(2,2-diphenylethyl)-1,4-benzoquinones in benzene[141]. Apart from similar substances, products resulting from the introduction of an alkoxy-group in the 2'-position [compounds (XXXVII)] are formed preferentially from 2-ethyl-, 2-isobutyl-, 2,5-dipropyl-,[139] 2-t-butyl-,[2,137] 2,5-di-t-butyl-, and 2,6-di-t-butyl-1,4-benzoquinones[2,137,142], probably via the interaction of the ROH alcohol molecule with a structure of type (XXVII) or (XXIX). *O*-Alkylation of the hydroquinones thus produced is possible[2], but data concerning the insertion of an alkoxy-group in the hydroquinone rings[143] are erroneous[2]:



(XXXVI) (XXXVII) (XXXVIII) (XXXIX)

The interaction of biradicals of type (XXVII), generated in the photolysis of t-butyl- and 2,5-di-t-butyl-1,4-benzoquinones with $SO_2$, leads to structures (XXXVIII), and the migration of hydrogen in the latter results in the formation of unstable sulphinic acids (XXXIX).[144]

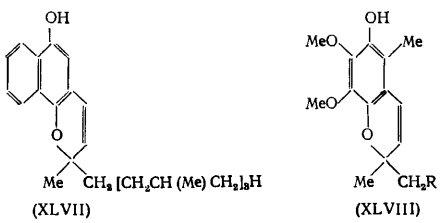
Structures (XL), formed by the intramolecular photochemical reduction of plastoquinones 1 [145,146] and plastoquinones 9 [146,147] on photolysis in benzenes, alcohols R'OH, and aqueous organic mixtures, are believed[145–147] to be stabilised by conversion into intermediate hydroxy-derivatives of *o*-methylenequinones (XLI) or into the corresponding anions. Their intramolecular cyclisation leads to compounds (XLII) and the reactions of the latter with addition of alcohol or water result in the formation of dihydrobenzofuran derivatives (XLIII); attack by a plastoquinone molecule yields the spiro-compound (XLIV). Compound (XLV) can be obtained from the intermediate structure (XL). The previously assumed[145] formation of dihydrobenzofurans (XLIII) in the interaction of alcohols (water) with the zwitter-ions (XLVI) and the involvement in this process of the radicals obtained by the intermolecular abstraction of a hydrogen atom are less likely:



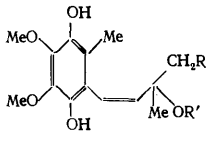
(XLa) (XLb) (XLI) (XLII) (XLIII) (XLIV) (XLV) (XLVIa) (XLVIb)

R = H, or $[CH_2CH=C(Me)CH_2]_3H$; or R = H, Alk.

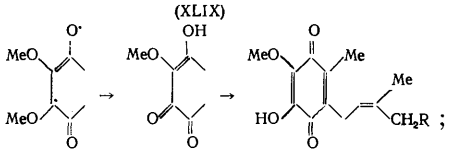
Irradiation of vitamin $K_1$ in benzene, ethanol, and water[148–151] and of certain coenzyme quinonoid structures in alcohols (R'OH)[2,152] leads in a similar manner—via the intermediate hydroxy-*o*-methylenequinones—to naphthopyranol (XLVII) and chromenols (XLVIII). The formation of the latter is accompanied by hydroquinones (XLIX), which are converted on oxidation into the corresponding quinones and the series of transformations (L) → (LI) → (LII) leads to demethylation products (LII):



(XLVII) (XLVIII)



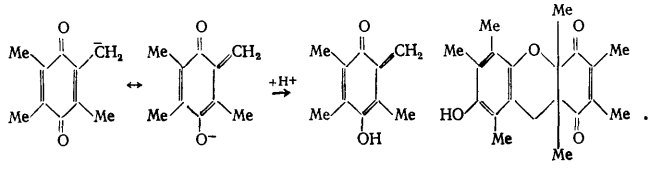
(XLIX)



(L) (LI) (LII)

R=[$CH_2CH$=C (Me) $CH_2$]$_n$H, $n$=3,6,9.

The formation of the adduct (LV) is also explained by the photochemical generation of hydroxy-*o*-methylenequinone (LIV) from tetramethyl-1,4-benzoquinone and its interaction with the unexcited substrate. The deprotonation of tetramethyl-1,4-benzoquinone in the $T$ state and the subsequent protonation of structure (LIII) at the oxygen atom is considered to be a possible reaction pathway [27,64,153]:

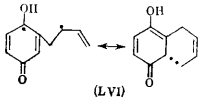


(LIII) (LIV) (LV)

The possibility that hydroxy-*o*-methylenequinones can indeed serve as intermediates in the processes discussed has been demonstrated by the detection of long-lived compounds of type (XLI) and their anions in the flash photolysis of 1-tocoquinone and vitamin $K_1$ in alcohols and hydrocarbons [154,155].

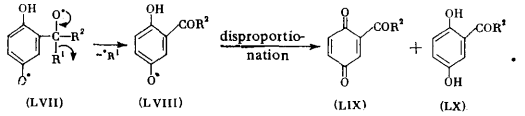
If there is a multiple bond in the 1-position in the side chain, as in 2-(1-methylvinyl)- and 2-(2,2-diphenylvinyl)-1,4-benzoquinones, then photolysis yields benzofuran structures exclusively [2].

The formation of 1,4-dihydro-5,8-dihydroxynaphthalene on irradiation of 2-(3-but-1-enyl)-1,4-benzoquinone under the same conditions is explained by the stabilisation of the biradical (LVI) [2]:



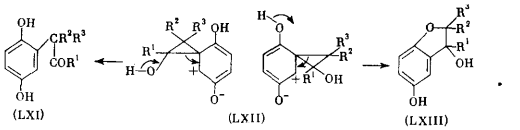
(LVI)

Quinones with oxygen-containing groups. A hydrogen atom may be abstracted during the intramolecular photochemical reduction of hydroxyalkylquinones both from the hydroxy-group and from a carbon atom in the side chain. The former mechanism operates with (1-hydroxyalkyl)quinones in the absence of a hydrogen atom in the 2′-position (hydroxymethyl-1,4-benzoquinone [2] etc.). The biradicals (LVII) formed from these quinones are stabilised either by the addition of a solvent molecule to the radical oxygen atom in the side chain or by the elimination of the alkyl substituent (hydrogen atom) with conversion into radicals (LVIII); disproportionation of the latter leads to the quinones (LIX) and hydroquinones (LX) with an oxidised side chain [2,156]:



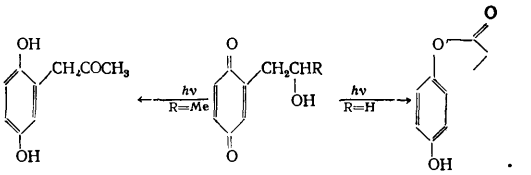

(LVII) (LVIII) (LIX) (LX)

The presence of a hydrogen atom in the 2′-position of (1-hydroxyalkyl)quinones, permits photochemical reduction via two pathways, the second of which gives rise to structures (LXII) analogous to those obtained from alkylquinones (see above). Subsequent reactions of these spirocyclopropane dipolar ions can lead to dihydrobenzofurans (LVIII); owing to the presence of the hydroxy-group, rearrangement to compounds (LXI) becomes possible at the same time [156]:



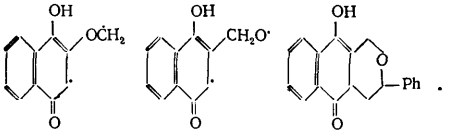
(LXI) (LXII) (LXIII)

The reactions of the biradicals formed as a result of the abstraction of a hydrogen atom exclusively from the 2′-position on photolysis of (2-hydroxyalkyl)-1,4-benzoquinones (LXV) leads to similar products [(LXIV) and (LXVI)]: [2]



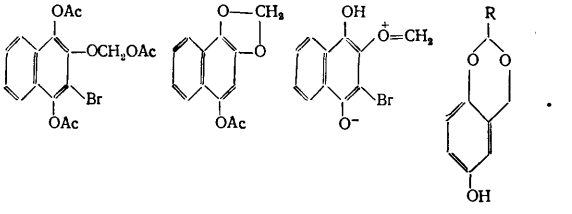

(LXIV) (LXV) (LXVI)

The biradical (LXVII), generated in the photolysis of 2-methoxy-1,4-naphthoquinone in benzene solution, apparently rearranges to the more stable biradical (LXVIII), to which styrene adds, forming compound (LXIX); [157] at the same time, there is sufficient time for the biradical (LXVII) obtained in acetic anhydride to react with the solvent, forming 1,4-diacetoxy-2-methoxynaphthalene [158]:



(LXVII) (LXVIII) (LXIX)

The photolysis in acetic anhydride of the same quinone but with a bromine substituent in the 3-position leads to compounds (LXX) and (LXXI), tentatively via the intermediate dipolar structure (LXXII): [158]

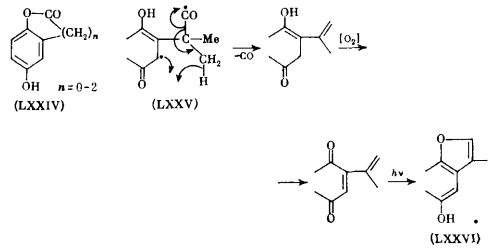


(LXX) (LXXI) (LXXII) (LXXIII)

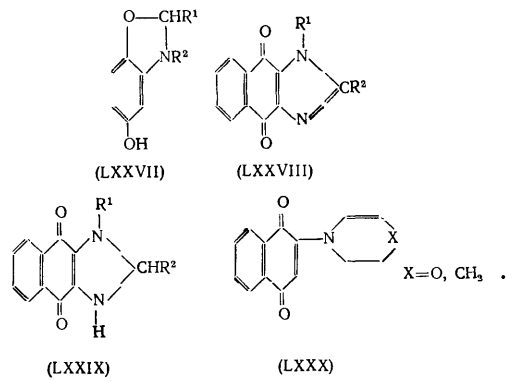
On photolysis, alkoxymethyl-1,4-benzoquinones yield polymeric phenolic acetals as a result of the intermolecular interaction of the substrate which has undergone intramolecular reduction. Benzo-1,3-dioxans (LXXIII) are sometimes formed, which may indicate the possible involvement of radicals generated by intermolecular photochemical reduction [2].

The presence of an ester group in the 2′-position of 1,4-benzoquinone does not lead to unexpected results following its photolysis: the corresponding benzofuran

derivative was obtained from 2-(2-ethoxycarbonylethyl)-1,4-benzoquinone in benzene[2]. If the side chain contains a terminal formyl group, the photochemical reaction products are lactones (LXXIV) or the corresponding hydroquinonecarboxylic acids[159]. The stabilisation of the biradicals (LXXV), obtained photochemically from 2-(1-formyl-1-methylethyl)-1,4-benzoquinone and the corresponding naphthoquinone, proceeds in a different way (with decarbonylation) and leads to benzo- and naphtho-furans of type (LXXVI) as a result of subsequent reactions[159]:

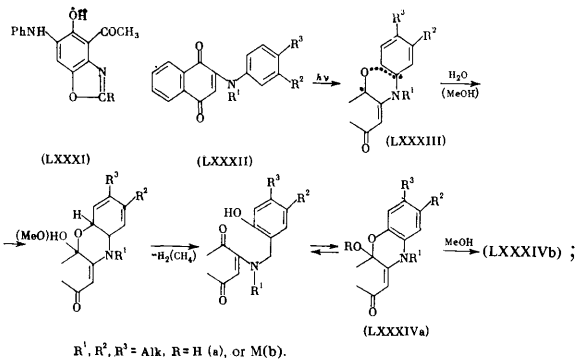



Aminoquinones. Amino-1,4-benzoquinones, containing the fragment $\rangle N-CH\langle$, give rise on photolysis to cyclisation products—derivatives of dihydro-oxazole (LXXVII).[2,160,161] Similar products were obtained from *NN*-dialkyl- or *N*-alkyl-2-amino-*N*-aryl-1,4-naphthoquinones when there was no amino-group in the 3-position[2,162,163]. Compounds (LXXVII) are unstable and undergo oxidative hydrolysis particularly readily, forming products resulting from the dealkylation of the initial quinones[2,161-163]:



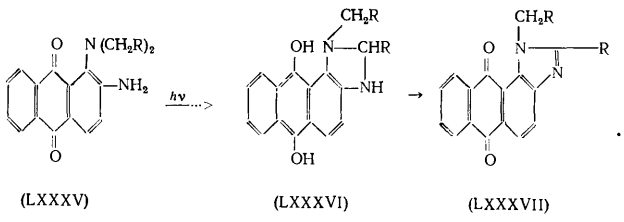

Naphthimidazoles (LXXVIII) and their dihydro-derivatives (LXXIX) have been obtained by the photolysis of 3-amino-2-dimethylamino(piperidino, morpholino)-1,4-naphthoquinones[164]. 2-Piperidino- and 2-morpholino-1,4-naphthoquinones do not cyclise but are dehydrogenated, forming compounds (LXXX).[165,166]. Although the mechanism of the formation of compounds (LXXVII)–(LXXX) has not been discussed, one cannot rule out intramolecular photochemical reduction as the first stage in such cases also.

The biradicals formed by the photochemical reduction of 2-acetyl-3-alkylamino-6-phenylamino-1,4-benzoquinones are converted, as a result of hydrogen transfer followed by ring closure and aromatisation (there is also a possibility of the formation of intermediate spiro-aziridines or imines) into the benzoxazole (LXXXI):[167,168]

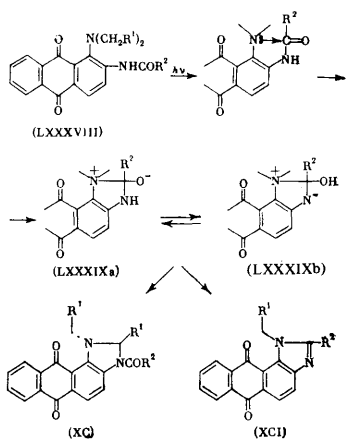



In the photolysis of *N*-substituted 2-phenylamino-1,4-naphthoquinones (LXXXII) in aqueous methanol solution, there is insufficient time for the intramolecular and intermolecular abstraction of a hydrogen atom by the biradical (LXXXIII) formed and the latter is stabilised by combining with a solvent molecule; the cyclisation products (LXXXIV) are formed ultimately[169].

The intramolecular photochemical reduction of the aminoanthraquinones (LXXXV) stabilises the intermediate biradicals by their conversion into anthrahydroquinones (LXXXVI), which are in turn converted into imidazoles (LXXXVII):[164]

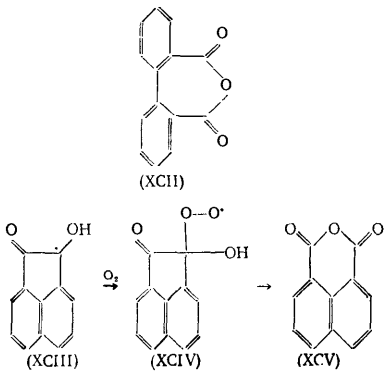



On the other hand, when an acylamino-group is present in the 2-position instead of the amino-group, it is reduced photochemically instead of the quinonoid moiety; the resulting dipolar structures (LXXXIX) are converted into imidazolines (XC) and imidazoles (XCI);[170,171] thus data[165,166] concerning the photochemical conversion of the acylamino-group of compounds (LXXXVIII) into the oxaziridine group were not confirmed:

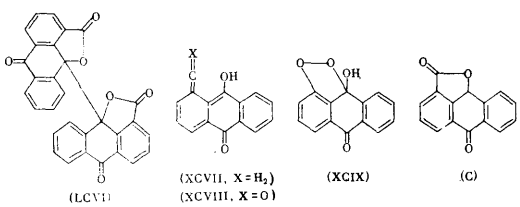


## III. PHOTOCHEMICAL OXIDATION

The photochemical oxidation of quinones reduces either to the oxidation of the side chain, which is characteristic of *p*-quinones or to the oxidative cleavage of the quinonoid fragment, which is characteristic of *o*-quinones. The primary step in the process is usually believed to be the photochemical reduction of the carbonyl group in one form or another. Thus the formation of the anhydrides (XCII) and (XCV) when aerobic solutions of phenanthrenequinone [3] and acenaphthenequinone [3,112] in acetonitrile, benzene, tetrahydrofuran, etc. are irradiated is attributed to the photochemical generation of a radical of type (XCII). The latter interacts with oxygen and gives rise to the peroxy-radical (XCIV), which is then converted into the anhydride (XCV):



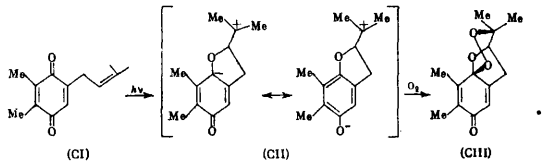

The photolysis of 1-methylanthraquinone in benzene saturated with oxygen yields compound (XCVI), while in the presence of air anthraquinone and anthraquinone-1-carboxylic acid are also formed [172,173]. In this case, the formation in the primary step of a photochemically enolised form of the quinone (XCVII) is postulated, the latter being converted by reaction with oxygen into the peroxide (XCIX) and then into 1-formylanthraquinone. The photochemical enolisation of the latter to the keten (XCVIII) and intramolecular attack by the hydroxyl on the keten group lead to the lactone (C) or its ketone tautomer. These compounds can be readily oxidised to the dilactone (XCVI). Anthraquinone is probably formed on photochemical decarbonylation of 1-formylanthraquinone:



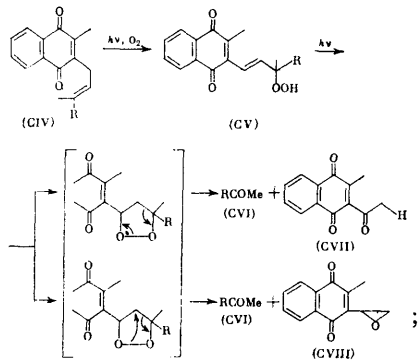

Products with a related structure have also been obtained from methyl-1,4-naphthoquinone [173].

1-Acetylanthraquinone was obtained by the photochemical oxidation of 1-ethylanthraquinone. The photochemical oxidation of the less reactive isomer (2-methyl- and 2-ethyl-anthraquinones) leads to anthraquinone-2-carboxylic acid and 2-acetylanthraquinone respectively [172,173], but the mechanism involving photochemical enolisation is apparently not applicable to these reactions.

The presence of a multiple bond (a $\pi$-electron donor) in the side chain of the quinone can lead to intramolecular cyclisation on excitation of the molecule. It has been suggested [145,174,175] that plastoquinone 1 (CI) is in fact converted in this way into the zwitter-ion (CII), which reacts with oxygen to form the peroxide (CIII). Oxygen is apparently involved in the process in its ground state, since the peroxide (CIII) is not formed when singlet oxygen generated with the aid of sensitisers acts upon compound (CI):

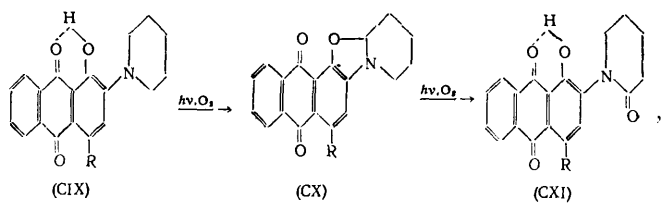



Other isoprenoid *p*-quinones (CIV) which have been investigated participate in the photochemical oxidation reaction in a different way: on reaction with singlet oxygen (generated in control experiments by means of dyes), they form hydroperoxides (CV). On irradiation, these substances are then converted into ketones (CVI) and compounds (CVII) and (CVIII); the latter were not isolated owing to their instability [176]:




R = Me, $CH_2CH_2CH{=}CHMe$, $(CH_2)_4Me$, $(CH_2CH{=}CMeCH_2)_2H$, or $(CH_2CH_2CHMeCH_2)_3H$.

The specific influence of the quinonoid fragment appears unlikely in the oxidative cyclisation of 2-dialkylamino-1-hydroxyanthraquinones (CIX) (but not the 1-amino-derivatives), leading to anthraoxazolines (CX), and in the photochemical oxidative cleavage of the heterocycle of the latter [177], as in the previous reaction:

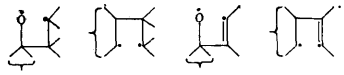



R=H,OH, or $NHCOCH_3$.

## IV. PHOTOCHEMICAL ADDITION

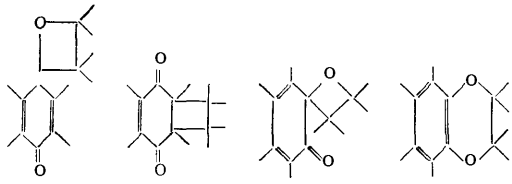
In almost all the processes examined, the reductant, a neutral molecule or an anion, behaves as a hydrogen atom or electron donor in relation to the excited quinone. We believe that one should not combine in a special group of reductants substances with multiple carbon–carbon bonds, differing from those described above by the nature of their interaction with quinones, since they are potential donors of $\pi$ electrons. Presumably the transfer of $\pi$ electrons from these substances to the oxygen or carbon

atom of the quinone leads to the formation of C–O and C–C bonds respectively in the photochemical step. The biradical structures (CXIIa) and (CXIIb) generated (by the addition of alkenes) or (CXIIIa) and (CXIIIb) (by the addition of alkynes) are subsequently stabilised by ring closure:



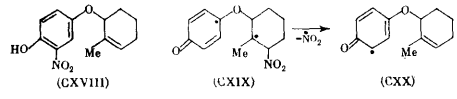
(CXIIa) (CXIIb) (CXIIIa) (CXIIIb)

As a result of photochemical addition to the C=C bond of such substances, *p*-quinones are converted into oxetans (CXIV) and cyclobutane derivatives (CXV), while *o*-quinones give rise to oxetans (CXVI) and 1,4-dioxens (CXVII); the photochemical addition of quinones to the C≡C bond of the reductant leads to the corresponding oxeten, cyclobutene, and 1,4-dioxin derivatives:



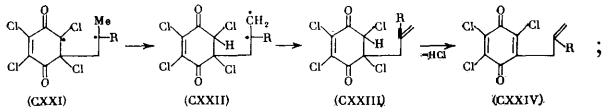
(CXIV) (CXV) (CXVI) (CXVII)

Substances with a different structure are formed much more rarely. Their generation is usually associated with the fact that there is insufficient time for the biradicals produced on addition of unsaturated hydrocarbons to undergo ring closure and they are stabilised in a different way. For example, the photochemical reaction of 1,4-benzoquinone with 1-methyl-6-nitro-1-cyclohexene gave compound (CXVIII), probably as a result of the elimination of the $NO_2$ group from the biradical (CXIX) with its subsequent addition to the radical (CXX):[178]



(CXVIII) (CXIX) (CXX)

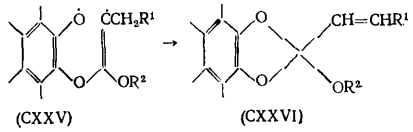
In another instance, the photolysis of tetrachloro-1,4-benzoquinone in the presence of 2-methylpropene or 2,3-dimethylbuta-1,3-diene produces biradicals (CXXI) which are converted as a result of hydrogen migration into (CXXII), after which pairing of electrons leads to (CXXIII); the latter compound is unstable, splits off HCl, and thus gives rise to compound (CXXIV):[179]



(CXXI) (CXXII) (CXXIII) (CXXIV)

R = Me or CMe = $CH_2$ .

The formation of dioxoles (CXXVI) on photolysis of phenanthrenequinone in the presence of alkyl- or alkoxyacetylenes has been explained[3,180,181] by a 1,2-hydrogen shift in the biradicals (CXXV) formed, which leads to allyl biradicals, stabilised by closure to a dioxole ring:



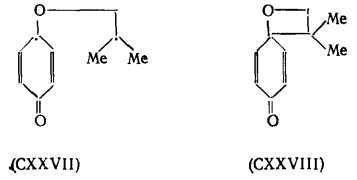
(CXXV) (CXXVI)

The quinone always participates in photochemical addition reactions in the excited state. In most but not all instances the triplet state of the substrate is then reactive and it is therefore desirable to explain the nature of the reactive excited state in each specific instance. The photochemical reaction of tetramethyl-1,4-benzoquinone with cyclo-octene is interesting from this point of view: in the presence of an excess of the quinone, the product is an oxetan and in the presence of an excess of cyclo-octene, it is a 1:2 adduct formed via the C=C bonds of the quinone[2]. It has been established that the oxetan is formed with participation of the *T* state of the quinone, while an increase in the concentration of the olefin should favour (in the absence of other complicating factors) the reactions of the quinone in the singlet state. If this interpretation is correct, significant differences between the photochemical reactions of quinones in the *S* and *T* states should naturally be expected.

Photochemical addition occurs successfully only when $E_T$ for the hydrocarbon (olefin, acetylene) is comparable or greater than $E_T$ for the quinone, so that there is no transfer of the energy of the triplet state. In particular, this factor is associated with the observation that simple ketones (for which usually $E_T > 60$ kcal mole$^{-1}$) rarely react with dienes and conjugated polyenes ($E_T < 60$ kcal mole$^{-1}$), whereas quinones ($E_T \leq 60$ kcal mole$^{-1}$) frequently enter into this reaction.

The following view appears to predominate at the present time concerning the $n,\pi^*$ or $\pi,\pi^*$ nature of the reactive state of quinones: quinones react via their C=C bonds in the $\pi,\pi^*$ state and via their C=O bonds in the $n,\pi^*$ state[2,179]. The distribution of the corresponding energy levels should be, from this standpoint, one of the principal characteristics determining the type of addition. The capacity of quinones for the simultaneous formation of different products can be accounted for either by the competition of processes involving energetically similar $n,\pi^*$ or $\pi,\pi^*$ states or by the fact that the excitation energy ($n,\pi^*$) is not fully localised in the carbonyl group, but is partly transmitted also to the C=C bonds of the quinone.

The photochemical addition of olefins to the carbonyl group of quinones is a specific instance of such a photochemical reaction in the series of ketones. It has been shown for the simplest ketones that the cryptoradical mechanism of such a process permits the correct prediction of the structure of the principal isomer among the oxetans formed: the oxetan corresponding to the most stable biradical with the largest number of alkyl or aryl groups at radical centres always predominates. This rule proved to be valid also in the photochemical reactions of certain *p*-quinones with olefins[2,179]: for example, the isomer (CXXVIII), formed from the biradical (CXXVII), predominates among the oxetans in the photolysis of 1,4-benzoquinone in the presence of 2-methylpropene:

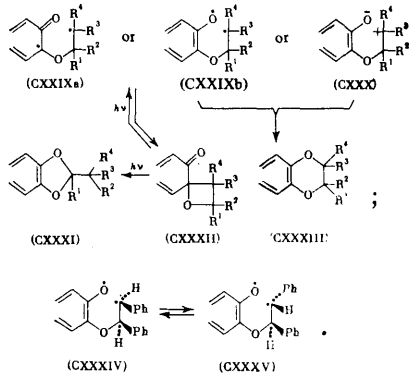


(CXXVII) (CXXVIII)

Predictions of this kind can probably be made for the photochemical reactions of both *p*- and *o*-quinones when the addition is to the carbonyl group; one cannot rule out the applicability of this rule also to photochemical addition to the C=C bonds of the quinone.

In the photochemical reactions of olefins with *o*-quinones, the biradical (CXXIX), obtained by the addition of the olefin to the quinone, gives rise to a dioxen (CXXXIII) and

(or) an oxo-oxetan (CXXXII), which, being unstable, is converted photochemically into the starting materials and (to a slight extent) into the dioxole (CXXXI):

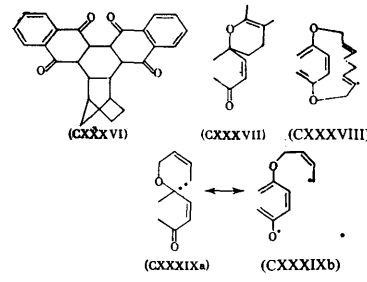



If the olefin contains the appropriate substituents, the above products [for example (CXXXIII)] can be obtained in the form of a mixture of stereoisomers. Thus the photochemical addition of phenanthrenequinone to simple *cis*- or *trans*-alkenes (but-2-ene, oct-4-ene, etc.) leads to a mixture of *cis*- or *trans*-dioxens [2,3]. Evidently the intermediate triplet biradical (CXXIX) is sufficiently long-lived for the establishment of conformational equilibrium, which in fact determines the proportions of the *cis*- and *trans*-adducts formed on pairing of the electrons. The observed stereospecificity in the photochemical reactions of tetramethyl-1,2-benzoquinone with *trans*-stilbenes and a certain selectivity in the photochemical addition of phenanthrenequinone to stilbenes [3] have been explained by the considerable contribution in such cases of the ionic structure (CXXX) to the resonance hybrid of the intermediate biradical; the interaction between the charges to a large extent limits the free rotation about the C–C bond, which should ensure steric control.

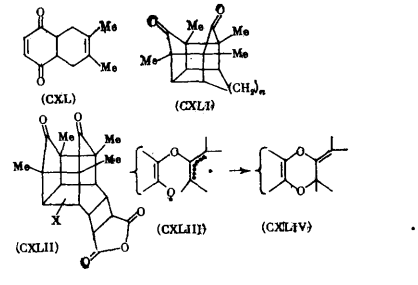
The above assumptions are in good agreement with the finding that the ratio of the *cis*- and *trans*-adducts formed from simple olefins does not depend on temperature, while the addition of phenanthrenequinone to stilbenes exhibits a decrease of selectivity with increase of temperature [3]. In the latter case, the interconversion of the radicals (CXXXIV) and (CXXXV) probable begins to compete with ring closure, since there is only a small energy barrier to rotation.

The simplest of the *p*-quinones (1,4-benzoquinone) forms only oxetans in photochemical reactions with non-conjugated acyclic and cyclic alkenes [2,179]. 2,3-Dimethyl- and tetramethyl-1,4-benzoquinones combine with alkenes only via the C=C bond [2,179,182]; tetrachloro-1,4-benzoquinone gives rise to both cyclobutanes and oxetans [2,179]; in the presence of an excess of the olefin, biscyclobutane structures may be obtained.

1,4-Naphthoquinone combines with alkenes to form oxetans and cyclobutanes [2,183,184]; its characteristic feature is the ability to form 2:1 quinone–olefin adducts [for example, the reaction with norbornene results in the formation of the adduct (CXXXVI) [185]]. The photolysis of anthraquinone in the presence of cyclo-octene and cyclo-octa-1,5-diene leads exclusively to oxetans [186]. All *o*-quinones give rise to oxetans or dioxens in reactions with alkenes; the addition to the C=C bond of the quinone has not been observed [1-3,187-193]:




Spirodihydropyrans (CXXXVII) are the products of the photochemical reactions of *p*-quinones (1,4-benzo- [2,282] and naphtho-quinones [179]) and certain conjugated olefins, while the macrocyclic adduct (CXXXVIII) is also formed in the reaction of buta-1,3-diene and 1,4-benzoquinone. The macrocyclic adduct is believed to be produced as a result of the addition of a second buta-1,3-diene molecule to the biradical (CXXXIXb), while compound (CXXXVII) is formed as a result of the intramolecular stabilisation of the mesomeric form (CXXXIXa) of the biradical. Depending on the photolysis conditions, compounds (CXXXVII) or (CXL) can be obtained for 2,3-dimethylbuta-1,3-diene. The reactions of tetramethyl-1,4-benzoquinone with certain conjugated dienes (cyclopentadiene, cyclohexa-1,3-diene) result in the formation of cage structures (CXLI), [194] while 1:1:1 adducts have been obtained in the photolysis of the benzoquinone in benzene derivatives ($C_6H_5X$, X = H, $CH_3$, or a halogen) in the presence of maleic anhydride [2]:



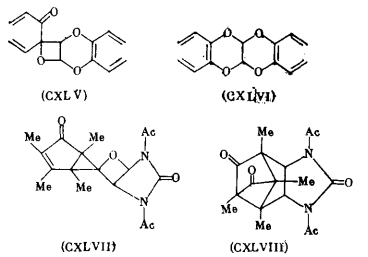

It is believed [195-197] that, in the photochemical reactions of allenes with *o*-quinones (phenanthrenequinone, tetrachloro-1,2-benzoquinone), the central carbon atom of the allene system is attacked with formation of the biradicals (CXLIII), whose stabilisation leads to dioxens (CXLIV).

Cyclobutene structures have been obtained in the photochemical addition of mono- and di-substituted acetylenes to 1,4-naphthoquinone and its methyl and acetoxy-derivatives [198,199]. The exclusive addition of acetylenes to the C=C bond of methoxy-1,4-naphthoquinones [2,200-203] has been explained [202] by the fact that the $OCH_3$ group localises the excitation at this bond and stabilises the intermediate biradical, promoting the formation of cyclobutene derivatives.

Phenanthrenequinone and tetrachloro-1,2-benzoquinone add to alkenynes with conjugated multiple bonds only at the C=C bond with formation of the corresponding oxetans and dioxens [204].

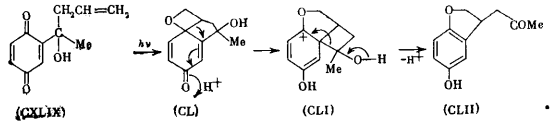
The primary products of the photochemical addition of unsaturated hydrocarbons to the C=C and C=O bonds of

quinones are frequently unstable and cannot be isolated, since they undergo further dark or photochemical reactions. For example, the photo-adducts of phenanthrenequinone with chloro-olefins split off HCl and the compound thus produced adds to the excited phenanthrenequinone, forming adducts with 2 : 1 quinone : olefin ratios [compounds (CXLV) and (CXLVI)]: [2,205]

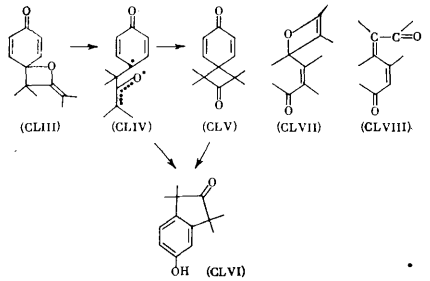



The oxetan obtained by irradiating tetramethyl-1,4-benzoquinone in the presence of 1,3-diacetyl-$\Delta^4$-imidazolin-2-one is converted photochemically into compound (CXLVII), from which compound (CXLVIII) is formed via a dark process [2].

The spiro-oxetan (CL) produced by the photolysis of compound (CXLIX) in benzene ultimately gives rise to dihydrobenzofuran (CLII); it is noteworthy that the conversion of (CXLIX) into (CL) is the only known example of the intramolecular formation of an oxetan from quinones with an unsaturated side chain [156]:




As in the examples quoted above, it is assumed that the photochemical reactions of *p*-quinones (1,4-benzo- and naphtho-quinones) with allenes result in the formation of an oxetan (CLIII), which rearranges to the phenolic derivative (CLVI) either directly or via an intermediate spirocyclobutanone (CLV): [206]



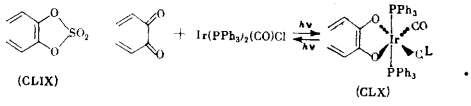

Mono- and di-substituted acetylenes undergo photochemical addition to the carbonyl groups of 1,4-benzoquinone, tetramethyl-1,4-benzoquinone, anthraquinone [2,179,186], 1,4-naphthoquinone, and its methyl and acetoxy-derivatives [198] with formation of quinonemethines (CLVIII) via the intermediate oxetens (CLVII). Phenanthrenequinone and tetrachloro-1,2-benzoquinone form 1 : 2 adducts of type (CXLVI) with individual acetylenes, since the initial dioxyns subsequently undergo a further photochemical addition reaction [3,180,181].

Apart from the instances described above, in photochemical addition processes the excited *p*-quinone molecule frequently reacts with another molecule of the same quinone but in its ground state; such examples are unknown for *o*-quinones. This type of photochemical dimerisation of the simplest *p*-quinones (1,4-benzo- and naphthoquinones and their derivatives) [2,207-211] and more complex natural products [2,212] takes place in solutions and in the solid state, resulting in the formation of spiro-oxetan, cyclobutane, and cage structures similar to those discussed above.

The ability to undergo photochemical dimerisation is determined to a large extent by the stabilisation energy of the exciplexes of quinones: those which are converted into stable adducts (for example, the species formed from 2,3-, 2,5-, and 2,6-dimethyl-1,4-benzoquinones) have a significantly greater stabilisation energy than those which do not form dimers (for example, the species formed from tetramethyl-1,4-benzoquinone) [213].

In contrast to solutions [2,214-216], the crystal structure, which determines the feasibility and direction of the reaction (the type of the product and its stereochemical characteristics), plays an important role in solid-phase photochemical dimerisation. Thus the process occurs when the reaction centres are separated by not more than 4 Å; on the other hand, the structure of the dimer is determined by the relative orientations of the monomers (the geometrical disposition of the parallel C=C and C=O bonds) in the crystal. The formation of polymeric materials in the photolysis of certain *p*-benzoquinones (1,4-benzoquinone, tetramethyl-1,4-benzoquinone) in the solid phase is attributed to the fact that the crystal structures of these compounds are characterised by an infinite chain of close C...C contacts between non-parallel C=C chains; their interaction leads to dimeric biradicals, which initiate polymerisation [2].

Whereas a characteristic feature of *p*-quinones is their capacity for photochemical dimerisation, a specific feature of *o*-quinones is their ability to combine on photochemical excitation with inorganic substances and organic derivatives of the elements with formation of C—element (element ≠ carbon) bonds. A reaction of this type, which has been known for a long time, is the so called "cyclosulphate synthesis" [2,3]—the addition of sulphur dioxide to the oxygen atoms of *o*-quinones (tetramethyl-1,2-benzoquinone, 1,2-naphthoquinone, its 3-nitro-derivative, phenanthrenequinone, its 2-, 3-, and 4-nitro-derivatives, chrysenequinone) with formation of compounds (CLIX):




The oxidative photochemical addition of $Ir(PPh_3)_2(CO)Cl$ to *o*-quinones (tetramethyl-1,2-benzoquinone, phenanthrenequinone, 1,2-naphthoquinone) [217] may be a convenient method for the synthesis of complexes of type (CLX). The process is reversible and takes place until the attainment of a specific equilibrium. Although both components are excited, the authors believe that the triplet state of quinones is reactive, by analogy with the cyclosulphate synthesis.

## V. PHOTOCHEMICAL SUBSTITUTION

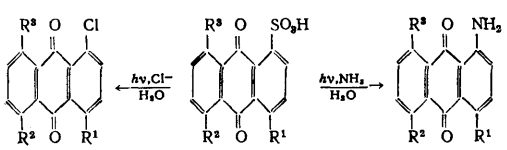
It is clear from the foregoing data, that the structure of the final photolysis products cannot in all cases constitute a sufficient criterion for the assignment of the photochemical reactions of quinones to a particular type. This is due to the formal nature of this feature, since the final products which can be isolated from the photolysed mixture do not always arise as a result of the photochemical

reaction of the excited quinone molecule with a given reactant. They are frequently formed in secondary dark or photochemical reactions, while the primary photochemical processes generate only the reactive species necessary for their occurrence. It is not even an obligatory condition that the quinone should participate in the secondary processes; the species produced by its primary reaction may be involved. All the foregoing considerations apply fully also to the photochemical reactions in which products resulting from substitution in the quinone ring or in its side chain are formed. For example, the photochemical process in the light-induced hydroxylation of sulphoanthraquinones, the elimination of their sulpho-group in reducing media, and the substitution of the $OCH_3$ group in methoxyanthraquinones by a hydroxy-group is the reduction of the quinone (see above), while the substitution of chlorine in tetrachloro-1,4-benzoquinone by an unsaturated hydrocarbon takes place as a result of the photochemical addition of hydrocarbons to the quinone (see section IV). One must therefore investigate in detail the mechanisms of such photochemical reactions before concluding that they are photochemical substitution reactions.

This section is concerned with the photochemical reactions of quinones which have been assigned on the basis of available data to photochemical substitution processes, and with reactions whose mechanism still has to be refined.

In concentrated aqueous solutions of inorganic acids, the sulpho-group is eliminated photochemically from 1-sulphoanthraquinone (but not the 2-derivative) via a hydrolytic mechanism with simultaneous formation of 1-hydroxyanthraquinone. The quantum yield of the photochemical hydrolysis is independent of the wavelength of the exciting light and its limiting value (approximately $10^{-3}$) is low, probably owing to the quenching of the excited substrate molecules by $H^+$ ions [15,135,136].

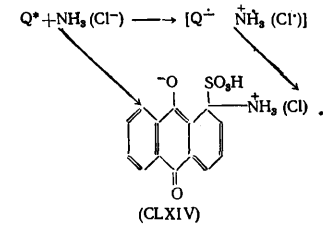
The irradiation of $\alpha$-sulphoanthraquinones (CLXII) in aqueous solutions containing chloride ions or ammonia results in the substitution of the sulpho-group by a chlorine atom or an amino-group respectively [15] (see also Eckert [218]). The yields of chlorination products are higher than those of the amination products, since the side products formed in the latter case (water-soluble hydroxy- and amino-sulphoanthraquinones) filter out photochemically active light. In contrast to electron-accepting substituents ($SO_3H$, $NO_2$, halogens), electron-donating substituents (OH, $NH_2$) inhibit the photochemical process; contrary to one report [54], the substitution of $\beta$-sulpho-groups always takes place with a very low efficiency. The photochemical substitution of $\alpha$- and $\beta$-sulpho-groups by alkyl- or aryl-amino-groups does not take place; traces of 1-methylaminoanthraquinone have been detected only when 1-sulphoanthraquinone was irradiated in aqueous methylamine solution with long-wavelength light ($\lambda_{exc} > 300$ nm): [15]




(CLXI) (CLXII) (CLXIII)

$R^1, R^2, R^3$ = H, Cl, $SO_3H$, or $NO_2$.

The available data suggest that the mechanisms of the photochemical chlorination and amination are the same and that the same excited state of the substrate (probably $n,\pi^*$) is reactive [15,136,219]. Two hypotheses have been put forward concerning the reaction pathways in the above processes. The first involves the nucleophilic substitution (in the classical sense, via an intermediate $\sigma$-complex) of the sulpho-group. The structure (CLXIV) can then be formed also as a result of the interaction of the radical (radical-ion) pairs generated by electron transfer in the solvent cage [15,54]:

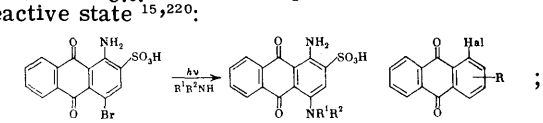



(CLXIV)

The second, alternative pathway involves the radical substitution of the sulpho-group. For example, the photochemical stage in the chlorination process may involve the generation of a Cl· atom by electron transfer from the $Cl^-$ ion to the excited substrate molecule; in the subsequent dark process, the sulpho-group is substituted by chlorine:

$$Q^* + Cl^- \rightarrow Q^{\cdot-} + Cl^\cdot; \; Q + Cl^\cdot \rightarrow QCl.$$

Apart from the sulpho-group, it is also possible to substitute photochemically the halogen atom in the anthraquinone ring by an amino-group. Thus the bromine atom is readily substituted by amino-, alkylamino-, and dialkylamino-groups in the photolysis of 1-amino-4-bromo-2-sulphoanthraquinone (CLXV) in aqueous aerated solutions of the corresponding amines. The increased rate of the process following the introduction of additives (MeCN > PrOH > dioxan > $H_2O$) is treated as evidence of the formation of a polar intermediate. The cleavage of the carbon–halogen bond under the influence of light is believed to be unlikely; the $S^1_{c.t.}$ state of compound (CLXV) is treated as the reactive state [15,220]:




(CLXV) (CLXVI) (CLXVII)

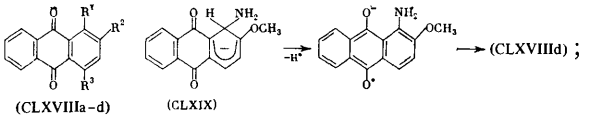
R = 4-OH, 2-$NH_2$, or 4-$NH_2$; Hal = Cl, or Br; $R^1, R^2$ = H, or Alk.

The capacity for the photochemical substitution of the halogen by an amino-group in aerobic alcoholic solutions of ammonia is characteristic of 1-halogenoanthraquinones when there are powerful electron-donating substituents in the 2- or (and) 4-positions, i.e. is characteristic of compounds of type (CLXVII). The process does not occur in the absence of substitutions, in the presence of only electron-accepting or weak electron-donating (methyl) groups, and also when strong electron-donating substituents are located in positions other than those indicated [221–224]. It has been possible to show that the $T^1_{c.t.}$ (or $\pi,\pi^*$) state is reactive in the case of 1-amino-4-chloroanthraquinone and 1-amino-4-bromoanthraquinone [223].

The role of oxygen is not merely oxidative, since the corresponding anthrasemiquinones and anthrahydroquinones are not involved in photoamination, while in deaerated media in the presence of other oxidising agents the halogen is not substituted (in polar solvents) [15,220,224]. The interaction of the substrate with singlet oxygen (obtained as a result of energy transfer from a triplet halogenoanthraquinone molecule) or attack by the amine (ammonia) on the exciplex of the excited substrate and oxygen is believed to be possible [220]. It has been shown for 1-amino-2,4-dibromoanthraquinone that the substrate

interacts in the $S^1_{c.t.}$ state in a polar solvent (MeCN), while in a non-polar solvent ($C_6H_6$) the compound in the $T^1_{c.t.}$ state is attacked by the amine and there is no necessity for oxygen. This change in the nature of the reactive excited state is attributed to a change in the disposition of the energy levels of the substrate when the nature of the solvent is altered [225].

The amino-group can substitute photochemically both the hydrogen atom and the $OCH_3$ group in the anthraquinone ring [226,227]. Thus compounds (CLXVIII, a–d) were obtained from 1- and 2-methoxyanthraquinones on irradiation in an acetonitrile–water mixture containing ammonia. Since the addition of radical acceptors does not decrease the rate of reaction, it is concluded that it is heterolytic. Whereas the formation of aminoanthraquinones is believed to proceed in the usual way, it is assumed that the $\sigma$-complex (CLXIX) is stabilised on formation of compound (CLXVIIId) by the abstraction of atomic hydrogen and not a hydride ion; accordingly, the rate of formation of compound (CLXVIIId) is reduced in the absence of oxygen. The $S^1_{n,\pi^*(\pi,\pi^*)}$ state of the substrate is assumed to be reactive:



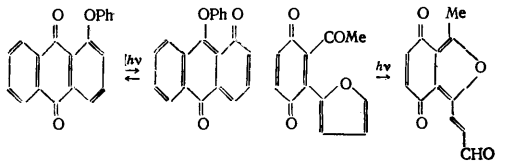
(CLXVIIIa–d) (CLXIX)

(a) $R^1 = NH_2$, $R^2 = R^3 = H$; (b) $R^1 = OCH_3$, $R^2 = H$, $R^3 = NH_2$;
(c) $R^1 = R^3 = H$, $R^2 = NH_2$; (d) $R^1 = NH_2$, $R^2 = OCH_3$, $R^3 = H$

When 1-phenoxyanthraquinone is irradiated with ultraviolet light in benzene solution, it is converted into a coloured form. If irradiation is not interrupted, the product is 1-hydroxyanthraquinone, which is also formed on contact between the light-induced coloured form of 1-phenoxyanthraquinone and $Al_2O_3$. The mechanism of the process has not been discussed [228,229].

## VI. UNIMOLECULAR PHOTOCHEMICAL REACTIONS OF QUINONES UNRELATED TO THEIR PHOTOCHEMICAL REDUCTION

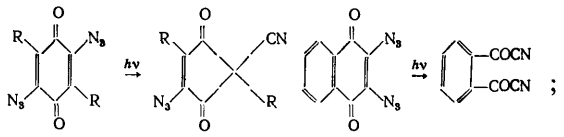
Reactions of the above type are few and are characterised by the fact that electronic excitation is localised in side chains; the primary photochemical reactions of the latter can be accompanied by secondary processes involving the quinonoid fragment. An exception is probably the formation, already mentioned, of the light-induced coloured forms of 1-phenoxy-, 1,5-diphenoxy-, and 1,8-diphenoxyanthraquinones and 10-phenoxynaphthacenequinone on their irradiation in non-polar solvents [228–230]. The spectra of the starting materials are restored when the irradiated solutions are kept in the dark or are irradiated with light corresponding to the new absorption band ($\lambda_{max} > 440$ nm). There are no exact data available for the mechanism of the photochromic transformations, but the authors assume that the colour of the light-induced form is associated with the polarisation of the carbonyl groups [229] or with the photoisomerisation of the *p*-quinone to an isomer with a higher oxidation-reduction potential—anaquinone [for example, (CLXX) → (CLXXI)]: [230]



(CLXX) (CLXXI) (CLXXII) (CLXXIII)

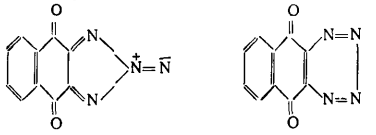
The photochemical rearrangement of the quinone (CLXXII) to compound (CLXXIII) is explained by the local excitation of the acetyl group [2].

Photolysis of 2,5-diazido-1,4-benzoquinones (CLXXIV) [231] and 2,3-diazido-1,4-naphthoquinone (CLXXVI) [232] leads to the elimination of one and two nitrogen molecules respectively; the resulting nitrenes are stabilised by conversion into compounds (CLXXV) and (CLXXVII). In the latter case, structures (CLXXVIII) and (CLXXIX) are postulated as intermediates which split off nitrogen:



(CLXXIV) (CLXXV) (CLXXVI) (CLXXVII)

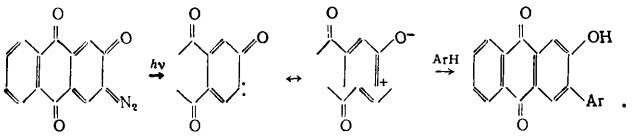
R=Me, $Me_3C$



(CLXXVIII) (CLXXIX)

The esters of 1,2-naphthoquinonediazosulphonic acids and di(tri)hydroxyanthraquinones, containing 1–2 free hydroxy-groups, also eliminate a nitrogen molecule on irradiation and the ketocarbenes formed rearrange to ketens [233]; a similar process is characteristic of *o*-quinone diazides, used as the main component in various light-sensitive layers [234]. The sensitisation of the photochemical decomposition by the anthraquinone residue is postulated in this case [233].

The electrophilic ketocarbenes (CLXXXI), formed by the photolysis of compound (CLXXX), interact with a solvent of type ArH and give rise to 2-hydroxy-3-arylanthraquinones (CLXXXII): [235]



(CLXXX) (CLXXXI) (CLXXXII)

## VII. THE INITATION AND INHIBITION OF PHOTOCHEMICAL REACTIONS BY QUINONES

One of the possible mechanisms of the initiation of photochemical reactions by quinones involves the transfer of the triplet state energy by the latter to various reactants. This sensitisation pathway§ is facilitated by the wide range of values of $E_T$ for different quinones (see Table) and the fairly high values of $\Phi_{ST}$ (as shown by the quantum yields of the photochemical reduction of many quinones, which are close to unity); for example, $\Phi_{ST} \simeq 0.9$ for anthraquinone [236].

The decomposition of 1-iodonaphthalene [242], the *cis-trans*-isomerisation of stilbenes, 2-, 3-, and 4-styrylpyridines, and 1- and 2-styrylnaphthalenes [243,244], and the

§ The term "sensitisation" is used here in a wide sense and implies the initiation of the photochemical process in the presence of an additive, regardless of the method by which initiation is achieved.

The energetic characteristics of the excited states of certain quinones.

| Compound | $E$, kcal mole$^{-1}$ | Compound | $E$, kcal mole$^{-1}$ |
|---|---|---|---|
| 1,4-Benzoquinone | 59 ($S^1$)[237]; 53.5 ($T^1$)[239]; 53 ($T^1$)[237]; 50 ($T^1$)[238] | 2,7-Disulphoanthraquinone (disodium salt) | 60 ($T^1$) |
| 1,4-Benzoquinone-$d_4$ | 53.5 ($T^1$)[239] | 1-Chloroanthraquinone | 60.5 ($T^1$) |
| 1-Methyl-1,4-benzoquinone | 54.7 ($T^1$)[239] | 1,5-Dichloroanthraquinone | 59.4 ($T^1$) |
| 2,5-Dichloro-1,4-benzoquinone | 55 ($T^1$)[239] | 1,8-Dichloroanthraquinone | 59.7 ($T^1$) |
| Tetramethyl-1,4-benzoquinone | 52 ($T^1$)[238] | 2-Chloroanthraquinone | 60 ($T^1$) |
| 1,4-Naphthoquinone | 62.8 ($S^1$)[239]; 58 ($T^1$)[237]; 53,7 ($T^1$)[239] | 1-Aminoanthraquinone | 52.2 ($S^1$) |
| 2-Methyl-1,4,-naphthoquinone | 63.3 ($S^1$)[239]; 53.8 ($T^1$)[239] | 2-Aminoanthraquinone | 54.1 ($S^1$) |
| 9,10-Phenanthrenequinone | 49 ($T^1$)[240] | 1-Amino-2-methylanthraquinone | 53 ($S^1$) |
| Anthraquinone | 67.8 ($S^1$)[239]; 62 ($T^1$)[238]; 60,5 ($T^1$)[241] | 1-Amino-5-chloroanthraquinone | 51.3 ($S^1$) |
| 2-Methyl-anthraquinone | 68 ($T^1$)[239]; 60,2 ($T^1$)[241] | 1-Amino-4-hydroxyanthraquinone | 48.9 ($S^1$) |
| 2-Sulphoanthraquinone (sodium salt) | 60 ($T^1$) * | 1,4-Dihydroxyanthraquinone | 53.8 ($S^1$) |
| 2,6-Disulphoanthraquinone (disodium salt) | 60 ($T^1$) * | 1,4-Di(methylamino)anthraquinone | 39.8 ($S^1$) |
| | | 1-Methylamino-4-*p*-toluidinoanthraquinone | 38 ($S^1$) |

*Data taken from Dearman and Chan [241].

reaction of anthracene with $CCl_4$ [245] may be quoted as examples of this type of sensitisation. In all cases, the systems were irradiated with light corresponding to the absorption band of the triplet energy donor (anthraquinone) and the occurrence of sensitisation confirmed the triplet nature of the excited states of the reactants.

Together with the solution of theoretical problems, energy transfer from quinone molecules has been used also for practical purposes. Thus the graft-copolymerisation of natural rubber with various monomers (styrene, methyl methacrylate) can be achieved in an emulsion under the influence of ultraviolet and visible light if 1-chloroanthraquinone is added to the mixture [246]. Various polycyclic quinones are used to initiate the photopolymerisation of acrylic or $\alpha$-alkylacrylic esters [247]. In order to "sensitise" layers based on organic azides towards light with wavelengths $> 300$ nm, anthraquinone is added to cyclorubber based on 4,4′-bisazidodiphenylmethane [248], while 1,4-benzoquinone and 1,2-benzanthraquinone are added to the polymer $[-CH_2CH.(O_2CC_6H_4N_3\text{-}p)-]_n$ [249].

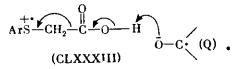
The photochemical oxidation of isopropylbenzene, tetralin, and benzaldehyde is sensitised by anthraquinone, 2-chloroanthraquinone, and 2-aminoanthraquinone [250–252]. It is believed that the biradical $^{\cdot}QO_2^{\cdot}$, formed on interaction between the excited quinone molecule and oxygen, is the initiator in this radical process; it is noteworthy that the yield of triplet quinone (Q) molecules increase under the influence of oxygen [253]. The intermediate form $^{\cdot}QO_2^{\cdot}$ either has a sufficiently large energy store to convert the substance being oxidised into a biradical (triplet) state or, if this condition is not fulfilled, it initiates the chain, dehydrogenating the substance AH undergoing oxidation:

$$Q\,(S^1) + O_2 \rightarrow {}^{\cdot}Q^{\cdot}\,(T^1),$$
$$Q\,(T^1) + O_2 \rightarrow {}^{\cdot}QO_2^{\cdot},$$
$${}^{\cdot}QO_2^{\cdot} + AH \rightarrow QO_2 + {}^{\cdot}AH^{\cdot}\,(T^1) \longrightarrow \text{chain},$$
$$\text{or } {}^{\cdot}QO_2^{\cdot} + AH \rightarrow {}^{\cdot}QO_2H + A^{\cdot} \longrightarrow \text{chain}.$$

Apart from the photochemical oxidation of alcohols sensitised by quinones, which was examined previously (see Section II), other photochemical reactions are known, whose initiation by quinones involves the photochemical reduction of the latter. This applies particularly to the decarboxylation of acids of the type $RXCH_2CO_2H$ (R = alkyl or aryl; X = O, S, or NH) in the presence of quinones (1,4-benzoquinone, tetrachloro-1,4-benzoquinone, anthraquinone). The process mechanism can be represented as follows [254]:

$$Q^{\cdot} + RXCH_2CO_2H \longrightarrow QH^{\cdot} + RX\dot{C}H_2 + CO_2,$$

$$QH^{\cdot} + RX\dot{C}H_2 \longrightarrow Q + RXCH_3,$$



(CLXXXIII)

One cannot rule out the possibility of decarboxylation in a cage formed by the charge-transfer complex (CLXXXIII) of the acid and the quinone, where the most mobile hydrogen atom of the carboxy-group approaches the oxygen atom of the carbonyl group of the quinone.

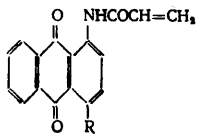
Anthraquinone-$\beta$-sulphonates which have been reduced photochemically in aqueous or aqueous alcoholic solutions (to sulphoanthrahydroquinone in neutral media or a radical anion at pH $> 11$) can serve as electron donors in relation to many compounds The process may involve only electron transfer (to stable radicals, quinones, and $Fe^{3+}$ ions) or the simultaneous initiation of a chain of chemical reactions (the reduction of nitro-compounds, certain decomposition reactions, etc.). $\beta$-Sulphoanthraquinones thus behave as sensitisers of the reduction of electron acceptors, which are themselves relatively inactive photochemically [255].

The introduction of anthraquinone during the irradiation of toluene increases the yield of 1,2-diphenylethane [256]. Since there is no energy transfer under these conditions [$E_T$(toluene) $> E_T$(anthraquinone)], the increase in process efficiency is probably caused by the greater number of benzyl radicals due to the photochemical dehydrogenation of toluene by anthraquinone.

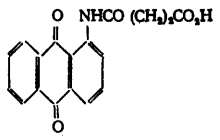
The photochemical degradation of *cis*-1,4-polyisoprenes in solutions is believed [257] to be caused by radicals formed from additives—quinones (1,4-naphthoquinone, anthraquinone, 1,2-benzanthraquinone, phenanthrenequinone).

Anthraquinone is used as the sensitising additive to photochemically polymerisable materials for photographic films [258] and to phototropic thermoplastic resins [259], while 1,5-diphenoxy-, 1,6-diphenoxy-, and 1,5-di-(*p*-methoxyphenoxy)-anthraquinones are also added to thermoplastic resins. The purpose of the addition of quinones to certain polymers is exactly the opposite; for example, 1,2- and 1,4-naphthoquinones, anthraquinones, and 1,2-benzanthraquinones are added to polystyrene in order to decompose it by photochemical oxidation [260].

It has been suggested that quinones can be used for this purpose also in compositions with other polymers in order to solve the problem of the degradation of packing materials. In this and many other examples enumerated above, it has not been established exactly how the photochemical reactions are initiated—by energy transfer from quinone molecules or by the reactive semiquinones formed on their photochemical reduction. Both initiation mechanisms may operate simultaneously:



(CLXXXIV)
R=H,OH



(CLXXXV)

Cases are known where quinones do not sensitise but actually inhibit photochemical processes: thus 1,4-naphthoquinone and anthraquinone diminish the extent of the photochemical degradation of vinyl polymers[261], while dyes of the anthraquinone series (CLXXXIV) and (CLXXXV) stabilise poly(methyl methacrylate)[262]. Such phenomena have so far been attributed only to the light filtration effect, but this explanation is probably not the only one possible.

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It has been found that excited quinones almost always behave as electron (hydrogen) acceptors in the primary photochemical step; on the other hand, the secondary processes reduce to intermolecular interaction with the reductant (solvent) or to the intramolecular stabilisation of the radical or biradical intermediates formed. We have endeavoured to demonstrate this in a logical manner in the description of the entire relevant data. This approach may not be entirely rigorous, since in many instances the formation of intermediates and the reaction mechanism as a whole have not been fully demonstrated and are tentative or have been assumed by analogy. Nevertheless, we believe that it can serve as a basis for a systematic treatment of the photochemical reactions of quinones.

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# The Reactions of Isatin and Its Derivatives with Aromatic and Heterocyclic *o*-Diamines

A.V.Ivashchenko and V.M.Dziomko

Studies on the reaction of isatin and its derivatives with aromatic and heterocyclic *o*-diamines are reviewed, and the mechanism of these reactions as well as the methods for the identification of their products are examined.
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## I. INTRODUCTION

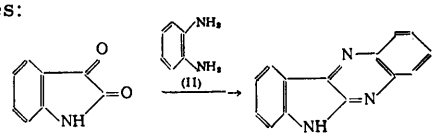
The reactions of isatin and its derivatives with aromatic and heterocyclic *o*-diamines, discovered in 1886 by Hinsberg[1], constitute an important method for the synthesis of condensed heteroaromatic systems, particularly purine analogues, as well as heteropolymers. The products of the reactions of isatins with aromatic heterocyclic *o*-diamines are of considerable interest as biologically active substances[2-15] (antimetabolites[2] and bactericidal[3-6], antifungal[7], antispasmodic, etc. agents), catalysts in colour photography[16], dyes for wool[17], and polydentate ligands capable of forming metal chelates stabilised by intramolecular hydrogen bonds[18-21], and are of interest as selective extractants[22].

It was believed for many years that the condensation of isatins with *o*-diamines always leads to derivatives of indolo[2,3-*b*]quinoxaline, but the latest data[15,20,21,23] have shown that the reaction does not proceed unambiguously and not only indolo[2,3-*b*]quinoxaline derivatives but also spiro-compounds are formed depending on the reaction conditions and the structures of the initial compounds.

Since the condensation of isatins with *o*-diamines has been attracting increasing attention in recent years, it is useful to survey the results of research on this reaction taking into account the latest data, with due attention to spectroscopic methods for the identification of the compounds formed.

## II. THE REACTIONS OF ISATINS AND ITS DERIVATIVES WITH AROMATIC *o*-DIAMINES

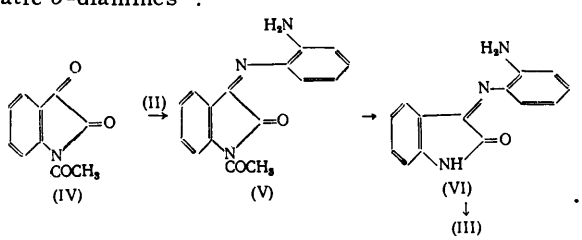
Schunk and Marchlewski[24-28] were two of the first investigators who studied the reactions of isatin (I) and its derivatives with aromatic *o*-diamines (II) in connection with the investigation of the properties of isatin. They obtained indolo[2,3-*b* quinoxaline] (III) and some of its derivatives:



(I) (III)

Subsequently the reactants employed in this reaction were isatin[1,15,17,21,23,24,27-35], *N*-substituted[6,23,28,30], alkyl- and alkoxy-[12,25,31,36-38], halogeno-[17,24,25,34,36,37], nitro-[17,34,36,37], naphtho-[37], and hydro-isatins[39,40] and isatin-carboxylic acids[8], on the one hand, and *o*-phenylenediamine[6,8,12,24-26,28,30,31,36,38-42], *o*-aminoalkylanilines and their salts[27,28,34,37,43-47], mono- and di-alkyl (alkoxy)-[1,17,21,26,28,33], mono- and di-halogeno[17], halogenoalkyl-[29], halogenonitro-[37], and nitro-*o*-phenylenediamines[31,37], *o*-diaminobenzoic acids[28], and *o*-naphthylenediamines[23], on the other. The reaction is usually carried out in aqueous or anhydrous acetic acid[23-25,33] and ethanol[15,23,48], more rarely in aqueous ethanol[38,48], benzene[32,33], and polyphosphoric acid[49,50], or without solvent[1].

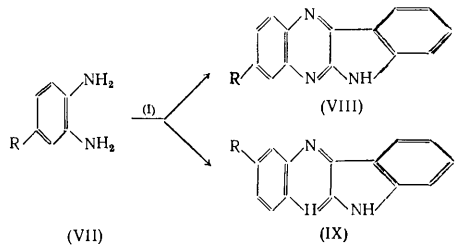
When 1-acetylisatin (IV) was condensed with *o*-phenylenediamine, Schunk and Marchlewski[38] obtained the acetylhydrazone (V), which was converted by hydrolysis into the hydrazone (VI), the latter being cyclised to 6*H*-indolo[2,3-*b*]quinoxaline (III). Similar hydrazones were obtained also by the reaction of 1-acetylisatin with other aromatic *o*-diamines[36]:



(IV) (V) (VI) (III)

When asymmetric *o*-diamines (VII) interact with isatin and its derivatives, there is a possibility of the formation of the structural isomers (VIII) and (IX), but, as a rule, one of the isomers is the dominant product[17], both isomers being obtained in approximately equal amounts only in the

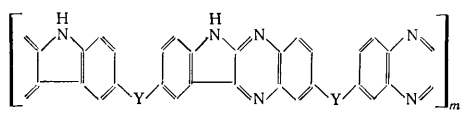
reactions of isatin with 4-ethoxy-*o*-phenylenediamine[28] and of 5-bromo-7-nitroisatin with 4-methoxy-*o*-phenylenediamine[17].



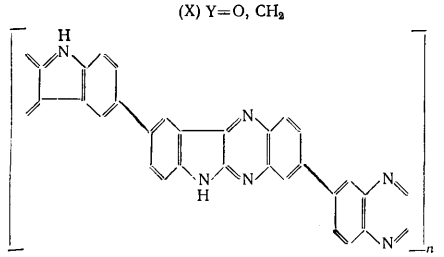
(VII) (VIII) (IX)

It is noteworthy that none of the structures of the indolo[2,3-*b*]quinoxalines obtained by the reactions of isatins with asymmetric *o*-diamines have been demonstrated.

The use as reactants in this process of 5,5′-oxybisisatinyl[49,50] and 5,5′-bisisatinyl[51], on the one hand, and oxybis-(3,4-diaminobenzene)[50], 4,4′-methylenebis-(*o*-phenylenediamine)[49], and 3,3-diaminobenzidine, on the other, made it possible to obtain the heteropolymers (X) and (XI). The condensation was carried out in polyphosphoric acid:

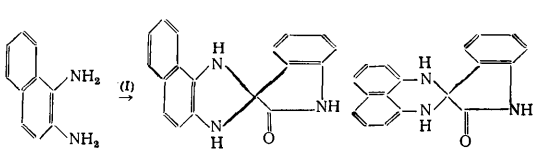


(X) Y=O, $CH_2$



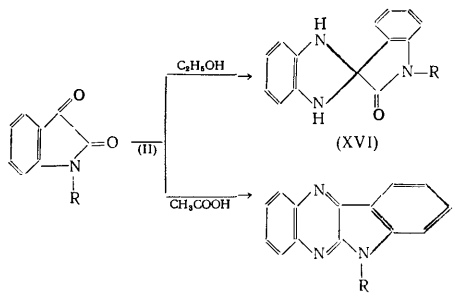
(XI)

Until 1958, it was believed that the only products of the reactions of isatins with *o*-diamines are derivatives of indolo[2,3-*b*]quinoxaline. However, Henseke and Lemke[48] established that the condensation of 1,2-naphthylenediamine (XII) with isatin proceeds with liberation of one water molecule. They suggested the spiro-structure (XIII) for the product of this reaction[48] by analogy with compound (XIV) obtained previously by Sachs[52] from 1,8-naphthylenediamine and isatin:



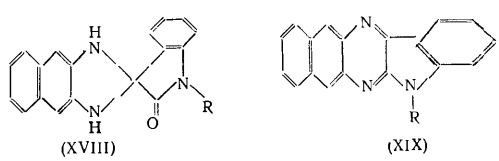
(XII) (XIII) (XIV)

Popp showed later[15,23] that, depending on the reactants and the reaction conditions (solvent), either linear products, or spiro-compounds, or both simultaneously may be formed. For example, the reaction of 1-methylisatin (XV) with *o*-phenylenediamine (II) in ethanol leads to the formation of 1′-methylspiro[benzimidazoline-2,3′-indolin]-2′-one (XVI), while in dilute acetic acid the product is 6-methylindolo[2,3-*b*]quinoxaline (XVII):



(XV) (XVI) (XVII)

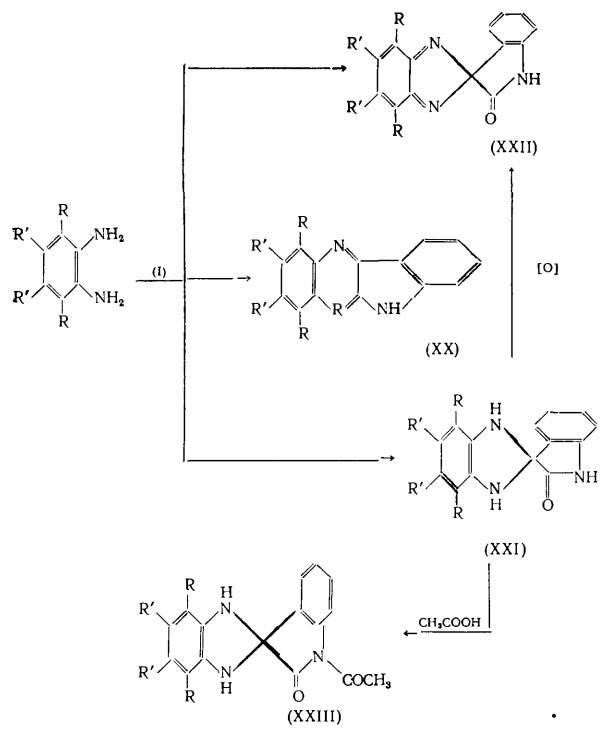
The reaction of 1-methylisatin with 2,3-diaminonaphthalene proceeds similarly. In contrast to its reaction with 1-methylisatin, 2,3-diaminonaphthalene reacts with 1-acetylisatin in ethanol to form a mixture of the spiro-compound (XVIII) and 8,9-benzo-6-acetylindolo[2,3-*b*]-quinoxaline (XIX), while the interaction in acetic acid of 9,10-diaminophenanthrene with 1-acetylisatin yields, in contrast to the reaction of the latter with *o*-phenylenediamine, only the spiro-compound:



(XVIII) (XIX)

The study of the reactions of 3,6- and 4,5-di-n-butoxy-*o*-phenylenediamines with isatin showed[21,33] that derivatives of spiro[2*H*-benzimidazole-2,3′-indolin]-2′-one (XXII) are formed together with derivatives of indolo-[2,3-*b*]quinoxaline (XX) and spiro[benzimidazoline-2,3′-indolin]-2′-one (XXI). When 3,6-di-n-butoxy-*o*-phenylenediamine interacts with isatin in 50% acetic acid, the product is a mixture consisting of indolo[2,3-*b*]quinoxaline (XX, R = n-BuO) and the spiro-compounds (XXI) and (XXII) with R = n-BuO and R′ = H, while in benzene in the presence of acetic acid only the spiro-compound (XXI, R = n-BuO, R′ = H) is formed. The mixture of products formed as a result of this reaction can be readily resolved owing to the different solubilities of these compounds in aqueous alcoholic solutions of alkalis and in benzene. The spiro-compound (XXI, R = n-BuO) is oxidised to the spiro-compound (XXII, R = n-BuO, R′ = H) by silver (I) oxide and is

acetylated by 80% acetic acid to the acetyl derivative (XXIII, R = n-Bu, R = H):

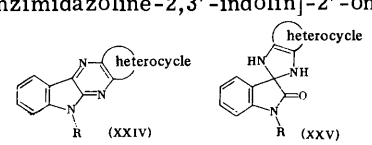


In contrast to 3,6-di-n-butoxy-*o*-phenylenediamine, the interaction of 4,5-di-n-butoxy-*o*-phenylenediamine with isatin in 50% acetic acid results in the formation of only the indolo[2,3-*b*]quinoxaline (XX, R = H, R′ = n-BuO) and the spiro-compound (XXII, R = H, R′ = n-BuO), while the reaction of these compounds in benzene in the presence of acetic acid results in the formation of only the indolo-[2,3-*b*]quinoxaline (XX, R = H, R′ = n-BuO).

## III. THE REACTIONS OF ISATINS WITH HETEROCYCLIC *o*-DIAMINES

The heterocyclic *o*-diamines employed in this reaction were 1,2-diamino-5-n-propyl-4-phenylimidazole[32], 2,3- and 3,4-diaminopyridines[23], 4,5-diaminopyrimidine[15,23] and its derivatives[23,33], and 4,5-diaminobenzothiazole[53], the products consisting of a series of heterocyclic systems.

In contrast to the reactions with aromatic *o*-diamines, the reactions of isatins with heterocyclic *o*-diamines yielded only analogues of indolo[2,3-*b*]quinoxaline (XXIV) and spiro[benzimidazoline-2,3′-indolin]-2′-one (XXV):

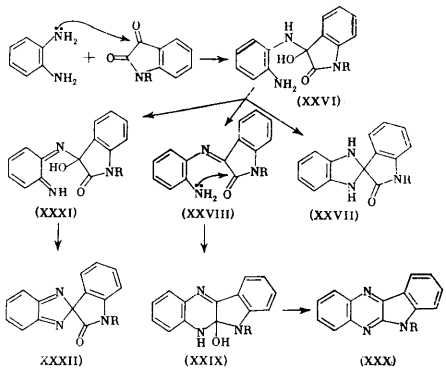


The structures of the initial compounds and the reaction conditions have a marked influence on the mode of reaction. Thus the interaction of 1,2-diamino-5-n-propyl-4-phenyl-imidazole[32], 4,5-diaminobenzothiazole[53], and certain derivatives of 4,5-diaminopyrimidine[33] with isatin yielded only linear products (XXIV). When 4,5-diamino-1,3-dimethyluracil was allowed to interact with isatin in acetic acid[23], the spiro-product (XXV) was obtained, while the interaction with 1-acetylisatin gave the linear product (XXIV).

The reaction of 3,4-diaminopyridine with isatin in ethanol leads to the formation of the linear product (XXIV), while 2,3-diaminopyridine and 4,5-diaminopyrimidine yielded the spiro-compound (XXV) under the same conditions[15]; the reactions of 2,3-and 3,4-diaminopyridines and 4,5-diaminopyrimidine with 1-acetylisatin also give rise to the spiro-compound (XXV).[15]

## IV. THE MECHANISM OF THE REACTIONS OF ISATINS WITH *o*-DIAMINES

The studies examined above suggest the following mechanism for the interaction of *o*-diamines with isatins. The first stage involves the formation of the hydroxy-compound (XXVI), which loses a water molecule and is converted either into spiro[benzimidazoline-2,3′-indolin]-2′-one (XXVII) or into a Schiff base (XXVIII):



It is noteworthy that the formation of the Schiff base (XXVIII) was observed by Schunk and Marchlewski[36,38] in the reaction of 1-acetylisatin with aromatic *o*-diamines.

The Schiff base (XXVIII) cyclises to the hydroxy-compound (XXIX), which liberates a water molecule and is converted into the indolo[2,3-*b*]quinoxaline (XXX).

The formation of spiro[-2*H*-benzimidazole-2,3′-indolin]-2′-one (XXXII) can be regarded as oxidation, during the reaction, of the hydroxy-compound (XXVI) to compound (XXXI), which cyclises to the spiro-compound (XXXII) with liberation of a water molecule. This mechanism of the formation of the spiro-compound (XXXII) may be put forward in view of the fact that the latter is not formed during the reaction from the spiro-compound (XXII).[33]

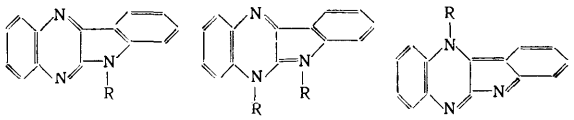
## V. METHODS FOR THE IDENTIFICATION OF THE REACTION PRODUCTS

Since the reactions of isatins with *o*-diamines do not proceed unambiguously, with the possibility of the formation of not only the isomeric indolo-[2,3-*b*]quinoxalines (VIII) and (IX) but also of the spiro-compounds (XXI) and (XXII), depending on the reaction conditions and the initial compounds, the problem arises of the identification of the reaction products.

Ultraviolet Spectra

The ultraviolet spectra of indolo[2,3-*b*]quinoxaline derivatives have been investigated by a number of workers[33,35,42,54-56], but systematic studies have been made only by Badger and Nelson[56], who investigated the ultraviolet spectra of 6*H*-indolo[2,3-*b*]quinoxaline and its *N*-methyl derivatives in neutral, acid, and alkaline media.

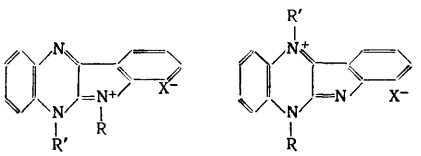
In theory, indolo[2,3-*b*]quinoxaline can exist in the form of three tautomeric forms (XXXIII)–(XXXV). By comparing its ultraviolet spectra with those of the *N*-methyl derivatives, it was shown[56] that indolo[2,3-*b*]quinoxaline exists preferentially in the 6*H*-form (XXXIII, R = H), since its ultraviolet spectrum is very similar to that of 6-methylindolo[2,3-*b*]quinoxaline and differs markedly from the spectrum of 5-methylindolo[2,3-*b*]quinoxaline in the range 400–520 nm.



(XXXIII) (XXXIV) (XXXV)

The spectrum of indolo[2,3-*b*]quinoxaline in sodium hydroxide solution is therefore similar to that of 5-methylindolo[2,3-*b*]quinoxaline, so that an appreciable proportion of the negative charge in the anion of indolo[2,3-*b*]quinoxaline is localised at the nitrogen atom in the 5-position.

The study of the spectra of the quaternary salts obtained by the protonation and methylation of indolo[2,3-*b*]quinoxaline showed that 6-methylindolo[2,3-*b*]quinoxaline is methylated and protonated in the 5-position with formation of the salt (XXXVI, R = R′ = $CH_3$; R = $CH_3$, R′ = H). 6*H*-Indolo[2,3-*b*]quinoxaline is also protonated in the 5-position, but this salt is capable of tautomerism and the solution probably contains both forms—(XXXVI) and (XXXVII) with R = R′ = H:



(XXXVI) (XXXVII)

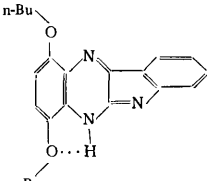
Methylation of 6*H*-indolo[2,3-*b*]quinoxaline by methyl toluene-*p*-sulphonate and methyl iodide as well as its protonation by toluene-*p*-sulphonic acid and HI lead to 5-methyl-11*H*-indolo[2,3-*b*]quinoxalinium iodide or toluene-*p*-sulphonate (XXV, R = $CH_3$, R′ = H, X = $CH_3C_6H_4SO_3^-$ or $I^-$). It is noteworthy that methylation of 6*H*-indolo[2,3-*b*]quinoxaline by methyl iodide or dimethyl sulphate in the presence of alkali as well as by diazomethane always yields a mixture of 5- and 6-methylindolo[2,3-*b*]quinoxalines. The formation of 11-methylindolo[2,3-*b*]quinoxaline was never observed under these conditions[56].

5-Methylindolo[2,3-*b*]quinoxaline is methylated in the 11-position with formation of 5,11-dimethylindolo[2,3-*b*]quinoxalinium toluene-*p*-sulphonate (XXXVII, R = R′ = $CH_3$, X = $CH_3C_6H_4SO_3^-$). Its ultraviolet spectrum resembles that of the protonated 5-methylindolo[2,3-*b*]quinoxaline, so that the latter is probably also protonated in the 11-position (XXXVI, R = $CH_3$, R′ = H, X = $CH_3C_6H_4SO_3^-$). Thus ultraviolet spectra can be used successfully for the identification of *N*-alkylindolo[2,3-*b*]quinoxalines.

Infrared Spectra

Owing to their low solubility in the corresponding solvents, the infrared spectra of the majority of the known indolo[2,3-*b*]quinoxalines and spiro[-2*H*-benzimidazole-2,3′-indolin]-2′-ones have not been investigated. The infrared spectroscopic data obtained by Ivashchenko and coworkers[21,33] are of interest, since they make it possible to interpret the structures of certain indolo[2,3-*b*]quinoxalines and demonstrate the possibility of using infrared spectroscopy for the identification of the products of the reactions of isatins with *o*-diamines.

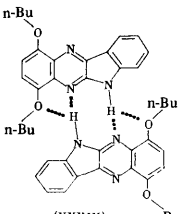
The infrared spectra of dilute solutions of indolo[2,3-*b*]-quinoxalines (XX) in chloroform have absorption bands characteristic of the stretching vibrations of the unassociated N–H bond (3425 and 3432 $cm^{-1}$). This shows that compound (XX) exists in the 6*H*-form, since otherwise the infrared spectrum of indolo[2,3-*b*]quinoxalines (XX, R = n-BuO, R′ = H) would be expected to exhibit a marked bathochromic shift of $\nu$(NH) relative to the spectrum of indolo[2,3-*b*]quinoxaline (XX, R = H, R′ = n-BuO) owing to the formation of an intramolecular hydrogen bond, as in formula (XXXVIII):



(XXXVIII)

The existence of the 6*H*-forms of compounds (XX) is also confirmed by their ultraviolet spectra[33] which do not have absorption bands in the long-wavelength region.

The infrared spectra of solid specimens of indolo-[2,3-*b*]quinoxalines (XX) differ markedly from one another in the presence of different substituents in the region of the stretching vibrations of the N–H bon[21]. On the other hand, the spectrum of compound (XX) with R = H and R′ = n-BuO has a broad absorption band in the range 3000–3300 $cm^{-1}$ with the fine structure characteristic of polyassociated compounds; the spectrum of compound (XX, R = n-BuO, R′ = H) has a single broadened band in this region at 3230 $cm^{-1}$), which apparently corresponds to the dimer. It is noteworthy that there is a possibility of two three-centre hydrogen bonds in the dimer of compound (XX, R = n-BuO, R′ = H), as in formula (XXXIX):



(XXXIX)

Since the formation of a "purely" three-centre hydrogen bond is extremely rare, it would be of undoubted interest to carry out X-ray diffraction studies on this compound.

The infrared spectrum of the spiro-compound (XXI, R = n-BuO, R′ = H) has an absorption band at 1668 $cm^{-1}$ (amide-I) and two bands in the region of the stretching vibrations of the N–H bond. The band intensities led to the following assignments[33]: the 3454 $cm^{-1}$ band ($\epsilon$ = 147)

to the stretching vibrations of the N–H bonds of the indoline ring and the 3370 $cm^{-1}$ band ($\epsilon$ = 428) to the stretching vibrations of the N–H bonds of the benzimidazoline ring. When this compound is acylated, the 3454 $cm^{-1}$ band disappears, while that at 3370 $cm^{-1}$ remains unchanged, which indicates the acylation of the spiro-compound (XXI, R = n-BuO, R′ = H) at the NH group of the indoline ring with formation of compound (XXIII, R = n-BuO, R′ = H).

The infrared spectra of the spiro-compounds (XXII) [33] contain bands due to the stretching vibrations of the N–H bond of the indoline ring at 3390 $cm^{-1}$ and the amide-I bands at 1732 and 1721 $cm^{-1}$.

## Mass Spectrometry

The mass spectra of indolo[2,3-*b*]quinoxaline and spiro-[-2*H*-benzimidazole-2,3′indolin]-2′-one have been studied in greatest detail in three investigations[21,33,57], where they were used successfully to identify the products of the reactions of isatins with aromatic heterocyclic *o*-diamines.

The mass spectra of the isatin–*o*-diamine reaction products contained intense peaks due to the molecular ions. The main decomposition pathways of indolo[2,3-*b*]quinoxaline, spiro[2*H*-benzimidazole-2,3′-indolin]-2′-one and spiro[benzimidazoline-2,3′-indolin]-2′-one in dissociative ionisation have been examined in detail[21,33,57].

In conclusion, we must emphasise that the reactions of isatins with aromatic and heterocylic *o*-diamines do not proceed unambiguously, so that they can lead to derivatives of indolo[2,3-*b*]quinoxaline, spiro-compounds, or both simultaneously. The study of the ultraviolet, infrared, and mass-spectra of derivatives of indolo[2,3-*b*]-quinoxaline, its analogues, and spiro[2*H*-benzimidazole-2,3′-indolin]-2′-one showed that these methods can be used successfully in many instances for the identification of the compounds formed in the condensation reactions of isatins with *o*-diamines.

Many studies carried out without taking into account the latest data and the evidence for the structures of the compounds obtained must be treated critically, since the structures of indolo[2,3-*b*]quinoxaline derivatives have been traditionally attributed without proof (and without demonstrating their individuality) to the products of the reactions of isatins with *o*-diamines.

The reactions have not been studied systematically and analysis of the data discussed in this review does not reveal systematic features in the formation of derivatives of indolo[2,3-*b*]quinoxaline and spiro-compounds as a function of the reaction conditions and the structures of the initial reactants. The study of these reactions is therefore of undoubted interest from both practical and theoretical points of view.

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# The Autoxidation of Azo-compounds and Certain Aspects of Associated Biochemical Processes†

V.Karnojitzky

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## I. INTRODUCTION

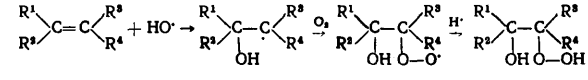
There is much interest at the present time in the role of organic peroxides in biochemical processes. After the discovery by Latarjet et al.[1] concerning organic peroxides in radiobiology, a study was published[2] on the biochemical importance of lipid peroxides, which subsequently served as a basis for a large review on this subject[3]. In recent years particular attention has been devoted to the oxidation of azo-compounds under the influence of molecular oxygen (in the triplet or singlet states). The studies published in recent years are concerned with the sensitised photochemical oxidation of aliphatic amines and oxides, various pyrrole, imidazole, oxazole, and isoindole derivatives, and also the oxidation of nucleic acid derivatives in the aqueous phase initiated by ionising radiation. Apart from the numerous original studies, the action of molecular oxygen on azo-compounds has been examined in a review[4] (containing 143 references to studies published up to 1967), while nucleic acids are dealt with in a major article[5] (70 references to studies published up to 1964). All these considerations led the present author to write a survey on the subject[132], combining all the latest and older studies on the autoxidation of aliphatic amines (in the gas phase), indoles, tetrahydrocarbazoles, dihydro-oxazines, tetrahydropyrazines, and hydrazones (in the liquid phase). Furthermore, in the studies published after 1967 (44 publications) the properties of the peroxides formed have been described in detail and an attempt has been made to relate, as far as possible, their formation to biological processes such as the decomposition of enzymes, the formation of pigments (kynurenine and melanin), the structural changes in alkaloids, and changes at the cellular level.

The results of 30 similar studies carried out in recent years, seven of which were published in 1975, are analysed in the present review. In particular, the review is concerned with the problem of the intermediate formation of peroxides in bioluminescence.

In the section dealing with oxidation mechanisms (oxidation by molecular oxygen), it was thought unnecessary to include the description of the classical chain mechanism of autoxidation.

## II. THE MECHANISMS OF OXIDATION UNDER THE INFLUENCE OF MOLECULAR OXYGEN

The classical mechanism of the oxidation of hydrocarbons under the influence of $O_2$ is applicable to aldehydes, ethers, and esters[6-10]. Initiation may be due to the radical generated from a source other than the substrate; for example, in the presence of ionising radiation, the autoxidation of unsaturated compounds in the aqueous phase is initiated by HO· radicals formed from $H_2O$. It is terminated by formation of hydroxyhydroperoxides via the mechanism



The H· atom is also formed from $H_2O$. The reaction involving nucleic acids proceeds in this way.

The oxidation of nitriles, hydroxylamines, (ketones and branched esters), and pyrazolones is very strongly accelerated in the presence of bases. It is suggested[12,13,183] that this type of oxidation proceeds via a mechanism similar to that described above but with participation of the anion $R^-$ (rather than the radical R·):

$$RH + HO^- \rightarrow R^- + H_2O;\ R^- + O^3 \rightarrow RO{-}O^-;$$
$$RO{-}O^- + HR \rightarrow RO{-}OH + R^- .$$

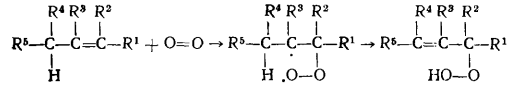
Sensitised photochemical oxidation proceeds in the presence of light and certain dyes (Methylene Blue, Rose Bengal, haematoporphyrin, and chlorophyll). In certain cases, for example in the presence of anthracene hydrocarbons, the substrate itself plays the role of the sensitiser. The sensitisation can be achieved via two different mechanisms.

1. In the first mechanism, the dye in the excited (biradical) state plays the role of a dehydrating agent, leading to the formation of a radical R·, which is then oxidised via the classical mechanism (involving $O_2$ as the triplet $^{\cdot}O{-}O^{\cdot}$).

†This review was written specially for the journal "Uspekhi Khimii". It was translated from French into Russian by T.V. Chernysheva.

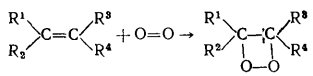
2. In the second mechanism, $O_2$ is involved in the singlet form O=O (formed in a certain amount under the conditions described above), which is capable of adding to ethylenic double bonds.

(a) In the oxidation of a mono-olefin having hydrogen atoms in the $\alpha$-position relative to the double bond, a hydroperoxide is usually formed in accordance with the equation



Many unsaturated hydroperoxides, for example those of $\alpha$- and $\beta$-pinenes [14] and of carvomenthene [15] have been obtained by this method. One should note that, in the presence of even one $\alpha$-methylene hydrogen atom at the double bond, two peroxide isomers are usually formed.

(b) In the absence of an $\alpha$-methylene hydrogen atom, O=O may add to the double bond with formation of a 1,2-peroxide:



This reaction proceeds more readily in the presence of nucleophilic substituents.

(c) In a system with conjugated double bonds, the addition in the 1,4-positions is stereospecific and proceeds only in the *cis,cis*-configuration. Numerous endoperoxides have been obtained in this way as a result of the sensitised photochemical oxidation of the corresponding 1,3-dienes (for example of ascaridole—from $\alpha$-terpinene in the presence of chloropyll [16]).

The mechanism of sensitised photochemical oxidation has been discussed in a number of publications [17-21,181,184]. The stereospecificity of the reaction has also been considered [21]. Schaap and Faler [22] and Hasty and Kearns [23] examined the photochemical oxidation of alkenes and dienes.

The biological importance of the photochemical oxidation sensitised by various dyes, inducing the decomposition of aminoacids (aromatic and heterocyclic), nucleic acids, and various proteins, as well as the inactivation of viruses and cells of multicellular organisms has been discussed by Spikes [176].

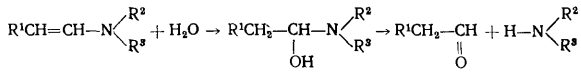
## III. THE AUTOXIDATION OF AMINES

### 1. The Reactions of Aliphatic Amines with Hydroperoxides

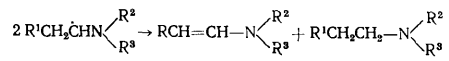
These reactions proceed via a mechanism different from that operating in the oxidation of amines by peracids (involving electrophilic attack by the oxygen of the peracid on the nitrogen atom of the amine). In the reactions with hydroperoxides, the dominant feature is the dehydrogenation of the amines simultaneously at the C and N atoms (when this is possible), which leads to the formation of an alcohol, water, or an imine. The hydrolysis of the latter leads to a carbonyl compound and the dealkylated amine:

$$RO{-}OH + R^1CH_2NHR^2 \rightarrow ROH + H_2O + R^1CH{=}NR^2,$$
$$R^1CH{=}NR^2 + H_2O \rightarrow R^1CHO + H_2NR^2.$$

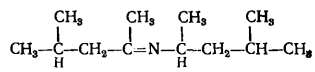
The molecules of the carbonyl compound may condense with one another (this reaction is favoured in an alkaline medium), with the initial amine, or with the dealkylated amine, forming respectively unsaturated carbonyl compounds and aldimines (or ketimines). The formation of a secondary amine and a carbonyl compound from a tertiary amine apparently proceeds as a result of the hydrolysis of the intermediate imine:



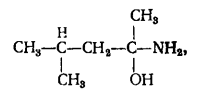
which is probably obtained as a result of the disproportionation of the radical $R^1CH_2CHNR^2R^3$:



The action of $O_2$ at 60–100°C on 4-methyl-2-pentylamine (I), 2,4,4-trimethyl-2-pentylamine (II), di-isopropylamine (III), and tri-n-propylamine (IV) has been considered [3] and it has been shown that $(CH_3)_3COH$, $H_2O$, and $NH_3$ (or $RNH_2$) are formed in satisfactory yields. In the reaction with the amine (I), the yields were 100, 82, and 60%; in addition, the compound



was isolated in 24–40% yield. The first compound, identified by infrared spectroscopy, is an aminoalcohol:



the subsequent decomposition of which to a carbonyl compound and $NH_3$ is facilitated by the formation of a hydrogen bond.

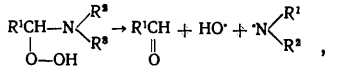
In the reaction with the amine (III), the yields of $(CH_3)_3COH$, $H_2O$, $(CH_3)_2CHNH_2$, and acetone were 85, 45, 88, and 95% respectively. The yields of t-butyl alcohol and dipropylamine from the amine (IV) were 80 and 32%.

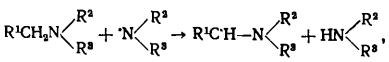
We may note that the corresponding nitro-derivative is formed in 2% yield from compound (II), which has no hydrogen atoms in the $\alpha$-position relative to the nitrogen atom, and that the reaction is very slow. The mechanism of the action of hydroperoxides on amines has been examined in detail [24,25] and the mobility of the hydrogen atom linked to the nitrogen atom and the carbon atom in the $\alpha$-position relative to the former has been discussed [26,27].

### 2. The Autoxidation of Aliphatic Amines in the Gas Phase

The autoxidation of aliphatic amines in the gas phase has been considered [28-34]. Studies have shown that the temperature of their oxidation (300°C) is lower by 200°C than the pyrolysis temperature. In contrast to hydrocarbons, ethers, and aldehydes, their oxidation is self-inhibited, but there is no appreciable induction period. The rate of oxidation depends on the structure of the amine and increases greatly as a result of branching both at the nitrogen and carbon atoms [30]. Table 1 presents the relative rates of oxidation $K$ of various amines at 310°C, the relative rate of oxidation of $CH_3NH_2$ having been adopted as unity.

The products of the reaction consist of carbonyl compounds and dealkylated amines, apparently formed from the intermediate hydroperoxides,



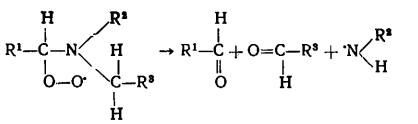


whose presence has been demonstrated in the oxidation of $CH_3NH_2$ at 350°C; their content reaches a maximum of $2 \times 10^{-6}$ mole/mole of amines after 2 min, decreasing subsequently and reaching zero after 4 min. In the light of the above, one may assume that the carbonyl compound and the dealkylated amine may be formed as a result of the decomposition of the intermediate aminoalcohol $R^1CH(OH).NR^2R^3$ produced by the action of the hydroperoxide $R^1CH(OOH)NR^2R^3$ on the initial amine. The absence of alcohols ROH shows that the hydroperoxide cannot be cleaved in the $\beta$-position.

Table 1. [30]

| Primary amine | $K$ | Secondary amine | $K$ |
|---|---|---|---|
| Methylamine | 1 | Dimethylamine | 19 |
| Ethylamine | 5.6 | Ethylmethylamine | 150 |
| Propylamine | 48 | Diethylamine | 255 |
| Butylamine | 230 | Methylpropylamine | 580 |
| Isopropylamine | 107 | Dipropylamine | 760 |
| Isobutylamine | 170 | | |

There is a possibility of the direct formation of a primary amine from the tertiary amine via the reaction [33]



The reactions of $C_1-C_9$ primary amines have also been discussed [28,29], while other workers considered secondary amines [31] and tertiary amines [32-34].

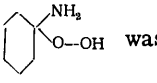
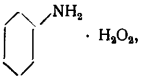
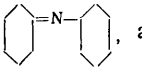
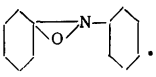
## 3. The Sensitised Photochemical Oxidation of Aliphatic and Aromatic Alkylamines in the Liquid Phase

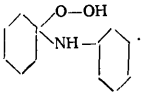
It has been shown [14] that primary amines (methyl-, ethyl-, propyl-, isopropyl-, and isobutyl-amines), secondary amines (diethylamine, pyrrolidine, and piperidine), and tertiary amines (triethylamine) are capable of absorbing oxygen and forming peroxides as a result of photochemical oxidation in the presence of chlorophyll, eosin, and haematoporphyrin. The amounts of absorbed $O_2$ (in moles per mole of the amine) are respectively 1, 2, and 2.6. On the other hand, $(CH_3)_3.CHNH_2$ does not absorb oxygen under these conditions owing to the absence of hydrogen atoms at the carbon atom in the $\alpha$-position relative to the nitrogen atom. These findings indicate attack on the carbon atom in the $\alpha$-position with the formation of a hydroperoxy-group in this position (as in the oxidation of amines in the gas phase).

The photochemical oxidation of the primary amines $C_3H_7NH_2$, $C_6H_5NH_2$, and $C_6H_5CH_2NH_2$, the secondary amine $(C_3H_7)_2NH$, and the tertiary amines $(C_2H_5)_3N$, $(C_3H_7)_3N$, $(C_6H_5CH_2)_3N$, $C_6H_5N(CH_3)_2$, and $C_6H_5N(C_2H_5)_2$, sensitised by benzophenone and dyes (Methylene Blue, eosin, and Rose Bengal) at room temperature in benzene or methanol solution, has been investigated in detail [35]. Primary and secondary amines proved to be relatively inactive and their decomposition products were not detected. In the reactions of tertiary amines, aldehydes and aldimines, formed as a result of the condensation of the aldehydes with initial amines or amines produced by dealkylation, were identified.

The formation of aldimines, corresponding to the formation of primary amines in the photochemical oxidation of tertiary amines, suggests the direct formation of the former from the latter (via a mechanism similar to that operating in the gas phase). Analogous results were obtained [36] in a study of the tertiary amines $(C_3H_7)_3N$, $(C_2H_5)_3N$, and $C_6H_5N(CH_3)_2$ using polycyclic aromatic hydrocarbons (naphthalene, perylene, anthracene, and phenanthrene) as sensitising agents. These investigations showed that the initial stage of the reaction involves the dehydration of the amines by the sensitiser and the formation of the radical $R^1CH_2\dot{C}HNR^2R^3$, the subsequent behaviour of which should be similar to but not identical with its behaviour in the gas phase.

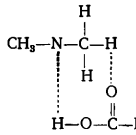
Indeed, apart from the cleavage in the $\alpha$-position, there is also a possibility of the cleavage in the $\beta$-position as a result of the addition of singlet $O_2$ to the double bond of the enamine produced by the disproportionation of the radical. In a study of the autoxidation [37] of mono-, di-, and tri-butylamines, it was shown that, apart from the postulated products (butylidenebutylamine, butylaldehyde, and propylamine), produced as a result of cleavage in the $\alpha$-position, considerable amounts of mono- or di-formamides are formed, indicating cleavage in the $\beta$-position. The reaction mechanism is discussed and the formation of reaction products as a function of the type of amine and solvent (ethanol, acetone, acetonitrile, and methyl methacrylate) is explained [37].

In certain cases it has been possible to isolate the corresponding hydroperoxide. In a study [28] of the benzophenone-sensitised photochemical oxidation of cyclohexylamine at temperatures between −20° and 20°C using ether and its mixtures with alcohol as solvents, the hydroperoxide  was isolated together with some of the decomposition products: the adduct  , the cyclohexylideneamine  , and the oxaziran  . Under conditions identical to those described above, the hydroperoxide



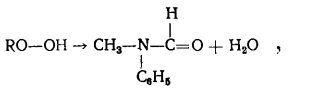
was also isolated from dicyclohexylamine [38].

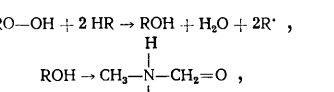
Aromatic alkylamines can also be oxidised in the absence of sensitisers. The autoxidation of *NN*-dimethylaniline (DMA), which has been investigated in particular detail by Horner and Knapp[40], has been described[29]. The autoxidation of DMA is catalysed by radical initiators—benzoyl peroxide[39], azobisisobutyronitrile[40], and particularly cobalt salts (manganese salts are less active and nickel and copper salts are completely inactive). Carboxylic acids also exhibit a catalytic activity, which is probably a consequence of the neutralisation of the amine and partly the formation of a cyclic complex in which a C–H bond in $CH_2$ is weakened, which favours attack by $O_2$ at this site:

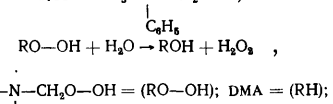


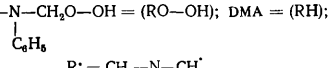
At 20°C, 80 mole % $O_2$ is absorbed in 90 min in the reaction catalysed by 0.2 mole % (relative to DMA) of cobalt stearate using a mixture of acetic acid, acetic anhydride, and benzene as solvent. The product consists of 50 mole % of peroxides (40% of $H_2O_2$ and 60% of organic peroxide), 90 mole % HCHO (45% in a free state), and 88 mole % $C_6H_5NHCH_3$. Apart from the compounds enumerated above, $(CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2$ can also be formed (as a result of the condensation of HCHO with DMA).

The nature of the products obtained and their relative amounts suggest the following mechanism of their formation from the hydroperoxide:

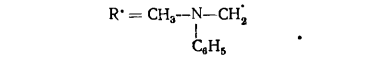


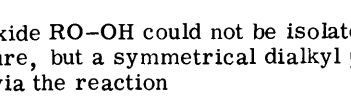




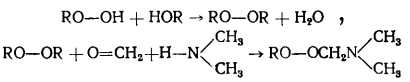


where

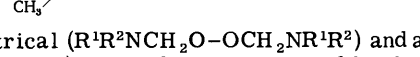




The hydroperoxide RO–OH could not be isolated from the reaction mixture, but a symmetrical dialkyl peroxide RO–OR, formed via the reaction



was isolated. The melting point of the peroxide RO–OR is identical with that of the peroxide obtained as a result of synthesis via the reaction described by Horner and Knapp[41]:



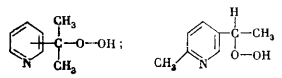
Symmetrical ($R^1R^2NCH_2O–OCH_2NR^1R^2$) and asymmetric ($R^1R^2NCH_2O–OR$) peroxides, synthesised by the action of secondary amines on formaldehyde in the presence of $H_2O_2$ or RO–OH respectively, are also known[42].

Similar results were obtained with certain DMA derivatives substituted in the benzene ring. We may note that nucleophilic groups increase and electrophilic groups decrease the rate of absorption of $O_2$.[39,40] On the other hand, aliphatic amines do not absorb $O_2$ in the presence of cobalt salts even at 40°C. All the methods and the complete composition of the products of the reactions are quoted by Horner and Knapp[40].

Primary aromatic amines absorb oxygen at room temperature only in a highly alkaline medium (in the presence of alkali metal alkoxides). The dominant process is dehydrogenation, leading to the formation of the corresponding diazo-compounds. This reaction may be inhibited by benzene derivatives disubstituted in the *ortho*- and *para*-positions; $\alpha$- and $\beta$-naphthylamines yield the corresponding phenazines. This reaction has been discussed in detail by Horner and Dehnert[43].

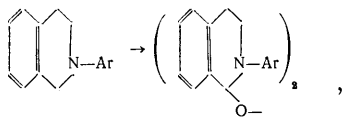
Non-hydrogenated or partly hydrogenated heterocyclic amines can also yield hydroperoxides or dialkyl peroxides as a result of autoxidation.

The stable crystalline hydroperoxides

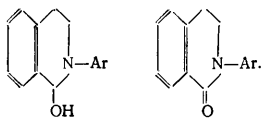


have been obtained by the autoxidation at 100–120°C of isopropylpyridines (the 2-, 3-, and 4-isomers) and 5-ethyl-2-methylpyridine.[46] Here the decomposition products are the alcohols $CH_3\diagdown$ / $CH_3—COH$ / Py and the ketone $CH_3–C(=O)–Py$. Preferential migration of the $CH_3$ group (in relation to pyridine) from carbon to oxygen always takes place in the cation $CH_3\diagdown$ / $CH_3—CO^+$ / Py. The synthesis and decomposition of hydroperoxides of this type have been described[44–46].

In other instances, dialkylperoxides were obtained. Thus *N*-aryltetrahydroisoquinolines yield, as a result of autoxidation, the peroxides

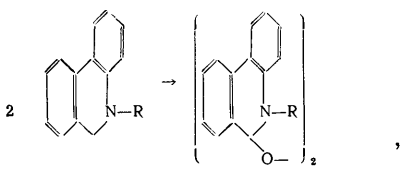


where Ar = $C_6H_5$, $C_6H_4$, or naphthyl. On boiling in $CHCl_3$, they undergo homolytic cleavage as a result of the rupture of the oxygen bridge. The radicals formed in this way disproportionate to a hydroxy-derivative and a ketone:



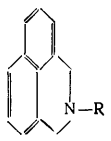
$\alpha$-Substituted derivatives of these compounds do not react with oxygen. The properties of peroxides and the methods used to synthesise them have been described[47].

As a result of autoxidation, dihydrophenanthridines also give rise to dialkyl peroxides:

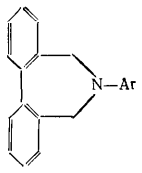


where R = $CH_3$ or $C_6H_5$ (they decompose on heating as in the previous case).

*N*-Substituted dihydroisoquinolines do not react[48]:



*N*-Aryldihydrobenzoazepines



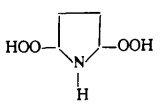
(Ar=$C_6H_5$, *p*-$CH_3C_6H_4$, *p*-$ClC_6H_4$, *p*-$CH_3OC_6H_4$)

form peroxides whose properties have been described[49].

We may note that these three types of dialkylperoxides can also be synthesised by treating the corresponding $\alpha$-bromo-derivatives with $H_2O_2$ and that $\alpha$-aminated hydroperoxides $R^1R^2C(COH)NHR$ have been obtained by treating the corresponding ketimines $R^1R^2C = NR$ with $H_2O_2$.[60] The simultaneous action of $H_2O_2$ and $NH_3$ on cyclic ketones gives rise to aminoperoxides of different structures[51].

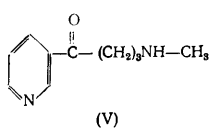
The different ways of obtaining peroxides from amines and related compounds have been described recently[52].

Pyrrolidinone absorbs two moles of $O_2$ at room temperature as a result of sensitised photochemical oxidation, forming a dihydroperoxide [14]:

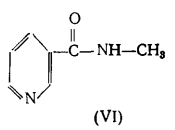


The sensitised photochemical oxidation of nicotine in an aqueous medium at 37° and 40°C has been investigated[53,54]. The structural changes apparently involve only the pyrrolidine ring, but the reaction goes beyond the hydroperoxide stage. Indeed the ring is cleaved, which entails the decomposition of the t-amino-group, resulting in a decrease of pH. The pyrrolidine ring is probably initially dehydrated with subsequent attack by $O_2$, causing the rupture of the ring owing to the formation of the very unstable intermediate 1,2-peroxide. This can probably account for the absorption of one mole of $O_2$ instead of two moles, as in another investigation[14]. The only peroxide detected was $H_2O_2$.

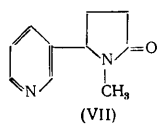
Methylaminopropyl pyridyl ketone (V), methylnicotinamide (VI), cotinine [1-methyl-5-(3-pyridyl)-2-pyrrolidinone] (VII), and methylmyosmine (VIII) have been isolated from tobacco leaves subjected to aerobic fermentation:



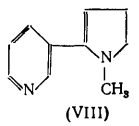
(V)



(VI)

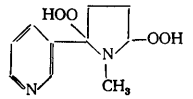


(VII)



(VIII)

The nature of these compounds suggests attack on the 2- and 5-positions of the pyrrolidine ring with formation of the corresponding mono- or di-hydroperoxides:



Compound (V) is probably obtained as a result of the decomposition of the monohydroperoxide with rupture of the ring between N and $C_{(2)}$, compound (VI) is produced by the decomposition of the dihydroperoxide with rupture of the ring between N and $C_{(2)}$ and between N and $C_{(5)}$, compound (VII) is formed by the dehydration of the hydroperoxide without the rupture of the ring, and compound (VIII) results from the dehydration of the alcohol without the rupture of the ring. The last compound is formed by the reactions

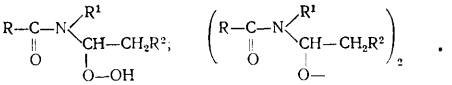
$$RO{-}OH \rightarrow RO^{\cdot} + {\cdot}OH\ ,$$
$$RO^{\cdot} + HR \rightarrow ROH + R^{\cdot}$$

(RH = nicotine).

## IV. THE REACTIONS OF AMIDES WITH MOLECULAR OXYGEN

### 1. The Autoxidation and Sensitised Photochemical Oxidation of Aliphatic Amides

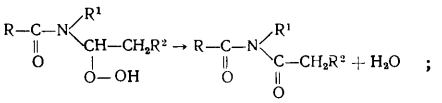
These reactions, involving aliphatic amides having the general formula $R{-}\underset{\underset{O}{\|}}{C}(R_1){-}N{-}CH_2{-}CH_2{-}R^2$, have been the subject of an extensive investigation[57]. It has been shown that in all cases the carbon atoms in the $\alpha$-position with respect to N are attacked with formation of a hydroperoxide or a dialkyl peroxide depending on the reaction conditions:



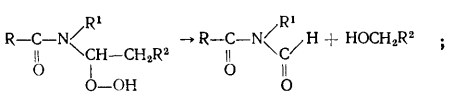
Using $^{14}C$, it had been shown earlier[58] for *N*-pentylhexanamide that valeraldehyde is formed from the carbon chain linked to the nitrogen atom and caproamide is formed from the chain linked to C=O.

The peroxides formed and decomposed into

(a) a diacylamide and water:

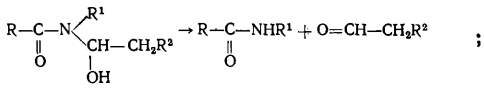


(b) an acylformamide and an alcohol:

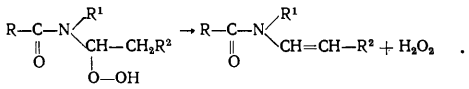


(c) an acylamino alcohol $R{-}\underset{\underset{O}{\|}}{C}{-}N(R_1){-}\underset{\underset{OH}{|}}{CH}{-}CH_2R^2$, the

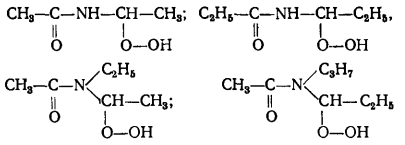
subsequent decomposition of which yields an amide and an aldehyde:



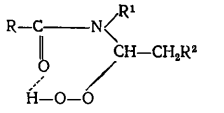
(d) an unsaturated amide and hydrogen peroxide:



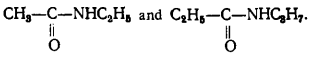
The hydroperoxides



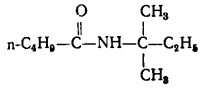
may be isolated in a pure state in a yield of the order of 2%. The autoxidation is carried out at 130° for 30 to 60 min. The excess amide is removed in a high vacuum at room temperature, the crude hydroperoxide being recrystallised from an appropriate solvent. These compounds are stable for several weeks at 0°C. Infrared spectroscopic and NMR data showed that they have a cyclic structure:



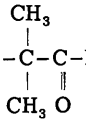
The photochemical oxidation at 0°C leads to the formation of dialkyl peroxides, which were isolated in a pure state in two instances:



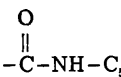
It is noteworthy that the rate of oxidation depends mainly on the structure of the carbon chain at the nitrogen atom and not at C=O; the oxidation does not occur in the presence of a tertiary carbon atom attached to the nitrogen atom; thus the amide



does not absorb oxygen in photochemical oxidation at 50°C,

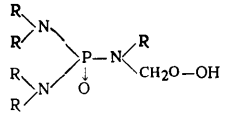


while the amide  absorbs it at the



same rate as the amide n-$C_5H_{11}$-C(=O)-NH-$C_5H_{11}$-n.[58]

The quite likely presence of the peroxide and the hydroperoxide

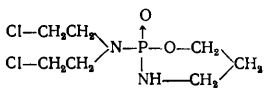


(R=$CH_3$)

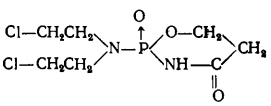
was proved[177] by iodometric and polarographic methods in the photochemical oxidation of hexamethylphosphoramide (HMP); owing to its instability, the hydroperoxide was not isolated in a pure state. The formation of formaldehyde following its thermal decomposition was demonstrated.

The phosphoramide (IX) is used in the treatment of various types of cancer. The reactions of this compound *in vivo* involve the carbon atom in the α-position relative to the nitrogen atom. Indeed the mixed amide (X) and the open-chain acid (XIII) have been found in the urine of animals receiving intravenous injections of the amide (IX) [178, 179]; however, when compounds (X) and (XIII) were injected, they proved to be less active than the amide (IX), while the hydroxy-compound (XI) and the hydroperoxide (XII) exhibit a strong cyclotoxic activity both *in vivo* and *in vitro*.

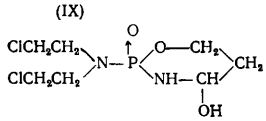
The hydroxy-compounds and mixed amides are probably formed via the intermediate hydroperoxide (XII), which can be obtained by treating the hydroxy-compound (XI) with Fenton's reagent[180]:



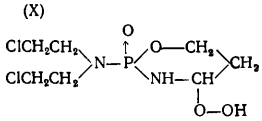
(IX)



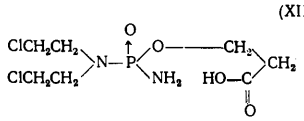
(X)



(XI)



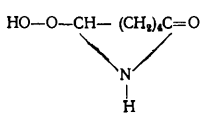
(XII)



(XIII)

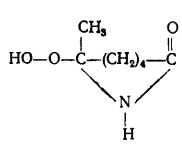
## 2. The Photochemical Oxidation of Lactams and Polyamides

The photochemical oxidation of ε-caprolactam (95°C, 48 h) led to the formation of the hydroperoxide



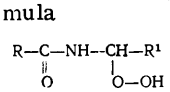
in 5% yield[59], the compound decomposing on heating in benzene solution into water and adipamide.

Under conditions identical with those described above, the lactam ring in methylcaprolactam is opened with formation of acetylvaleramide; the intermediate hydroperoxide

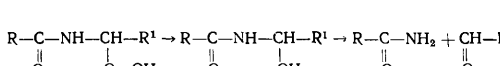


could not be isolated.

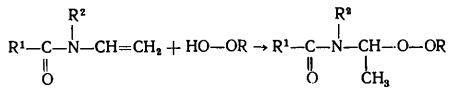
It is interesting to note that, when various polyamides are heated in the presence of oxygen, hydroperoxides having the general formula



are also formed. Depending on the experimental conditions, they give rise to the cross-linking of the chains accompanied by the formation of bridges with and without oxygen atoms, or to degradation of the type

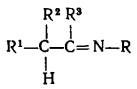


The autoxidation of polyamides has been discussed[60-62]. We may note that certain amide peroxides can be obtained by treating vinyl derivatives of amides with hydroperoxides[185]:

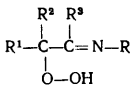


## V. THE OXIDATION OF IMINES AND ENAMINES

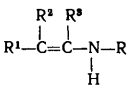
Imines having the general formula



with a hydrogen atom in the $\alpha$-position relative to the nitrogen atom and in the $\beta$-position relative to the double bond, undergo autoxidation with conversion into the corresponding hydroperoxides:

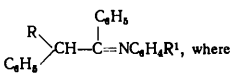


The same may be said of the enamines



containing a hydrogen atom linked to the nitrogen atom, which give rise to the same hydroperoxides after their isomerisation to the corresponding imines.

There are also several examples where the double bond and the nitrogen atom are outside a ring; these are the anils[63] derived from *p*-methoxyaniline, methylphenylacetaldehyde (XIV), and diphenylpropionaldehyde (XV) and the anils of *p*-methylaniline and diphenylacetophenone (XVI):[64]

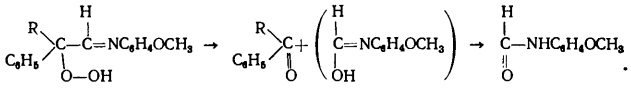


R=CH$_3$, R$^1$=OCH$_3$ ; (XIV)

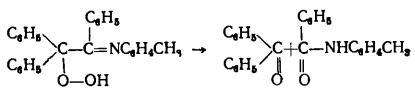
R=C$_6$H$_5$, R$^1$=OCH$_3$ ; (XV)

R=C$_6$H$_5$, R$^1$=CH$_3$ . (XVI)

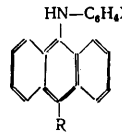
At room temperature in ether or ethyl acetate, compounds (XIV) and (XV) rapidly absorb one mole of $O_2$, forming hydroperoxides (iodine is liberated from iodides), which decompose fully into the corresponding ketone and formylamisidine (R = $CH_3$ or $C_6H_5$); in the case of compound (XV), the peroxide vanishes completely after 2 h at room temperature:



The same may also be said of the anil (XVI) from which only benzophenone and *p*-methylphenylbenzamide could be isolated:

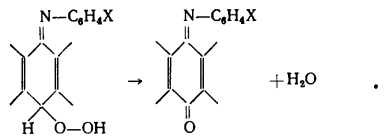


Derivatives of 9-aminoanthracene



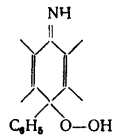
are of considerable interest. The rate of autoxidation depends on the nature of the substituent X in the *para*-position in the benzene ring linked to the nitrogen atom. For example, at room temperature (in ethereal solution) when R = $C_6H_5$ and X = $NO_2$ the absorption of $O_2$ is not observed for 7 days, while with X = $OCH_3$ or $N(CH_3)_2$ one mole of $O_2$ is absorbed after 4 days or after several hours respectively[65].

The stability of the hydroperoxide obtained depends not only on the nature of X but also on that of R. Thus, with R = H and X = $OCH_3$ or $N(CH_3)_2$, it was possible to obtain only quinone imines, formed as a result of the decomposition of the corresponding hydroperoxides:



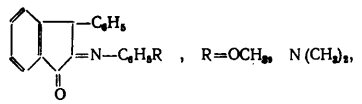
With R = $C_6H_5$, the corresponding hydroperoxides were isolated, but the hydroperoxide with X = $N(CH_3)_2$ was obtained only in a crude form and were not purified owing to its instability and low solubility in organic solvents. The hydroperoxide with X = $OCH_3$ was obtained in a pure form in a yield of 65%.

The hydroperoxide[66]

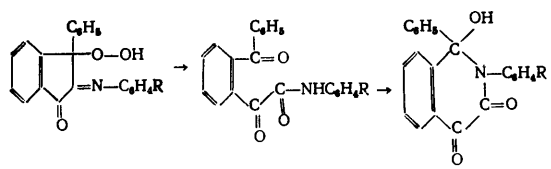


without substituents at the nitrogen atom, was isolated in 35% yield; the autoxidation was carried out in an ethereal solution at 0°C. The hydroperoxide decomposes fully into the corresponding quinone imine and phenol in several hours at 0°C. The methods of synthesis are described and the reaction is discussed in detail by Cauquis[65].

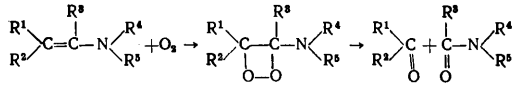
The autoxidation of the indandione anil



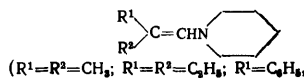
leads to the formation of the corresponding hydroxyisoquinolinedione.[67] Although the presence of the peroxide has not been established chemically, nevertheless one can postulate the intermediate formation of a very unstable hydroperoxide, the decomposition of which is probably due to the corresponding isoquinoline derivative:



Enamines without a hydrogen atom linked to the nitrogen atom can combine with singlet $O_2$ in certain cases and give rise to a carbonyl compound and a substituted amide via the intermediate formation of a very unstable 1,2-peroxide:



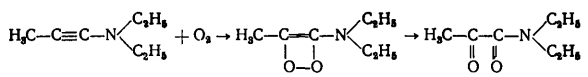
It has been shown[68] that the sensitised photochemical oxidation of the compound



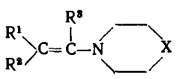
$(R^1=R^2=CH_3;\ R^1=R^2=C_2H_5;\ R^1=C_6H_5,\ R^2=CH_3)$

(solvent—benzene, sensitiser—haematoporphyrin) at room temperature leads to the rapid absorption of one mole of $O_2$ with formation of the ketone $R^1R^2C{=}O$ (in a high yield) and formylpiperidine.

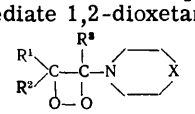
Under the same conditions, *NN*-dimethylpropynylamine yields the *NN*-dimethylamide of pyruvic acid:

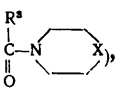


The photosensitised oxidation at room temperature of enamines of the type

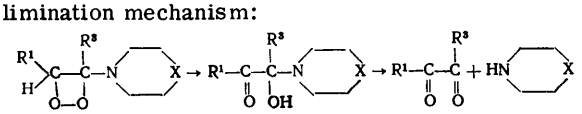


where X = $CH_2$ or O, has been examined[186]. It involves the rapid absorption of 1.2 moles of $O_2$ with formation of a very unstable intermediate 1,2-dioxetan

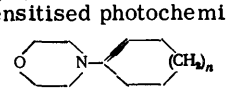
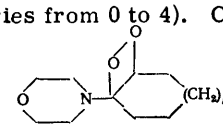
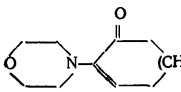
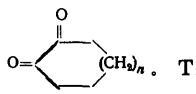
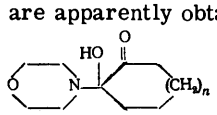


which may decompose as a result of the dissociation of the C–C bond, with formation of the monoketone $R^1R^2C{=}O$ and the amide,  , or the C–N bond with formation of the $\alpha$-diketone $R^1{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}R^3$. The latter reaction depends to a large extent on the nature of $R^3$. For $R^1 = R^2 = CH_3$ and X = O, the degree of dissociation of the C–N bond is 32% when $R^3 = C_6H_5$, falling to zero when $R^3 = H$.

The presence of the hydrogen atom in the $\beta$-position relative to the nitrogen atom ($R^1$ or $R^2$ = H) also promotes the dissociation of the C–N bond in accordance with the $\beta$-elimination mechanism:

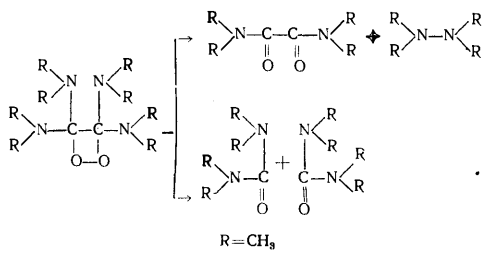


Thus, when $R^1 = CH_3$, $R^3 = C_6H_5$, and X = O, the degree of dissociation of the C–N bond increases from 32 to 71% following the replacement of $R^2 = CH_3$ by $R^2 = H$.

An interesting instance[187] of the sensitised photochemical oxidation of morpholine enamines  has been discovered (*n* varies from 0 to 4). Crystals of the intermediate dioxetans  , were isolated at −78°C in dimethyl ether (for *n* = 1, 2, or 3), but at room temperature the main compounds are the monoketone enamines  and the diketone  . They are apparently obtained from the aminohydroxyketone  by dehydrogenation in the former case and by the dissociation of C–N bond in the latter. The aminohydroxyketone may be formed from the dioxetan on dissociation of the peroxy-bridge and subsequent hydrogen transfer (the $\beta$-elimination mechanism).

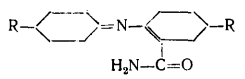
The photochemical oxidation of 3-morpholinocholest-3-ene in ether at −78°C leads to the formation of cholestane-2,3-dione and 3-morpholinocholest-3-en-2-one.[187]

The autoxidation of tetrakisdimethylaminoethylene in polar and non-polar solvents has been investigated[69]. The mechanism of this reaction is very complex, depends on the nature of the solvent, and has been investigated inadequately. The principal autoxidation products (the composition of the products varies depending on the nature of the solvent) are dimethylurea, tetramethyloximide, and tetramethylhydrazine. They are probably obtained from a very unstable intermediate peroxide:

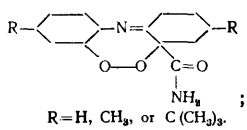


R=$CH_3$

Conjugated unsaturated imines, in which one nitrogen atom and one of the double bonds are outside the ring and which are described by the formula



constitute an interesting case[70]. At room temperature in chloroform they rapidly absorb one mole of $O_2$ (the reaction is appreciably accelerated by the addition of 0.1% of cobalt naphthenate) with formation of endoperoxides:



R=H, $CH_3$, or $C(CH_3)_3$.

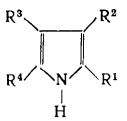
## VI. THE AUTOXIDATION OF COMPOUNDS WITH A DOUBLE BOND AND A NITROGEN ATOM IN THE RING

### 1. Pyrroles

The pyrrole rings are important components of compounds which are of great biological significance: chlorophyll, haemoglobin, and certain alkaloids (chydrine and

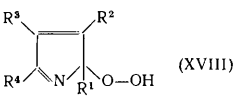
stachydrine). The various methods for their oxidation by oxygen are therefore of special interest. Numerous, very important studies have been devoted to them in recent years [72-84]. Non-sensitised autoxidation at room temperature yields only a mixture of compounds which are difficult to determine [71], the rate of absorption of $O_2$ increasing sharply in the presence of alkali metal alkoxides. Two moles of $O_2$ are absorbed and trimers with two pyrrole rings are formed [72]. Sensitised photochemical oxidation leads to the formation of readily identifiable compounds, which are probably obtained as a result of the isomerisation of the 1,4-endoperoxide, formed initially with or without the rupture of the pyrrole ring. The nature and proportions of the products depend on the structure of the pyrrole derivative and the conditions of preparation. In certain cases a hydroperoxide may be formed.

The tetrasubstituted pyrrole (XVII)



(XVII)

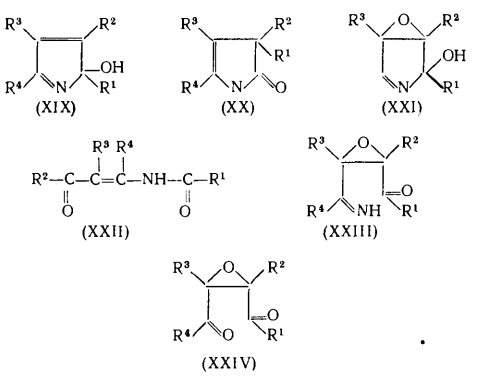
can lead to the formation of the hydroperoxides (XVIII)



(XVIII)

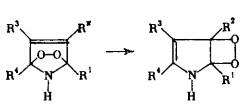
(a) $R^1=R^2=R^3=$ t-Bu, $R^4=H$;
(b) $R^1=R^2=$ t-Bu, $R^3=R^4=H$;
(c) $R^1=R^2=R^3=R^4=C_6H_5$;
(d) $R^1=R^4=C_6H_5$, $R^2=R^3=H$,

as well as an alcohol (XIX), a lactam (XX), an epoxyalcohol (XXI), a chalcone (XXII), an epoxyketoimine (XXIII), and its hydrolysis product (XXIV):



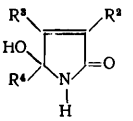
(XIX) (XX) (XXI) (XXII) (XXIII) (XXIV)

In order to account for the formation of some of the above products, obtained in consequence of the dissociation of the $C_{(1)}-C_{(2)}$ bond, the formation of the intermediate 1,2-peroxide (XXVI) as a result of the isomerisation of the 1,4-endoperoxide (XXV) was examined:



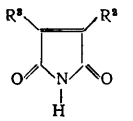
(XXV) (XXVI)

Pyrroles unsubstituted in the 1- and 4-positions can give rise to the formation of the hydroxylactam (XXVII)



(XXVII)

as a result of the base-catalysed rearrangement of the endoperoxide (XXV) and its more far-reaching oxidation products, for example derivatives of maleimide (XXVIII):



(XXVIII)

(in the case of pyrroles unsubstituted in both 1- and 4-positions).

Unsubstituted pyrrole (as well as its *N*-methyl derivative), subjected to photochemical oxidation at room temperature (with eosin as the sensitiser), yields a hydroxylactam (XXVII). [73] On photochemical oxidation in benzene solution, 2,4-dimethylpyrrole gives rise to the hydroxylactam (XXVII), $R^1 = R^3 - H$, $R^2 = R^4 = CH_3$) but with the OH group in the 2-position (the 4-position is blocked). It is apparently obtained on rearrangement of the 1,2-peroxide (XXVI). [74] The photochemical oxidation of 2,3-diethylpyrrole in solution in methanol (with Rose Bengal as sensitiser) gives a methoxy-derivative of the hydroxylactam (XXVII) and the corresponding maleimide (XXVIII) in a yield of the order of 35%. [75]

We may note that in certain cases the hydroxylactam and maleimide are formed as a result of the dealkylation of the $C_{(4)}$ atom. Thus the photochemical oxidation of 3-ethyl-2,3,4-trimethylpyrrole and 3-ethyl-2,4-dimethylpyrrole (in methanol solution with Rose Bengal as the sensitiser) gives rise to the hydroxylactam (XXVII) and the corresponding maleimides in yields of 40 and 3% respectively [75].

The sensitised photochemical oxidation of 1,4-di-t-and 1,2,4-tri-t-butylpyrroles (in methylene chloride with Methylene Blue as sensitiser) gives rise to hydroperoxides with a strong hydrogen bond [76].

The behaviour of 1,2,3,4-tetraphenylpyrrole, the photochemical oxidation of which has been investigated [77-79], is most characteristic of pyrroles. This compound is similar to lophine (1,3,4-triphenylimidazole), the sensitised photochemical oxidation of which gives rise to a hydroperoxide and not an endoperoxide, as was believed previously. The irradiation of a 2% solution of compound (XVII, $R^1 = R^2 = R^3 = R^4 = C_6H_5$) at room temperature or −50°C in $CS_2$, $CH_3OH$, $CHCl_3$, or ether for 10–15 min in the presence of 1% of the sensitiser (heterocoerdianthrone, dibenzoperylenequinone) leads to the formation of a hydroperoxide in 35% yield. It is noteworthy that this hydroperoxide, like that of lophine, can decompose into the initial pyrrole and $O_2$.

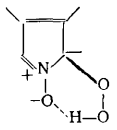
When compound (XVII) is subjected to autoxidation without a solvent at 120–130°C or refluxed in propanone, dioxan, or benzene, 2,4-substituted pyrroles are formed preferentially in yields of 66, 75, and 82% respectively. When the compound is refluxed in methanol, the main products are compounds (XXI) and (XXII) in yields of 30 and 15% respectively.

The reduction of the hydroperoxide (XVIII) at room temperature (KI solution in acetic acid) gives rise to

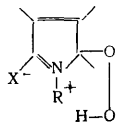
compound (XIX) (90% yield). Decomposition in a sealed tube in benzene solution with added anhydrous KOH results in the formation of compounds (XX) and (XXII) in yields of 28 and 10% respectively. The formation of a hydrogen bond between the H atom of the HO–O group and the nitrogen atom of the pyrrole ring facilitates the dissociation of the CO–OH and HO–O–C linkages with evolution of $O_2$, which proceeds more readily the lower the degree of association of the solvent. We may note that compounds (XXI) and (XXII) are formed in the sensitised photochemical oxidation of compound (XVII) without the preliminary isolation of the hydroperoxide (XVIIIc).

The sensitised photochemical oxidation of 1,4-diphenylpyrrole also leads to the corresponding hydroperoxide (XXVIId), but the latter is very unstable, which makes it impossible to reduce it by iodides. Its thermal decomposition *in vacuo* at 80°C leads to the formation of a tarry residue with slight evolution of $O_2$.[79]

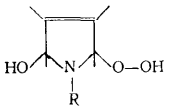
The sensitised photochemical oxidation of 1,2,3,4-tetraphenylpyrroles substituted at the nitrogen atom by OH,[80] $C_6H_5$,[81] benzoyl,[82] and $NH_2$ [83] groups has been investigated. When R = OH, the product is a nitrone peroxide



which is converted into the corresponding hydroxynitrone on reduction with KI solution in acetic acid. Similar results were obtained for R = $C_6H_5$ [81] and benzoyl.[82] In both cases the initial product (a 1,4-endoperoxide) isomerises to the 1,2-peroxide, which was detected iodometrically in the course of photochemical oxidation in ethereal solution at −65°C. In the first instance, the peroxide may be isolated as the hydroperoxide salt, which readily hydrolyses to compound (XIX) and $H_2O_2$ (X = halogen or $CH_3C_6H_4SO_3$):

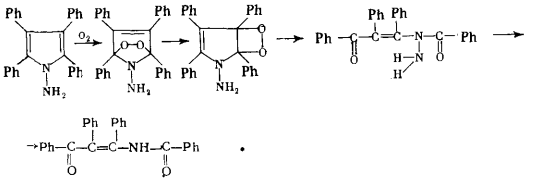


If R = benzoyl, treatment with the above acids leads to the hydrolysis of the initial hydroperoxide and the formation of a hydroxyhydroperoxide



The decomposition products of these two peroxides are similar to the products obtained from tetraphenylpyrrolyl hydroperoxide (XVIIc) unsubstituted at the nitrogen atom. In both cases the chalcone (XXII) is formed in chloroform solution with $C_6H_5$ and $C_6H_5COO$ groups respectively at the nitrogen atom; when R = $C_6H_5COO$, the second reaction product is the epoxyoxoimine (XXIII); when R = $C_6H_5$, the epoxyoxoimine hydrolyses with formation of the epoxyketone (XXIV).

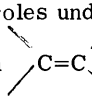
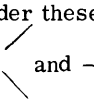
If R = $NH_2$, [83] the formation of a peroxide could not be observed even at −60°C regardless of the solvent. The main products of this sensitised photochemical oxidation were benzoyltriphenylpyrazole and tetraphenylpyridazine. The former compound is apparently formed from a very unstable intermediate peroxide:



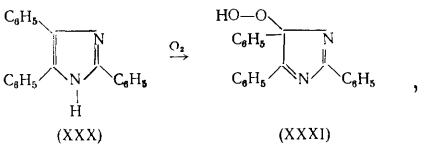
The sensitised photochemical oxidation of *N*-phenylpyrrole unsubstituted at the carbon atoms, which is used to synthesise the hydroxylactam (XXVII, $R^1 = R^2 = R^3 = R^4 = H$), necessary for the synthesis of various mitomycins, has been investigated[87].

The sensitised oxidation of pyrroles substituted and unsubstituted at the nitrogen atom has also been examined[85,86].

## 2. Imidazoles

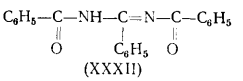
The behaviour of imidazoles under autoxidation and sensitised photochemical oxidation conditions is similar to that of pyrroles under these conditions except that compounds with  and  bonds are formed respectively in the two cases.

Triphenylimidazole (lophine) (XXIX) gives rise to a hydroperoxide,



(XXX) (XXXI)

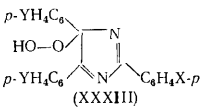
as a result of non-sensitised (in $CS_2$) [87] or sensitised (in chloroform) photochemical oxidation[88] in yields of 20 and 68% respectively. The hydroperoxide is relatively stable at room temperature in the solid state but is very unstable in solution (particularly in acid or alkaline solutions). On heating, it decomposes into lophine (with a yield of 50%) and $O_2$. This reaction is accompanied by luminescence and the formation of *MN*-dibenzoylamidine (XXXII):



(XXXII)

The latter compound is also formed as a result of the oxidation of compound (XXX) in organic solvents.

Certain hydroperoxides derived from lophine, described by the formula



(XXXIII)

have been obtained by the photochemical oxidation of compound (XXXIII) in solution in a mixture of methylene chloride (95%) and ethanol (5%).[89]

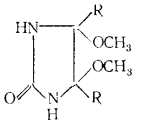
The pure hydroperoxides have been obtained for X = $H_3CO$, Y = H and X = $H_3CO$, Y = $H_3CO$; for X = $(CH_3)_2N$, Y = H and X = $(CH_3)_2N$, Y = $H_3CO$, the hydroperoxides proved to be very unstable[89]. The luminescence of hydroperoxides

of this type has been discussed[89]. It is probably associated with the formation of *NN*-dibenzoylamidine in an excited state.

The luminescence in the case where the substituents in the three benzene rings of compound (**XXXIII**) are chlorine atoms (one chlorine atom in the *ortho-*, *meta-*, or *para*-position and two chlorine atoms in the 2,4- and 3,4-positions) has been discussed in another investigation[90].

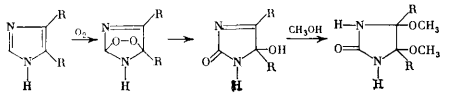
We may note that the sensitised photochemical oxidation of *N*-phenyl-lophine in solution gives rise to a very unstable peroxide, which was detected iodometrically at −60°C. The product in this instance is probably a 1,4-endoperoxide, the hydrolysis of which results in the formation of hydroperoxide salts, similar to those of *N*-substituted pyrroles[91].

The sensitised photochemical oxidation (in solution in methanol) of unsubstituted imidazole and 1,2-diphenylimidazole has been examined[92]. The final reaction products are methoxyimidazolidinones (**XXXIV**) (in 45% yield):



(XXXIV)

Their formation with participation of the solvent can be represented as follows on the basis of the formation of a 1,4-endoperoxide:

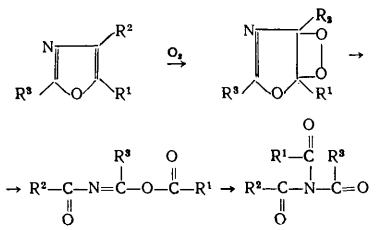


The decomposition of the imidazoline ring of histidine on sensitised photochemical oxidation of enzymes in the aqueous phase is associated with a decrease of their activity. A relation between the degree of decomposition of the imidazole ring of histidine in bovine insulin and the biological activity of this hormone can be established[93]. We may note that the absorption of 2.25 moles of $O_2$ lowers the histidine content from 5.4 to 0.1%, while the content of other aminoacids remains almost constant [93].

Similar phenomena have been observed for phosphoglucomutase [94] and chymotrypsin.[95] The change in the properties of lactoglobulin [96] is also associated with the decomposition of the imidazole ring in histidine.

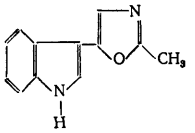
## 3. Oxazoles

The sensitised photochemical oxidation of oxazoles leads to the formation of triamides. A study[97] of the photochemical oxidation of 3-methyl-1,2-diphenyl- and 2-methyl-1,4-diphenyl-oxazoles (at room temperature in methanol) showed that the final product of the reaction is *N*-acetylbenzamide in both cases. It is probably formed as a result of a rearrangement of the 1,2-peroxide (which is apparently in its turn a product of the isomerisation of the 1,4-endoperoxide):

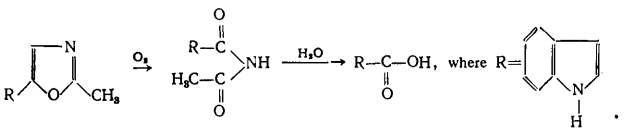


The mechanism of this reaction has been considered in detail[97,98].

The conversion of pimprinine

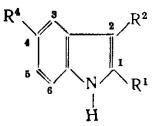


in sensitised photochemical oxidation into indolecarboxylic acid is a reaction of this type[97,99]:



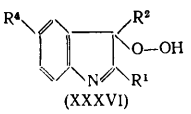
## 4. The Autoxidation of Indoles

Alkylindoles (**XXXV**) having the general formula



(XXXV)

give rise to the corresponding hydroperoxides (**XXXVI**)



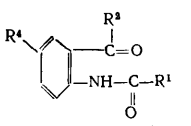
(XXXVI)

on autoxidation. Their formation requires the presence of a hydrogen atom linked to the nitrogen atom. The nature of the group $R^2$ in the pyrrole ring (in the β-position relative to N) is very important; for example, the reaction does not occur when $R^2 = C_6H_5$. The nature of the group $R^4$ in the 4-position of the benzene ring (in the β-position relative to the common double bond) also influences the reaction; the latter proceeds more readily in the presence of a nucleophilic group, for example $OCH_3$. The results are presented in Table 2.

Table 2. Data on the autoxidation of indoles.[100]

| Группа | | | Yield of hydroperoxide |
|---|---|---|---|
| $R^4$ | $R^1$ | $R^2$ | |
| H | $CH_3$ | $CH_3$ | 25 |
| $CH_3O$ | $CH_3$ | $CH_3$ | 50 |
| $CH_3O$ | $C_6H_5$ | $CH_3$ | 100 |

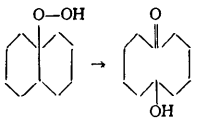
On being refluxed with dilute acids or alkalis, indolyl hydroperoxides are converted into amidoketones (**XXXVII**)



(XXXVII)

via two possible mechanisms:

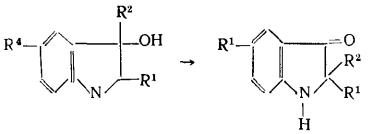
(1) The mechanism described by Criegee, which consists in the conversion of decalinyl hydroperoxide into hydroxycyclodecanone:



The reaction proceeds with heterolytic dissociation of the O–O bond followed by rupture of the $C_{(1)}$–$C_{(2)}$ bond and the migration of the OH group from O to $C_{(6)}$.

(2) The mechanism (operating in the case of tetraphenylpyrrolyl hydroperoxide) involving the heterolytic dissociation of the O–H bond (in RO–O–H), resulting in the formation of $RO-O^-$ and $H^+$, and the addition of the anion $RO-O^-$ and the proton $H^+$ to the $-N=C\langle$ double bond.

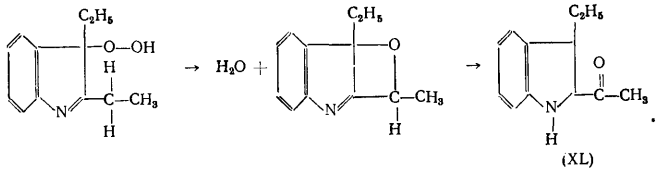
On being reduced with hydrosulphites, hydroperoxides are converted into the corresponding alcohols (XXXVIII), which are further converted into lactams (XXXIX) in an alkaline medium. This reaction is analogous to that which occurs with pyrrole derivatives:



(XXXVIII) (XXXIX)

The methods for the synthesis and decomposition of hydroperoxides of this type have been described [100].

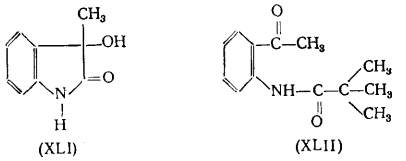
The behaviour of 1,2-diethylindole is interesting [102]. The hydroperoxide (XXXVI, $R^3 = H$, $R^1 = R^2 = C_2H_5$), with the OOH group in the 2-position, is converted into 1-acetyl-2-ethylindole (XL):



(XL)

(The presence of the N=C double bond renders the hydrogen atoms in $CH_2$ mobile). One should note that (XL) is formed from diethylindole at room temperature in the presence of atmospheric oxygen in the light.

The behaviour of 1-isopropyl-2-methylindole is more complex [103]. The resulting hydroperoxide with the OOH group in the 2-position, gives rise on decomposition to compounds (XLI) and (XLII):



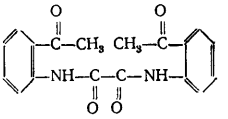
(XLI) (XLII)

The mechanism of these anomalous reactions has already been discussed [103–105].

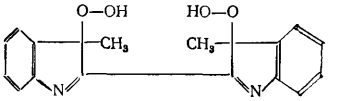
The formation of 1-acylindoles during the *in vivo* oxidation of derivatives of 1,2-dialkylindoles in alkaloids such as dregamine [106], voacafrine [107], and vobasine [108] apparently proceeds via a mechanism similar to that operating with 1,2-diethylindole.

A more complex instance involving indoles (XXXV, $R^4 = H$, $R^2 = CH_3$, $R^1$ = methylindolyl) has been examined [109].

The monohydroperoxide (XXXVI) is formed initially and its subsequent oxidation (on passing $O_2$ into a boiling xylene solution) yields the oxamide (XLIII):



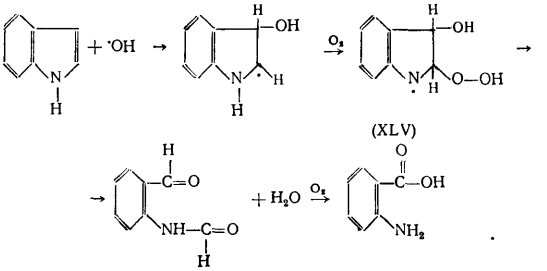
which is apparently formed from the intermediate dihydroperoxide (XLIV):



(XLIV)

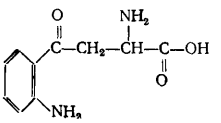
The formation of indolyl hydroperoxides is probably associated with the bioluminescence of certain marine organisms. This hypothesis has been confirmed by studies on the hydroperoxides (XXXVI, $R^4 = H$, $R^2 = CH_3$, $R^1 = CH_3$ of $p$-$CH_3OC_6H_4$). [110]

The action of $\gamma$-radiation in the presence and absence of $O_2$ on indole, $N$-methylindole, 2,$N$-dimethylindole, and 1,2-dimethylindole in aqueous solution has also been investigated [111]. It was shown that attack by the $^{\cdot}OH$ radicals formed from $H_2O$ is initially directed to the 2-position (the $\beta$-position relative to the nitrogen atom) of the pyrrole ring (which does not in any way exclude attack on the benzene ring) and that, depending on the presence or absence of oxygen, different reaction products are obtained. In particular, anthranilic acid is formed from indole only in the former case—probably as a result of the formation of the intermediate hydroxyhydroperoxide (XLV) in accordance with the equation



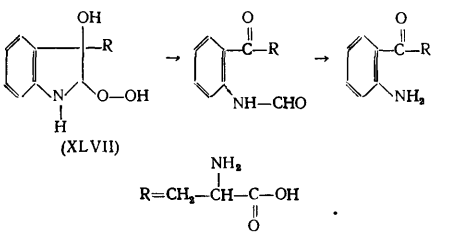
(XLV)

The formation of kynurenine (XLVI)



(XLVI)

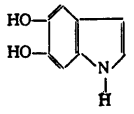
from tryptophan apparently proceeds via a mechanism similar to that involving the formation of the intermediate hydroxyhydroperoxide (XLVII):



(XLVII)

This reaction was achieved *in vitro* when an aqueous solution of tryptophan (at a concentration of 0.001 M) was exposed to X-rays at room temperature in the presence of oxygen[112]. Kynurenine is a product of the decomposition of tryptophan in living cells and in micro-organisms and is one of the controlling factors in transmitting hereditary information[113]. It has been shown[114] that the conversion of tryptophan into kynurenine in rat liver proceeds via the intermediate formation of formylkynurenine. Various metabolic aerobic transformations of tryptophan have been examined[192].

The role of indolyl hydroperoxides in the formation of melanin pigments has not been completely elucidated as yet. These pigments are formed as a result of the biological oxidation of tyrosine with intermediate formation of 4,5-dihydroxyindole:[115]

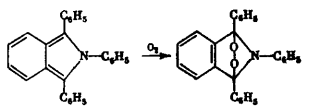


The attempts to oxidise 4,5-dihydroxyindole and its 1- and 2-methyl derivatives in an aqueous alkaline medium have shown[115] that $O_2$ is absorbed in all cases, but a black deposit is formed only from the 2-methyl derivative; the 1-methyl derivative gives rise to an amorphous blue precipitate, while the unsubstituted derivative is converted into a purple solution. Presumably these three indole derivatives are oxidised via different mechanisms.

## 5. The Autoxidation of Isoindoles

The non-sensitised photochemical oxidation of isoindoles has been the subject of several studies[116-119]. In the autoxidation of *N*-substituted isoindoles the intermediate is apparently an endoperoxide, the stability of which and hence the nature of the final product depend to a large extent on the nature of the 1,2-substituents in the pyrrole ring.

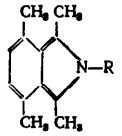
The corresponding endoperoxide (XLIX)



(XLVIII) (XLIX)

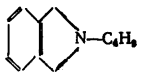
was isolated in the autoxidation of 2,3-*N*-triphenylisoindole (XLVIII). This endoperoxide decomposes on heating in oxygen up to 118°C; acid hydrolysis leads to the rupture of the pyrrole ring with formation of dibenzoylbenzene and aniline[116].

The autoxidation of *N*-alkyl-1,2,4,7-tetramethylisoindoles (L)

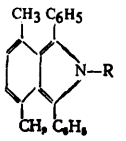


(L)
R=$CH_3$, $C_6H_5$, $C_6H_5$

has been examined[117]. The final oxidation products in boiling tetrahydrofuran (THF) are the corresponding phthalimides, which are believed to be formed on decomposition of the intermediate endoperoxides as a result of the elimination of $CH_3$ groups. The $CH_3$ groups are abstracted from the pyrrole ring (which is retained, in contrast to the previous case).

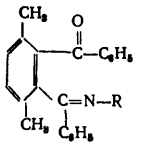
The autoxidation of *N*-butylisoindoline 

has been investigated[118] and it has been shown that the first reaction stage involves the dehydrogenation of the corresponding isoindole and depends to a large extent on the nature of the solvent. The products of this reaction are phthalimidines and a phthalimide. The reaction has a non-classical mechanism, which is believed to involve peroxy-radicals[118]. The autoxidation of the isoindoles

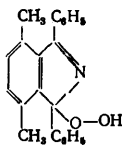


(R=H, $CH_3$, $C_6H_5$, or $C_6H_5CH_3$)

(in boiling THF) has been studied[188] and it has been shown that, owing to the greater difficulty of the elimination of $C_6H_5$ groups compared with $CH_3$ groups, the ketimines



are formed instead of phthalimides (R can be any group other than a hydrogen atom) as a result of the rupture of the pyrrole ring. When R = H, the product is the hydroperoxide

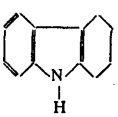


which is rapidly converted into the corresponding alcohol.

## 6. The Autoxidation of Tetrahydrocarbazoles

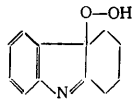
The autoxidation of tetrahydrocarbazole derivatives has been studied in detail[120-127]. It is to some extent similar to the autoxidation of dialkylindoles, in particular in view of the necessity for the presence of a hydrogen atom linked directly to the nitrogen atom and as regards the influence of the substituent in the benzene ring. The formation of hydroperoxides at the beginning of the reaction (which have been isolated in many instances) is accompanied by the formation of interesting products on their decomposition.

The unsubstituted tetrahydrocarbazole (LI)



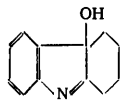
(LI)

gives rise, under conditions analogous to those in the reactions of dialkylindoles, to the hydroperoxide (LII)



(LII)

which may be reduced to the alcohol (LIII)

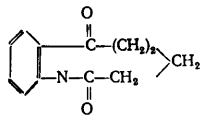


(LIII)

by an aqueous solution of $Na_2S_2O_4$ in the presence of NaOH.

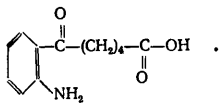
Here one should note that the catalytic hydrogenation of compound (LII) in the presence of palladium yields the tetrahydracarbazole (LI), while in the presence of $PtO_2$ the hydrogenation proceeds with formation of hexahydrocarbazole.

The formation of the lactam (LIV)



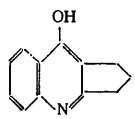
(LIV)

from compound (LII) proceeds at room temperature in polar solvents and is strongly catalysed by acids [121]. Under the influence of acids, the lactam is converted into *o*-aminobenzoylvaleric acid (LV):



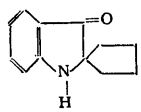
(LV)

Compounds of two types are formed in an alkaline medium (2 *N* NaOH) at room temperature: hydroxycyclopentanoquinoline (LVI)



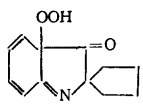
(LVI)

as a result of the internal condensation of the lactam (LIV) and the oxospiran (LVII)



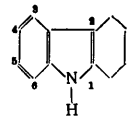
(LVII)

which is a product of the isomerisation of the hydroxy-derivative. As a result of catalytic hydrogenation, the oxospiran is converted into the corresponding dihydro-derivative, which yields the hydroperoxide (LVIII) on autoxidation [120,121]:



(LVIII)

The autoxidation of tetrahydrocarbazoles substituted in the benzene ring has been investigated [122-124]:



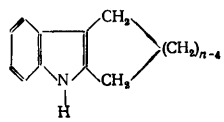
(LIX)

| substituent | position |
|---|---|
| $OCH_3$ | 4,5 |
| Br | 4 |
| $NO_2$ | 6 |
| $H_2N-C(=O)-CH_3$ | 4 |
| $COOCH_3$ | 3 |
| $COOCH_3$ | 4 |

In the presence of the same substituent, the rate of autoxidation is a maximum for the isomer substituted in the 3-position and a minimum for the isomer substituted in the 6-position. Thus the reaction proceeds in a different manner when the 6-position is occupied by the $NO_2$ and $COOCH_2$ groups. Particular attention has been devoted to the study of derivatives with the $COOCH_3$ and COOH substituents in the 3-, 4-, 5-, and 6-positions.

In the first case, the autoxidation proceeds only in an organic solvent. The corresponding hydroperoxides have been isolated (except for the isomer substituted in the 6-position). In the second case the autoxidation occurs only in an aqueous alkaline medium and intermediate peroxides could not be isolated. The corresponding hydroxyquinolines have been obtained for 6- and 8-bromo-derivatives and the 3-methoxycarbonyl-derivatives.

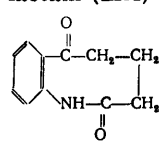
A study has been made of the influence of the size of the hydrogenated ring in compound (LX)



(LX)

(where *n* is the number of carbon atoms in the ring) on the rate of autoxidation and on the nature of the products [125]. It was found that the rate decreases with increase of *n* and the corresponding hydroperoxides could not be isolated in any of the instances considered (except for $n = 6$).

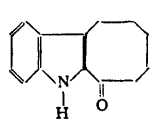
The corresponding lactam (LXI)



(LXI)

formed from the compound with a five-membered ring is readily hydrolysed to *o*-aminobenzoylbutyric acid, but the corresponding hydroxyquinoline (LVI) could not be isolated. The hydroxyquinoline is formed from the compound with a seven-membered ring, but the OH group is in the $\alpha$- and not the $\gamma$-position as in compound (LVI).

It is interesting to note that attack by $O_2$ on the compound with the eight-membered ring is directed to the $\alpha$-position of the hydrogenated ring relative to the nitrogen atom with formation of the corresponding cyclic ketone (LXII)



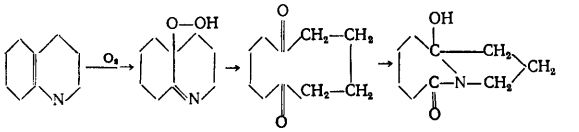
(LXII)

probably via a mechanism similar to that of the formation of 1-acetyl-2-ethylindole from 1,2-diethyl-2-hydroperoxyindole.

The rearrangements occurring in the series of indoles and tetrahydrocarbazoles in connection with structural changes in alkaloids such as quinamine and cinchonamine has been examined in a major article [126].

### 7. The Autoxidation of Octahydroquinoline

The autoxidation of octahydroquinoline (LXIII) [127] at room temperature in ethyl acetate leads to the absorption of 0.9 mole of $O_2$ per mole of compound with formation (in 87% yield) of the crystalline hydroperoxide (LXIV), which is relatively unstable at room temperature but is fairly stable at −5°C. In polar solvents, it is transformed into 7-hydroxy-1-azabicyclo[5,3,0]decan-2-one (LXVI)

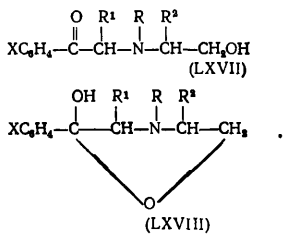


(LXIII) (LXIV) (LXV) (LXVI)

as a result of the rearrangement of the intermediate lactam (LXV).

### 8. The Autoxidation of Dihydro-oxazines

β-Hydroxyethylaminoacetophenones can exist in linear and cyclic forms. This tautomerism and its dependence on steric and polar factors have been discussed [128,129]:

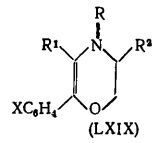


(LXVII)



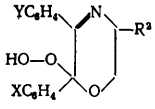
(LXVIII)

Some of these compounds have antimalarial and carcinolytic properties [128]. They readily split off $H_2O$, being converted into dihydro-oxazines [129]:

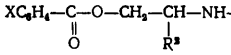


(LXIX)

When R = H and $R^1$ is a *para*-substituted phenyl group *p*-$YC_6H_4$, compounds (LXIX) readily give rise to hydroperoxides under the influence of atmospheric $O_2$:



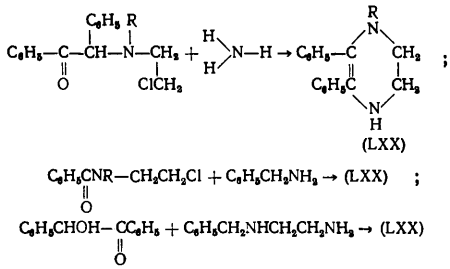
The hydroperoxides are unstable and decompose rapidly close to their melting points. On heating in an acid medium, they are converted into esters:



The hydroperoxides were isolated for the following substituents: $R^1 = CH_3$, X = Y = H or Cl; $R^2 = C_2H_5$, X = Y = H or Cl; $R^2 = C_6H_5$, X = Y = H, Cl, or $CH_3O$; $R^2 = C_6H_5CH_2$, $X = CH_3O$, Y = H. On the other hand, they could not be obtained in the presence of the following substituents: $R^2 = C_2H_5$, $X = CH_3O$, Y = H; $R^2 = C_6H_5CH_2$, $X = CH_3O$, Y = H, X = Y = Cl or X = Y = $CH_3O$.

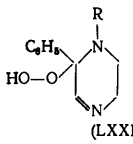
### 9. The Synthesis of 1,2-Dehydropiperazinyl Hydroperoxides

The attempts to synthesise *N*-alkyl(or aryl)-1,2-diphenyl-1,2-dehydropiperazines (in ethereal solution at 70–80°C) in the presence of atmospheric oxygen according to the mechanisms



(LXX)

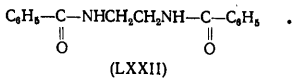
led to the formation of the hydroperoxides (LXXI) [130]:



(LXXI)

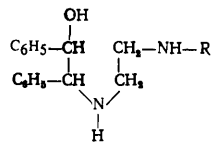
which are crystalline compounds, rapidly decomposing close to their melting points when R = $C_2H_5$, $C_6H_5CH_2$, or $C_6H_5$.

Their decomposition in an acid medium (3 *N* HCl) leads to dibenzoylalkylethylenediamines, e.g.



(LXXII)

Catalytic hydrogenation results in ring opening with formation of compound (LXXIII):



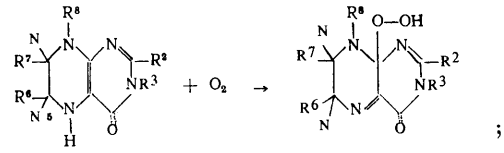
(LXXIII)

while reduction with $LiAlH_4$ yields the corresponding piperazine. The experiment has been described and discussed [130].

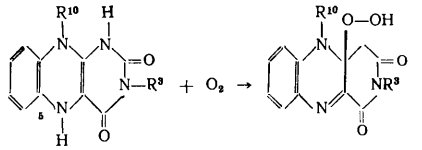
The attempts to synthesise compound (LXXI) with R = H by treating 1,2-diphenyl-4,5-dihydropyrazine with $H_2O_2$ led to the synthesis of its decomposition products only, which included, apart from the expected dibenzoylethylenediamine, a multiplicity of compounds, the nature and content of which varied as a function of the experimental conditions (for example, depending on the presence of water). It is interesting to note that in certain cases the ring may contract with formation of imidazolines [131].

Partly hydrogenated pyrazines and isoalloxazines, such as tetrahydropteridines (LXXVI) or dihydroisoalloxazines (LXXV), also give rise to the intermediate hydroperoxides

(XXVI) and (XXVII) as a result of autoxidation[132] (their presence has been established chemically and polarographically in some instances). An exception is the case where the nitrogen atom in the 5-position has a substituent:

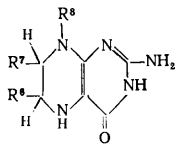


(LXXIV) (LXXVII)



(LXXV) (LXXVI)

In the pteridine series, 2-amino-4-hydroxy-derivatives have been investigated:



(1) $R^6=R^7=CH_3$ and $R^8=H$;
(2) $R^6=R^7=CH_3$ and $R^8=C_2H_5$ or $CH_2—CH_2OH$;
(3) $R^6=R^7=C_6H_5$ and $R^8=C_2H_5$ .

The first case has been investigated in particularly great detail. The initial solid compound is stable at room temperature, but in solution absorbs $O_2$ rapidly. The intermediate hydroperoxide interacts with the initial compound, forming a dihydro-derivative via the mechanism

$$H_3PterO—OH + H_4Pter \rightarrow 2H_2Pter + 2H_2O .$$

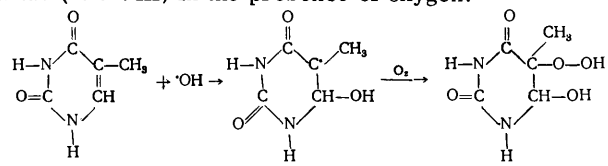
Tetrahydropteridines (cases 2 and 3) and the corresponding isoalloxazine with R = H behave similarly. In the presence of an appropriate reducing agent, $H_2Pter$ can be reconverted into $H_4Pter$. It has been noted that $H_4Pter$ has an accelerating effect on the oxidation of various compounds, for example thiols ($\beta$-mercaptoethanol, cysteine) as well as more complex compounds, for example dihydronicotinamide-adenine nucleotide. This effect has been examined in detail[132]. The possible involvement of tetrahydropteridine and dihydroisoalloxazines in biochemical hydroxylation is discussed in the same report[132].

5,6,7,8-Tetrahydrofolic acid and its 5-methyl derivative have been recently reinvestigated[189]. Traces of an organic peroxide could not be detected, but $H_2O_2$ was found in the distillation products. Hence one can apparently conclude that the oxidising radicals (chain-transfer agents) are HO–O· and not RO–O·, which leads to the formation of $H_2O_2$ and not ROOH.

## 10. Nucleic Acid Derivatives

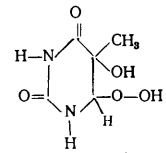
The influence of ionising radiation on the organism causes cell damage such as aberrations in chromosomes, mutation, and carcinogenesis, which are a result of changes at the molecular level. Radiation has a particular influence on the cell nucleus, since it has been established that the latter is twenty times more sensitive to radiation than cytoplasm. It is now believed that exposure to ionising radiation leads mainly to the formation of ·OH radicals, produced by the radiolysis of the aqueous medium. It was found previously that, in the radiolytic process, attack by the ·OH radicals is directed to the extent of 80% towards the pyrimidine base and only to the extent of 20% towards the sugar component of DNA. Purine bases are apparently more resistant to this attack. The foregoing findings suggest that the action of ionising radiation on pyrimidine bases *in vitro* in an aqueous medium is of considerable interest: since 1966, it has been the subject of numerous studies[133-150]. In particular, much attention has been devoted to thymine.[139-147]

The studies have shown that attack is directed mainly to the $C_{(5)}=C_{(6)}$ double bond; the preferred site of the initial attack by ·OH radicals is the 6-position, with formation of a hydroxy-radical, which gives rise to the hydroxyhydroperoxide (LXXVIII) in the presence of oxygen:



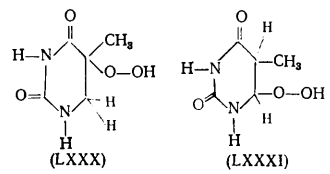
(LXXVIII)

Apart from the hydroxyhydroperoxide (LXXVIII) (consisting of a mixture of the *cis*- and *trans*-isomers), compound (LXXIX) was also obtained (as a result of attack by ·OH radicals in the 5-position):



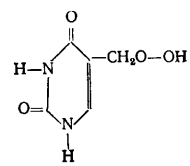
(LXXIX)

and the hydroperoxides (LXXX) and (LXXXI) as a result of attack by H· atoms in the 5- or 6-position:



(LXXX) (LXXXI)

Apart from the $C_{(5)}=C_{(6)}$ double bond, the $CH_3$ group in the side chain can also be attacked by ·OH radicals, which leads to the formation of the primary hydroperoxide (LXXXII):

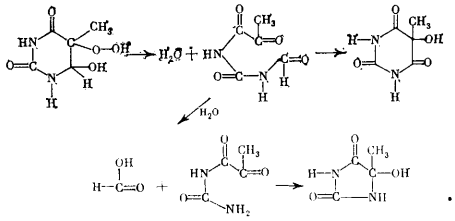


(LXXXII)

In a neutral medium, the rate of this reaction is very insignificant, but increases with increase in alkalinity owing to the aromatisation of the pyrimidine ring[143,147].

Hydrogen peroxide is also formed as a result of the dimerisation of ·OH radicals and the hydrolysis of the hydroxyhydroperoxides (LXV). The existence of these different peroxy-compounds has been established chromatographically[146] and spectroscopically (mass spectrometry, infrared and ultraviolet spectroscopy, NMR, ESR)[144]. NMR and particularly ESR made it possible to demonstrate the existence of intermediate radicals.

At 12°C, pH 5, and an irradiation dose of $9 \times 10^3$ rad $min^{-1}$, a reaction time of 1 h, and a concentration of 0.001 M, the contents of the hydroperoxides (LXXVIII), (LXXIX), (LXXX), and (LXXXI) were respectively 4.0, 4.4, 2.4, and 2.1%. The hydroperoxides (LXXVIII) and (LXXIX) were synthesised (by treating the corresponding glycol with $H_2O_2$). The hydroperoxide (LXXVIII) is fairly stable, decomposing slowly at 30°C. When thymine is radiolysed in an aqueous medium in the presence of $O_2$, the decomposition products of the hydroperoxide (LXXVIII) are formed, namely 5,6-dihydroxy-5,6-dihydrothymine, pyruvylurea, 5-hydroxy-5-methyl-barbituric acid, 5-hydroxy-5-methyl-hydantoin, urea, and formic and pyruvic acids:

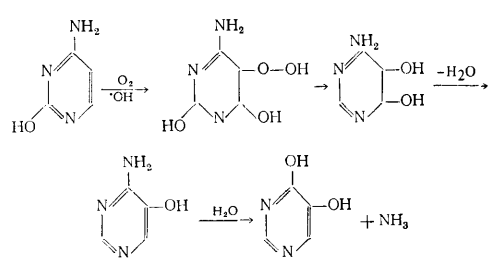


The results of a study of the radiolysis ($^{60}Co$ $\gamma$-radiation) of an aqueous solution of thymine (12°C, pH 5, dose $9 \times 10^3$ rad $min^{-1}$) have been published[145] and the kinetics of the formation of various compounds as a function of the irradiation dose (between $2 \times 10^2$ and $10^6$ rad) under the above conditions have been investigated[143,144].

Under analogous conditions, uracil also yields a hydroxyhydroperoxide, since the O–OH group is likewise located in the 5- or 6-position, but it is much more unstable than in the case of thymine; its presence has been detected by NMR.[148] Its decomposition products are similar to those of the hydroperoxide derived from thymine (with the $CH_3$ group replaced by an H atom); they include hydroxybarbituric acid, hydroxyhydantoin, formylglyoxylurea, and products of more extensive oxidation—alloxane, parabanic acid, and dialuric acid.

The complete list of compounds and the methods for their isolation in the radiolysis of uracil in an aqueous medium (at room temperature, pH 6, a concentration of 0.001 M, and a $\gamma$-radiation dose of 90 rad) has been published[148].

The hydroxyhydroperoxide derived from cytosine is still less stable than that derived from uracil. Thus irradiation of this base (under conditions similar to those described above) leads to the formation of isobarbituric acid via the mechanism[136,149]



Products of more far-reaching oxidation are formed from isobarbituric acid: alloxan, dialuric acid, and parabanic acid.[150]

Pyrimidine nucleosides and nucleotides also form peroxides under conditions similar to those in the formation of the corresponding bases[133]. Attack by ·OH radicals is mainly directed to the 6-position, in the double bond of the 5,6-pyrimidine ring, and not to the bond between the nitrogen-containing base and the monosaccharide or between the monosaccharide and phosphoric acid.[154]

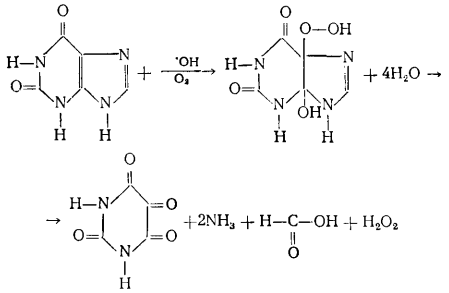
The radiolysis of thymidine has been investigated at 16°C, pH 6, and an irradiation dose of $8 \times 10^3$ rad.[152,190] Molecular asymmetry at the level of the sugar component indicates the occurrence of diastereoisomerism leading to the formation of two forms of the *cis*-peroxide derived from 5-hydroperoxy-6-hydroxy-5,6-dihydrothymidine and two forms of the corresponding *trans*-hydroperoxide. These hydroxyhydroperoxides have properties similar to those of the hydroxyhydroperoxide derived from thymine. In particular, they are readily hydrolysed to the corresponding glycols (with retention of the configuration), which are the main reaction products.

The presence of the sugar component makes the pyrimidine ring appreciably resistant to the dissociation of the $C_{(5)}=C_{(6)}$ bond. Indeed hydroxymethylribofuranylbarbituric acid, which can be obtained as a result of the rearrangement of formylpyruvylribofuranylurea, could not be detected[152].

The formation of organic peroxides and $H_2O_2$ was also established following the irradiation of an aqueous DNA solution (at 22°C, a concentration of 0.001 M, and a dose of $7 \times 10^3$ rad).[163] The kinetic curves for the decomposition of these peroxides at 52°C, 62°C, 72°C, and 79°C indicate the existence of two different peroxy-compounds[153], which are in all probability hydroxyhydroperoxides derived from thymine and cytosine nucleotides. These hydroperoxides probably play an important role in the development of the consequences of the irradiation of organisms as a result of their further decomposition into the products discussed above[153].

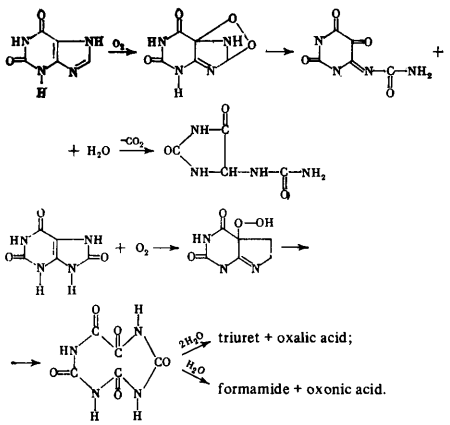
It is noteworthy that only pyrimidine compounds are formed. Indeed not even traces of a peroxide could be detected after the irradiation of an aqueous solution of quanine and adenine as well as their nucleosides and nucleotides[133].

However, purine bases can be subjected to oxidative degradation under the influence of $\gamma$-radiation in an aqueous solution with rupture of the imidazole ring. Thus xanthine is converted into alloxan, formic acid, $NH_3$, and $H_2O_2$. The preferred site attacked by the ·OH radical is apparently the $C_{(4)}=C_{(5)}$ double bond. In order to account for the formation of the above compounds[155], the formation of very unstable hydroxyhydroperoxides was postulated:



In addition, purine bases (in contrast to pyrimidine bases) decompose at room temperature as a result of sensitised photochemical oxidation. For example, in an aqueous alkaline medium containing added dyes, they absorb approximately one mole of $O_2$ following exposure to light with formation of various decomposition products consisting of allantoin in the case of xanthine and triuret in the case of uric acid.

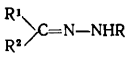
In order to account for the formation of these compounds, it was suggested that a very unstable endoperoxide (in the case of xanthine) and a very unstable hydroperoxide (in the case of uric acid) are formed as intermediates:



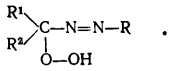

The compounds formed in accordance with the experimental conditions have been described and their formation discussed [156,157].

## VII. THE OXIDATION OF HYDRAZONES

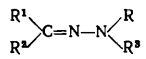
Hydrazones having the general formula



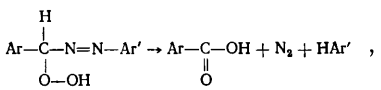
yield hydroperoxides on autoxidation at room temperature in an organic solvent:



Hydrazones disubstituted at the nitrogen atom are not oxidised under these conditions.

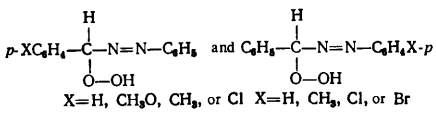


The hydroperoxides derived from hydrazones are yellow crystalline substances, which explode in the dry state, are more or less stable in solution, are soluble in alcohol and ether, and are sparingly soluble in petroleum ether. They decompose to a carboxylic acid, a hydrocarbon, and nitrogen,



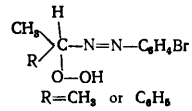
and on reduction (with KI in acetic acid) give rise to the corresponding hydroxy-derivatives, which rearrange to acylhydrazines.

Hydroperoxides of the type



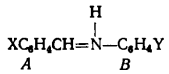

have also been investigated.

Apart from the above hydroperoxides, there exist a further two hydroperoxides:



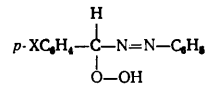

Hydrazone hydroperoxides were obtained for the first time by Bush and Dietz [158] and their structures have been established by Pausacker [159] and Criegee and Lohaus [160].

Any substituent in ring *A* of the hydrazone having the general formula



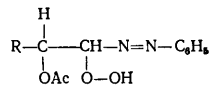
decreases the rate of autoxidation; the autoxidation is accelerated in the presence of nucleophilic substituents and is retarded in the presence of electrophilic substituents in ring *B*. [159]

The stability of the hydroperoxides

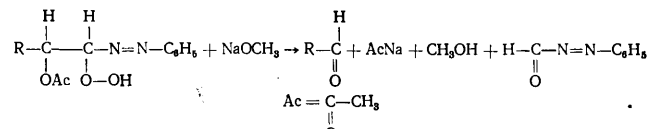


increases in the presence of nucleophilic substituents and diminishes in the presence of electrophilic substituents. For example, when **X** = $CH_3O$, the hydroperoxide decomposes very slowly at room temperature and can be stored for several weeks at 0°C, while in the case where **X** = Cl it decomposes already during crystallisation [161].

Interesting results have been obtained for hydrazones derived from monosaccharides. [162] Thus when a stream of $O_2$ is passed into a benzene solution of penta-acetylgalactose phenylhydrazone, the product is the hydroperoxide



which decomposes under the influence of sodium methoxide in methanol solution to lyxose and *N*-phenyldi-imine formate:



Deoxyarabinose is formed similarly from rhamnose.

Thus the above method can be convenient for the synthesis of $C_{n-1}$ monosaccharides from a $C_n$ monosaccharide.

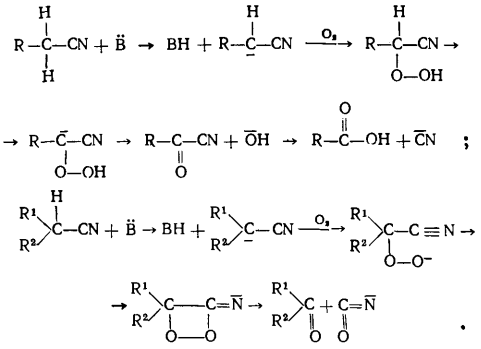
## VIII. THE BASE-CATALYSED AUTOXIDATION OF AZO-COMPOUNDS VIA AN IONIC MECHANISM

### Nitriles

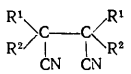
The autoxidation of a number of mono- and di-substituted nitriles (phenyl-, diphenyl-, and cyclohexylphenyl-acetonitriles) has been examined [163,164] and it has been established that there is no absorption of $O_2$ at room temperature even in solvents such as pyridine, but it begins rapidly after the addition of a strong base (sodium methoxide, benzyltrimethylammonium hydroxide), reaching a maximum

of 0.7–0.8 mole of $O_2$ in the course of several hours. Disubstituted nitriles lead to the formation of ketones and cyanates, while monosubstituted nitriles yield benzoic and hydrocyanic acids (in the form of alkali metal salts). The yield of benzophenone from diphenylacetonitrile is 65%.

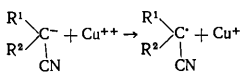
The following reaction mechanism has been proposed [164]:



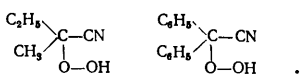
In the presence of copper ions (1–2 mole %), the acceleration of the absorption of $O_2$ is accompanied by the formation of the dinitriles



which are apparently a result of the dimerisation of the radicals formed via the mechanism

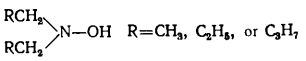


When the oxidation was carried out at −40° and −75°C with added $(CH_3)_3COK$ in solution in $CH_3OCH_2CH_2OCH_3$, pure hydroperoxides were obtained from the corresponding nitriles in 67% yield:



## Hydroxylamines

The study of the autoxidation of symmetrical disubstituted aliphatic hydroxylamines (in the form of oxalates) [165,166]



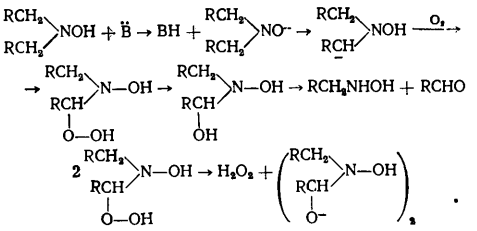
shows that alkalis have a marked accelerating effect on the absorption of $O_2$. $Mn^{2+}$ and particularly $Cu^{2+}$ ions greatly accelerate the absorption of $O_2$.

A monosubstituted hydroxylamine ($RCH_2NHOH$) aldehydes (RCHO), and peroxy-compounds are formed in the autoxidation reaction. The content of peroxides passes through a maximum, then falls, but does not reach zero. The formation of $H_2O_2$ and of an organic peroxide from the compound



has been demonstrated by the polarographic method [166]. However, the latter could not be isolated in a pure state.

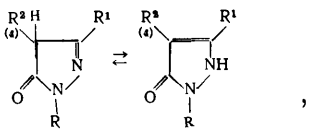
The following mechanism of the reaction involving the formation of a hydroperoxide, a dialkyl peroxide, and $H_2O_2$ is possible:



The accelerating effect of metal ions can probably be accounted for by the conversion of anions into radicals, as for nitriles.

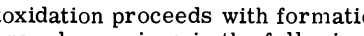
## Pyrazolones

Pyrazolones, which exist in two tautomeric forms,

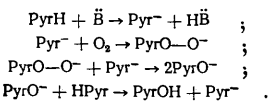


are converted in the presence of atmospheric oxygen into the corresponding dimers linked via the carbon atoms in the 4-positions. The study of the autoxidation of pyrazolones with R = $C_6H_5$, $R^1 = CH_3$, and a variable $R^2$ shows that one mole of $O_2$ is absorbed in an alkaline medium [167].

The primary autoxidation products are apparently pyrazolones hydroxylated in the 4-position, which yield dimers as a result of the reaction with the initial pyrazolone [167]:



The autoxidation proceeds with formation of intermediate pyrazolone anions in the following manner:



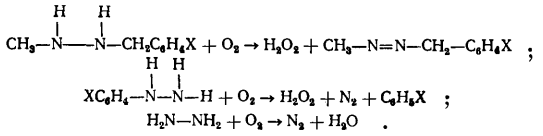
This mechanism has been discussed in detail with changes caused by any change in the nature of the base [167].

The autoxidation of 3,4-dialkyl-1-(methylpiperidinyl)-5-pyrazolones, which have interesting pharmacological properties, has been examined. A study has also been made of pyrazolidine-3,5-diones [169].

# IX. THE INTERACTION OF HYDRAZINES WITH OXYGEN

Hydrazines containing at least one hydrogen atom linked to each nitrogen atom undergo autoxidation at room temperature (in the form of salts in aqueous solution) with dissociation of N–H bonds and the formation of $H_2O_2$ and a diazo-compound. The latter may decompose into $N_2$ and a hydrocarbon. The rates of the reactions of *N*-benzyl-*N'*-methylhydrazines [170], *N*-arylhydrazines [171], and

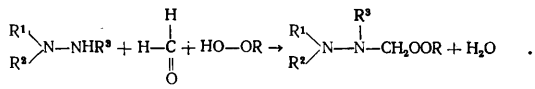
unsubstituted hydrazine [172] at room temperature are consistent with the following equations:



The reactions are vigorously catalysed by $Cu^{2+}$ ions.

In the presence of $O_2$, hydrazines exhibit a cytotoxic activity owing to the possible formation of $^{\cdot}OH$ radicals (via the reaction between $H_2O_2$ and the initial hydrazine), which disrupt the structure of nucleic acids by adding to the $C_{(5)}=C_{(6)}$ double bonds of the pyrimidine bases. We may note that benzyl-*N*-isopropyl-*N*-methylcarbamoylhydrazine is present in the blood and in urine and is probably capable of being oxidised *in vivo*, exhibiting a cytotoxic activity [170,173-175].

Despite the absence of hydroperoxides from the autoxidation products of hydrazines, it has been possible to obtain several peroxides (derived from these compounds) by treating hydrazines with RO–OH in the presence of formaldehyde [191]:



We may note that in certain instances hydroperoxides can be obtained when RO–OH is replaced by $H_2O_2$.

## X. THE INTERMEDIATE FORMATION OF PEROXIDES IN THE BIOLUMINESCENCE PROCESS

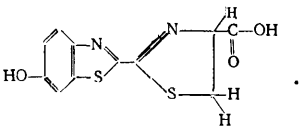
Since many substrates exhibiting bioluminescence contain nitrogen, it was thought useful to examine briefly the intermediate formation of peroxides at the instant of the manifestation of bioluminescence.

Luminescing organisms are frequently encountered among animals, particularly among the marine fauna. The only luminescing organisms among vertebrates and plants are fish and fungi respectively. Luminescence is also characteristic of certain bacteria. However, only a few of the many thousands of the existing species of organisms have so far been investigated owing to the difficulty of collecting them and the very low content of the active compound (several milligrams per tens of thousands of individuals).

All the reactions associated with the manifestation of bioluminescence require oxygen or a peroxide formed beforehand. In the presence of the enzyme luciferase, the substrate called luciferin is oxidised. During the last decade, bioluminescence has been the subject of serious research and development [195-200].

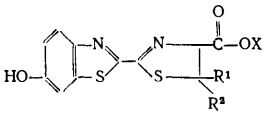
### Luciferins

Particular attention has been devoted to the study of the luciferin of the North American *Photinus pyralis*, which emits a bright yellow light. The luciferin from *Photinus pyralis* was isolated in a pure form and characterised by elemental analysis infrared spectroscopy [201], and by the identification of the decomposition products [202]. It is a benzothiazole derivative having the formula



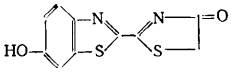
It was synthesised by treating cysteine with 2-cyano-4-hydroxybenzothiazole. [202] The corresponding luciferase was also isolated. Its molecular weight is 100 000 and it has an isoelectric point of 6.2–6.3. [203]

Numerous luciferin derivatives having the general formula [215]

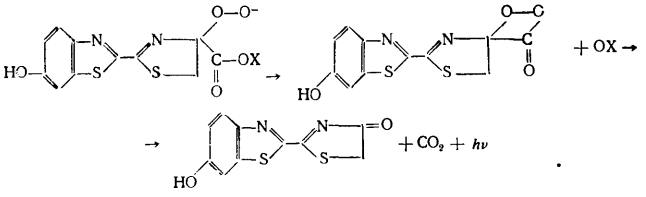


where X = $C_6H_5$ or adenyl, $R^1 = R^2 = CH_3$, or $R^1 = H$, and $R^2 = CH_3$, have also been synthesised. The disubstituted derivative ($R^1 = R^2 = CH_3$) is particularly interesting because it cannot decompose via dehydroluciferin (which is readily formed when $R^1 = R^2 = H$). The bioluminescence arises as a result of the enzymatic oxidation of luciferyl adenylate formed when adenosine triphosphoric acid is acted upon by luciferin in the presence of luciferase and $Mg^{2+}$ ions.

The light emitting compound is the lactam

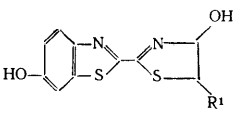


(in the excited state), which is probably formed via the very unstable dioxetan:

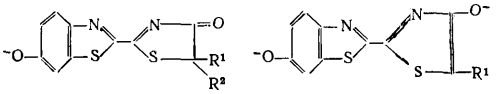


Indeed one mole of $O_2$ per mole of compound is absorbed and one mole of $CO_2$ per mole of compound is evolved in the bioluminescence process.

The above lactam was identified and isolated (in the form of the diacetate) from glow worm extracts [204]. Furthermore, the chemiluminescence spectrum of luciferin is identical with the fluorescence spectrum of the lactam, synthesised [204] by the condensation of the above nitrile with ethyl thioglycolate. Similar lactams have also been obtained from various substituted luciferin derivatives [205]. The chemiluminescence of these lactams varies with pH owing to the possibility of their existence in the enolic form



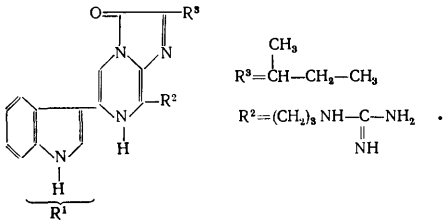
which can lead to the formation of a mono- or di-anion in an alkaline medium:



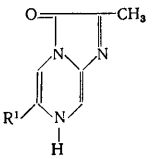
When $R^1 = R^2 = CH_3$ in the disubstituted derivative, only the monoanion can exist.

## The Bioluminescence of Cypridina hilgendorfi

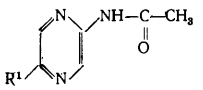
This crustacean lives in the Sea of Japan and near the shores of Jamaica. When the contents of two glands containing luciferin and luciferase respectively are introduced into air-saturated water, a blue glow is observed. The luciferin of this crustacean was identified[208] as an indolopyrazine derivative having the formula



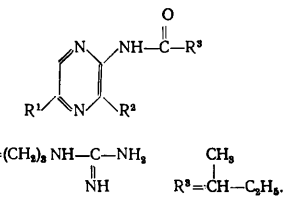
Simpler model compounds



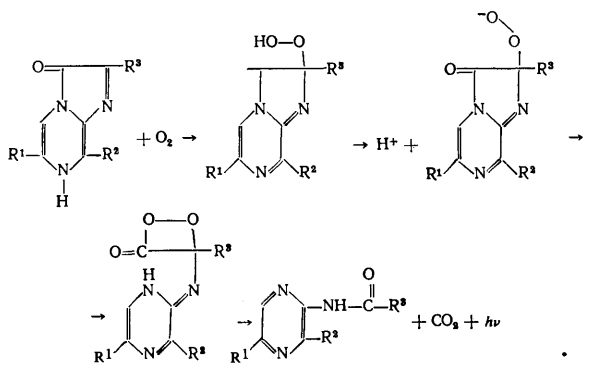
where $R^1 = C_6H_5$ [209] or β-indolyl [210], have also been synthesised. They inhibit luminescence and decompose after the absorption of $O_2$ into the corresponding amides:



Luciferin itself (obtained from natural extracts) absorbs $O_2$ in the presence of luciferase and evolves $CO_2$ in equimolar amounts[211,212]. The reaction yields the amide

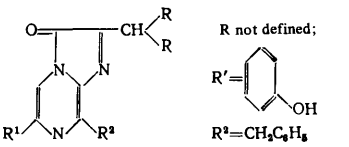


All the foregoing facts suggest the following sequence of reactions proceeding via an intermediate dioxetan, yielding an amide in an excited state:

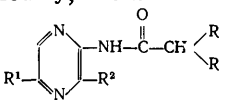


## The Bioluminescence of the Jellyfish *Renilla* and *Aequorea*

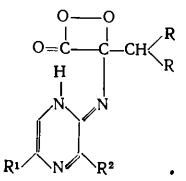
The mechanism of the bioluminescence of the jellyfish *Renilla* is similar to that of Cypridina, but is more complex. Since a photoprotein, containing a peroxide formed beforehand, is present in this organism apart from luciferin identical with that from Cypridina [213], light emission begins only after the addition of ions (in the presence of $O_2$). The luciferase from *Aequorea* [214] has the following structure:




In conformity with a sequence of reactions analogous to that described previously, the amide

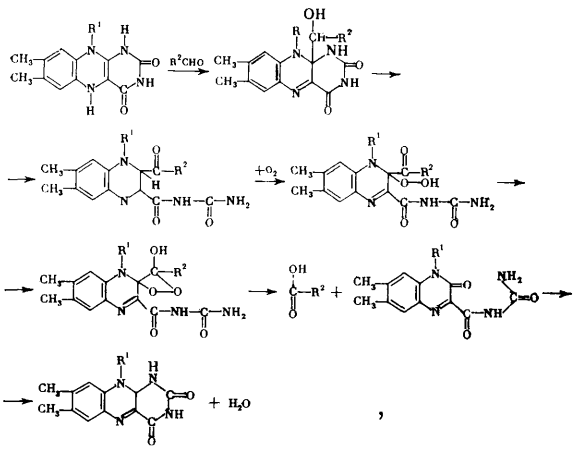


is obtained in an excited state via the intermediate dioxetan



## The Bioluminescence of Bacteria

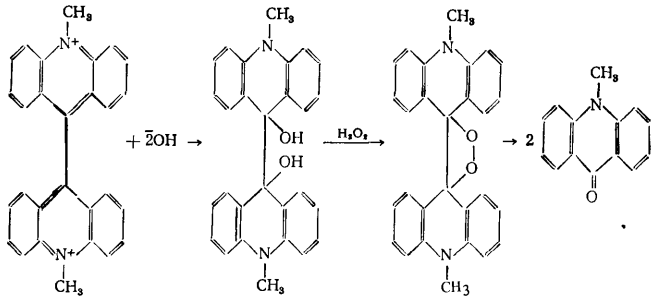
The luminescence of fish, dead animal tissues, and plants is caused by bacteria, various species of which have been described[215]. In this case, there is no luciferin or luciferase, but two other compounds are active: flavinmononucleotide (in a reduced form) ($FMNH_2$) and a linear long-chain aliphatic aldehyde. The aldehyde is apparently oxidised to the corresponding acid[217,218] in an excited state via the peroxide in accordance with the mechanism



where $R^1$ = ribosyl and $R^2$ = aldehyde group.

Synthetic Luminescent Compounds

Studies have shown that the conversion of lucigenin (*NN*-dimethyl-2,9-biacridinium dinitrate) under the influence of $H_2O_2$ in an alkaline medium into *N*-methylacridone (in an excited state), accompanied by the emission of a green light, proceeds via the formation of an intermediate peroxide[218]:



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# Photochromic Polymers

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The chief methods of preparation and the photochromic properties of polymers containing covalently bound photochromic groups in the main or a side chain of the macromolecule are surveyed. The properties of such polymers differ from those inherent in analogues of low molecular weight or in mechanical mixtures of the latter compounds with polymers. The difference in behaviour is explained by the steric and polar influence of the macromolecule on the initial and the photo-induced forms of the photochromic compound. A list of 55 references is included.

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## I. INTRODUCTION

The phenomenon of photochromism—a reversible change in colour under the influence of light of definite wavelength—is observed in many classes of organic compounds, and during recent years has been intensively studied in connection with the wide prospects for its application. Photochromic materials may be used to obtain images and as memory units in electronic computers and light filters of variable density, automatically varying the transmission according to the conditions of illumination[1,2].

Comparatively recently several papers have appeared on the preparation and study of a new class of photochromic compounds—polymers containing covalently attached photochromic groups in the main or a side chain. Methods for preparation and the photochromic behaviour of polymers containing mainly spiropyran groups have been surveyed by Smets[3].

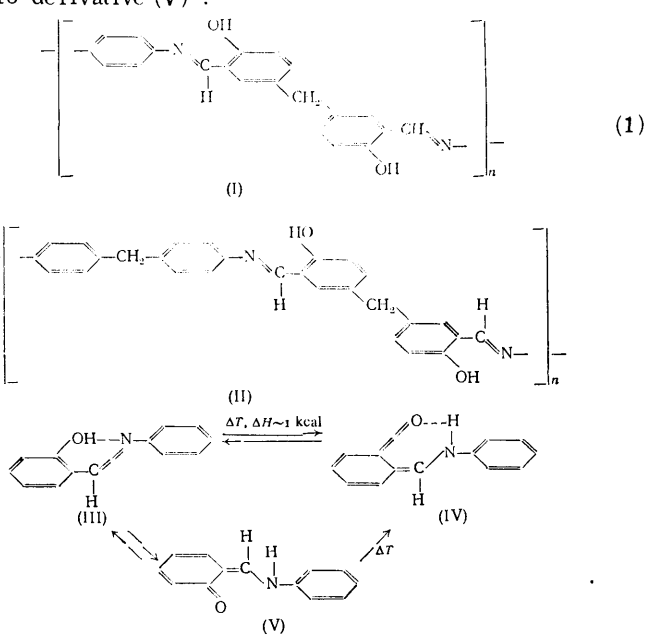
The photochromism of the simpler organic compounds may be due to isomerisation, heterolytic and homolytic bond cleavage, tautomerism, redox reactions, dimerisation, and triplet transitions. Various aspects of the photochromism of organic substances have been covered in a number of reviews and monographs[4-6]. The development of photochromic polymers is based on the assumption that the same mechanisms underly their action.

Distinctive features of the photochromism of polymers are the restricted mobility of the photochromic groups contained in the macromolecule, the dependence of their properties on the conformation, and the influence of the polarity of the comonomer. The present Review considers the main methods of preparing polymers containing covalently linked photochromic groups, the kinetic and spectral behaviour of the polymers in solutions and in films as functions of their chemical nature and structure, and also the photochemical reactions of the polymers. In order to study the steric and polar influence of the macromolecule on the behaviour of the photochromic groups, the properties of copolymers are compared with those of relatively simple photochromic compounds (model compounds), and also with solid solutions of photochromic compounds in a polymer matrix (photochromic matrix polymers).

The Review does not cover many papers on matrix polymers in which attention was paid mainly to investigating the mechanism of photochromic transitions in relatively simple compounds, with the polymers used merely as media for such investigations.

## II. PHOTOTAUTOMERISATION WITH MIGRATION OF HYDROGEN

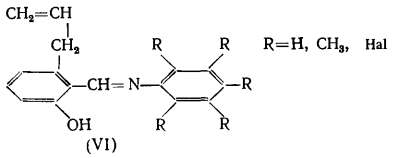
The photochromism and thermochromism of polyazomethines containing a salicylidenanil group in the main polymer chain (I) and (II) was studied by Laverty and Gardlund[7]. The phototautomerisation of anils involves intramolecular migration of hydrogen from an *o*-hydroxy-substituent (III) to the azomethine group to form a *trans*-keto-derivative (V)[7]:




(1)

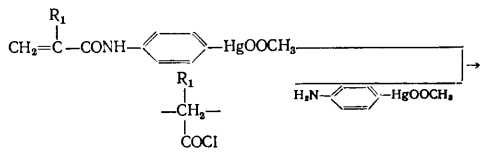
The *trans*-keto-form of the anil isomerises thermally into the *cis*-keto-form (IV), which is converted into the *cis*-enol (III) before equilibrium is established. The polymers (I) and (II), which are insoluble in the usual organic solvents, are not photochromic: they exhibit only the thermochromic transition (III) → (IV), but the bathochromic shift when heated from 25 to 100°C is merely 20 nm.

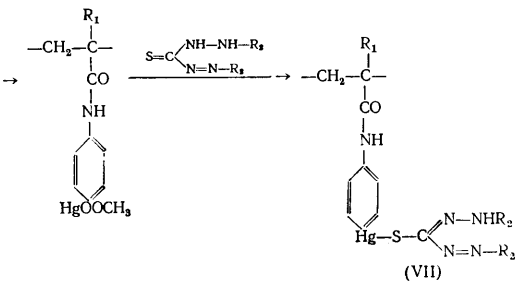
Photochromic polyazomethines can be obtained[8] by the copolymerisation of styrene and methyl methacrylate with the unsaturated salicylidenanil derivative



(VI)

Photochromic transitions in copolymers of the two monomers with unsaturated derivatives of mercury dithiozonates were subjected to detailed investigation by Kamogawa et al.[9,10] Such polymers were obtained by various polymer-like conversions[9-12]:

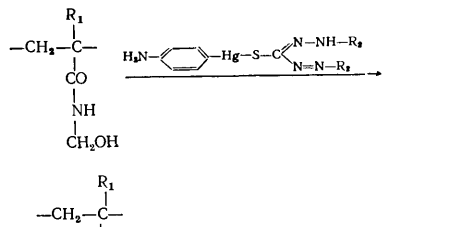


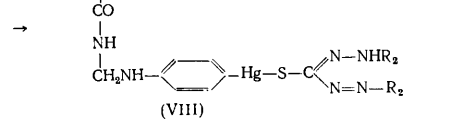



(VII)

(2)

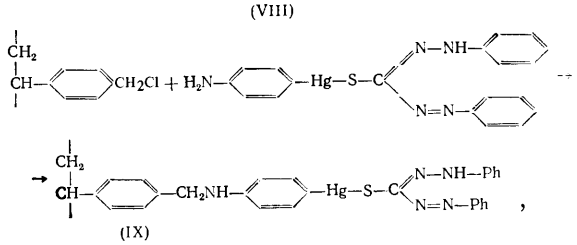
(3)



(VIII)

(4)

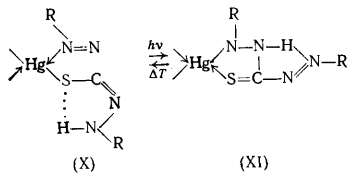


(IX)

(5)

where $R_1$ = H, $CH_3$ and $R_2$ = $C_6H_5$, 2-$C_{10}H_7$, *p*-$C_6H_4Br$, *p*-$C_6H_4Cl$, *p*-$C_6H_4CH_3$, *o*-$C_6H_4CH_3$, *o*-$C_6H_4OCH_3$, *o*-$C_6H_4CF_3$.

The photochromism of metal dithiozonates is due to geometrical isomerisation of the ligand about the C=N bond with migration of hydrogen (X) → (XI):



(X) (XI)

(6)

In the copolymers (VII)–(IX) the initial form (X) absorbs at 500 nm, but the photoinduced (XI) in the region of 600 nm. Photocoloration and thermal decoloration are described by first-order equations. The rates of forward and reverse reactions depend on the composition of the copolymer, the chemical structure of substituents in the dithiozonate group, and the viscosity of the system.

The steric influence of the macromolecule depends on the mobility of the comonomer. The rate of thermal fading of copolymers of (VII) with styrene is lower than that of copolymers containing more mobile residues (the copolymer with methyl acrylate)[9]. Both forward and reverse reactions are slowed down by the introduction into the dithiozonate group of electron-accepting substituents ($R_2$ = *o*-trifluoromethylphenyl) or substituents that cause steric hindrance ($R_2$ = 2-naphthyl, *o*-tolyl)[10]. Electron-donating and electron-accepting substituents produce bathochromic and hypsochromic shifts respectively in the spectra of initial and photoinduced forms.

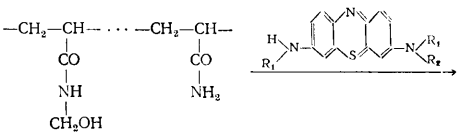
Photoconversion and decolorisation are greatly retarded in films of copolymers of (VII)–(IX) owing to the considerable steric hindrance to *cis–trans*-isomerisation. This is confirmed by the shortening by a factor of 50 in the half-period of the dark reaction of copolymers of (VII) with styrene when the temperature is raised from 15 to 65°C, and also by the lowering of the glass point $T_{gl}$ of the polymer and the increase in the rate of photochromic conversions of the copolymers with increase in the content of butyl acrylate groups[9].

## III. REDOX POLYMERS

The reversible photodecolorisation of thionine introduced into a polymer chain in the presence of a reductant ($Fe^{2+}$), which was accompanied by photochemical redox reactions, was first observed by Kamogawa[13]. Photochromic polymers have been obtained also by the copolymerisation of a thionine monomer (XII) with acrylamide[14] and by chemical reactions on polymers[14-16]:

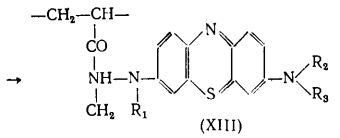


(XII)




(8)†

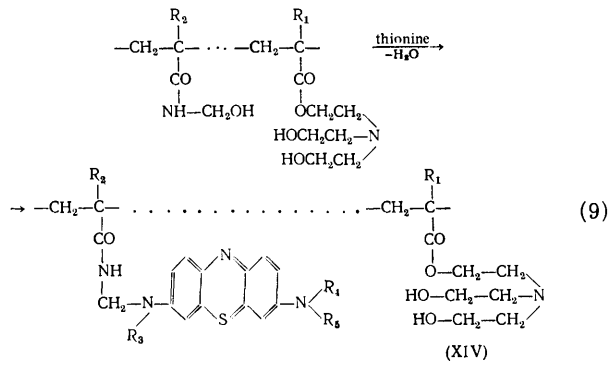
† Equation (7) is absent from the Russian text (Ed. of Translation).



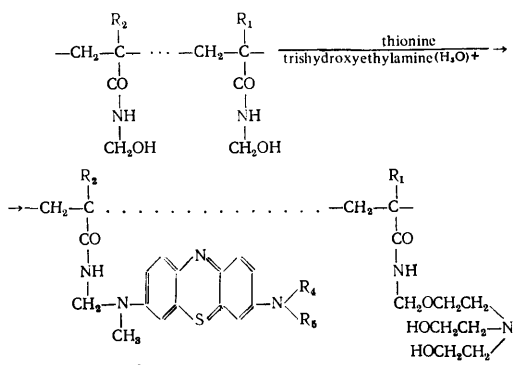
(XIII)

$R_1=R_2=R_3=H$; $R_1=H$, $R_2=R_3=CH_3$;
$R_1=R_2=R_3=CH_3$; $R_1=R_2=H$, $R_3=CH_3$; $R_1=CH_3$, $R_2=R_3=H$

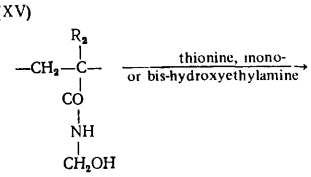
Polymers containing thionine dye and hydroxyethylamine residues have been synthesised[16]:

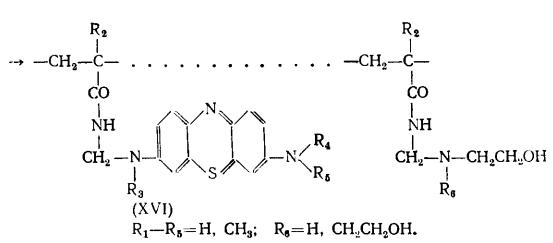


(XIV) (9)



(XV) (10)

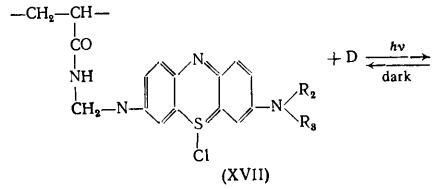




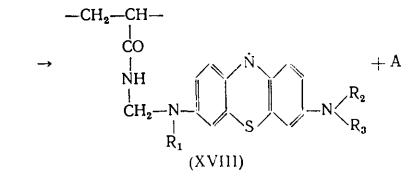
(XVI) (11)

$R_1$—$R_5$=H, $CH_3$; $R_5$=H, $CH_2CH_2OH$.

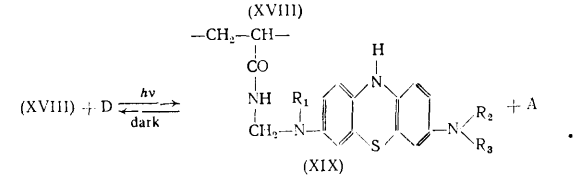
In the solid state thionine polymers fade reversibly (absorption diminishes in the region of 600 nm) on exposure to visible light. Kamogawa[15] attributed this reaction to photoactivated reduction of the coloured form of thionine (**XVII**), in the presence of an electron donor D, to the colourless semiquinone form (**XVIII**), which disproportionates rapidly into the colourless leuco-thionine (**XIX**) and the coloured thionine (**XVII**) forms:



(XVII)



(XVIII) (12)



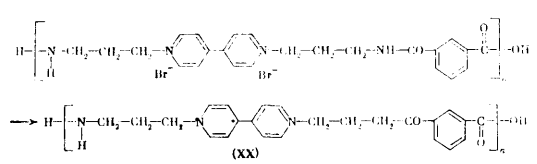
(XIX)

The reverse reaction takes place in the dark, and involves slow oxidation of leuco-thionine successively to the semiquinone and to the coloured thionine form in the presence of an electron acceptor A.

Introduction of electron-donating components such as $Fe^{2+}$ ions, poly(vinyl alcohol), hydroxyethylamines, certain enzymes (e.g. papain) confers considerable photosensitivity on the polymers. However, the mechanism of reaction (12) is probably more complicated, since the photochromic behaviour of thionine systems depends in considerable measure on the moisture content of the polymer film. It is suggested[15] that water molecules adsorbed on active groups in the polymer, just like atmospheric oxygen, are involved in redox reactions. Increasing the concentration of the donor D in the polymer chain somewhat enhances the sensitivity to photochromic reactions, but hydroxyethylamine residues inserted into the polymer chain are comparable with the monomeric analogues in effectiveness[16].

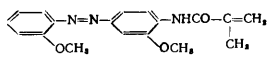
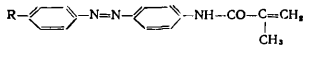
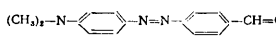
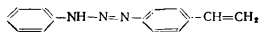
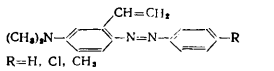
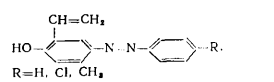
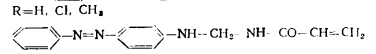
The rate of fading is somewhat affected by the method of preparation of the thionine polymers. Increasing the acidity of the polymer films (**XV**) diminishes the electron-donating power of the hydroxyethylamine residues, with a consequent slower rate of fading of the polymer[16]. The rate of restoration of the colour diminishes on introduction of the iron(II)–(III) system as carboxylate salts[15].

Photochromic redox polymers containing an *NN'*-dialkyl-4,4'-bipyridinium group (a viologen) have recently been prepared and studied[17]. New polyviologens (**XX**) and (**XXa**) possessing film-forming properties have been obtained by the interfacial polycondensation of *NN'*-bis-aminoalkyl-4,4'-bipyridinium salts with di-, tri-, or tetra-functional acid derivatives. On chemical and electrical reduction or exposure to light the polymer films become coloured owing to formation of a viologen radical:



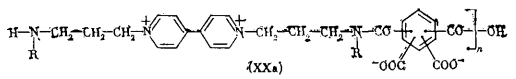
(XX) (13)

**Table 1.** Photochromic polymers containing azo-groups, obtained by radical copolymerisation.

| Copolymer | Photochromic monomer | Comonomer or comonomer mixture (mole %) | $10^{-3}$ *M* | Photochrome, mass % | Ref. |
|---|---|---|---|---|---|
| (XXI) a |  | $CH_2=C(CH_3)-COOH$ | — | 3.6 | 20 |
| b | | $CH_2=CH-COOH$ | 50—200 | 1.2 | 20 |
| (XXII)* a | | $CH_2=C(CH_3)-COOH$ | 150 | — | 21 |
| | | | | | 24 |
| b |  | $CH_2=C(CH_3)-COOH$ $CH_2=C(CH_3)-COOCH_3$ (60 : 40) | 225 | — | 21 |
| c | | $CH_2=C(CH_3)-COOCH_2CH_2N(CH_3)_2$ | 75 | 0.8—1.0 | 21 |
| d | | $CH_2=C(CH_3)-COOH$ $CH_2=C(CH_3)-COOCH_2CH_2N(CH_3)_2$ (50 : 50) | 88 | — | 21 |
| e | |  | 0.15** | 5*** | 27 |
| f | | $CH_2=C(CH_3)-COOCH_3$, $CH_2=C(CH_3)-COOC_2H_5$ | 0.12—0.16** | 9—10*** | 27 |
| g | | $CH_2=C(CH_3)-COOH$ | — | — | 24 |
| (XXIII) a |  |  | 0.13* | 2.5—2.9** | 14,25 |
| b | | $CH_2=C(CH_3)-COOCH_3$ | 0.15* | 0.7—1.3** | 14,25 |
| (XXIV) |  |  | — | — | 14 |
| (XXV) |  R=H, Cl, $CH_3$ |  | — | — | 14 |
| (XXVI) |  R=H, Cl, $CH_3$ | $CH_2=C(CH_3)-COOCH_3$ and $CH_2=CH-COOC_2H_5$ | — | — | 14 |
| (XXVII) |  |  | — | — | 14 |
| (XXVIII) |  | $CH_2=C(CH_3)-COOCH_3$ | 0.26* | 3*** | 27 |

* R = $N(CH_3)_2$ and $^+N(CH_3)_3$ for copolymer (XXIIg); R = H for the remaining copolymers (XXII).
** Intrinsic viscosity of the polymer.
*** Photochrome content, mole %.

With pyromellitoyl chloride a betaine type of polymer is formed:



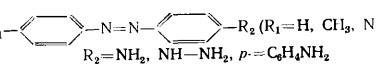
(XXa)

(R = H, $CH_2CH_2CH_3$)

Decolorisation of the films takes place in air in the dark after 8 h, or under the influence of water after 1 min.

## IV. *cis–trans*-ISOMERISATION OF AZO-GROUPS

The principle of *cis–trans*-isomerisation about the N=N bond has been utilised for the preparation of photochromic polymers containing an azo-group. Copolymers containing an azo-group in the side-chain have been obtained by the radical copolymerisation of vinyl derivatives of azo-compounds with unsaturated monomers. Similar photochromic copolymers can be prepared also by chemical modification of poly-*o*-hydroxystyrene with diazonium salts of aniline derivatives or of a ternary copolymer of *N*-hydroxymethylacrylamide with derivatives of *p*-aminoazobenzene[14,18]



$R_2 = NH_2$, $NH-NH_2$, $p$-$C_6H_4NH_2$

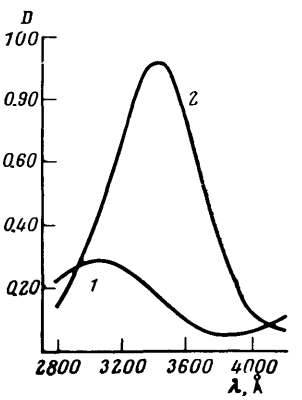


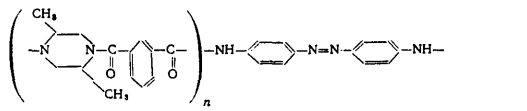
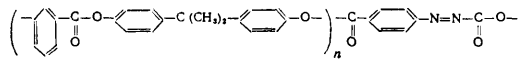
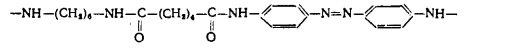
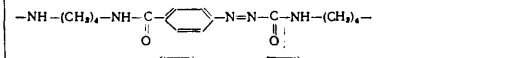
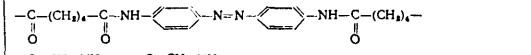
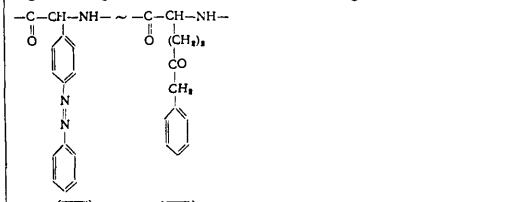
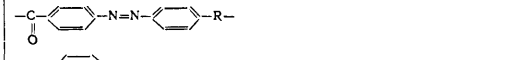
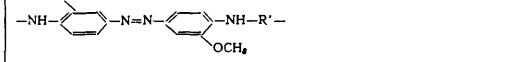
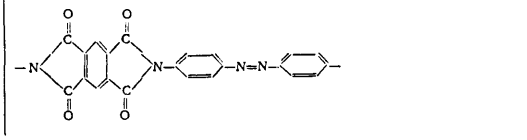

Figure 1. Absorption spectra of *p*-acetamidoazobenzene (0.01 M at pH 8): 1) initial form; 2) photoinduced form.

Polycondensation has been used to introduce an azo-group into the main chain of the polymer. Data on the structure and the composition of copolymers obtained by radical copolymerisation and copolycondensation are summarised in Tables 1 and 2 respectively.

Initial and photoinduced forms of the azo-group usually have absorption bands close together in the near ultraviolet or the visible spectrum (Fig. 1).

Goodman and Falxa showed[19] that the photoisomerisation of azo-groups on introduction into a polypeptide chain (XXXIII) (Table 2) is accompanied by a change in the optical activity of the isomers. The photochromic properties of polymeric azo-compounds are strongly influenced by the conformation of the macromolecule. This effect is especially clearly developed in polyelectrolytes containing an azo-group in the side-chain. Polymers of this type were first obtained by Lovrien[20] (XXIa, b) and later by Fink[21] (XXIIa, c, d) (Table 1).

Table 2. Photochromic polycondensation polymers.

| Polymer | Repeating unit | Ref. |
|---|---|---|
| (XXIX) |  | 27 |
| (XXX) |  | 27 |
| (XXXI) |  | 27 |
| a (XXXII) |  | 26 |
| b |  | |
| (XXXIII) |  | 19, 33 |
| (XXXIV) |  | |
| a |  | 32 |
| b |  | |
| c |  | |
| (XXXV) |  | 32 |
| a |  | |
| b |  | |
| (XXXVI) |  | (29) |

Both photoinduced and dark reactions are influenced by conformational transitions of polyelectrolyte macromolecules depending on their degree of ionisation, so that the isobiestic wavelength in the absorption spectra of copolymers of acrylic acid and 4-acrylamido-2,2′-dimethoxyazobenzene (XXIa, b) depends on the pH and becomes considerably shorter with increase in the reduced viscosity (pH 5–7) owing to uncoiling of the polyelectrolyte chains[20]. This is responsible also for the diminution in the rate of the dark reaction of (XXIb) at pH 6–10, although the rate of transition of the model monomeric azo-compound increases in the same pH range because of the catalytic effect of hydroxide ions[20].

The pH dependence of the rate of the dark *cis–trans*-isomerisation of azo-groups is influenced by the type of polyelectrolyte[21]. At pH < 8–9 the macromolecule of the polyanion of (XXIIa, b) is coiled up, which slows down the isomerisation; conversely, this transition is facilitated when the macromolecule has straightened out (pH > 8–9). The rate constant of the dark reaction of (XXIIa, b) has its minimum value at pH = 8–9. The opposite dependence is observed for the polycation (XXIIc), for which the minimum rate constant occurs at pH 5–6. The polyampholyte (XXIId) is similar in behaviour to the model photochromic compound, for which a minimum rate constant is observed at pH ≃ 7. The uncoiling of the polypeptide (XXXIII) macromolecule in trifluoroacetic-acid solution increases the yield of the *cis*-isomer on photoexcitation relative to that observed in dioxan solution, in which the polypeptide has a coiled conformation[19].

On the other hand, photoisomerisation of constituent azo-groups in the polyelectrolyte changes the conformation of the macromolecule and hence the viscosity of the polymer solutions (the "photoviscous effect")[22], which opens up the possibility of photocontrolling the conformation of a polyelectrolyte by means of photochromic compounds. An example of one of the two main mechanisms distinguished by Lovrien[22] is provided by a copolymer of methacrylic acid such as (XXIIa). In the absence of irradiation the balance between two types of interaction—van der Waals cohesion of hydrophobic lateral *trans*-azo-groups and electrostatic repulsion of like charges—determines the degree of coiling of the polyelectrolyte. On *trans–cis*-photoisomerisation the hydrophobic interaction of the azo-groups diminishes owing to the increased polarity of the *cis*-isomer, leading to uncoiling of the macromolecule and increase in the viscosity of the polyelectrolyte solutions.

An example of the second type of system is a macromolecule of polymethacrylic acid with adsorbed ligands of a charged azo dye (e.g. anions of Chrysophenine). The addition of photochromic ligands uncoils the polyelectrolyte macromolecule as a consequence of interaction of like charges. On *trans–cis*-conversion the increased dipole moment of the *cis*-isomer makes the ligand more hydrophilic, which leads either to its desorption from the macromolecule or to an increase in the dielectric constant along the chain. In either case the macromolecule coils up: i.e., in contrast to the first mechanism, solutions of the polyelectrolyte will become less viscous after exposure‡. With degrees of ionisation of polymethacrylic acid < 0.075 (pH < 4.9) the addition of ligands—Chrysophenine anions—coils up the polymer chain and lowers the dissociation constant (p$K$) of the carboxy-groups on *trans–cis*-photoisomerisation[23].

Photocontrol of the conformation of polymethacrylic acid in solution at degrees of ionisation of 0.2 (pH 4.5–5.5), at which the polyelectrolyte macromolecule uncoils, is

‡ It is undoubtedly of interest to study such processes, since this would open up the possibility of using membranes and photochromic polyelectrolytes for the photoregulation of biological processes.

possible with the use of cationic ligands based on *p*-phenylazophenyltrimethylammonium iodide or the copolymers (XXIIa)[24]. Solutions of polymethacrylic acid with cationic ligands exhibit a decrease of 0.2 in the p$K$ on *trans–cis*-photoisomerisation, caused by a change in the degree of coiling of the polyelectrolyte molecules. The photochromic copolymers (XXIIa) also display an induced photochemical jump in p$K$ when the azo-groups pass into the *cis*-form. Since

$$pK = pH + \lg[(1+\alpha)/\alpha],$$

the degree of ionisation of polymethacrylic acid modified by photochromic groups, and hence the conformation of the polyelectrolyte, should be controlled photochemically in buffered solutions.

A usual consequence of the addition of azobenzene groups to a polymer chain is steric hindrance to *cis–trans*-isomerisation, which is apparent in a diminished rate of photochromic transitions of copolymers in comparison with model compounds[14,21,19,25]. An increased rate of thermal isomerisation relative to the reaction with model compounds has been observed with the copolymers (XXIIIa), (XXV), and (XXXII)[14,26]. Such anomalous behaviour was attributed to diminished aggregation of azobenzene groups when separated by an inert comonomer. This is supported by the decrease in the rate of photochromic transitions with increase in the aggregation of azobenzene molecules due to polar groups capable of forming hydrogen bonds, e.g. in the copolymer (XXIV)[14].

Thus the effects of aggregation of azobenzene groups and steric hindrance by the macrochain tend to balance each other, and the photochromic behaviour of the macromolecule will depend on the relation between them. Another view[26] is that the introduction of azobenzene groups into the main chain of the polyamide (XXXII) does not impede isomerisation, since the time required for conversion of the macromolecular conformation into a form corresponding to the transition state in the *cis–trans*-isomerisation of azo-groups is comparable with the time of isomerisation of these groups in a model compound.

The steric effect of a polymer chain on *cis–trans*-isomerisation is evident also in the dependence of the rate of photochromic transitions on the mobility of the macromolecule. The rate of the thermal *cis–trans*-isomerisation of copolymers on methyl methacrylate with *p*-dimethylamino-*p'*-vinylazobenzene (XXIIIb) in benzene solution exceeds that of copolymers with styrene (XXIIIa) because of the greater mobility of poly(methyl methacrylate). For the polystyrene macromolecule, which has a straight conformation in benzene solution, isomerisation processes in side-chains are difficult[25]. Analogous results were obtained by Kamogawa et al.[14]: the rate of the thermal *cis–trans*-isomerisation of copolymers falls with decrease in the flexibility of the macromolecule—polystyrene and poly(methyl methacrylate) compared with poly(butyl acrylate).

Since the mobility of a macromolecule in solution depends on the interaction of the polymer with the solvent, the rate of a photochromic transition is influenced by the parameter $\chi$ of this interaction. The higher value of $\chi$ for polystyrene than for poly(methyl methacrylate) in benzene is responsible for the lower *cis–trans*-isomerisation rate constant of vinyldimethylaminoazobenzene in copolymers with styrene than in those with methyl methacrylate (XXIIIa) and (XXIIIb)[25]. The decrease in the rate constant with increase in the content of vinyldimethylaminoazobenzene in the copolymer (XXIIIb) is also explained by an increase in $\chi$. The departure from this relation observed for simultaneous increase in the content of this monomer and increase in the concentration of the copolymer in the solution is probably due to inter- and intra-molecular transfer of excitation energy[25].

The loss of mobility of a macromolecule in a film results, as would be expected, in a considerable decrease in the rates of photochemical transitions relative to those observed in solution, especially if the polymer has a rigid chain[14,27]. Sometimes the longer-wavelength absorption band of the polymer undergoes a bathochromic shift in a film in comparison with the maximum in solutions[14].

However, it was found[27] that, after a photostationary state had been reached in a film, the dark *cis–trans*-isomerisation of photochromic copolymers containing azobenzene groups—whether in side-chains (XXIIe), (XXIIf), and (XXVIII) or in the main chain (XXIX)–(XXXI)—takes place at a constant rate differing little from that in dilute solutions of analogous polymers. This unexpected phenomenon was explained in terms of the fundamental postulate of the theory of rate processes that the transition state in a reaction is in equilibrium with the initial state, and the reaction velocity is unaffected by the reduced mobility of the reactants imposed by increase in the viscosity of the medium.

In solutions of polymers photochemical *trans* $\rightleftharpoons$ *cis*[25,19] and thermal *cis–trans*-isomerisation[21,25,26,19] are usually first-order reactions. The latter type of isomerisation in dilute formic-acid solutions of the polyamide (XXIIa) containing azobenzene groups in the main chain diverged from this rule[27]. Its kinetics are described by the equation

$$c/c_0 = \alpha \exp(-k_1 t) + (1-\alpha)\exp(-k_2 t)$$

where $c_0$ is the concentration of the *cis*-isomer at zero time, $c$ is its concentration at time $t$, and $k_1$ and $k_2$ are rate constants of the *cis–trans*-isomerisation of the azobenzene groups. Here $k_1 \simeq 3k_2$, with the latter approaching the isomerisation constant of a model compound. The presence of rapidly isomerising azo-groups in the polyamide is probably connected with their oxidation to azoxy-derivatives. This view is supported by the decrease in the ratio $k_1/k_2$ in a more acid medium.

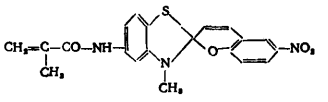
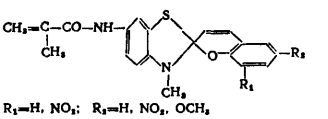
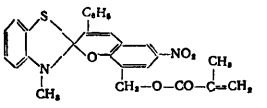
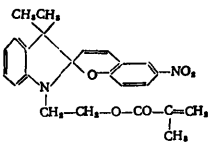
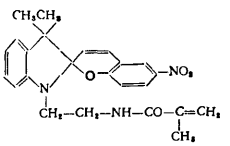
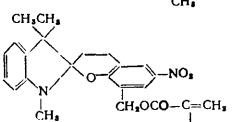
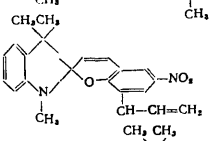
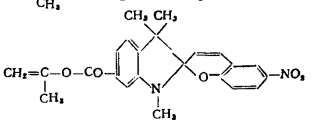
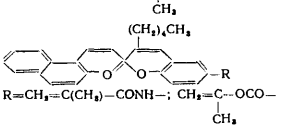
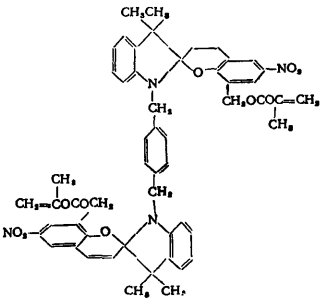
Kinetic investigation of the thermal *cis–trans*-isomerisation in a film of polymers containing azobenzene and azonaphthalene groups in side-chains—(XXIIe), (XXIIf), and (XXVIII)—revealed a relation between the glass point and the departure from first-order kinetics[27]. A first-order equation was obeyed by polymers in a state of rubber-like elasticity. A proportion of rapidly isomerising azoarene groups and the associated departure from first-order kinetics appear at temperatures below the glass point. Such anomalous behaviour of polymer films was attributed[27] to the non-equilibrium character of the vitreous state, which causes a non-uniform distribution of free volume in the polymer. Similar results were obtained for solid solutions of 2,2'-azonaphthalene or *p*-ethoxyazobenzene in polystyrene[28]. The content of *cis*-isomers in the photostationary state decreases with increase in the viscosity of the medium, but the kinetics of the dark reaction deviates from a first-order equation at temperatures below the glass point.

It has recently been reported[28] that the photoisomerisation of polymers containing azo-groups in the main chain may be accompanied by mechanical changes. When poly-*pp'*-azobenzene–pyromellitimide (XXXVI) was subjected to temperature cycles involving heating to 200°C under constant pressure, shrinkage and expansion of the film were

observed. With the length of the film maintained constant, on the other hand, the stress applied to the film during exposure increased with time.

Since the activation energy of compression of a film is insignificant, whereas the activation enthalpy of isomerisation of azo-compounds in solution is ~ 20 kcal mole$^{-1}$,

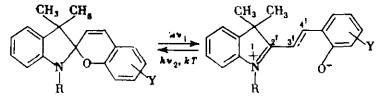
Table 3. Spiropyran polymers obtained by radical copolymerisation.

| Copolymer | Shiropyran monomer | Comonomer or comonomer mixture | Photochrome in polymer, mole % | $10^{-4}$ *M* | Ref. |
|---|---|---|---|---|---|
| (XLII) a |  | methyl methacrylate | 3.3—21.5 | 0.77—9.0 | |
| b | | styrene | 10 | 0.55 | 34 |
| c | | methacrylonitrile | 10.2 | — | |
| d | | dodecyl methacrylate | 17.9 | 3.08 | |
| e | | 1- or 2-vinylnaphthalene | 9—13 | 0.19—0.87 | |
| (XLIII) |  $R_1$=H, $NO_2$; $R_2$=H, $NO_2$, $OCH_3$ | methyl methacrylate | 10 | — | 35 |
| (XLIV) |  | methyl methacrylate | 10 | 42.6 | 3 |
| (XLV) a |  | methyl methacrylate (MMA) | 0.6—50 | (—100) | 3,35,36,37, 38,39 |
| b | | styrene | 2.5 | — | 37,40 |
| c | | MMA-*p*-acrylamidophenol-*p*-azidoxy-carbonylbenzoic acid | 3.2 | — | 37 |
| d | | 2-vinylnaphthalene | 2.1 | 0.28 | |
| e | | 9-vinylanthracene | 50.6 | 0.12 | |
| f | | 5-methacryloyl-2-methoxybenzaldehyde | 3.3 | 0.27 | |
| g | | 4-vinylpyridine | 2.1 | 0.53 | 40 |
| h | | acrylonitrile | 2.0—3.3 | 0.17 | |
| i | | 2-hydroxyethyl methacrylate | 2.2 | 0.15 | |
| j | | 1-methacryloylmethyl-*o*-carborane | 2.5 | 0.30 | |
| k | | homopolymer | 100 | 0.16 | |
| (XLVI) |  | n-propyl or isobutyl methacrylate | — | — | 3 |
| (XLVII) a |  | styrene | 1.5—100 | — | 41 |
| b | | methyl methacrylate | 2.1 | 37.9 | 3,41 |
| (XLVIII) |  | methyl methacrylate | 0.2—0.8 | 12—26 | 35,38 |
| (XLIX) |  | methyl methacrylate | 5 | — | 37 |
| (L) |  $R=CH_2=C(CH_3)-CONH-$; $CH_2=C(CH_3)-OCO-$ | methyl methacrylate | — | — | 42 |
| (LI) |  | methyl methacrylate, ethyl acrylate | 0.5—1 | — | 3,30 |

Agolini and Gay [29] suppose that the rate of expansion or contraction is determined by the elastic properties of the polymer rather than by the rate of *cis–trans*-isomerisation. This seems a very probable interpretation in view of data obtained [27] for polyamides and polyesters containing azoarene groups and the absence of a direct relation between the rates of isomerisation of the polymer and of expansion or contraction of the film. Water-swollen membranes of a copolymer of 2-hydroxyethyl methacrylate and ethylene dimethacrylate with adsorbed molecules of Chrysophenine shrink by 1.2% on illumination, and return to their original dimensions in the dark [30,31]. This phenomenon was explained [30,31] by a change in the conformation of the polymer chain resulting from the difference between the solubilities of *trans*- and *cis*-isomers in the hydrophobic part of the macromolecule.

## V. POLYMERS BASED ON SPIROPYRANS

The photochromism of polymers containing spiropyran residues has been subjected to most detailed investigation. Ultraviolet irradiation causes dissociation of the carbon–oxygen bond, with coloration of the colourless photochromic systems [34]. The reverse process of ring closure takes place either in the dark or under the influence of visible light in the region of absorption by the merocyanine form:



(14)

Polymers containing spiropyran units in the side-chain have been obtained by the copolymerisation of unsaturated photochromic monomers with vinyl comonomers (Table 3), as well as by chemical reactions on polymers.

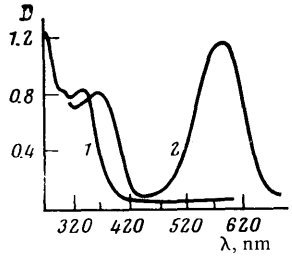
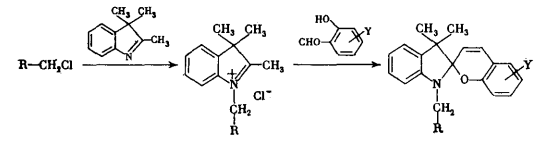


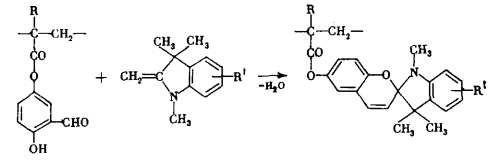

Figure 2. Absorption spectra of forms of copolymer (XLVa): 1) initial; 2) photoinduced.

The absorption bands of the coloured form $\lambda_{max}^{vis}$ are located over the range 470–600 nm depending on the structure of the spiropyran and the nature of the comonomer. Fig. 2 shows typical spectra of initial and photoinduced forms of an indolinospiropyran copolymer.

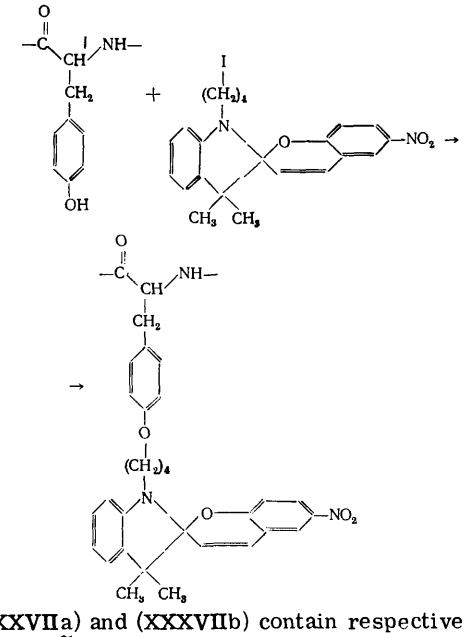
Polymers may be obtained by reaction between chloromethylated polystyrene and Fischer's base [43]:



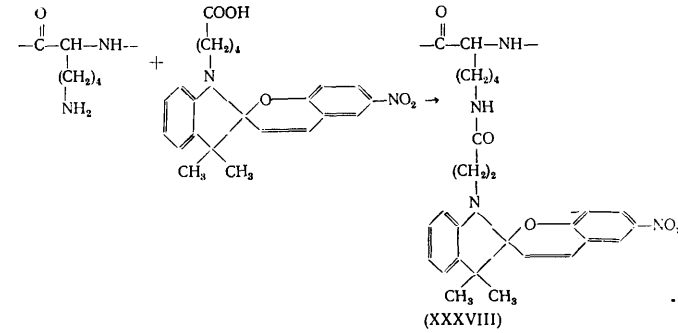
(R represents a macroradical and Y different substituents—$NO_2$; $NO_2$, $NO_2$; $NO_2$, $OCH_3$; $NO_2$, Hal). An alternative reaction is [44]



where R = H, $CH_3$, Hal and R′ = $CH_3$, $NO_2$, Hal, AlkO, AlkS). Some Japanese workers [45] have obtained photochromic polymers by the action of "live" polymers, such as the polystyrene or the poly-α-methylstyryl anion, on a spiropyran having a chloromethyl, bromoaryl, or ester group as reactive centre. Photochromic polypeptides were obtained [46] by the reaction of *N*-ω-halogenoalkylindolinospiropyrans with poly-L-tyrosine:

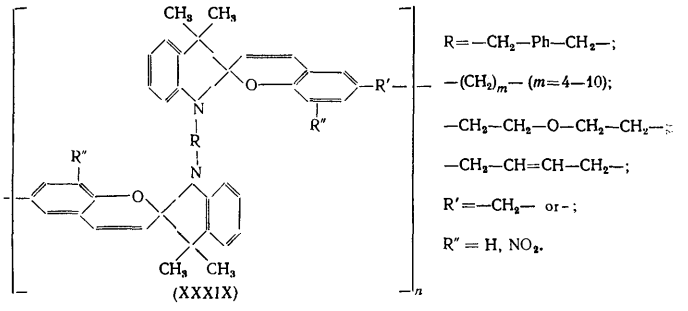


where (XXXVIIa) and (XXXVIIb) contain respectively 54.7 and 72.3 mass % of the photochrome. Alternative reactants are an *N*-carboxyalkyl derivative of indolinospiropyran and polylysine [3]:



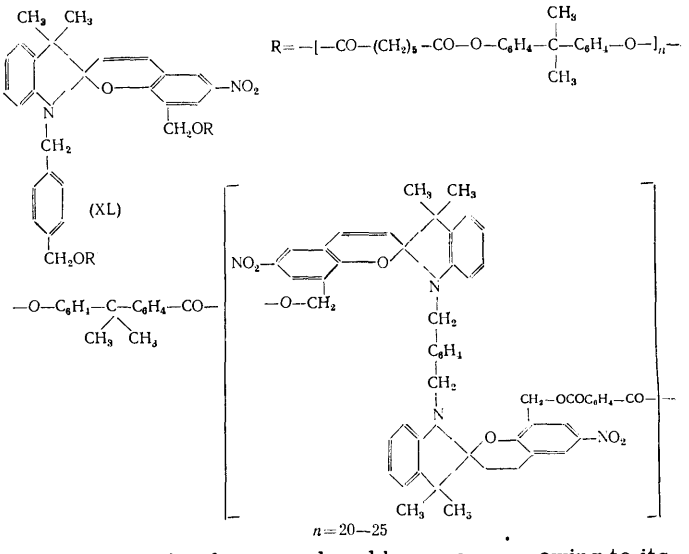
(XXXVIII)

Smets[3,47] used the polycondensation of bisindolenines with bis-salicylaldehydes to introduce photochromic groups into the main chain of the polymer:




(XXXIX)

Because of the sparing solubility of the condensation products (XXXIX), only oligomers having $n = 5$–$10$ were obtained. The copolycondensation of a bishydroxymethyl derivative of indolinospiropyran or a bisindolinospiropyran or of bisphenol A with pimeloyl chloride or a mixture of iso- and tere-phthaloyl chlorides gave polyesters (XL) and (XLI) containing respectively 4.0 and 9.5 mass % of the photochrome[3,30]:




The merocyanine form produced by exposure, owing to its zwitterionic nature, possesses strong negative solvatochromism (especially in benzothiazolinospiropyrans), which affects both $\lambda^{vis}_{max}$ and the rate of decolorisation. As a consequence, the specific effect of the polymer chain on the photochromic transitions of spiropyran units can be determined by comparing the photochromism of simple spiropyrans with that of their copolymers.

The kinetic and spectral behaviour of spiropyran polymers differs depending on whether the polymer is in solution or in the solid state. Furthermore, differences have been found in the behaviour of polymers into which spiropyran groups have been introduced chemically and of solid solutions of the corresponding photochromic monomers in the homopolymers.

## 1. Photochromic Transitions in Solution

The steric and polar effects of the macrochain depend on the polarity of the solvent[34,36]. In strongly polar media (e.g. dimethylformamide, pyridine) the copolymers (XLIIa–e) (Table 3) exhibit strong negative solvatochromism similar to that of model compounds[34]. The thermal decolorisation of such copolymers obeys a first-order kinetic equation. The activation energy in dimethylformamide solution varies from 24.9 to 25.6 kcal mole$^{-1}$ depending on the comonomer, which compares with the value of 22.1 kcal mole$^{-1}$ for the model benzothiazolinospiropyran.

The photochromic polypeptides (XXXVIIa, b) also undergo first-order thermal decolorisation in dimethylformamide[46]. In strongly polar protic solvents (ethylene glycol and formamide) both polytyrosine (XXXVII) and its model compound, the latter obtained by reaction between 1-(4-iodobutyl)-3,3-dimethyl-6′-nitrospiro(indolino-2,2′-[2*H*-1]-benzopyran) and the methyl ester of *N*-acetyltyrosine, exhibit reverse photochromism, a phenomenon due to the high content of the merocyanine form in thermal equilibrium with the spiropyran[46].

In solvents of low polarity (acetone, dichloromethane, oxolan) the copolymers (XLIIa–e) and (XLVIIa, b) differ considerably from the model compound in photochromic behaviour[34,41]. In such solvents the polar influence of the comonomer becomes appreciable. Interaction of the merocyanine form of the spiropyran with the comonomer is confirmed by the hypsochromic shift in $\lambda^{vis}_{max}$ of the copolymers relative to the lower spiropyrans[34,40,41], which increases with the polarity of the comonomer. If the macromolecule is not solvated, the merocyanine form may also interact with spiropyran units to produce a hypsochromic shift in $\lambda^{vis}_{max}$ and a decrease in the rate of decolorisation with increase in the spiropyran content of the copolymer[34,41].

Thermal decolorisation of the copolymers (XLIIa–e), (XXXVIIa, b), (XLVIIa, b), and (XXXIX) in solvents of low polarity, in contrast to that of model compounds, diverges from first-order kinetics, and can be represented by the sum of at least two first-order reactions[3,34,41,46]. The variation in optical density of the $\lambda^{vis}_{max}$ band can be described by the equation

$$D = a\exp(-x_1 t) + b\exp(-x_2 t) \quad . \qquad (15)$$

which presupposes the existence of several *trans*-isomers—with respect to the central bond 3′–4′ in Eqn. (14)—of the merocyanine form, the rate of whose interconversion is far smaller than their rate of decolorisation. In formula (15) $a$ and $b$ are the contributions of each geometrical isomer to the optical density at $t = 0$, while $x_1$ and $x_2$ are their decolorisation rate constants.

The above regularities have been attributed[34,41] to the steric and polar effects of the macromolecule in raising the potential barrier separating the geometrical isomers. The polar influence of the comonomer diminishes with increase in the polarity of the medium, so that, when a polar precipitant (t-butyl alcohol) is added to a solution of the copolymer (XLIIa) in chlorobenzene, the first-order kinetics of decolorisation are restored up to degrees of conversion of 60%[34].

As a consequence of incomplete solvation of polytyrosine macromolecules by solvents of low and high polarity the photochromism of solutions of copolymers (XXXVIIa, b) is almost independent of the polarity of the solvent, in contrast to that observed for the model compound. The specific effect of the polypeptide chain is evident also in the appearance of two absorption maxima in the visible range, due to different geometrical isomers of the merocyanine form[46].

Equilibrium between spiropyran and merocyanine forms is established in solutions of copolymers (XLVc–j) of indolinospiropyran with comonomers differing in polarity and in three-dimensional structure[40]. The equilibrium constant depends on the polarities of the solvent and of the comonomer.

Furthermore, the spectra of the homopolymer (XLVk) and of the copolymers (XLVc–e) contain a band due to a *cis*-cisoid isomer ($\lambda_{max}$ = 470 nm) formed immediately after dissociation of the carbon–oxygen bond in the pyran part of the molecule. The absence of such a band in the spectrum of the model compound, as well as in those of mixtures of the corresponding homopolymers with the model compound, suggests that steric hindrance by the macromolecule to interconversion of colourless and coloured forms is responsible for the appearance of this isomer. A polar solvent, as well as a polar comonomer, promotes rapid transition through the stage of formation of the *cis*-cisoid isomer, and stabilises the merocyanine form (*trans*-isomer)[40].

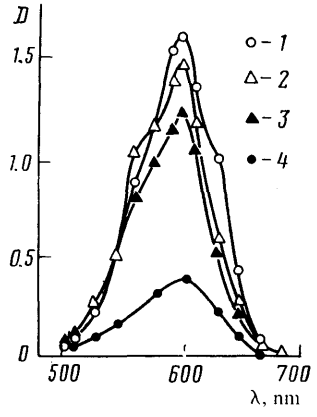



Figure 3. Absorption spectra of coloured form of copolymer (XLVc) (0.3 mM solution in benzene) after: 1) 40 μs; 2) 0.66 ms; 3) 0.1 s; 4) 15 s.

The use of flash photolysis[48] to investigate photochromic processes, including those accompanied by formation of short-lived intermediates on photoexcitation of copolymer (XLVc), confirms the existence of geometrical isomers of the merocyanine form having different lifetimes. The mechanism of photoconversion of the copolymer involves the formation of a short-lived *cis*-cisoid isomer ($\lambda_{max}$ = 490 nm), which passes rapidly (lifetime < 1 s) into more stable interconvertible geometrical isomers having absorption maxima at 560, 600, and 640 nm (Fig. 3). At times exceeding 1 s the spectrum still contains the band due to the thermally stable isomer ($\lambda_{max}^{phot} \simeq$ 600 nm), the decrease in whose optical density monitors the kinetics of the dark decolorisation after long periods of time.

The thermal decolorisation rate constants of copolymers in solution depend on many factors—the structure of the spiropyran, the nature of the comonomer, and the polarity of the solvent[34,41,39] (Tables 4 and 5). The copolymers (XLVIIb) and (XLIX) fade more slowly than do model compounds. The opposite effect is observed with the copolymers (XLVa) and (XLVI). This confirms that the rate of decolorisation is affected by the site at which the photochrome is attached to the polymer chain[39]. In the case of the benzothiazolospiropyran (XLIV) the rate of decolorisation of the copolymer is about half that of the model compound. Steric hindrance to rotation of the polymer chain about the 3′–4′ bond operates here[3].

Table 4. Photochromic behaviour of copolymers of spirobenzopyrans with methyl methacrylate (sp.) and their model compounds (mod.) in acetone solution[3,39].

| Structure | (XLVa) | | (XLVIIb) | | (XLIIa) | | (XLIX) | | (XLVI) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | mod. | sp. | mod. | sp. | mod. | sp. | mod. | sp. | mod. | sp. |
| $\lambda_{max}^{vis}$, nm | 577 | 577 | 567 | 567 | 526 (506) | 478 (504)* | 569 | 569 | 572 | 572 |
| $10^3 k_1$ (20°C), $s^{-1}$ | 8.2 | 9.9 | 1.3 | 1.0 | 1.7 (4.8) | 1.7** (3.8) | 2.0 | 1.05 | 2.8 | 4.7 |
| $E_a$, kcal mole$^{-1}$ | 22.3 | 22.4 | 24.3 | 24.5 | (22.1) | (25.6) | 21.6 | 23.0 | 24.7 | 24.5 |

*In all cases parentheses enclose values in dimethylformamide.
**Apparent initial rate constant.

Table 5. Kinetics of the decolorisation of copolymers of methyl methacrylate with 1-methyl-5-methacrylamido-6-nitrospiro(thioindolino-2,2′-[2*H*-1]benzopyran) (XLIIa) in solution[3].

| Solvent | *t*, °C | $10^3 k^*$, $s^{-1}$ | $10^3 x_1$, $s^{-1}$ | $10^3 x_2$, $s^{-1}$ | Isomer, %*** | |
|---|---|---|---|---|---|---|
| | | | | | *a* | *b* |
| Acetone | 20.5 | 1.7 | 1.7 | 0.27 | 36 | 64 |
| Dichloromethane | 20.0 | 3.4 | 5.7 | 0.48 | 66.7 | 33.3 |
| Oxolan | 22.2 | 38.0** | 4.6 | 0.70 | 68 | 32 |

*Rate constants for the model compound.
**Extrapolated value.
***The coefficients *a* and *b* from Eqn. (15).

The viscosity of the medium has a considerable influence on the kinetics of the photoconversion of copolymers[34,38]. Thermal decolorisation diverges from a first-order reaction as solutions of the copolymers become more viscous[34].

The introduction of the photochrome into the polymer molecules (XLVa) and (XLVIII) does not lower the quantum efficiencies of coloration and decolorisation.

The substantial decrease in mobility of photochromic groups on introduction into the main chain of the oligomers (XXXIX) halves the rate of decolorisation in comparison with the corresponding dimers, and the thermal process diverges from the first order even in polar solvents[3].

Solutions of benzothiazoline polymers (XLII) are less strongly coloured than are the indolinospiropyran copolymers (XLV). When a solution of the polymer (XLIII) is cooled, the fluorescence becomes more intense, while the efficiency of the photodecolorisation of coloured solutions diminishes[35].

## 2. Photochromism of Copolymers in the Solid State

The photochromism of copolymers in the solid state is of especial interest in connection with practical application. The rate of the thermal decolorisation of copolymer films and solid solutions depends significantly on the glass point of the polymer, especially when the spiropyran forms part of the macromolecule. This effect is most clearly developed in copolymers containing the photochrome in the main chain[30]. The rates of the dark decolorisation of copolymers and solid solutions of spiropyran monomers in a polymer matrix drop sharply (by factors of 100–500) at temperatures below the glass point[3,38,39,41,49,50]. The optical density of the absorption band of the copolymer $\lambda_{max}^{vis}$ decreases by 90% after a few minutes in solution, but after several months in a film[41]. A long-lived coloured state of spiropyrans has been obtained in polymer matrices containing reactive groups, which may undergo photochemical cross-linking[36].

The kinetics of the thermal decolorisation of copolymer films is described by a first-order equation at temperatures above the glass point, but diverges from it below this temperature. Such behaviour of films is consistent with the existence of two or more geometrical isomers, the rate of interconversion of which differs considerably depending on the mobility of the macromolecule at temperatures below and above the glass point[50,51]. In the latter case the rate is so high that decolorisation is a first-order reaction, whose velocity is comparable with that for solutions of spiropyrans[50]. Below the glass point isomerisation slows down considerably, and decolorisation can be regarded as the sum of two or more parallel first-order processes, each characterised by its own rate constant and activation energy[3,50].

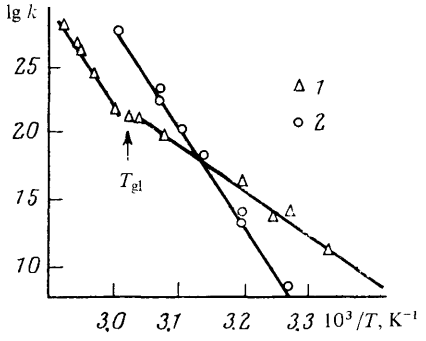



**Figure 4.** Temperature dependence of rate constant of dark decolorisation plotted in Arrhenius coordinates for: 1) copolymer (XLVI); 2) matrix mixture.

However, Lawrie and North[52], studying the rate of decolorisation of 1,3,3-trimethyl-6′-nitrospiro(indolino-2,2′-[2*H*-1]benzopyran) in various polymer matrices, concluded that the deviation from first-order kinetics for copolymers in a film below the glass point must be attributed to the non-uniform distribution of free volume in the vitreous state of the polymer and its relatively uniform distribution in the rubberlike elastic state. Thermal decolorisation of this spiropyran dispersed in a poly(methyl methacrylate) matrix is a first-order reaction below the glass point, owing to the short relaxation times (10–100 s) of the free volume in the polymer. The time of decolorisation of solid solutions of the above spiropyran increases in the sequence poly(methyl methacrylate) < poly(vinyl chloride) < polystyrene < poly-*p*-chlorostyrene owing to the intensifying polar and steric influence of the macromolecule[52].

The mechanism of the thermal decolorisation of three different indolinospirobenzopyrans in amorphous polymer matrices—poly(methyl methacrylate), poly-(n-butyl methacrylate), poly(vinyl acetate), and poly(vinyl n-butyrate)—has also been discussed in terms of a discrete distribution of free volume in a vitreous matrix[53]. The presence of two decolorisation rate constants, together with the change in activation energy below the glass point, is due to the existence of kinetic units of the macromolecule differing in ability to relax (e.g. end and side groups) and also to interaction of the photochromic molecule with the matrix[53].

The decolorisation of films of copolymers differs from that of solid solutions of a spiropyran in a polymer matrix: whereas the Arrhenius plot (Fig. 4) for a solid solution of 1-(2-methacryloyloxyethyl)-3,3-dimethyl-6′-nitrospiro-(indolino-2,2′-[2*H*-1]benzopyran) in poly(isobutyl methacrylate) exhibits a rapid increase in rate of decolorisation with rise in temperature, a film of the copolymer (XLVI) gives a curve with an inflexion near the glass point. The increase in the effective activation energy above this temperature is due to the additional activation energy of viscous flow[3]. The effect of a polymer matrix on the rate of decolorisation of spiropyrans is determined mainly by the polarity of the polymer and is fully consistent with the strong negative solvatochromism of the merocyanine ring system[3,50,52,39,53]. This fact, as well as the sensitivity of the merocyanine form to steric factors, enables benzopyrans to be used as indicators of molecular interaction of polymers[3,49,50,52].

Photochromic conversions in spiropyran copolymers in the solid state, in contrast to solutions, are accompanied by photodecomposition and oxidation. This phenomenon, which has been termed *fatigue*[54], is a result of two photoprocesses involving the colourless and coloured forms respectively. A scheme suggested[38] for photochromic conversions of copolymers (XLVa) and (XLVIII) can be written

$$C \xleftarrow{h\nu} A \underset{h\nu_1}{\overset{h\nu}{\rightleftarrows}} B \xrightarrow{h\nu} E,$$
$$\qquad\qquad\quad \downarrow h\nu_1$$
$$\qquad\qquad\quad F$$

where A and B are initial and coloured forms of the spiropyran, and C, F, and E are products of photodecomposition under the influence of ultraviolet radiation $h\nu$ and visible light $h\nu_1$. Fatigue of the copolyester (XL) at temperatures above the glass point is illustrated[55] by Fig. 5, which shows that the optical density of the coloured form in the photostationary state decreases after each period of exposure. This effect is considerably less well defined in a vacuum, which indicates that the process is influenced by oxygen.

It has recently been found[38] that the quantum efficiencies of the photodecolorisation of copolymers (XLVa) and (XLVIII) are one-third of those observed in solid solutions of spiropyrans in a polymer matrix. This is due to

inhibition of the relative rotation of parts of the spiropyran molecule, as a consequence both of the great structural viscosity of the medium and of the attachment of one part of the photochrome molecule to a polymer chain[38].

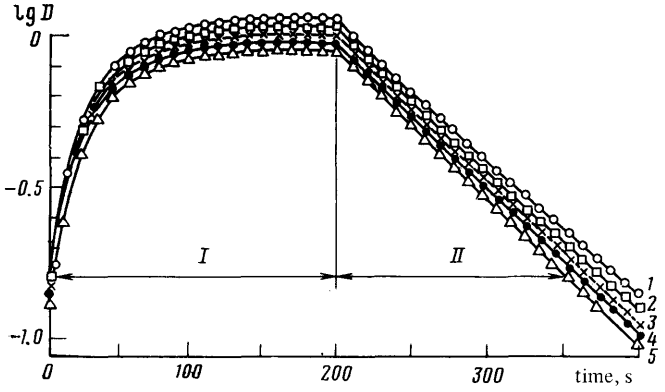



Figure 5. Photochromic behaviour of copolyester of bisindolinospiropyran at 65.3°C: I) period of irradiation; II) dark period; 1)–5) curves after first, second, etc. exposure cycles.

Interesting phenomena associated with the photochromism of spiropyran polymers—enhanced stability of copolymers with spiropyran groups during degradation induced by light and radiation[35] and a photomechanical effect[3,30]—have been discovered recently. The latter is observed on filaments and films prepared from photochromic cross-linked poly(ethyl acrylate) (LI). A shrinkage of 2–3% occurs on ultraviolet irradiation under strictly isothermal conditions; the original dimensions are regained in the dark. These photomechanical phenomena show good reproducibility, and are caused by the increase in entropy of the polymer chain resulting from the enhanced flexibility of open-chain merocyanines in comparison with rigid spiropyrans[30]. The amount of shrinkage depends on the applied stress, the temperature, the degree of cross-linking, and the position of attachment of the photochrome. The considerably lower activation energies than in dark decolorisation and shorter times of returning to the initial dimensions in the dark indicate that the photomechanical behaviour of photochromic polymers not only is controlled by isomerisation but also is connected, as in the case of azo-compounds[29], with the properties of the polymer matrix.

## VI. CONCLUSION

Investigation of the spectral and kinetic properties of photochromic polymers, as well as the quantum efficiencies of their photodecolorisation, has revealed in several cases differences from the lower analogues. Furthermore, marked differences are observed in the behaviour of photochromic polymers in the solid state and in solution. With strong interaction between solvent and polymer the photochromic properties of the latter approach those of the simple analogues. When such interaction is less clearly defined, as e.g. in the case of copolymers of styrene and methyl methacrylate with indolinospiropyran in solvents of low polarity, the mechanism of the dark decolorisation of the polymers differs from that for the model compound, and is determined by the polar and steric influence of the macromolecule. The variation with solution pH in the conformation of polyelectrolytes containing azo-groups correlates with the rate constant of the dark reaction.

In the case of solid polymers the photochromic behaviour of groups forming part of the macromolecule depends on the physical state of the polymer. If an appreciable change in conformation of photosensitive groups, e.g. *cis–trans*-isomerisation, accompanies a photochromic transition, the latter is slowed down significantly in the solid, vitreous state because of strong steric hindrance. In the rubberlike elastic state deviations from the behaviour of the polymer in solution are less marked.

The behaviour of copolymers having covalently bound photochromic groups, especially when the latter form part of the main chain of the macromolecule, differs from that of matrix polymers. Smets[55] has recently shown experimentally that the rate constant of the dark decolorisation of a matrix mixture containing indolinospiropyran is only around 10% of the value for photochromic copolyesters.

Thus by varying the polymer structure and the orientation of the polymer matrix it is possible to obtain materials having various photochromic characteristics ($\lambda_{max}^{vis}$, rate constant of dark decolorisation—i.e. colour and stability of the image). These factors, together with the improved technology for obtaining photochromic materials from photochromic copolymers rather than introducing a low-molecular-weight photochromic compound into a polymer matrix, explain the increasing interest taken by research workers during recent years in the study of photochromic copolymers.

Nevertheless, despite the extensive study of the spectral and kinetic characteristics of photochromic transitions, little attention has been paid to the photochemical characteristics of polymers such as the quantum efficiency of photocoloration and photodecolorisation, as well as photosensitivity. Few papers have appeared on the mechanism of photoreactions in polymers. Because of the lack of such information it is impossible in several cases to assess the possibility of practical application of the synthetic photochromic polymers.

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# Structural Peculiarities of Homo- and Co-polyurethanes

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Recent advances in the investigation of polyurethanes are surveyed. Considerable attention is paid to copolyurethanes based on multicomponent initial constituents, which may exhibit thermoplastic or thermoelastoplastic properties depending on the distribution of the components in the chain and the length of the glycol constituent. A list of 142 references is included.

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## I. INTRODUCTION

Almost all technically valuable polymeric materials—rigid and elastic fibres and rubbers, film materials, coatings, adhesives, rigid and elastic foam plastics, etc.—can be based on polyurethanes. The possibility of obtaining such diverse materials is governed by peculiarities of the chemical structure of the polyurethanes, which in turn are determined by the structure of the initial components and the conditions of synthesis. Because of the variety exhibited by the chemical structure it is especially important to establish the fundamental relations between chain structure and properties, and to elucidate specific aspects of structure formation in polyurethanes. Information on structure and properties has been summarised previously [1], but new advances have been made during recent years, and a tendency has appeared to develop new lines of investigation, primarily in the field of random copolyurethanes and segmented polyurethanes (block copolyurethanes). Moreover, the literature reveals no uniform approach to the separation of polyurethanes into individual groups or types on the basis of their structure or properties. Depending on their chemical structure these polymers may acquire the properties either of thermoplasts or of elastomers and thermoelastoplasts, so that the segregation of polyurethanes as a single class of polymers is extremely arbitrary. In this connection it is very convenient to classify polyurethanes according to the molecular mass of the glycol component [2].

The present Review discusses mainly the principal papers that have appeared during the past five years on the structure and the physicochemical properties of polyurethanes and related compounds [polyurethanureylenes, poly(urethane semicarbazides), polyamidourethanes, etc.]. We shall base our survey on one of the main parameters of the chemical structure of a polyurethane—the molecular mass of the glycol component of the polyurethane chain.

At the present time polyurethanes comprise a very large class of polymers, often differing significantly in chemical nature and chain structure, but invariably containing a number of urethane groups $-NH.COO-$, [1-4] e.g. polyesterurethanes based on oligoesters, etc. The chemical structure of linear polyurethanes can be represented by the general formula

$$[-R_1-OCONH-R_2-NHCOO-]_x \quad (1)$$

where $R_1$ and $R_2$ are chain segments of the initial glycol and di-isocyanate components respectively. Hence, by varying the structure and the chemical nature of $R_1$ and $R_2$, we can obtain polyurethanes of diverse molecular structure, with different concentrations of urethane groups governed by the length of the glycol component. The latter factor largely determines the type of polymer properties acquired by the polyurethane materials. The use of mixtures of glycols differing in molecular mass, as well as trifunctional compounds to provide a three-dimensional structure, provides wide opportunities for controlling the properties of polyurethanes.

In view of the above considerations we have divided polyurethanes into two main classes, obtained respectively from lower glycols and from oligomeric glycols, for the discussion of their structure and properties.

## II. POLYURETHANES BASEDON LOWER GLYCOLS

### 1. Linear Homopolyurethanes†

One of the chief representatives of this type is that obtained from tetramethylene glycol and hexamethylene di-isocyanate (4,6-polyurethane)

$$[-OC(OCH_2CH_2CH_2CH_2)_nOCONH(CH_2)_6NH-]_x \quad (2)$$

($n = 1$), which, because of its good fibre-forming properties, has long been the subject of comprehensive investigation [2]. This polymer crystallises well, with a lattice exhibiting sharply defined anisotropy [5,6], for it comprises "planar networks", between which van der Waals bonds operate; within a network the macromolecules are combined by regular hydrogen bonds. This is a necessary condition for the establishment of a fully crystalline structure within 4,6-polyurethane, and is responsible for the peculiarities of its formation and its breakdown. The crystal lattice contains both di-isocyanate and glycol units. Thermographic and calorimetric investigations have shown [7-9] that structural features of 4,6-polyurethane also effect the variation in its thermodynamic properties.

Calorimetric investigations were made [10] on a series of polyurethanes synthesised from carbon-chain glycols $HO.[CH_2]_n.OH$ ($n = 2-10$) and various di-isocyanates—hexamethylene, methane-*pp'*-diphenylene, and 4-methyl-1,3-phenylene di-isocyanates. The melting points of the polyurethanes investigated, like those of polyamides,

† We apply the term *homopolyurethanes* to polyurethanes formed from single initial components (glycol and di-isocyanate).

depend on whether $n$ is odd or even. The maximum glass point is found with specimens obtained from the diphenylmethane derivative, for which it falls uniformly with increase in $n$. For the tolylene series the glass points vary irregularly with increase in $n$, and the glass points of the hexamethylene polymers are independent of $n$.

Structural changes [11] and structure [12] were investigated in oligourethanes of general formula $CH_3.CO.\{O.[CH_2]_5.NH.CO\}_nO.CH_3$ ($n = 2-5$, $8-10$) as well as in a specimen of high molecular weight. Crystals grown from solution were studied. In oligourethanes having $n = 2-8$ the size (height) of the crystallites was independent of the conditions of heat-treatment, but for the remaining oligourethanes it increased on annealing at high temperatures, which indicates structural rearrangement with transition of chains from a folded to an elongated conformation (for $n = 9$, 10). The heat of fusion and the crystallinity of the oligourethanes diminish with increase in $n$. The crystallites have a two-phase structure, consisting of a very dense crystalline phase and a less dense intercrystalline phase containing mobile free ends of macromolecules.

When the length of the glycol component is increased and an oxygen atom is introduced to give 5-oxanonane-1,9-diol, the resulting polyurethane [formula (2) with $n = 2$] has a lower melting point and exhibits a characteristic change in crystalline structure, becoming polymorphic [13,14]. Infrared spectroscopy reveals three modifications, denoted $\alpha$, $\alpha'$, and $\beta$. [13] The transition $\alpha \rightarrow \beta$ is a polymorphic process accompanied by change in the conformation of the chain with rotation of the urethane group. The transition from the $\alpha$ to the $\alpha'$ structure does not fit into a simple scheme of fusion of the former and appearance of the latter at this temperature, but involves an "intermediate" structure, which subsequently melts [14]. The change from the $\alpha$ to the intermediate structure is a transition from one crystal lattice to another, accompanied by a change in the chain conformation, which in this case, however, does not involve urethane group. The transition from the intermediate to the $\alpha'$ structure is in turn also accompanied by changes in crystal lattice and chain conformation, which become the same for the $\alpha'$ as for the $\alpha$ structure.

It will be of interest to examine the structure and properties of polyurethanes based on ethylene glycols [8,15-26], whose general formula can be written

$$[-OCO(CH_2CH_2O)_nCONH(CH_2)_6NH-]_x \quad , \qquad (3)$$

where $n = 1-6$. The structure [15,21] and the thermodynamic properties [16] of the product having $n = 2$, i.e. polyurethane-2 based on diethylene glycol and hexamethylene di-isocyanate, have been investigated. Conditions were found for the appearance of two different crystallographic modifications, $\alpha$ and $\beta$, melting at 124 and 128°C respectively. The dimorphism of polyurethane-2 must explain the complicated fusion peak on the heating thermogram [8] and the temperature dependence of the heat capacity [16]. Furthermore, polyurethane-2 is able to form two types of supermolecular structure (annular and needle-shaped spherulites) [21]: the former correspond to only one of the two crystallographic modifications, but the latter spherulites contain crystals of both modifications.

A multiplicity of thermal transitions [8,17,25-27] and a variety of supermolecular structures [19] are found also when $n = 3$. Optical microscopic investigation of the spherulitic crystallisation of polyurethane-3 (from triethylene glycol and hexamethylene di-isocyanate) has shown [19] that extremely diverse structures (annular and radial spherulites, lamellar spherulitic aggregates, etc.) may appear depending on the conditions of crystallisation (temperature, from solution or melt, thickness of crystallising film). X-Ray examination has in turn revealed [18] the presence of two crystalline modifications ($\alpha$ and $\beta$). However, calorimetry indicates [25,27,28] a more complicated pattern of structural changes when this polyurethane is heated. Indeed, more detailed investigations of the structure and structural transitions of polyurethane-3 shows [26] that it can crystallise in at least four crystallographic modifications $\alpha-\delta$, and many transitions appearing in particular on the heating thermograms and the temperature dependence of the heat capacity are a consequence of polymorphic transitions and the melting of individual modifications, in one case of melting followed by recrystallisation. These polymorphic transitions are realised only with relatively slow heating.

At least two crystalline modifications $\alpha$ and $\beta$ may appear in polyurethane-4 [based on tetraethylene glycol and hexamethylene di-isocyanate—formula (3) with $n = 4$]. [23] This polymer is also characterised by a variety of supermolecular structures (positive and negative annular spherulites of different degrees of perfection, sheathlike spherulites). A significant feature is the coexistence of two crystalline modifications—positive rings comprising $\alpha$-crystallites, and negative rings of $\beta$-crystallites—in an annular spherulite of polyurethane-4. This provides further confirmation of the formation of annular spherulites by "rhythmic" crystallisation [29-31]. However, the opposite phenomenon has been observed with polyurethane-2 [21] and polyurethane-3: [26] i.e. annular spherulites grew in the temperature range of one crystalline modification, and their optical patterns were consistent rather with a structural hypothesis suggested by other workers for annular spherulites [32,33].

Calorimetric investigations [34] on polyurethane-4 and polyurethane-6 (the latter from hexaethylene glycol and hexamethylene di-isocyanate) have yielded information on their thermodynamic properties. In particular, true values were obtained for the enthalpy and entropy of fusion of polyurethane-4: $\Delta H_f = 28.5$ cal $g^{-1}$ and $\Delta S_f = 29.0$ cal $mole^{-1}$ $deg^{-1}$; the corresponding values for polyurethane-6 were 30 cal $g^{-1}$ and 40.0 cal $mole^{-1}$ $deg^{-1}$. The contributions of urethane groups to the entropies of fusion of these polyurethanes were estimated. It is interesting that the contributions of methylene groups and of urethane groups differ not only in absolute magnitude but also in sign, respectively 2.4 and $-4$ cal $mole^{-1}$ $deg^{-1}$. The negative entropy indicates that the presence of urethane groups diminishes the number of conformations of the chain in the melt: i.e. it lowers the configurational entropy of the melt. Hence increasing the concentration of urethane groups in the chain should raise the melting point of the polyurethanes (with closely similar true heats of fusion). Such regular rise in the melting point is indeed observed on passing from polyurethane-6 to polyurethane-2. [8,9,16,17,34].

It is significant also that the glass points of this series of polyurethanes increase linearly [27] with the concentration of urethane groups. Extrapolation to zero concentration then gives $T_{gl} = -83$°C, which will yield the glass point of poly(ethylene oxide), the macromolecular polymer-homologue of the glycol chain segments of these polyurethanes. For polyurethane-4 and polyurethane-6 the excess entropy at the glass point has also been obtained, as well as the contributions thereto made by urethane groups. The energy of hydrogen bonds involving urethane groups in these polyurethanes was estimated as ~4 kcal $mole^{-1}$.

A new structural feature of this series of polyurethanes (formula 3) has been revealed by the X-ray examination of oriented fibres and films[24]: the observed identity periods were shorter than the theoretical values $C_{exp} < C_{theor}$. The difference was due to the divergence between the $c$ axis of the inverse lattice and the texture axis of the polyurethanes, and was increased by any spatial position of the crystallite axes relative to the orientation drawing axis. The parameters of the unit cell of polyurethane-3 were found to be

$$\begin{aligned} a &= 9.24\ \text{Å}; & \alpha &= 77°; \\ b &= 8.01\ \text{Å}; & \beta &= 90°; \\ c &= 23.90\ \text{Å}; & \gamma &= 68°; \\ \rho_{exp} &= 1.23; & \rho_{X\text{-ray}} &= 1.31; \\ & N = 4. \end{aligned}$$

with the presence of sloping crystallites taken into account. Another peculiarity of the orientational behaviour of crystallites of polyurethane-3 in the $\beta$ form was that on elastic deformation they underwent three-dimensional rotation until the axes of the molecules coincided with the texture axis. Furthermore, elastic deformation of a polyurethane-3 specimen containing the $\gamma$ modification leads to breakdown of the $\gamma$ form with transition to the $\beta$ modification.

Replacement of the aliphatic di-isocyanate unit in polyurethane-3 by an aromatic unit, i.e. passing to a polyurethane based on triethylene glycol and methane-*pp'*-diphenylene di-isocyanate (polyurethane-F3), [35] results not only in loss of the ability to crystallise but also in a rise in the glass point and an anomalous process of vitrification. This is indicated by the occurrence of two successive jumps in heat capacity in the region of the glass point. Analysis of the process suggested that the first abrupt change in heat capacity corresponded to the development of mobility in microregions of the polyurethane in which were concentrated glycol chain segments, whereas the higher-temperature jump was due to disintegration of microregions with associated methanediphenylene di-isocyanate chain segments.

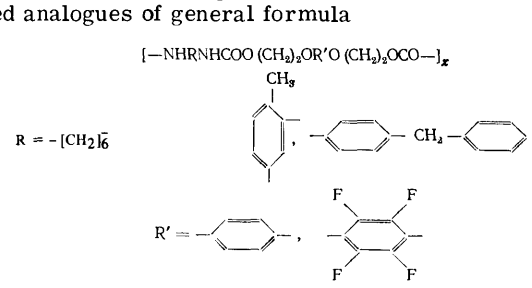
The diminished degree of hydrogen bonding on passing to *N*-substituted polyurethanes is responsible for several structural and thermal peculiarities. This was demonstrated in an investigation by infrared spectroscopy and thermography of *N*-methylated and *N*-benzylated polyurethanes based on ethylene glycol and 4-methyl-1,3-phenylene di-isocyanate[36].

Analogues of the polyurethanes

$$[-OCO(CH_2)_nOOCNH(CH_2)_6NH-]_x \qquad (4)$$

($n = 4-6$) in which 2–4 methylene groups have been replaced by difluoromethylene groups, in either or both di-isocyanate and glycol units, have been examined thermographically[37–41]. The introduction of fluorine atoms into one of the components results in anomalous melting, with two extrema on the fusion peak of the thermogram obtained when the polyurethane is heated. Such anomaly depends on the previous history of the specimen, and is due to the polymorphism of the crystalline phase, as with polyurethanes based on glycols containing oxygen in the chain. The ability to form a polymorphic crystalline structure diminishes as the number of difluoromethylene groups introduced into the chain decreases. When glycol and di-isocyanate components contain the same number of difluoromethylene groups, the resulting polyurethane exhibits no tendency to polymorphism. Conformational changes in the chain due to the sequence of difluoromethylene units are held responsible for the polymorphism of fluorinated aliphatic polyurethanes.

Fluorinated aromatic polyurethanes and their unfluorinated analogues of general formula




both crystallise poorly[42]. Those based on an aliphatic di-isocyanate exhibit the greatest tendency to crystallise. With an aromatic di-isocyanate the polyurethane has a higher melting point. Thus those obtained from hexamethylene, 4-methyl-1,3-phenylene, and methane-*pp'*-diphenylene di-isocyanates melt at 188, 190, and 222°C respectively, the corresponding glass points being 42, 47, and 49°C. It is significant that two glass points—as with the polyurethane from methane-*pp'*-diphenylene di-isocyanate and triethylene glycol[35]—are not observed here, which indicates that the introduction of a benzene ring into the glycol unit leads not only to an increase in the general rigidity of the polyurethane chain but also to a "levelling out" of the mobilities of di-isocyanate and glycol units. Probably this is responsible also for some tendency to crystallise shown by these polyurethanes based on aromatic di-isocyanates and glycols.

Formula (5) shows fluorine introduced into the benzene ring of the glycol unit, which should not affect the thermodynamic flexibility of the polyurethane chain. However, both the melting points and the crystallinity of all three types of fluorinated aromatic polyurethanes are lower than those of their unfluorinated analogues. The explanation is that the replacement of hydrogen by fluorine atoms leads to weakening of interchain interaction and of the tendency to associate at the fluorinated benzene rings. This is evidenced by the fall in the glass point of a polyurethane based on an aliphatic di-isocyanate when fluorine is introduced into the benzene ring of the glycol unit. However, the introduction of fluorine into polyurethanes based on an aromatic di-isocyanate, in which its benzene rings are also able to associate, does not affect the glass point of the polyurethane.

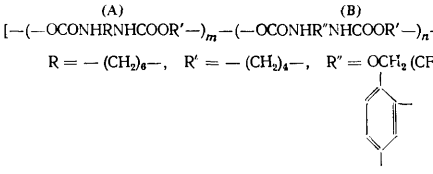
The above results indicate that, depending on the previous thermal, mechanical, etc. history of linear homopolyurethanes based on the lower glycols, their structure and physicochemical properties are predetermined by the chemical structure of the whole polymer chain. This implies that the main method of regulating the properties of polyurethanes of this type is, as before, to vary the chemical structure of the chains, not their physical structure.

## 2. Linear Copolyurethanes‡

Copolyurethanes of the simplest type are obtained from two di-isocyanates and one glycol or from two glycols and one di-isocyanate. They can be regarded as binary

‡ The term *copolyurethane* indicates that one of the initial constituents (di-isocyanate or glycol) comprises more than one component.

copolymers, in which units of two initial homopolyurethanes can be distinguished. Three types of random binary copolyurethanes have now been obtained, differing in their property–composition diagrams[41,43–47]. An example of the first type is based on tetramethylene glycol, hexamethylene di-isocyanate, and a fluorinated aromatic di-isocyanate having a structure resembling that of 4-methyl-1,3-phenylene di-isocyanate but with the methyl group replaced by a polyfluoroalkoxyl[45]. The chemical structure of this copolyurethane-I can be represented by the formula



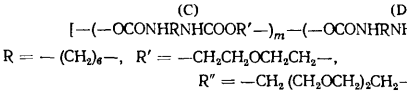

(6)

containing two kinds of units—4,6-polyurethane (A) and a polyurethane based on tetramethylene glycol and the fluorinated di-isocyanate (B)—corresponding to the initial homopolyurethanes. The latter, in contrast to 4,6-polyurethane, cannot crystallise. Thus copolyurethane-I contains units capable (A) and incapable (B) of crystallising. Thermographic examination has shown that the introduction of non-crystallising units causes the crytallisation and melting points of copolyurethane-I to fall and lowers the heats of crystallisation and fusion[45]. The reason is the diminished ability of the copolymer to crystallise with increase in the proportion of non-crystallising units, with a consequent lower degree of crystallinity and the formation of a less perfect crystal structure: copolyurethane-I containing >50 mole % of non-crystallising units is amorphous. This phenomenon leads to anomalous variation of the density of the copolymers, which increases linearly with the content of fluorinated units only for the amorphous copolymers. This is because the density is determined over the initial composition range (<50 mole % of non-crystallising units) by competition between two processes: the introduction of fluorinated units tends to increase the density by the substitution of fluorine atoms, but tends to diminish the density by disrupting the crystalline phase of the crystallising units (4,6-polyurethane).

Flory's equation for random binary copolymers comprising crystallising and non-crystallising units was applied to the depression of the melting point of copolyurethane-I. The calculated melting point was closely similar to the experimental value only for low contents of the non-crystallising units, but was above the latter at higher contents. Such anomaly is attributed to the presence in the non-crystallising units of long polyfluoroalkoxy-groups, which act as an internal plasticiser and intensify the general irregularity of the copolyurethane-I chains.

A copolyurethane of the same type is obtained from triethylene glycol with hexamethylene and methane-*pp*′-diphenylene di-isocyanates[47]. The initial homopolyurethanes are the crystallisable polyurethane-3 and the amorphous polyurethane-F3 (see Section I). In this case the melting point and the crystallinity of the copolyurethane also fall with increase in the proportion of non-crystallising units, but the copolymer becomes completely amorphous only when the content reaches 80 mole %. This provides further conformation that polyfluoroalkoxy-groups do indeed intensify the general irregularity of the copolyurethane-I chain.

An example of the second type of random binary copolymers is copolyurethane-II based on di- and triethylene glycols with hexamethylene di-isocyanate, whose chemical structure can be represented by the formula[43,44,46]

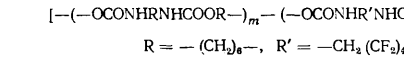



(7)

which shows that the initial homopolyurethanes are the above polyurethane-2 and polyurethane-3 (units C and D respectively). In contrast to copolyurethane-I, both kinds of units in copolyurethane-II are able to crystallise. Infrared spectroscopy and X-ray diffraction reveal a crystal structure identical with that of one of the initial homopolyurethanes. Transition from one type of structure to another is observed when the copolyurethane-II contains 60 mole % of C units. The composition dependence of the melting point contains a "eutectic minimum" at intermediate compositions, but no eutectic—mixture of crystals of the initial homopolyurethanes—is present. The occurrence of the eutectic minimum is due to the appearance of a less perfect crystal structure, owing to disruption of the regularity in the alternation of urethane groups that is necessary to produce a perfect crystal structure in polyurethanes of this type. The copolyurethanes, like the initial homopolyurethanes, are capable of a polymorphic crystal structure, but this ability diminishes with the transition to an equimolecular copolyurethane-II composition. Structural investigations have shown that the polymorphic transitions in the copolymer and in the initial homopolymers are a consequence of conformational changes in the chain, which may involve both the urethane group and the glycol unit. Thermographic and structural examination of mixtures of the initial homopolyurethanes crystallised together has shown that they are not isomorphous and cannot cocrystallise.

The copolyurethane obtained from hexamethylene di-isocyanate and mixtures of ethylene and hexaethylene glycols is of the same type[48]. Both kinds of units are also capable of crystallising, and their melting point also falls as the equimolecular composition of the copolymer is approached. Yet several mechanical properties of the copolyurethane vary irregularly, which can be attributed to the absence of a random or nearly random distribution of glycol units and the presence of long sequences (blocks) of the same glycol units in the chain. This may be due to a difference in the conditions of preparation of the copolyurethane[49].

Binary copolyurethanes of the third type may have the chemical structure[41]




(8)

As with copolyurethane-II, the initial homopolyurethanes of copolyurethane-III can crystallise, but they are isomorphous and able to form a combined crystal structure. Further, the composition dependence of the melting point does not pass through a "eutectic minimum", but is linear, owing to isomorphism. Another difference is that the tendency to form a polymorphic crystal structure inherent in a fluorinated homopolyurethane is not suppressed by the introduction of units of the second homopolyurethane, and a polymorphic structure appears even when the copolyurethane-III contains 70 mole % of the unfluorinated homopolyurethane.

A series of copolyurethanes based on hexamethylene di-isocyanate and mixtures of glycols of general formula $HO[C_2H_4O]_nH$ ($n = 1-4$, 6) (copolyurethane-M) had a constant mean concentration of hydroxy-groups in the mixture equal to their concentration in triethylene glycol [27,49-51], so that the empirical formula of the copolymers corresponded to formula (3) with $n$ adopting simultaneously all the above values. The properties of these copolyurethanes are compared with those of polyurethane-3, since they possess the same concentration of urethane groups, and differ only in the distribution of the latter in the chain. As in the case of copolyurethane-II, on passing from polyurethane-3 to copolyurethane-M not only the tendency to crystallise but also the ability to form a polymorphic crystal structure diminishes. The structure of copolyurethane-M containing 60% and 70% of triethylene glycol in the initial glycol mixture is identical with that of polyurethane based on triethylene glycol (polyurethane-3). Copolyurethanes having about the same contents of different glycols may have different types of structures depending on the conditions of crystallisation (from different solvents). The glass point of copolyurethane-M, in contrast to those of the initial homopolyurethanes, is determined not only by the concentration of urethane groups but also by their distribution in the chain. The temperature range of the glass transition also becomes wider, owing to the expansion of the spectrum of relaxation times resulting from differences in the mobility of individual chain segments caused by the irregular distribution of urethane groups in these copolyurethanes. Enthalpies and entropies of fusion as well as crystallinities have been determined for copolyurethanes-M. As in the cases of polyurethanes-4 and -6, the contribution of urethane groups to the entropy of fusion of the copolyurethanes identical in structure with polyurethane-3 has been estimated: they lower the entropy of fusion of the crystalline phase as in the other cases, the observed decrease being similar in magnitude to that of NHCOO groups in polyurethanes-4 and -6, and of NHCO groups in polyamides.

The data given on the structure and properties of linear polyurethanes obtained from the lower glycols indicate that their relation to the chemical structure of the chain is governed by the same laws as with other types of thermoplastic polymers capable of specific interactions (e.g. polyamides). Nevertheless, results for various random copolyurethanes obtained from multicomponent initial constituents suggest that the structure and properties of thermoplastic polyurethanes can be controlled extremely effectively by varying not only the chemical structure and nature of the initial constituents but also the distribution in the chain of polar—primarily urethane—groups, which determine the regularity of intermolecular hydrogen bonds in polyurethanes of this type.

## III. POLYURETHANES BASED ON OLIGOMERIC GLYCOLS

### 1. Cross-linked Polyurethanes

Increasing the molecular weight of the glycol constituents of polyurethanes while chemically cross-linking their chains leads to a qualitatively new type of polymeric materials—elastomers (rubbers)—which have been the subject of many studies, mainly on their strength, elastic, and other operating properties. Since most of this information has been summarised in monographs, reviews, and symposia [1,3,4,52-54], we shall discuss here only some of the main conclusions that can now be reached concerning the relation between the chemical constitution of cross-linked elastomers and their structure and physicochemical properties.

Cross-linked polyurethane elastomers are characterised by the alternation in their macromolecules of oligomeric blocks differing in flexibility and nature, as well as rigid di-isocyanate units, and the presence of various polar functional groups capable of forming various types of physical cross-links and transverse chemical bonds, etc. All this combined determines the macroscopic properties of the polyurethanes (glass point, temperature and range of phase transitions in crystallisable polymers, mechanical and other properties). As a consequence, the three-dimensional network in cross-linked polyurethanes is formed by both chemical cross-links and physical (hydrogen) bonds [1,3,4], and the structure of the effective three-dimensional framework, together with other parameters, acquires especial importance [1]. The most convenient procedure in estimating the contributions of individual parameters to the variation in the properties of cross-linked polyurethanes is to study successively the initial components (oligoglycols), intermediate products in the synthesis (linear polyurethanes), and the final cross-linked polyurethanes, as has been done in several studies [2,55-58].

Blocks of oligomeric glycols have the predominant role in determining the structure and properties of polyurethanes derived from them. Thermodynamic analysis and structural investigations have shown [56-59] that the ability of these polymers to crystallise is determined by the corresponding ability of the oligomeric blocks, and increases with the molecular mass of the latter. The crystal structure appearing both in linear and in cross-linked polyurethanes is identical with that of the oligoglycol blocks and their high-polymer homologues, but is less perfect, since the di-isocyanate units—and in cross-linked polyurethanes also branch points of the chemical network with adjacent units—act as defects in the crystal lattice. Formation of a crystalline phase in cross-linked polyurethanes is responsible for the development of properties inherent in energy-elastic materials [2,60,61], but the action of temperature or mechanical stresses breaks down this phase and restores to the polyurethanes the properties characteristic of entropy-elastic materials.

An abrupt rise in the glass point is observed on passing to polyurethanes only from oligoglycols (oligoethers) comprising polar chains, as a consequence of the formation of a secondary physical network diminishing their kinetic flexibility [1,2]. In cross-linked polyetherurethanes the glass point (like that of linear polyurethanes, largely determined by the thermodynamic flexibility of the chain) depends mainly not on the frequency of chemical cross-linking but on the concentration of urethane groups forming branch points of the physical network. Indeed, calculation of effective and chemical densities of cross-linking for polyurethanes based on oligoethers showed that physical links constitute about 80% of the total three-dimensional network, whereas the corresponding proportion in cross-linked polyurethanes based on carbon-chain oligoglycols is 10–30% [63].

With oligomeric blocks of the same molecular mass, the same di-isocyanate structure, and the same degree of chemical cross-linking the fall in the glass point of the polyurethanes with decrease in the polarity of the oligomeric blocks is accompanied by extension of the temperature range of vitrification, owing to a change in the character of the intermolecular bonds in the polymers.

Application of the theory of the free volume to vitrification of the initial oligoethers and the resulting polyurethanes established[58,64] that the macromolecules of polyurethanes based on oligoesters are thermodynamically more flexible than those based on oligoethers, but kinetically less flexible. The high thermodynamic flexibility of oligoester blocks is due to the great mobility of the secondary physical network formed, so that the latter readily rearranges under the influence of temperature or mechanical stress[1]. The presence in polyetherurethanes of a dense physical network capable of structural reorganisation influences also the thermodynamics of their deformation: in contrast to ordinary rubbers, the deformation of polyetherurethane elastomers is accompanied not only by a decrease in entropy but also by a change in internal energy[61,65,66].

The dominant role of glycol blocks in determining structure and properties is indicated by the fact that the flexibility of the molecules in polyurethane networks is due not only to the formation of long sequences of relatively short oligomeric chains but also the intrinsic flexibility of the oligomeric blocks. The cleavage and redistribution of secondary physical bonds in amorphous polyesterurethane elastomers, which occur under the influence of temperature and mechanical stress, are then a consequence of the preservation of oligoester blocks of high thermodynamic flexibility (mobility) even after their introduction into the polyurethane[2]. The high mobility of the secondary network in polyesterurethanes suggests an analogy between these polymers and the thixotropic structures studied in colloid chemistry[1,67].

Polyurethanes based on oligoglycols and individual di-isocyanates can be regarded as block copolymers, but the individual properties of the di-isocyanate units do not develop in the polyurethane, owing to their small size and the small fraction of the volume of the polymer that they occupy.

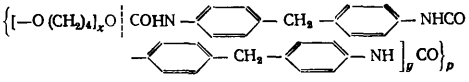
## 2. Segmented Polyurethanes

The introduction into the chain not only of oligomeric glycols but also of lower glycols or other bifunctional compounds (diamines, hydrazine, dihydrazides of dicarboxylic acids, etc.) leads to the formation of polyurethanes that, being linear or weakly cross-linked, develop under certain conditions the properties of elastomers, but at high temperatures or under the influence of solvents behave as ordinary thermoplastic polymers (polymeric materials).[1,68-73] Since the oligoglycol blocks are accompanied in the chain by relatively long sequences (segments, blocks) comprising di-isocyanate units and lower functional units, these polymers are usually termed *segmented polyurethanes*. The term "block copolyurethanes" is also fully applicable, but these compounds differ from traditional block copolymers (butadiene–styrene copolymers, etc.) in the relative smallness of the blocks, whose molecular mass reaches only a few thousands, so that the number of them in the chain is far larger. Since segmented polyurethanes have the properties both of thermoplasts and of elastomers, they have been termed *thermoplastic elastomers* (*thermoelastoplasts*).

During recent years quite a large number of studies have been published on segmented polyurethanes, concerned with their fine and supermolecular structure[71,74-93], their thermal and thermomechanical behaviour[94-110], and their physicochemical and physicomechanical properties[111-128]. The latter are related to the chemical constitution and to the supermolecular structure present in segmented polyurethanes.

### (*a*) Structure

The chemical structure of segmented polyurethanes can be demonstrated by that based on an oligo-oxytetramethylene glycol, methane-*pp'*-diphenylene di-isocyanate, and tetramethylene glycol (chain lengthener)



(9)

one of the most thoroughly studied examples. Two types of blocks can be distinguished (separated by the broken line)—flexible (oligether) and rigid, comprising di-isocyanate and lower glycol (chain lengthener) units—the first of which exhibit relatively weak intermolecular interactions and are responsible for the elasticity of the system, whereas the second ensure strong intermolecular interactions in the chain, the total effect of which may be comparable with that of cross-linking of the chains by chemical bonds[129]. Investigation of intermolecular links, primarily hydrogen bonds, therefore becomes especially important in segmented polyurethanes. An additional reason is that both the concentration and the distribution of hydrogen bonds should depend significantly not only on the chemical structure of the blocks but also on the length of the rigid blocks—the values of $y$ in formula (9)—as well as their proportion and distribution in the chain.

Information on chemical bonds, including hydrogen bonds, and physical interactions in polyurethanes has already been summarised[1]. Different types of hydrogen bonds may be formed in polyetherurethanes, involving either urethane or ether groups of the oligoether blocks. The type of hydrogen bond is largely determined by the concentration of urethane groups in the chain, increase in which results in hydrogen bonds formed predominantly between urethane groups. Fresh information on hydrogen bonds in polyurethanes has been obtained by the quantitative infrared spectroscopy of segmented polyetherurethane[77-81]. Examination of the efficiency of hydrogen-bonding in polymers based on methane-*pp'*-diphenylene di-isocyanate, tetramethylene glycol, and an oligo-oxytetramethylene glycol—formula (9)—or an oligo(tetramethylene adipate) of molecular mass 1000 has shown that almost all the NH groups in the urethane groups are hydrogen-bonded, with only about 60% bound to urethane carbonyls, and the remaining 40% to ethereal oxygen. Qualitatively similar results have been obtained for polyurethanes based on either oligoethers or oligoesters. A considerable number of hydrogen bonds between NH groups and ethereal oxygen in flexible chain segments are found in polyetherurethanes based on 2- and 4-methyl-1,3-phenylene di-isocyanates[81].

Whereas the presence of hydrogen bonds between urethane groups indicates the association of rigid blocks to form rigid domains[69], a high content of hydrogen bonds involving ethereal oxygen is evidence that segregation of rigid blocks in segmented polyurethanes does not (may not) go to completion. This may indicate that such bonds are formed at the boundary between the rigid domains and the flexible medium (matrix) formed by the oligoether blocks. Consequently, the spectral investigations of segmented polyurethanes are not inconsistent with

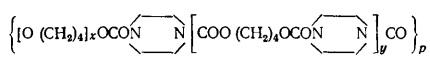
the conclusion that phase separation takes place in these polyurethanes, as in traditional block copolymers[68]. This is confirmed also by an investigation of the infrared dichroism of segmented polyurethanes[78], but in this case the regions of rigid urethane blocks and those of flexible oligoether blocks partly overlap.

X-Ray investigations have also been made[71,82-85,89] of the physical structure of the cross-links in segmented polyurethanes based on methane-*pp'*-diphenylene di-iso cyanate, an oligoether and an oligoester, and various chain lengtheners (tetramethylene glycol, ethylenediamine, hydrazine), both initially and after considerable deformation. The diffraction patterns of initial specimens containing hydrazine as lengthener show, besides a broad amorphous halo, a weak reflection with an interplanar spacing of 12 Å, which is a consequence of intermolecular packing of urethane segments[71]. Stretching the specimen by 200 to 300% results predominantly slanting orientation of rigid segments, while flexible segments are oriented in the direction of deformation. Further stretching leads to reorientation of rigid blocks. Heat-treatment in turn results in almost complete disorientation of flexible blocks, but does not affect the orientation of rigid blocks.

Furthermore, structural differences may be observed in stretched polyurethanes depending on the structure of both flexible and rigid blocks. The differences in intensity of scattering of X-rays by various segmented polyurethanes are attributed to different degrees of aggregation of the rigid blocks[83]. Rigid urethane domains constructed from methane-*pp'*-diphenylene di-isocyanate and tetramethylene glycol units[85] possess a lamellar structure, with mean distances of 100–200 Å between their centres. Both X-ray and spectral studies indicate that the rigid segments of segmented polyurethanes form isolated domains within a rubberlike matrix of flexible blocks.

Electron microscopy of segmented polyurethanes also indicates a two-phase structure[88]. They are micro-heterogeneous two-phase systems with rigid domains of size 30–100 Å. The micrographs suggest that the domains are three-dimensional.

Structural investigation of the polyurethane[87,88]



(10)

from which hydrogen bonds should evidently be absent, also indicates the presence of domains. Furthermore, such segmented polyurethanes, with a narrow range of lengths of flexible blocks and a different (definite) length of rigid blocks, may contain structural formations ("superstructures" or "superdomain structures") substantially larger than the domains. These stable structural formations, which may extent to 1 μm, are revealed by the scattering of polarised light. Although they resemble spherulites, the pattern of scattering is somewhat different. The nature of these structures is related to the possible crystallisation of rigid chain segments, since flexible segments do not crystallise in the undeformed state. This indicates that the appearance of a domain structure in segmented polyurethanes is not a consequence solely of the presence in the rigid blocks of polar groups capable of forming hydrogen bonds. Phase separation in segmented polyurethanes, as in traditional block copolymers, is predetermined also by the limited compatibility of different blocks in the chain, differing in nature and flexibility.

(*b*) Thermal and thermomechanical behaviour

Both the chemical constitution and the structure of segmented polyurethanes govern also their thermal and thermomechanical behaviour. Calorimetric, differential thermal, dilatometric, thermomechanical, and other studies indicate that segmented polyurethanes undergo a multiplicity of temperature transitions, due to the occurrence of various processes. Thermal transitions have been investigated[95] in a segmented polyurethane based on an oligoethylene glycol adipate, tetramethylene glycol, and various di-isocyanates (methane-*pp'*-diphenylene, tolylene, etc.), in which several thermal transitions have been detected, three of which can usefully be distinguished. Thus a transition in the region of −40°C is due to the segmental mobility of units of the oligoether block, i.e. its vitrification, as in cross-linked polyurethanes based on the above adipate[1]. The temperature of this transition in the polyurethane is higher than the glass point of the initial oligoether. Yet the glass point varies little with the structure of the di-isocyanate units in polyurethanes, with the exception of tolylene di-isocyanate, which may raise the glass point of a segmented polyurethane.

The other two transitions, observed around 70–80° and 150–180°C, depend on the structure of the rigid blocks and represent processes occurring in the micro-regions formed by them. The higher glass point and somewhat lower temperatures of the high-temperature transitions in the polyurethane based on tolylene di-isocyanate are attributed to the diminished segregation of rigid blocks due to the large number of bonds formed between them and the oligoether blocks. Hence interaction between rigid and flexible blocks may lead to disordering of the rigid domains, resulting in depression of the transition temperatures characterising these domains. It was also concluded that rigid segments may achieve a high degree of order, but the high-temperature transition points in segmented polyurethanes are lower than those for the initial rigid blocks owing to their small proportion in the polyurethane or low percentage crystallinity resulting from their copolymerisation with flexible blocks or from branching. However, cases are possible in which the degree of order in the rigid domains is so great that the high-temperature transition point in the segmented polyurethane is almost identical with that in the initial rigid block.

The glass point in a segmented polyurethane can be lowered[96] by increasing the chain length of flexible blocks, shortening rigid blocks, replacing aromatic by aliphatic urethane units, and restricting the intermolecular interactions of flexible blocks. The introduction into a segmented polyurethane of oligoether blocks having a wide molecular-mass distribution leads in turn to widening of the temperature range of vitrification and crystallisation of the polyurethane (flexible blocks)[97].

Calorimetric investigations have been made on segmented polyurethanes obtained from various oligoethers—oligo-oxypropylene glycol, oligo-oxytetramethylene glycol, oligo(ethylene butylene glycol adipate)—varying in molecular mass, methane-*pp'*-diphenylene di-isocyanate, and tetramethylene glycol[101]. The concentration of urethane groups was controlled by varying the content of lower glycol units in the chain. As with cross-linked polyurethane elastomers[1], the glass points of these polymers depend on the total concentration of urethane groups in the chain, but this relation becomes less marked with increase in the molecular mass of the oligoether block.

In addition to the low-temperature vitrification, a high-temperature transition develops at 110–120°C, whose character depends on the length of the rigid block. It was suggested that this latter transition was due to the dissociation of hydrogen bonds between rigid blocks, caused by "thermal perturbation of adjacent polyether segments of the chain" [101].

Three thermal transitions have been revealed by thermographic and thermomechanical studies of segmented polyurethanes (polyurethane semicarbazides) [99,108] prepared from methane-*pp'*-diphenylene di-isocyanate, oligoethers (oligo-oxytetramethylene glycol, oligo-oxypropylene glycol), and chain lengtheners (hydrazine, adipo- and isophthalo-dihydrazines). The first transition occurs between −25 and −55°C depending on the chemical structure and the molecular mass of the oligoether block, as well as on the concentration of urethane groups, and is due to the segmental mobility of the oligoether blocks. The third transition, which begins around 70°C and is diffuse in character, represents the breakdown of association complexes formed from rigid blocks (devitrification of rigid blocks). The second transition occurs in the region of 25°C, and is probably due to dissociation of bonds between oligoether and rigid (di-isocyanate–lengthener–di-isocyanate) blocks. In a segmented polyurethane [100] having longer blocks capable of crystallisation the latter two transitions correspond to higher temperatures (50–100 and 140–200°C); in addition a new transition appears in the range 200–300°C, caused by the melting of paracrystalline ordered domains constructed from rigid blocks.

Thermal transitions and thermomechanical behaviour have been investigated also in segmented polyurethanes [103] obtained from 2- and 4-methyl-1,3-phenylene di-isocyanates, differing also in the proportions of the initial components and the previous history of the test specimens. Polyurethanes obtained from the symmetrical di-isocyanate crystallise; those containing the unsymmetrical 4-methyl-1,3-phenylene di-isocyanate unit are amorphous. Three temperature transitions are observed depending on the structure of the di-isocyanate unit, the composition of the segmented polyurethane, and the previous thermal history. The transition in the range 20–80°C is attributed to dissociation of bonds between loosely packed domains of rigid blocks, and that above 150°C to fusion of crystalline formations of rigid blocks.

Thermomechanical and structural investigations of segmented polyurethanes based on oligoethers and oligoesters, methane-*pp'*-diphenylene di-isocyanate, and aliphatic diamines $NH_2[CH_2]_xNH_2$ ($x$ = 0, 2–6) have established [106] that preliminary softening takes place at 60–70°C in specimens from diamines having $x$ = 3, 5, which is attributed to interaction between phases formed by flexible and rigid blocks, leading to some mutual dissolution. The softening temperature of the polyurethanes varies from 130 to 190°C with change in $x$ from 0 to 6. Softening temperatures are in all cases lower for polyurethanes containing oligomeric ester blocks than for segmented polyurethanes based on oligoethers. Small-angle scattering of X-rays shows that the softening temperature rises with increasing degree of isolation of rigid blocks. Varying the number of methylene groups in a segmented polyurethane alters the degree of aggregation of rigid blocks, although the content of urethane and urea groups remains the same. The aggregation of rigid blocks involves the formation of hydrogen bonds between functional groups in the blocks, which is governed by the number of methylene groups in the diamine unit. Aggregates of rigid segments act as an active filler or as branch points in the three-dimensional network of the segmented polyurethane.

The temperature of annealing has a complicated influence on transitions in and the structure of a segmented polyurethane [98]. It is concluded that annealing results in two types of microstructural changes: homogenisation of the system of hydrogen bonds includes the observed increase in order; and conversion into an ordered structure (perhaps microcrystalline) may involve reorientation of the domain structure. The effect of quenching (amorphisation) on thermal behaviour has been demonstrated in a thermographic investigation of a segmented polyurethane based on an oligo-oxytetramethylene glycol, hexamethylene di-isocyanate, and diethylene glycol [108]. Six temperature transitions were observed, associated with vitrification, crystallisation, and fusion of microregions formed by blocks of differing rigidity. The polar nature of the blocks leads to interaction between microregions differing in rigidity, which affects the transition temperatures. Nevertheless, the melting point of a rigid block remains almost unchanged after introduction into a polyurethane. This agrees well with an earlier conclusion [95] that a high degree of order may be possible in rigid domains.

Investigation of a polyurethane based on an oligobutylene glycol adipate, hexamethylene di-isocyanate, and an aliphatic (tetramethylene glycol) and an arylated chain lengthener has revealed [109] that the previous thermal history has a significant influence on the thermomechanical behaviour and other properties of segmented polyurethanes. The structure and the properties of these polymers depend on their state of phase aggregation, which depends both on the structure of the rigid blocks (governed by that of the chain lengtheners) and on the previous thermal history of the copolyurethane. The polyurethane based on the aliphatic lengthener exhibits considerable residual elongations, which are attributed to orientation crystallisation on stretching. The rather lower values found with aromatic lengtheners are consistent with the smaller tendency to crystallise shown by the resulting blocks than by those based on tetramethylene glycol.

Investigations on segmented polyurethanes [110] in which the chain lengtheners contain either non-polar or polar substituents have shown that increase in the polarity of a rigid block is accompanied not only by the regular rise in the flow point owing to the breakdown of rigid domains but also by a fall in the glass point of the flexible oligoether blocks. This phenomenon is attributed to an increase in the degree of segregation of rigid blocks with increase in their polarity.

Study of the thermal behaviour of the above segmented polyurethane devoid of hydrogen bonds (based on piperazine—formula 10) revealed [94] the properties of cross-linked elastomers over a wide temperature range, but at high temperatures this polymer melts, and can be processed by the methods used for plastics and fibres. Their three-dimensional network is formed by the association (crystallisation) of rigid blocks bound by intermolecular bonds. It is concluded that the flexible blocks act as a diluent and do not mix with the rigid blocks.

A multiplicity of transitions in segmented polyurethanes has been detected in an investigation of their relaxation properties by dynamic, mechanical [111,116,117], and dielectric [125–127] methods. Thus two principal transitions have been observed [111], corresponding to the glass points of

oligoether and rigid blocks (containing urethane groups). Several transitions corresponding to the movement of various groups in the blocks have also been found. All relaxation transitions depend on the molecular mass and the content of rigid blocks, as well as on the previous thermal history. Increasing the molecular mass of the rigid block leads to the formation of a semicrystalline material. Relaxation mechanisms in segmented polyurethanes depend not only on the crystallinity but also on the nature of the domain structure. The properties of segmented polyurethanes from oligoethers are determined by both the size and the structure of the rigid blocks [112,117]. In the case of a polyurethane having a non-polar flexible block the glass point of the latter is in turn independent of the nature and the concentration of the rigid urethane blocks [116].

Investigation of the influence of block dimensions and molecular-mass distribution on the properties of a segmented polyurethane shows [123] that a narrower distribution of rigid blocks gives a higher elastic modulus in the region of the plateau. The reason is that the domains formed in such a polyurethane are more perfect that those in a polyurethane having a wider molecular-mass distribution.

(*c*) Orientation and deformation behaviour

Application of infrared dichroism to orientation processes in segmented polyurethanes containing [90,91] and devoid of [92,93] hydrogen bonds reveals two different mechanisms of orientation for crystalline and amorphous segments formed by rigid blocks. In amorphous segments such blocks are oriented in the direction of stretching at small deformations. The orientation of crystalline segments takes place in two stages, the first of which consists in positive orientation of crystalline regions as a whole, leading to negative orientation of the blocks. In the second stage the primary crystalline segments break down, and the blocks are packed in microregions parallel to the stretching force. Segmented polyurethanes containing no hydrogen bonds exhibit enhanced deformability of rigid blocks and hysteresis in comparison with the hydrogen-bonded segmented polyurethanes. This difference applies to the decrease in energy of intersegmental bonds and the increase in crystallinity of the rigid blocks. Calorimetric examination of the stretching of segmented polyurethanes from crystallisable and non-crystallisable oligoethers indicates [119] in turn that mainly the flexible blocks are deformed when the polyurethane is stretched. Comparison of the energy of the probable hydrogen bonds with the quantity of heat evolved on stretching shows that these bonds are completely realised in the undeformed state. Crystallisation occurs in some polyurethanes even at small deformations, as is confirmed by X-ray diffraction. If the chain structure permits crystallisation, large residual deformations may be observed, which become reversible on subsequent heating.

Investigation of the structure of initial and stretched fibres of a segmented polyurethane showed [74] that orientation drawing is accompanied by a transition of flexible blocks from an unordered (amorphous) state to an ordered (crystalline) state. During drawing the chains slide over one another until the strong dipole–dipole interaction between rigid blocks inhibits such slippage. It was concluded that the deformed polyurethane contained an oriented supermolecular structure, whose character depended on the chemical structure and on the conditions of fibre formation. The influence of temperature and the previous history of stretching on molecular orientation in various blocks in a segmented polyurethane has also been examined [130]. A two-phase model is suggested for interpreting the morphology of polyurethane. It envisages two regions—one containing urethane blocks, and the other flexible oligoether blocks—which are semi-continuous and mutually overlapping. Those having a high elastic modulus, containing aromatic urethane units, reinforce the flexible phase. Since these phases are interpenetrating, both are deformed when stress is applied. On removal of the load, the flexible regions relax, whereas the rigid regions remain plastically deformed. Other investigations on the orientation of rigid and flexible blocks [131] are consistent with a model in which a segmented polyurethane consists of hydrogen-bonded crystallites formed by rigid blocks, which are distributed in a matrix of flexible blocks.

Several studies have been made of the optical [114,118] and mechanical [118,120–122] properties of various segmented polyurethanes. The optical behaviour on deformation [114] indicates a segregated spherical structure comparable with that observed by electron microscopy in hydrocarbon block copolymers. Investigation of the optical and mechanical properties of various segmented polyurethanes containing optically anisotropic regions of size 50–200 $\mu$m, as well as spherulitic structures, has shown that both the anisotropy of their distribution and the mechanical properties of these polyurethanes are functions of composition. Some specimens are deformed with formation of a neck and the appearance of small hump on the stretching curve, and others have a curve characteristic of elastomers; the moduli of elasticity also differ. Such variation in mechanical properties is attributed to the formation of different domain structures, which explain also the low-temperature deformability of the segmented polyurethane obtained from an oligo-oxytetramethylene glycol, methane-*pp'*-diphenylene di-isocyanate, and isophthalodihydrazide [121]. The mechanism is assumed to resemble that of the large low-temperature deformations developed for crystalline polypropylene [132]. However, the deformation is due in this case to the slippage not of units of the supermolecular (spherulitic) structure but of domains or their units formed by rigid blocks. Hence the structural features of segmented polyurethanes govern also their typical orientation and deformation behaviour.

Thus, in spite of some ambiguity and occasionally contradictions in the results of individual investigations, there are nevertheless grounds for reaching definite conclusions on the structure and properties of segmented polyurethanes. Like hydrocarbon block copolymers, these materials possess a two-phase structure. Rigid domains, made up of rigid blocks, are distributed in a medium (matrix) of flexible oligomeric (oligoethereal) blocks and act as branch points of a physical network or as an active thinner. In the present case, however, the rigid domains are usually hydrogen-bonded and may possess a crystalline (semicrystalline) structure, depending on the chemical structure, the molecular mass and its distribution, and other properties of the rigid blocks determining their degree of segregation. The polar nature of blocks differing in rigidity and the presence in them of functional groups capable of specific interaction prevent the segregation of rigid blocks and favour the appearance of "transition" (mutually overlapping) regions. However, the presence in rigid blocks of polar groups capable of forming hydrogen bonds and other physical interactions is not the only factor responsible for the domain structure in segmented polyurethanes. As in hydrocarbon block copolymers, separation into phases is

due also to the limited compatibility of blocks differing in structure and rigidity. Segmented polyurethanes can be regarded as microheterogeneous systems.

### 3. Segmented Polyetherurethanes

The term "segmented polyetherurethanes" can also be applied in most cases to the polyurethanes discussed above (Section III, 2), but we have decided to use it for copolyurethanes whose chains contain two kinds of oligoether blocks, usually differing either in ability to crystallise or in flexibility, and linked by a di-isocyanate (lengthener). The general formula of such a polymer can be written

$$(-A-OCONHRNHCOO-)_{1-n}-(-B-OCONHRNHCOO-)_n \qquad (11)$$

in which A and B are segments (blocks) of different oligoethers, and R is part of the di-isocyanate unit. Several studies of these products [124,133-142] have examined such aspects as the influence on structure and properties of the chemical constitution, molecular mass, molecular-mass distribution, mole fraction, etc. of various oligoether blocks. Several properties of these polyetherurethanes have already been surveyed [1].

Study of the properties of segmented polyetherurethanes [134] prepared from an oligoethylene glycol adipate, an oligo-*p*-phenylenebisethylene glycol adipate, and hexamethylene di-isocyanate with different molar proportions of the blocks and different molecular masses of the acrylated oligoether established that each block could crystallise as a separate phase. The ability to form a crystalline phase decreases as the oligoether block becomes smaller. Polyetherurethanes with roughly the same number of blocks of each kind exhibit the smallest tendency to crystallise, which is responsible for their highest elastic properties. The increase in the content of urethane groups resulting from decrease in the length of the block raises the glass and melting points of homopolyurethanes of comparable molecular mass. The crystallinity of a segmented polyetherurethane is usually due to crystallisation of the oligoether block present in excess [133]. The glass and melting points of segmented polyetherurethanes are largely determined by the structure and the molar content of the oligoether blocks.

Investigation of segmented polyetherurethanes with crystallising blocks of oligo-*o*-phenylenebisethylene glycol adipate and amorphous blocks of oligo(diethylene glycol adipate) suggested [135] that the primary units of the spherulitic structures were formed only by crystallising blocks. Blocks of the amorphous component chemically combined with them, also present in the spherulite, were arranged on the periphery of the primary crystalline structures, acting as an interstructural plasticiser. Crystallisation processes taking place with time then result not in a rise but in a fall in the glass point, since crystallisation is accompanied by accumulation of the interstructural component in the spherulites. An analogous fall in glass point has been observed in other investigations of segmented polyetherurethanes containing crystallising and non-crystallising oligoether blocks [136-138], which indicates that during crystallisation the non-crystallising block forms a separate phase with its own inherent properties.

Thermographic investigations of a segmented polyetherurethane obtained from oligo-oxytetramethylene glycols of various molecular masses and an oligoethylene glycol sebacate have shown [140,142] that crystallisation occurs predominantly in the latter, but when the first block is sufficiently long both may crystallise. These polyetherurethanes exhibit two separate melting ranges, that at lower temperatures due merely to weakening of the "physical network" (fusion of the crystalline phase comprising oligo-oxytetramethylene glycol blocks) with a corresponding change in elastic properties, whereas the higher-temperature range (melting of the crystalline phase of oligoethylene glycol sebacate blocks) represents transition of the polyurethane to a state of viscous flow. The flow point of segmented polyetherurethanes can be raised by introducing tetramethylene glycol units into their chain, so that the concentration of urethane groups is increased, with an increase in branch points of the physical network. Strictly speaking, such modification of properties leads to the formation of a kind of "hybrid" segmented polyurethane, between the above segmented polyurethanes and segmented polyetherurethanes, since sequences of di-isocyanate and tetramethylene glycol units are produced (formation of a rigid block). Investigation of the structure of an analogous segmented polyetherurethane but with oligo-oxytetramethylene glycol blocks differing in polydispersity indicates [124] that the properties of these polymers are determined mainly by the structure and the properties of the crystalline phase, and to a less extent by the structure of the more flexible block. However, the most labile, easily reorganised crystal structure should be more readily achieved in copolymers with mobile fragments of the more flexible block. This should apply also to segmented polyetherurethanes with greater polydispersity of the oligo-oxytetramethylene glycol blocks, in which the network of physical bonds formed by the urethane group is most imperfect and labile.

Thus the above results for segmented polyetherurethanes indicate that they also can be included among thermoelastoplasts, but the crystalline structure produced in them, acting as branch points of the physical network, cannot provide adequate thermal and physicomechanical constants. This makes it necessary to introduce also lower glycols, which increase the concentration of urethane groups in the chain and localise them in separate microregions (domains). Strictly speaking, we return to the above segmented polyurethanes with two kinds of flexible oligoether blocks in their chains.

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# Gas-chromatographic Analysis of Unstable Inorganic and Organoelement Compounds

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The present state of the gas-chromatographic analysis of unstable and reactive substances if reviewed and described systematically in terms of the characteristic reactions of such compounds, such as hydrolysis, oxidation, thermal and catalytic degradation, and isomerisation. The requirements which must be met by the carrier gas, the solid carrier, and the stationary phase in the analysis of these compounds are discussed together with the characteristics of the qualitative analyses, as well as the apparatus employed.
The bibliography includes 218 references.

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## I. INTRODUCTION

Gas-chromatography is the most universal method for the solution of various analytical problems. However, the application of the usual version of gas chromatography in the analysis of unstable substances is impossible owing to the high reactivity of the compounds analysed. In the analysis of such substances, it is therefore necessary to carry out methodological modifications involving the elimination of the causes responsible for these reactions or the latter must be carried out either before injection into the column or in the column.

One of the trends in the development of gas chromatography is the development of special methods whereby gas chromatography can be used to analyse unstable compounds.

Several reviews have been published on chromatographic analysis, which include, in particular, data on the analysis of relatively unstable compounds[1-4]. However, they mainly describe isolated data for specific classes of substances combined because of the similarity of their molecular structures. We thought it most useful to give a systematic account of the gas-chromatographic analysis of unstable compounds on the basis of their characteristic reactions, such as hydrolysis, oxidation, thermal and catalytic degradation, and isomerisation.

In order to prevent the above reactions in chromatographic analysis, it is necessary to take special precautions in the preparation of the carrier gas and in the selection of the solid carrier, the stationary phase, the apparatus, etc. In the first place, more stringent requirements must be met by the carrier gas as regards its nature and purity, in particular its content of oxygen and moisture. In the analysis of unstable compounds, much attention is devoted to the selection of the solid carrier on the basis of diatomite and polytetrafluoroethylene. The structures and properties of solid carriers have been described in detail[5]. On the other hand, the choice of the carrier in the analysis of readily hydrolysable, oxidisable, and thermally and catalytically active compounds has its own characteristic features. Important properties of the carrier are its specific surface, mechanical strength, surface pH, and adsorption and catalytic activities. Its chemical properties (acidity or alkalinity) to a large extent determine the error in qualitative or quantitative analysis. In order to eliminate the chemical, catalytic, or adsorption activity of the carrier, it is modified by thermal, acid, or alkaline treatment, by coating the surface with a continuous film of an inert material, by deactivating the adsorption-active centres as a result of the introduction of small amounts of adsorption-active additives, and by chemical conversion of the polar hydroxy-groups into non-polar groups. Inert polymeric sorbents based on Teflon are used successfully.

In the first place, the mobile phase should be incapable of dissolving oxygen, should be chemically inert, with respect to the substances analysed, and should be hydrophobic. Specific requirements in the analysis of compounds of the type under consideration must be met by the material of the column, the metering device, and the detector, and the conditions during analysis. In order to prevent the decomposition of thermally unstable compounds, the percentage impregnation of the mobile phase is low and use is made of solid carriers with small surface areas, vacuum, low temperature, short columns, and high carrier gas flow rates. In many cases the instability of certain compounds makes it possible to analyse them on the basis of the stable products of their characteristic reactions; the reactions are carried out in the column or before injection into the latter (the method of reaction chromatography). Stable compounds in unstable products are analysed by the same method involving a preliminary reaction with the unstable compound in order to remove it and subsequent separation of the stable compounds.

The gas-chromatographic study of the reactions of unstable substances (hydrolysis, oxidation, isomerisation, etc.) constitutes a separate problem and is not discussed in this review.

## II. ANALYSIS OF READILY HYDROLYSABLE SUBSTANCES

One of the large groups of substances which are analysed by gas chromatography are those which can be hydrolysed. These include metal chlorides, chlorosilanes and organochlorosilanes, boron, hydrides, chlorine, bromine, and iodine fluorides, and alkylated derivatives of boron, aluminium, beryllium, and gallium. The following reactions may be quoted as examples of hydrolysis:

$$BCl_3 + 3H_2O \rightarrow 3HCl + H_3BO_3,$$
$$BHCl_2 + 3H_2O \rightarrow 2HCl + H_2 + H_3BO_3,$$
$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl.$$

Evidently hydrolysis results in the evolution of gaseous substances (such as HCl and $H_2$) and solid products (silicon dioxide and boric acid). The occurrence of such reactions cannot be allowed in gas-chromatographic analysis, because, on the one hand, it distorts the quantitative result and, on the other hand, leads to corrosion of the apparatus (HCl) and the formation of a solid deposit which blocks the metering device, the detector, and the connecting capillaries. Furthermore, the formation of a solid deposit on the stationary phase impairs the separation and alters the chromatographic characteristics of the substances analysed.

Numerous studies have been devoted to the direct gas-chromatographic analysis of readily hydrolysable substances. The first publications on this problem appeared in 1957–1960[6,7] and subsequently their number greatly increased[8–45]. Table 1 presents the fundamental groups of substances which are readily hydrolysable. Direct gas-chromatographic quantitative analysis of compounds of this type requires careful drying of the carrier gas until its water content is such that it does not affect the analytical results. The drying agents employed in gas chromatography are listed in Table 2, which shows that the best drying effect is achieved in the presence of phosphorus pentoxide. Furthermore, moisture is removed by condensing water vapour at the temperature of liquid nitrogen. In the majority of studies involving the analysis of readily hydrolysable substances, drying is achieved with a combination of drying systems. Thus, in the analysis of inorganic hydrides[46,47], the carrier gas (nitrogen) was dried by being passed through a system of five series-connected columns filled with granulated copper, KSK silica gel, activated granulated alumina, type 5 Å molecular sieve, and a liquid eutectic mixture of sodium and potassium. After passage through the system, up to $8 \times 10^{-5}$% of water remained in the nitrogen. However, in another investigation[7] oxygen-free nitrogen for the analysis of boron hydrides was dried with magnesium perchlorate alone, the drying effect being regarded as sufficient.

In the analysis of inorganic corrosive gases, the drying agents employed were 5 Å molecular sieve (nickel column 12.5 mm in diameter and 107 cm long) subjected to preliminary activation by heat treatment (at 300–325°C, and a residual pressure less than 1 mmHg) for 2 h. The authors[48] claim that such activation makes it possible to employ the drying agent without reactivation for several months, and that the water content in the gas is reduced to $< 5 \times 10^{-4}$%. A gas-chromatographic method has also been proposed for the determination of residual moisture in the carrier gas by condensing water at −78°C and then removing it by reaction with calcium hydride with determination of the oxygen formed. The drying capacities of KSK silica gel, Anhydrone, 5 Å and 4 Å molecular sieves, and phosphorus pentoxide have been tested[49]. The maximum attainable drying effect has been achieved, for example, in the drying of chlorosilanes with the aid of phosphorus pentoxide ($5 \times 10^{-3}$ mg litre$^{-1}$). In order to increase the period during which the $P_2O_5$ column is serviceable (the $P_2O_5$ is deposited on lumps of pumice), some other drying agent must be placed before this column: molecular sieves, Anhydrone, or silica gel. In some investigations[50,51], three columns (100 cm long and 40 mm in diameter), made of glass and filled with 5 Å molecular sieve, were used as the drying train. The moisture content in the nitrogen emerging from the chromatographic column was less than $5 \times 10^{-4}$ mole %, which is permissible for the analysis of germanium tetrachloride and trichlorosilane.

Table 1. Conditions in the gas-chromatographic analysis of readily hydrolysable substances.

| Substance analysed | Carriers and stationary phases | Carrier gas and requirements which it must meet | Detector | Refs. |
|---|---|---|---|---|
| Boron hydrides | Celite 545, Chromosorb W, Chromaton N, Embacel, liquid paraffin, tricresyl phosphate, Octoyl S, silicone oil 702, OV-17, SE-30, E-301, OV-1, Apiezon L | helium and nitrogen: oxygen content not more than $1 \times 10^{-3}$ mg litre$^{-1}$ | katharometer, flame-photometric detector | 6-13 |
| Metal chlorides, $BCl_3$, $SiCl_4$, $SnCl_4$, $TiCl_4$, $PCl_3$, $TaCl_5$, $NbCl_5$ | Celite 545, Teflon, Chromosorb AW-HMDS, graphite heated in a stream of $Cl_2$, Sterchamol, silicone oils, DC-703, DC-550, XE-60, Kel-F, Apiezon L, saturated n-alkanes, paraffin, $BiCl_3$–$PbCl_2$ eutectic mixture | helium, nitrogen, and hydrogen with a water content up to $1 \times 10^{-3}$ mg litre$^{-1}$ | katharometer, thermionic detector, electron capture detector | |
| Chlorosilanes and organochlorosilanes | infusorial earth, tiles, Celite 545, INZ-600, Sterchamol, treated DMDXC, Spherochrome, Chromaton NWA, nitrobenzene, benzophenone, liquid paraffin, diethyl- and dibutyl phthalates, tricresyl phosphate, silicone oils NF-M50150, DC-703, PFMS-4, F-169, FS-16, OE-4178, SF-96, DC-LS, K-3-0295, SKTFT-50, and E-301 | helium and nitrogen, argon with a water content up to $1 \times 10^{-3}$ mg litre$^{-1}$ | electrical conductivity detection, katharometer, flame-ionisation detector | 23-36 |
| Corrosive inorganic gases | PTFE, solid Kel-F polymer, silica gel, NaF, LiF, liquid Kel-F, oil. dimethyl galcarbonic ether of triethylene glycol, chlorofluorohydrocarbons | helium, nitrogen, and argon | nickel katharometer, thermistors coated with Teflon | 37-45 |

Thus specially activated 5 Å molecular sieve and phosphorus pentoxide may be regarded as the most effective drying agents in the analysis of readily hydrolysable compounds. The degree of drying of the carrier gas can be usefully inferred from the chromatograms of readily hydrolysable products, for example trichlorosilane.[52] When moisture is present in amounts exceeding $5 \times 10^{-4}$ mole %, two peaks due to trichlorosilane and its hydrolysis product (hydrogen chloride) appear on the chromatogram. When the degree of drying was inadequate, the sorbent was additionally dried by passing trichlorosilane vapour through the column.

In the drying of the carrier gas, account must be taken of the tendency for the moisture content in the carrier gas–sorbent system to reach equilibrium. The dew point in the carrier gas does not therefore characterise the moisture content of the system as a whole, which is the most important parameter.

We shall now consider a number of drying procedures. Thus, in order to prevent the decomposition of boron trichlorides in the chromatograph, the sample injection system is coated with Teflon and the connections between the latter, the column, and the detector are made of Teflon tubes [15]. The carrier gas is carefully dried by means of a molecular sieve and a trap cooled with a mixture of acetone and ice and is treated with 1% of boron trichloride†.

Table 2. Comparison of the drying capacities of various substances.

| Drying agent | Residual concentration of water vapour at 25°C, mg litre$^{-1}$ |
|---|---|
| Fused $CaCl_2$ | 0.36 |
| Granulated $CaCl_2$ | 0.14–0.25 |
| $Al_2O_3$ | 0.03 |
| $Mg(ClO_4)_2.3H_2O$ | 0.002 |
| Anhydrous $Mg(ClO_4)_2$ | 0.0005 |
| Molecular sieves | 0.0005 |
| Phosphorus pentoxide | 0.000025 |

In many cases the gas system of the chromatograph is dried by substances more readily hydrolysable than the compound analysed. For example, before the analysis of dichloro-(β-cyanoethyl)methylsilane, trichlorosilane or silicon tetrachloride are introduced several times into the apparatus after the column has been flushed with dry helium [35]. Alkylated boron derivatives are analysed after the entire system has been flushed with the carrier gas at 150°C and above, with subsequent repeated passage of boranes through the column [53]. On the other hand, in the analysis of readily hydrolysable compounds, for example, boron trichloride, the final drying is carried out using the compound analysed [54,55].

A scheme with circulation of the carrier gas [56] is of interest. The authors showed that the passage of 1.5 litres of the carrier gas (containing water at a concentration of $1 \times 10^{-4}$%) through the column at a rate of 50 ml min$^{-1}$ causes the decomposition of 0.002 ml of the bisisopropyl benzenechromium specimen. On the other hand, circulation of the carrier gas makes it possible to reduce its moisture content by its interaction with the first portion of the substance chromatographed. The employment of stepwise chromatography in the analysis of readily hydrolysable substances is also of considerable interest. In this case, hydrolysis does not affect the results of the quantitative analysis [52].

†We believe that the cooling of the carrier gas described above is not a rational procedure, because the drying capacity of molecular sieves is extremely high and there is a possibility of the formation of a mist in the trap, which would prevent the complete drying of the carrier gas.

As already mentioned, special requirements must be met by the solid carrier in the analysis of readily hydrolysable and corrosive compounds. In the first place, it is necessary to remove physically adsorbed moisture, which leads to the instantaneous hydrolysis of the substances analysed. However, drying should not remove the water which is used to deactivate the active centres of the carrier [57]. Thus it has been noted‡ that, in the analysis of boron trichloride on Celite (Chromaton) subjected to preliminary vacuum drying at 300°C, boron trichloride undergoes complete irreversible adsorption. The HCl peak is not then observed, which indicates the absence of moisture from both the system and the solid carrier. On the other hand, partial removal of water from the active centres of the solid carrier led to a sharp increase of the retention time of boron trichloride (the peak remained asymmetric). In the drying of the solid carrier, it is therefore necessary to select optimum conditions.

Various methods are used to eliminate the adsorption activity of the carrier. Together with the generally accepted procedures described above, the most effective method for modifying the solid carrier involves its treatment with the substances analysed. In the analysis of primary amines, the preliminary steps involve the repeated admission of the mixture analysed, after which quantitative analysis becomes possible [58]. A study of the influence of irreversible adsorption on the analysis of 1-butanol showed that the error in the determination of 1-butanol decreases appreciably with the increase of the number of successive analyses. If the strongly adsorbed compounds are then desorbed by heating the solid carrier in a stream of carrier gas, saturation is again necessary in the subsequent analyses [59].

The INZ-600 carrier modified by chloromethylsilanes has been used in the analysis of readily hydrolysable chlorosilanes and organochlorosilanes. It was shown that the best modifying agent is dichlorodimethylsilane. [52,60–62] Boron trichloride has been analysed on non-modified Celite 545. [55] In subsequent studies, additional treatment of the solid carrier with boron trichloride proved to be necessary in order to obtain reproducible quantitative results. The method of treatment was as follows: the solid carrier was dried *in vacuo* at 200°C for 3 h, after which it was treated with boron trichloride vapour for 1 h, freed from the trichloride which failed to be adsorbed on the surface by a stream of dry carrier gas, and the stationary phase was deposited (avoiding contact with air). Fig. 1 presents two chromatograms for boron trichloride obtained on untreated and treated carriers.

The solid carrier is also modified when substances of a similar type are introduced into the carrier gas. It is recommended that, in the analysis of amines, a volatile amine or ammonia be added to the carrier gas [63]. In another investigation [15], 1% of boron trichloride was added to the carrier gas in order to achieve additional drying. In this case, boron trichloride probably also behaves as a modifying agent in relation to the carrier surface.

It is claimed [64] that diatomite carriers such as Celite 545 and Chromosorb are unsuitable for the analysis of hydrogen chloride and chlorine even after they have been washed with acid. Further studies showed that this view is

‡N. I. Ivanova, L. D. Prigozhina, S. V. Syavtsillo, G. V. Avdonin, and L. A. Frangulyan, "Protsessy v Khromatograficheskikh Konokakh" (Processes in Chromatographic Columns), Karpov Physicochemical Institute, Moscow, 1975, No. 26, p. 65.

invalid[65-69]. However, the usual silanised diatomite carriers do not always permit the separation of corrosive mixtures. Carriers based on polymeric materials, a major proportion of which have a hydrophobic surface and low adsorption and catalytic activities, are used to separate such mixtures. Carriers based on polytetrafluoroethylene[5], which is manufactured in the USSR under the names Ftoroplast, Polykhrom-1, and Polykhrom-2, have found extensive applications. Outside the USSR, analogous materials are manufactured under the names Teflon (USA), Fluon (England), Algoflon (Italy), Hostaflon (German Federal Republic), and Soreflon (France). Methods have been described[70] for the preparation of an effective Teflon carrier (Polykhrom-1 and Polykhrom-2) and it has been shown that they can be used for the separation of phosphorus, silicon, germanium, strontium, titanium, and arsenic halides and oxide halides. PTFE type carriers are also used for the analysis of corrosive inorganic gases (chlorine fluorides, chlorine oxide fluoride, hydrogen fluoride, hydrogen chloride, and chlorine)[71-75].

Mainly gas–liquid chromatography is used for the analysis of readily hydrolysable compounds. Gas–adsorption chromatography (GAC) has been applied in only a few studies. Graphite, heated beforehand in a stream of chlorine and then evacuated, is used in the analysis of metal chlorides[18]. Studies have shown[76-78] that GAC employing Carbochromes and Silochromes is the best method for the separation of structural and steric isomers of organic derivatives of Group IVB elements. Studies have been made on the analysis of reactive substances on a graphitised carbon black[79]. Furthermore, artificial diamond has been used as the solid carrier for the analysis of hydrogen fluoride, hydrogen chloride, fluorine, and chlorine trifluoride [80], while the alkali metal fluorides KF, RbF, and CsF have been used for the separation of $SF_4$, $SOF_2$, $COF_2$, and $SO_2F_2$.[81]

In the analysis of readily hydrolysable unstable substances, the stationary phase must not be hygroscopic and must not contain hydroxy-groups; it must be thermally stable under the conditions of the gas-chromatographic experiment and must not react with the compounds analysed. Before being deposited on the solid carrier, the stationary phase is dried. In the analysis of chloromethylsilanes, the stationary phase was subjected to preliminary distillation from phosphorus pentoxide and stored over anhydrous sodium sulphate[82]. The high-boiling liquids employed as stationary phases are dried by evacuation at appropriate temperatures. Nitrobenzene was used as the stationary phase in early studies on the analysis of chlorosilanes and organochlorosilanes[23-29,81-83]. However, despite the satisfactory selectivity of this phase in relation to chlorosilanes, it is highly volatile (b.p. 210°C); it can be used only at room temperature and for a short time, since the separating capacity of the column is impaired as the stationary phase is carried away.

Stationary phases based on organosilicon liquids, which are hydrophobic, thermally stable, and exhibit different polarities depending on the nature of their organic group, began to be used to an increasing extent[25-35,84,85]. Alkyl-, aryl-, and fluorine-containing liquid polysiloxanes were tested as stationary phases for the analysis of organochlorosilanes. It was shown that the separating capacity in relation to chromomethylsilanes increases with the polarity of the stationary phase. Liquids containing fluorinated groups, for example the FS-16 liquid, exhibit a high selectivity. In terms of selectivity, the FS-16 liquid is close to organic stationary phases such as diethyl and dibutyl phthalates. The PFMS-4 and PFMS-6 liquids as well as silicone rubbers and elastomers are used in the analysis of more high-boiling organochlorosilanes. Silicone oil 703 has been employed to analyse boron trichloride, diborane, dichloroborane, and monochlorodiborane, while glycols, the Apiezon grease, phthalates, sulphides, and phosphates reacted with these compounds[54].

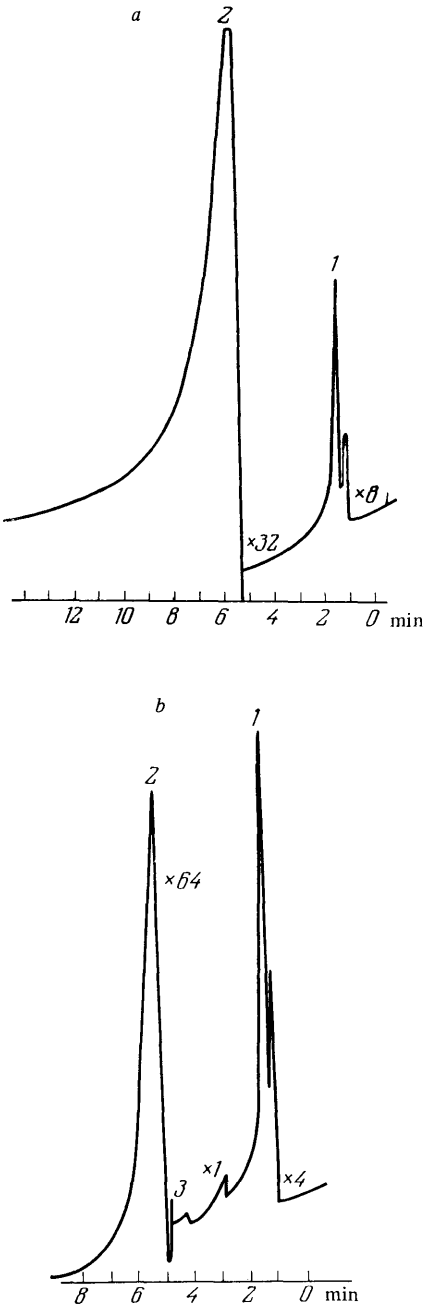



**Figure 1.** The chromatogram of $BCl_3$ on untreated (*a*) and $BCl_3$-treated (*b*) Chromaton N: 1) HCl; 2) $BCl_3$; 3) $COCl_2$.

**Table 3.** The interaction of hydrides with water and oxygen.

| Group in Periodic System | Element | Interaction with water | | Interaction with oxygen | |
|---|---|---|---|---|---|
| | | nature of interaction | example of reaction | nature of interaction | example of reaction |
| III, IV | B, Si | decomposition with evolution of $H_2$ | $SiH_4 + 4H_2O \rightarrow 4H_2 + Si(OH)_4$ | explosive decomposition | $SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$ |
| IV, V | Sn, Sb, P, As, Ge | does not react | — | quiet oxidation | $4AsH_3 + 6O_2 \rightarrow 2As_2O_3 + 6H_2O$ |
| V | N | addition of $H^+$ ions | $NH_3 + H_2O \rightleftarrows H_4^+ + OH^-$ | — | — |
| VI | O, S, Se, Te | weak oxidative dissociation | $H_2S \rightleftarrows H^+ + HS^-$ | weak interaction | $2H_2Se + 3O_2 \rightarrow 2SeO_2 + 2H_2O$ |
| VII | F, Cl, Br, I | vigorous acid dissociation | $HCl \rightleftarrows H^+ + Cl^-$ | — | — |

Only a few studies have been made on the analysis of the very readily hydrolysable boron trichloride and extremely contradictory results have been obtained.

Some authors believe [86] that boron trichloride is bound in an involatile complex with PMS-100 which conflicts with the results of other investigations [54,87,88] where liquid polyorganosiloxanes were used as the stationary phases in the analysis of this compound. The authors of this review showed that the hydrophobic properties and lack of reactivity of liquid silicones permitted the employment of these compounds, such as VKZh-94, PMS-100, and E-301, for the analysis of boron trichloride, boron hydrides, and alkylated boron derivatives§. Readily hydrolysable boron hydrides have been analysed in most cases on silicone stationary phases [6-13]. It has been shown that liquids containing unsaturated compounds and hydroxy-compounds cannot be used as stationary phases.

However, despite the careful selection of the stationary phase and its preparation, analysis cannot be achieved immediately. The above procedure, involving the drying of the system by passing the most readily hydrolysable component through it before analysis, is applicable also in the final drying of the stationary phase. Apart from the generally adopted silicone stationary phases [22,87,88], the $BiCl_3$–$PbCl_2$ eutectic mixture, melting at 217°C, has been used in the analysis of metal chlorides and for the separation of titanium tetrachloride and antimony trichloride.

Thus the assortment of stationary phases for the analysis of readily hydrolysable substances is limited. For this reason, their selection for the analysis of various groups of substances is highly specific.

## III. THE USE OF HYDROLYTIC REACTIONS FOR ANALYTICAL PURPOSES

Hydrolytic reactions can be used in the analysis of readily hydrolysable compounds for the following purposes: (1) when a direct determination is impossible; (2) in the detection of non-hydrolysable substances which do not exhibit corrosion activity; (3) in order to increase sensitivity by employing detectors selective in relation to the hydrolysis products.

The hydrolytic reaction is employed in the analysis of organometallic derivatives of Group I–IV elements (organolithium, organosodium, organopotassium, organomagnesium, organocalcium, and organoaluminium compounds) in order to convert these substances into stable volatile compounds, which are then subjected to gas-chromatographic analysis. Thus vinyl-lithium was determined on the basis of its hydrolysis product—ethylene [89]. The hydrolytic reaction has been used for the analysis of organopotassium, organolithium, and organosodium compounds [90-95]. In the analysis of complexes of phenylcalcium and *m*-tolylcalcium iodides with dioxan and of phenylcalcium in tetrahydrofuran (THF) solution, their hydrolysis products ($C_6H_6$ and $C_6H_5CH_3$) were analysed by gas–liquid chromatography [96]. Ethylmagnesium iodide was hydrolysed by phosphoric acid in the reactor and the gaseous reaction products were then injected into the chromatographic column [97].

Different versions of the analysis of trialkylaluminium compounds, based on their reaction with hydroxy-compounds, which leads to the formation of the corresponding hydrocarbons, have been described [98]. Rapid analysis of $C_1$–$C_5$ aluminium and zinc alkyls has been achieved on the basis of their gaseous hydrolysis product [99,100]. A method has been proposed for the determination of (iso-$OC_4H_9$)Al(iso-$C_4H_9$)$_2$ and (iso-$OC_4H_9$)$_2$Al(iso-$C_4H_9$) in tri-isobutylaluminium on the basis of the hydrolysis product—the alcohol [101]. Alkylaluminium derivatives have also been analysed using their hydrolysis products [102,103].

Since substances containing active hydrogen are hydrolysed, quantitative gas-chromatographic determination of, for example, B–H and Si–H bonds is possible on this basis. A rapid method for the quantitative determination of the total content of B–H bonds in chloroboranes and boron hydrides, based on the hydrolysis of these substances followed by the detection of hydrogen with a thermistor-based thermal conductivity detector, has been developed [104]:

$$BHCl_2 + 3H_2O \rightarrow B(OH)_3 + 2HCl + H_2,$$
$$B_2H_5Cl + 6H_2O \rightarrow 2B(OH)_3 + HCl + 5H_2,$$
$$B_2H_6 + 3HOH \rightarrow 2B(OH)_3 + 3H_2 \quad \text{etc.}$$

A method has been described for the determination of hydride hydrogen in boron compounds and of hydroxyl hydrogen in alcohols [105]. Si–H bonds are determined by the gas-chromatographic estimation of hydrogen after the hydrolysis of the substances in the presence of KOH. [106]

Diborane and dichloroborane have been determined in hydrogen, nitrogen, and boron trichloride using hydrolytic reactions [107]. The same report [107] describes the apparatus and experimental technique. Furthermore, there is a possibility of reactions with the HCl hydrolysis products. Hydrogen chloride mixed with acetylene and methylene chloride was determined on the basis of the $CO_2$ formed via the reaction [108]

$$HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2.$$

§N. T. Ivanova, L. D. Prigozhina, S. V. Syavtsillo, G. V. Avdonin, and P. A. Frangulyan, Symposium, "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1975, No. IV, Part 1, p. 75.

The same reaction can be carried out with the hydrogen chloride evolved after the hydrolysis of the corresponding compounds and the reaction mechanism can be represented as follows:

$$CO_2 \xrightarrow[\text{catalyst}]{H_2,\ T} CH_4.$$

This makes it possible to improve the sensitivity of the determination by using the more sensitive flame-ionisation detector [109].

In the analysis of readily hydrolysable reactive substances, the problem arises of the determination of stable organic and inorganic impurities. The determination of the impurities requires the employment of highly sensitive detectors, or concentration of the impurities, or reactions must be carried out with the impurities in order to improve the sensitivity of the analysis. When highly sensitive ionisation detectors such as the thermionic detector (TID), the electron capture detector (ECD), and the flame-ionisation detector (FID) are used, the entry of the main organoelement derivative into the detector is prevented, since this puts it out of order. Thus microimpurities consisting of chlorinated hydrocarbons of the methane series have been determined in boron trichloride using a thermionic detector after binding $BCl_3$ into a complex with diphenylamine, which was deposited (in an amount corresponding to 20%) on the INZ-600 carrier. [110] Certain organic chloroderivatives and inorganic substances have been determined in boron trichloride with the aid of a thermionic detector also after their binding into involatile complexes [86]. Using the ability of arsenic trichloride to form a complex with tricresyl phosphate, its organic impurities were determined with the aid of a flame-ionisation detector. Chromosorb W with 15% of tricresyl phosphate was placed in the initial section of the column, while the rest of the column was filled with Chromosorb, containing 10% of PEG-400. [111] In addition, a method is used where the main substance is removed after emerging from the column and before reaching the detector. $CCl_4$, $C_6Cl_6$, $C_2H_5Cl$, and $C_2H_4Cl_2$ impurities in arsenic trichloride have been determined with the aid of a flame-ionisation detector, $AsCl_3$ being removed before reaching the detector [112].

## IV. ANALYSIS OF READILY OXIDISABLE SUBSTANCES

The next group of substances which must be analysed by gas chromatography comprises those which are oxidised by atmospheric oxygen. They include boron, silicon, phosphorus, arsenic, tellurium, and selenium hydrides as well as alkyl derivatives of boron, aluminium, gallium, and silicon. However, the majority of oxidisable substances are also capable of interacting with water to some extent. Table 3 presents examples of the interaction of hydrides with water and oxygen.

The oxidation reaction proceeds with formation of water and the solid metal oxide, i.e. with decomposition of the substance. Special precautions are therefore necessary in the chromatographic analysis of certain substances in order to prevent the oxidation reaction. In gas-chromatographic analysis, the products may be oxidised by the oxygen contained in the carrier gas, adsorbed on the solid carrier, and dissolved in the stationary phase. Furthermore, the products may also be oxidised outside the chromatograph at the instant of the removal and injection of the sample. The gases produced by the USSR industry and used as carrier gases, namely helium, nitrogen, and argon, contain the oxygen impurity in amounts of 0.001 to 0.003, 0.1–1, and 0.003–0.4% respectively. For a valid analysis, one must therefore select a carrier gas with the minimum oxygen content and, when necessary, additional elimination of oxygen must be carried out.

In the analysis of silicon, germanium, arsenic, and phosphorus hydrides, the carrier gas was freed from moisture and oxygen by means of a system [46] comprising granulated copper, KSK silica gel, active granulated alumina, 5 Å molecular sieves, and the sodium-potassium eutectic mixture. This made it possible to eliminate oxygen from nitrogen down to $1 \times 10^{-3}$%. It is noteworthy that in most instances substances with a tendency towards being oxidised are also hydrolysed. For this reason, a system of drying and oxygen-removing columns is used as a rule. In another study [47], the authors thought that the elimination of oxygen in a granulated copper column alone was sufficient for the analysis of silicon, germanium, phosphorus, and arsenic hydrides.

It has been shown that the removal of the oxygen impurity from technical helium is necessary, since the presence of oxygen (0.003%) lowers the sensitivity of the determination of phosphine approximately by an order of magnitude. Oxygen must be removed from helium at 300°C on a column 1 m long and 3 cm in diameter and filled with a granulated chromium–nickel catalyst. The catalyst was reduced beforehand in a stream of hydrogen until the complete elimination of the water evolved. Table 4 presents the results of the calibration of the chromatograph by Lovelock's method against phosphine with and without the removal of oxygen from helium. It is seen that the area of the peak corresponding to the same concentration of phosphine (0.08%) is almost ten times greater when helium is additionally freed from oxygen. Evidently the lower the concentration of the substance, the more harmful the presence of oxygen in the carrier gas; this is particularly the case in the analysis of impurities. With the aid of such purification, it has been possible to achieve a sensitivity in relation to arsine (by the direct method) of $5 \times 10^{-3}$%.

Furthermore, it has been suggested that MnO, obtained from manganese acetate, be used for the absorption of oxygen from the gas stream [113]. According to the authors, this makes it possible to reduce the concentration of oxygen in nitrogen to $10^{-7}$%.

Table 4. The influence of the elimination of oxygen from the carrier gas on the analytical results.

| Calc. concn. of phosphine, % | Phosphine peak areas, cm² | |
|---|---|---|
| | with elimination of $O_2$ | without elemination |
| 3.87 | 38.4 | 28.6 |
| 2.38 | 23.8 | 15.5 |
| 1.51 | 15.2 | 8.6 |
| 0.77 | 7.6 | 2.38 |
| 0.28 | 2.88 | 0.35 |
| 0.16 | 1.54 | 0.16 |
| 0.08 | 0.81 | 0.08 |

However, the carrier gas always contains some residual oxygen. In order to prevent the reaction or reduce the percentage decomposition of the substance analysed, the method involving a decrease of contact time is used. Thus nitrogen freed from oxygen and moisture, a column 50 cm long at 34.5°C, and Celite 545 with 30% of silicone 702 were used in the separation of boron hydrides ranging from $B_2$ to $B_5$. [7] By passing the separated

components through the chromatographic column again, it was established that the compounds $B_2H_6$, $B_4H_{10}$, and $B_5H_9$ are not decomposed at all under the conditions of the analysis, while $B_5H_{11}$ decomposes to the extent of 10% during each pass through the column. We believe that drying with Anhydrone, suggested in the above investigation for the analysis of boron hydrides, is inadequate, and this may be the reason for the decomposition of $B_5H_{11}$.

The scheme involving the circulation of the carrier gas discussed in the preceding section is of undoubted interest also for the elimination of oxygen from the carrier gas [56]. The carrier gas is freed from oxygen following the injection of the first samples containing the readily oxidisable compounds to be analysed. The reactivities of such substances are not the same and an individual approach to the selection of drying agents and of the oxygen-elimination system is therefore necessary [114,115].

In the analysis of boron trialkyls, attention was drawn to their extremely high reactivity in relation to moisture and oxygen, which necessitated the "complete" absence of the latter [114,115]. However, it is known that trimethylboron is resistant to water and is not oxidised in air and that triethylboron and tripropylboron are less steadily hydrolysed than boron hydrides and triethyl aluminium [116]. One of the authors of the present review [117] tested the influence of the removal of oxygen from the carrier gas by the chromium–nickel catalyst on the decomposition of triethylboron. The experiments demonstrated a slight change in the results of the analysis for the main product (97.0% with elimination of oxygen and 96.9% without). The "complete absence" of oxygen and moisture is therefore not obligatory in the analysis of boron alkyls. The use of technical helium dried over phosphorus pentoxide without additional elimination of oxygen is quite feasible.

Table 5. Conditions in the chromatographic analysis of oxidisable substances.

| Substances analysed | Carriers and stationary phases | Carrier gas and requirements which it must meet | Detector | References |
|---|---|---|---|---|
| Boron, silicon, germanium, phosphorus, arsenic, selenium, tellurium, and tin hydrides | Celite, Chromosorb W, Embacel, liquid silicones Apiezones, BAU charcoal, Polysorb-1 | helium, nitrogen, and argon freed from $H_2O$ and $O_2$ to within $1 \times 10^{-3}$% | katharometer, FID PPD | 6,10,13,46,47,53, 79,113,117,118, 121–124 |
| Alkylated boron, aluminium, gallium, tin, and silicon derivatives | refractory brick, Polychrom-1, Kieselguhr, Stercha-mol, Celite, liquid silicones | ditto | katharometer | 113–116 |

The requirements which must be met by the solid carrier in the analysis of substances showing a tendency towards both hydrolysis and oxidation (boron hydrides, alkylated derivatives of boron, aluminium, and gallium, and silicon hydrides), on the one hand, and substances which can only be oxidised (phosphorus, arsenic, tellurium, and selenium hydrides), on the other, are different. In the former case, apart from the drying procedures described in the previous section, the carrier must be degassed in order to remove physically adsorbed oxygen. Furthermore, the impurities in the solid carrier can serve as oxidation catalysts. In the analysis of such products, one therefore uses as a rule solid carriers such as Celite 545 [9], Embacel [10,11], and Chromosorb W. [12,13] In the latter case, one can use gas-adsorption chromatography. Thus the adsorption of silicon, arsenic, germanium, and phosphorus hydrides on BAU activated charcoal has been investigated [118,119] in the temperature range from 0° to 100°C, and it was shown that the substances do not decompose in this temperature range and undergo physical adsorption. This justified the employment of BAU charcoal as the adsorbent in the analysis of the above hydrides.

A necessary condition for the employment of gas-adsorption chromatography is careful elimination of adsorbed oxygen from the adsorbent by evacuation at high temperatures, and careful removal of oxygen from the carrier gas in order to prevent the adsorption of oxygen on the solid carrier. In one investigation [79], graphitised carbon black was subjected to a preliminary treatment with hydrogen at 1000°C. This process should have limited the number of active centres formed by the surface oxygen complexes which are always present on the surface of adsorbents. In this case, the carbon black behaves as an inert carrier.

Readily oxidisable substances are separated on polymeric sorbents. Polysorb-1 has been used to determine arsine and phosphine in the effluent gases from phosphorus furnaces and as impurities in acetylene [120,121]. The requirements which must be met by the stationary phase are analogous to those mentioned previously and, in addition, the stationary phase must not dissolve oxygen. The method of preparation involves vacuum heat treatment followed by stabilisation of the column. Mainly liquid silicones and Apiezon are recommended as the stationary phases for the analysis of readily oxidisable substances [10,12,13,53,113,122–124].

In certain cases, the oxidation of the main substance does not interfere with the analysis, for example in the determination of stable non-oxidisable impurities in a readily oxidisable compound. Thus, in the determination of hydrocarbons in arsine [125], the mixture was passed through a tube containing copper heated to 130°C, where arsine was bound and the impurities were then separated on a chromatographic column and detected with the aid of a flame-ionisation detector. In addition, one sometimes uses the method where the main reactive substance is removed before entering the detector [126], and stable impurities are detected. The impurities are also concentrated by employing two columns, where silicon, boron, or germanium hydrides are separated in the first column from the organic impurities, which are collected in a cooled trap and then separated on the second column: the hydrides are removed and subjected to thermal decomposition [127].

Table 5 presents the conditions necessary for the chromatographic analysis of oxidisable substances.

## V. ANALYSIS OF SUBSTANCES CAPABLE OF THERMAL AND CATALYTIC DEGRADATION AND ISOMERISATION

Chromatographic analysis of substances showing a tendency towards thermal and catalytic degradation is possible when a number of conditions preventing the occurrence of such reactions are maintained. These include the employment of reduced evaporator, column, and detector temperatures, the use of inert and catalytically inactive solid carriers and stationary phases, careful

selection of the material for the metering device and column, and purity of the carrier gas. The requirements which must be met by the carrier gas are similar to those described above. In contrast to the hydrolytic and oxidation reactions, which are as a rule instantaneous, the catalytic and thermal degradation and isomerisation reactions take place over a period of time. In the analysis of such substances it is therefore important to bear in mind the duration of the analysis.

The gas-chromatographic method has been used in the analysis of thermally unstable substances. Dichloroborane and monochlorodiborane are known to decompose at room temperature [128]. In the separation of a mixture of dichloroborane, monochlorodiborane, hydrogen chloride, boron trichloride, and hydrogen, a temperature of 0°C, and a column 10 mm long and 6 mm in diameter filled with Chromosorb W containing a silicone oil as the stationary phase were therefore used. It has been suggested [107] that diborane and dichloroborane be determined in hydrogen, nitrogen, and boron trichloride below 0°C. The hydrogen–diborane or hydrogen–dichloroborane–boron trichloride sample is directed to a column 25 cm long, filled with quartz sand, and cooled to −173°C, where diborane (or boron trichloride–dichloroborane) condenses, while hydrogen does not and passes subsequently through the hydrolysis column (molecular sieves treated with ethanol) and is detected. The condensation column is then warmed and the diborane (or boron trichloride–dichloroborane) sample is directed to the hydrolysis column, where it decomposes with evolution of hydrogen, which passes to the detector. This permitted the determination of diborane and dichloroborane with a high sensitivity.

The metal carbonyls $Fe(CO)_5$, $Ni(CO)_4$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are readily oxidised and thermally unstable. However, at a reduced temperature and when the percentage impregnation of the stationary phase was low, it was possible to analyse them by gas–liquid chromatography. A column 2 m long and 6 mm in diameter, filled with molybdenum glass containing 0.5% of liquid polymethylethylsiloxane (VKZh-94), was used at 30°C for the analysis of iron pentacarbonyl and nickel tetracarbonyl, boiling at 102° and 42°C respectively [129]. Chromium, molybdenum, and tungsten carbonyls were separated at 76°C on a 3 m × 3 mm column filled with 10% of 1,2,3-tris-2-cyanoethoxypropane on diazolide [130].

As a rule thermally unstable substances undergo hydrolysis and oxidation at the same time. Their chromatographic analysis therefore requires a combined approach involving precautions against both hydrolysis and oxidation. Substances of this kind include alkylated derivatives of boron, aluminium, and gallium. The possibility of using gas-chromatographic analysis for the investigation of catalytic exchange reactions between boron trialkyls and for the determination of the rates of these reactions has been demonstrated [53,114]. This was achieved by employing high carrier gas flow rates. At relatively low temperatures, boron alkyls are known to split off olefins via the reaction

$$R_2BCH_2CH_2R' \rightarrow BR_2H + CH_2 = CHR' \ .$$

The selection of the temperature of the metering device and the column is therefore very important in the analysis of these substances. It is claimed [37] that the above reaction does not play a significant role in gas-chromatographic analysis. The authors of the present review [117] determined the maximum permissible evaporator temperature, which is 100°C for tripropylboron (B.p. 160°C) and 80°C for triethylboron (B.p. 96°C). The analysis of these substances is carried out under programmed conditions. Methyldiboranes have been determined at 0°C. [131]

Not only temperature parameters but also the selection of the solid carrier and its treatment are important for substances undergoing thermal and catalytic degradation and polymerisation. A gas-chromatographic method has been proposed for the analysis of dichloro-(β-cyanoethyl)-methylsilane, which boils at 210°C and is extremely reactive, being readily hydrolysed by water and polymerising at elevated temperatures and in the presence of a number of metals [35]. In order to prevent the decomposition of the substance, a glass tube was inserted into the metallic metering device of the chromatograph, which was responsible for the non-reproducibility of the chromatograms obtained, in such a way that its end entered the initial section of the chromatographic column; the temperature of the metering device did not exceed 150°C, because decomposition was observed already at 180°C. Before analysis, the column was flushed with the dry carrier gas at 200°C for 2 h and the sorbent was then additionally dried by introducing several trichlorosilane samples in succession; the column was stabilised by injecting samples of the substance to be analysed.

A direct gas-chromatographic method for the analysis of triethylaluminium and triethylgallium, which are also readily oxidised and thermally unstable, has been proposed [132]. The boiling point of triethylaluminium is 186.6°C and it begins to decompose in an inert atmosphere already at 120–125°C. The authors propose a method for the removal and injection of these substances into the chromatograph without coming into contact with air, but do not indicate the range of evaporator temperatures and do not quote quantitative data, which precludes an assessment of the reliability of this procedure. In most studies, reaction chromatography is used for the analysis of organoaluminium compounds [99–103].

The fundamental conditions in the selection of the solid carriers are its complete catalytic inertness, the employment of modifying carriers [133], and the stabilisation of the sorbent by passing through the column compounds resembling those to be analysed. Thus, in the analysis of bisethylbenzenemolybdenum, the column was first modified by passing bisarene complexes of chromium through it, 3–5 analyses were carried out, and the column was then modified [134].

An interesting procedure has been proposed for the analysis of organophosphorus compounds, which tend to isomerise [135]. An isomerisation inhibitor was added to the stationary phase, which permitted the gas-chromatographic analysis of these substances. The separation of dichloroborane and monochlorideborane [54] at 40°C on a column filled with Chromosorb containing 30% of n-hexadecane, saturated with boron trichloride, is based on the same principle. Since it was known that dichloroborane and monochlorodiborane are most stable in the presence of boron trichloride, the saturation of the stationary phase by the latter made it possible to achieve the separation [54].

A decrease of the resonance time of the unstable substance in the column should undoubtedly improve the results results of the chromatographic analysis. A study has been made [136] of the influence of the solid carrier, of the percentage content of the stationary phase and its nature, and of the residence time of the sample in the column (i.e. the carrier gas flow rate) on the separation of the isopropylphenyl hydroperoxide. It was shown that tricresyl phosphate (TCP), which has the smallest acid number, is the best stationary phase; common salt and silanised Chromosorb W were used as the solid carriers and it was

shown that the degree of decomposition diminishes with increase of the percentage of the stationary phase and with the carrier gas flow rate. Conditions were selected on the basis of the percentage decomposition for the separation of a mixture of isopropylbenzene, acetophenone, and isopropylphenyl hydroperoxide. Glass columns, high carrier gas flow rates, and low temperatures are as a rule employed in the analysis of hydroperoxides. Thus *n*-butyl hydroperoxide was isolated on a glass column (Celite with 30% of dinonyl phthalate) at 40–60°C and a helium flow rate of 120 ml $min^{-1}$, the sample being injected directly into the column[137]. A mixture containing isopropylphenyl hydroperoxide was analysed on Chromosorb treated with dichlorodimethylsilane (DCDMS) with 1.5% of TCP at 80°C; after preliminary flushing of the column for 8 h at 100°C and the injection of 15–16 hydroperoxide samples into the chromatograph, the decomposition of isopropylphenyl hydroperoxide was not observed[138]. Ethylphenyl hydroperoxide was analysed on Chromaton treated with DCDMS containing 5% of poly(ethylene glycol) (PEG) distearate at a nitrogen flow rate of 210 ml $min^{-1}$.[139]

We considered specially the procedures used in the analysis of organic peroxides which are thermally and catalytically unstable, since analogous methods are used in the analysis of organoelement compounds. For example GLC analysis of alkylmercury derivatives showed that RHgX and $R_2Hg$ are effectively separated on glass and metallic columns when the sample size is $10^{-5}$ g; when the sample size is reduced to $10^{-8}$ g, RHgX decomposes on a steel column[140]. Similar experiments showed that stable MgHgX peaks may be obtained by increasing the mass of the chromatographed sample[141]. To prevent a long residence time of the unstable hydrides in the column, a short column (40 cm long, containing Celite with 30% of silicone 702) was used in a study of the pyrolysis of diborane[7].

## VI. IDENTIFICATION OF UNSTABLE COMPOUNDS AND QUANTITATIVE INTERPRETATION OF CHROMATOGRAMS

Several methods are available for the identification of compounds. They include identification on the basis of chromatographic parameters, i.e. the determination of the dependence of the retention time on the nature of the substance and the determination of the relation between the retention volume and the number of similar groups or atoms (analogously to the relations observed in homologous series of organic compounds), preparative isolation followed by the employment of physicochemical methods of analysis, and chromato-mass-spectrometry. The use of chromatographic relations (the dependence of the retention volume on the number of atoms and on the boiling point) is difficult, because a high reliability of the analysis requires the determination of the retention volume in stationary phases of different polarities and at different temperatures. However, this is not always possible, since the number of stationary phases and the feasible temperature ranges are limited in the analysis of unstable substances. Furthermore, the extremely high reactivity of the products may distort the measured retention volumes when the sample interacts with the solid carrier and the material of the column.

However, attempts to find relations which would assist in the identification of substances of this kind have been made. For example, the behaviour of alkoxychlorosilanes $Cl_nSi(OR)_{4-n}$ (where $n$ = 1, 2, 3, or 4 and R = Me, Et, Pr, or Bu) at 50–90°, 80–120°, 150–190°, and 160–200°C respectively has been studied by GLC on 1 m × 3 mm columns filled with different weakly polar and polar stationary phases on Resorb and Hexasorb[142,143]. When the fluorosilicone FS-16 was used as the stationary phase, a linear relation was obtained between the heats of solution and boiling points of alkoxychlorosilanes, which may be used for the identification of these compounds. The retention indices of alkyl-, aryl-, akylaryl-, and chloroaryl-chlorosilanes have been determined[144,145] and it has been shown that the indices for substances on a non-polar stationary phase are satisfactorily correlated with their boiling points. The retention volumes of decaborane and its 1- and 2-halogeno-substituted derivatives $B_{10}H_{13}X$, where X = Cl, Br, or I, have been determined at 141°, 151°, and 161°C.[146] Using these data and the specific retention volumes of pentadecane and eicosane, the retention indices were calculated. The sorbent employed was Chromosorb W with 3% of silicone oil QF-1. It was shown that Carbowax 20 M, polyesters, and unsaturated compounds react with the substances analysed.

The retention indices of boron hydrides ranging from $B_2$ to $B_{10}$ have been calculated for a column with 6% OV-17 on Chromosorb. It was found that the indices vary approximately linearly with the number of boron atoms in the boron hydride molecules, which made it possible to identify hexaborane in the mixture, the result being subsequently confirmed mass-spectrometrically[12]. Linear relations have been obtained between the logarithm of the absolute retention volume ($\lg V_g^{abs}$) and the number of atoms in silicon hydrides from $Si_2$ to $Si_6$ and between the logarithm of the relative retention volume ($\lg V_g^{rel}$) and the number of germanium atoms in germanium hydrides and silicogermanes[147]. The data for metal chlorides are contradictory. Thus it has been found[148] that the variation of $\lg V_g^{abs}$ with the boiling points of Si–Ti tetrachlorides is non-linear, while other workers[149,150] obtained a linear relation between $\lg V_g^{abs}$ for metal tetrachlorides and the reciprocal of the absolute column temperature ($1/T$), the boiling point, and the molecular refraction. There are also contradictory data for organotin compounds. It was found in a study of the chromatographic properties of $Me_4Sn$, $Et_4Sn$, and $Bu_4Sn$ on eight stationary phases that the dependence of $\lg V_g$ on $1/T$ and the number of carbon atoms in the molecule is linear[151], while another investigation[152] demonstrated a non-linear variation of $\lg V_g$ for compounds of the type $R_4Sn$ with the total number of carbon atoms.

Since the temperature and the stationary phase cannot always be varied in the analysis of unstable compounds, which is necessary in qualitative analysis, the preparative isolation of the unknown compounds followed by their identification by infrared spectroscopy, mass-spectrometry, etc. is the most reliable procedure. Comparative chromatography combined with infrared spectroscopic analysis of the compounds isolated has been used to identify admixtures in dichlorodiphenylsilane and trichlorophenylsilane[153]. Certain compounds, obtained in the direct synthesis of chloromethylsilanes, were identified by preparative gas chromatography followed by the study of their physicochemical constants, elemental composition, and infrared spectra[154]. Chromato-mass-spectrometry has been used to identify trialkylboranes[155] and boron hydrides[156].

The specificity of the chromatographic analysis of unstable compounds is also reflected in the quantitative interpretation of the chromatograms. The method of absolute calibration, normalisation without the introduction of calibration coefficients, and, more rarely, the internal standard method are used in quantitative analysis. When an absolute calibration is carried out, it is necessary to prepare artificial mixtures. For substances with high vapour pressures and boiling points up to 100°C, a vacuum system for the preparation of the calibration mixture is used. This procedure, proposed for the preparation of a calibration mixture of nickel and iron carbonyls [129], can be modified as a function of the reactivity of the product. A similar system can be made wholly from glass and metallic taps can be replaced by glass and Teflon taps[50,51]. Provision can be made for several flasks at once, in which the calibration mixtures are prepared. For substances with a tendency towards oxidation accompanied by explosion, the mixtures are usually prepared in metallic cylinders, their composition being followed from the pressure. Naturally the material of the cylinder should not react with the mixture. Finally, the exponential dilution method proposed by Lovelock [157] is used for the calibration.

In the calibration of sulphur compounds, a method is used which combines permeability and exponential dilution. It has been shown that the application of the exponential dilution method alone with injection of the sample into the vessel from a syringe does not yield a result with an error less than 5%. [158] On the other hand, the combination of the two methods results in a relative standard deviation not exceeding 1%. When calibration mixtures of readily hydrolysable compounds are prepared, there is a risk of an error due to their hydrolysis during the preparation of the mixture. In the study of the possibility of calculating low concentrations of readily hydrolysable chloromethyl- and chlorophenyl-silanes by a normalisation method without calibration coefficients, the errors were determined and the limits of the applicability of the method were found [159]. It was shown that, in the analysis of trichloromethylsilane (TCMS) microimpurities in chlorodimethylsilane (CDMS) up to a content of 0.75%, the systematic absolute error associated with failure to take into account the coefficients does not exceed 0.10%, which implies that, in the analysis of commercial organosilicon monomers containing 98–99% of the main substance, the concentrations of the impurities may be calculated with adequate accuracy by the normalisation method without taking into account calibration coefficients. Calculations by the normalisation method from the areas without the use of calibration coefficients have been employed by various investigators in the analysis of chlorosilanes [31], dichloro(β-cyanoethyl)methylsilane [15], alkylated boron derivatives, and boron trichloride [117].

In the absolute calibration of readily hydrolysable substances, it is possible to suppress the hydrolysis of the admixture, having prepared its calibration mixture with a more readily hydrolysable substance. This is particularly important in the determination of microimpurities. Thus mixtures of $SiCl_4$ and boron trichloride containing between 0.01 and 0.08% $SiCl_4$ have been prepared and the analytical error was about 10 rel.%. The absolute calibration method has been used in the analysis of mixtures of phosphorus, $PCl_3$, $POCl_3$, and $PSCl_3$ [160] (the relative error of the determination varied in the range ±6%), in the analysis of alkylchlorosilanes and chloroalkyl derivatives [161], and in the analysis of chloromethylsilanes [29,162].

The internal standard method is more rarely used in the analysis of reactive substances owing to the difficulty of selecting an internal standard and of its introduction into the mixture. As examples of the application of the internal standard method, we shall only quote studies [34,163] where ether was used as the internal standard in the analysis of chloromethylsilanes (analytical error 2%) and the study where trichloro-*n*-propylsilane chlorination products were analysed using trichloro-*n*-propylsilane as the internal standard. We believe that the employment of a substance having a similar structure and properties as the internal standard is more justified.

In order to obtain accurate quantitative results, it is desirable to use a density detector, which does not require calibration, for the analysis of unstable substances with different molecular weights. Corrosive halogen gases have been analysed quantitatively by means of a Martin nickel densitometer [164].

One should also note that, using the capacity of reactive substances for interaction with some other substance or their thermal instability, in the analysis of such substances one can carry out the reaction beyond the column and before the detector in order to detect the inert substance or the inert mixture in the detector and to calibrate the apparatus with respect to the reaction products. In the experiments on the analysis of volatile inorganic hydrides of a number of Group IV–VI elements ($SiH_4$, $GeH_4$, $AsH_3$, $PH_3$, $H_2S$, etc.), the furnace (10 to 15 cm long and 1.5 cm in diameter) was placed beyond the chromatographic column in order to decompose the hydrides to hydrogen at 1000°C. [46] This enabled the authors to increase the sensitivity of the determination and also to avoid (under the conditions of complete conversion) the calibration of the apparatus with respect to the hydrides, using hydrogen for this purpose. The apparatus was calibrated similarly after the decomposition of chlorophenylsilanes [165,166]. Using the hydrolysis of chlorosilanes to HCl and carrying it out before the detector with subsequent conversion into $CO_2$ via the reaction $HCl + NaHCO_3 = NaCl + H_2O + CO_2$, it is also possible to calibrate the apparatus with respect to the stable carbon dioxide instead of the readily hydrolysable substances. A method has been proposed [37] for the analysis of $F_2$, ClF, $ClF_3$, and $ClF_5$ on the basis of the products of their reaction with silicon, which results in the formation of $SiF_4$ and $Cl_2$ ($Si + 2F_2 \rightarrow SiF_4$; $Si + 4ClF \rightarrow SiF_4 + 2Cl_2$, etc.).

This is of interest also from the standpoint of quantitative interpretation, since calibration with respect to one component undoubtedly gives rise to a smaller error than calibration with respect to four different components (naturally provided that one can be certain that all the reactions go to completion). Iron carbonyls have been detected [167] by a flame-ionisation detector after conversion via the mechanism $Fe(CO)_5 \xrightarrow{T} Fe + 5CO$ and the transformation of CO into methane; after the decomposition in the column, organolead compounds were passed through a tube with a nickel catalyst and the methane formed in the presence of the catalyst from the substances separated was detected [168]. In all the instances described, the calibration procedure is simplified and can be carried out with a high accuracy, but the chromatographic set up becomes much more complex, requiring the calculation (or selection) of optimum reactor parameters and careful monitoring of the reaction conditions.

## VII. CHARACTERISTICS OF THE APPARATUS USED IN THE ANALYSIS OF UNSTABLE COMPOUNDS

Analysis of readily hydrolysable, corrosive, and toxic compounds imposes additional requirements on the materials of the metering devices and it is also essential to protect the injected sample from the surrounding medium.

There is no universal metering device in chromatography; there are several possibilities for the metering of various types of samples, from which the optimum procedure must be selected. The most widely used materials for the construction of sample injection systems and metering in chromatographic analysis of the compounds under consideration are Teflon, polyethylene, glass, nickel, stainless steel, and Monel metal.

Metering by means of a syringe, whereby samples ranging from several millilitres can be injected depending on the design, is simple and fairly reliable. The possibility of using a microsyringe for the metering of corrosive readily hydrolysable compounds depends on the materials used for its construction and design solutions ensuring a fully hermetic seal. Syringes produced by U.S. and East German (GDR) firms to a large extent meet these requirements, being used, in particular, in the metering of organometallic compounds [169,170].

In the analysis of extremely reactive and toxic compounds, the authors of the present review¶ used a hermetically sealed syringe having a volume up to 10 μl with a Teflon piston, isolated from the external medium and ensuring the localisation of the sample in case of accidental breakage of the glass cylinder.

A system consisting of a glass 50 ml nitrogen-flushed cuvette with two outlets has been proposed for the removal of samples which must not be allowed to come into contact with air, for example those of organic compounds of certain metals [169]. After the insertion of the needle into the cuvette through the stopper, nitrogen was passed through the syringe until the product was collected, which ensured that the sample was preserved in the syringe until its injection into the evaporator of the chromatograph. During the transfer of the syringe to the chromatograph, the needle of the former remained inserted in an elastic stopper, which prevented its contact with air. The sample was injected with simultaneous piercing of both the stopper on the needle and the rubber membrane on the chromatograph inlet unit. A similar procedure to ensure a hermetic seal on the syringe needle was used when liquid alkylated boron [53], aluminium, and gallium [132] derivatives and dichloro-(β-cyanoethyl)methylsilane [35] were injected into the chromatograph. Triethylboron and tripropylboron were sampled in an inert atmosphere or in a stream of an inert gas [117]. One of the varieties of metering device for the injection of liquid and solid samples has been described by Wong and Schwartz [171].

In the removal of gaseous samples, vacuum sample removal and sample injection systems are used in most instances. One of such systems has been used in the analysis of trichlorosilane, germanium tetrachloride, and arsenic, phosphorus, germanium, and silicon hydrides [46,50,51]; an analogous system, with slight modifications, has been employed in the analysis of fluorine and chlorine fluorides [37,38], alkylated boron derivatives [53], and metal carbonyls [129]. Various systems made of glass, incorporating multiway taps and metering reservoirs [172-174], including experiments *in vacuo* at residual pressures down to $10^{-3}$ mmHg, are used in the analysis of many corrosive inorganic gases, for example nitrogen oxides, HCl, and fluorine compounds (other than HF) [175-177]. Precautions are taken to eliminate a sealing grease by employing glass and Teflon taps [50]. Samples ranging from several millilitres [175] to $10^{-5}$ mole have been metered with the aid of such systems [177]. Samples of readily hydrolysable corrosive and toxic substances, such as, for example, organochlorosilanes, boron hydrides, and boron and silicon chlorides, are frequently introduced into the chromatograph by means of breakable glass bulbs.

A device has been proposed [178] for the injection of very small samples (0.001–10 mole) of gases of vapours by means of a sealed glass tube, the upper, breakable part of which is made in the form of a hemisphere with a drawn out portion, where it can be sealed off. The sealed tube constitutes the lower part of an outer Pyrex tube (with an internal diameter of 15 mm and a polished inner surface) which is fitted onto the cylindrical shell of the Teflon metering device into which the carrier gas is supplied via a capillary. When the capillary comes into contact with the upper part of the sealed tube, the latter is broken and the sample is blown out by the stream of carrier gas via a side arm of the metering device directly into the chromatograph. The hermetically sealed bulb metering device, in which a sealed glass bulb with the sample of the test substance was placed, has been used in the analysis of organochlorosilanes, boron trichloride, and other products [179]. The metering device is joined directly to the evaporator of the chromatograph. The bulb is broken by a rod activated at a distance by an electromagnet; the sample is then introduced into the evaporator by the stream of carrier gas. The metering device is freed from glass fragments via a special aperture after 25–30 analyses.

The metering systems in which glass is used are unsuitable for the injection of samples containing hydrogen fluoride and highly toxic substances. Furthermore, in the removal of samples from systems under an excess pressure, glass is unsuitable because of its low mechanical strength. A metallic metering tap made of a corrosion-resistant material with a Teflon seal makes it possible to inject samples of reactive and highly toxic gases from the cylinder, provision being made for the flushing of the tap and the connecting tube by a dry inert gas with the aid of a system of valves [107]. The removal of the sample directly from the technological line can be achieved similarly, provided that conditions permit it. For the cyclic injection of liquid hydrolysable substances, particularly into an industrial chromatograph, a slide-valve metering device with a pneumatic actuator was developed; in it, a stainless steel plate is made to move through a definite cycle by means of the pneumatic device [180]. The plate, moving between stationary PTFE plates, causes the injection of the sample into the column or its flushing with the carrier gas as it allows appropriate channels to be connected. A similar system was also used in the metering of metal chlorides and phosphorus compounds [181,182].

Methods for the injection of samples by special gas tube systems and blocking devices, permitting the alteration of the direction of the stream of the carrier gas and the injection of the sample directly into the chromatograph, have been described in a number of studies [48,54,183-186]. Thus, a system consisting of sections of polyethylene capillary tubes 0.38 mm in diameter and blocking devices have been used to meter mixtures of chlorine and hydrogen fluoride [185]. Tubes were connected by nickel capillaries to a T-shaped socket made of Monel metal. In order to alter the direction of the gas streams, the tubes were closed by

¶See the footnote to p. 175.

clamping them to a solid plate by means of five bronze screws. Metallic or Teflon washers between the screw and the tube protected the latter from being crushed. By opening and closing the tubes to the gas stream in different combinations, it is possible to achieve in succession the passage of the carrier gas through a by-pass into the chromatograph with simultaneous removal of the sample into the metering reservoir, its isolation, and injection into the column. The size of the dose is determined by the length of the corresponding section of the polyethylene tube (the dose is $6.5 \times 10^{-3}$ mm for a tube 50 mm long).

A system acting on a similar principle has been proposed for the removal *in vacuo* of samples of corrosive halogen-containing gases from the technological stream[48]. The gas streams are controlled by glandless needle valves made of bronze with nickel-plated inner surfaces. The gas system is welded using a silver solder. Such valves remain effective for 12–18 months of continuous operation according to the authors, after which the system is completely renewed. One of the varieties of the systems described with cut-off valves, controlled by compressed air, has been used for the injection of samples of mixtures of chlorofluoroalkanes with uranium hexafluoride. The materials used for their preparation were nickel, Monel metal, and Teflon[186]. The latter systems have definite advantages over multiway taps and slide-valve metering devices from the standpoint of reliability of operation and the hermetic seal, although their control requires a large number of operations.

In many instances, particularly in the industrial control of a technological process, the sample removed must be transported over a certain distance for its chromatographic analysis. It is then necessary to employ samplers which ensure that the sample is representative, is preserved, and can be injected into the chromatograph. A version of a 10 ml sampler, made of Teflon, for sulphur-containing gases ($H_2S$, $SO_2$, etc.) has been described[187]. A transportable sampler has been proposed† for corrosive, toxic, and readily hydrolysable gaseous media in which the volume of the working chamber is 250 $cm^3$ (Fig. 2). The device makes it possible to remove a sample from gaseous systems under an excess pressure or under the conditions of rarefaction. The Teflon shell of the sampler is clamped together with an elastic membrane between Textolite flanges. The membrane is connected to a plunger with a rigid centre and is moved by a guide screw with a handle, located in a guide bracket. The sampler tube is connected to the shut-off valve by a polyethylene capillary. Samples containing compounds capable of diffusing through Teflon are removed by a modified sampler with a stainless steel bellows replacing the membrane unit.

The choice of column materials is as a rule preceded by a careful analysis of their behaviour under various conditions[188]. For example, Teflon is completely inert and can be used in the separation of any substances, including HCl, HF, etc., but the temperature must not exceed 200°C. Like Teflon, glass and quartz are not catalytically active, while metallic columns can exhibit catalytic effects, particularly at high temperatures, and the sorption phenomena on their surfaces are manifested to a greater extent than for glass and Teflon. The disadvantages of metallic columns are compensated by their high resistance to heat, optimum thermal conductivity, and the technological ease of their manufacture. Thus the choice of column material depends on the nature of the substance analysed, the conditions of the analysis, and the technology of the column manufacture. Despite its disadvantages, glass is in many cases the only material suitable for the preparation of columns used in the analysis of chemically unstable compounds. For example, studies carried out with copper, stainless steel, Teflon, and glass on the chromatographic analysis of mixtures of nitrogen dioxide and air showed that materials other than glass cannot be used because of sorption on the column surface[189]. Nor could glass columns be replaced in the analysis of admixtures of hydrogen chloride, chlorine[172,190], halogenohydrocarbons[173], organic derivatives of boron, beryllium, aluminium, phosphorus, zinc, and tin[169], and phosphates, amines, and triazides[191], and in the determination of organic chloro-impurities in germanium tetrachloride and hydrocarbons[50,51]. The replacement of Teflon columns by glass columns in the analysis of tetraethyl pyrophosphate decomposition products increased the sensitivity of the determination by a factor of five[192].

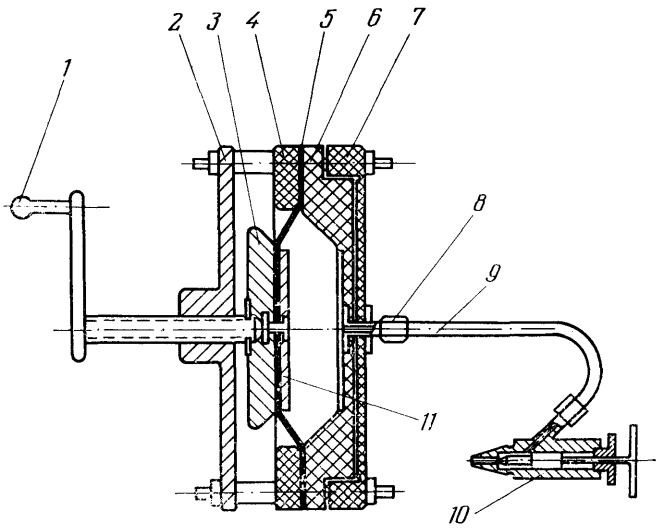



Figure 2. Gas sampler: 1) guide screw; 2) bracket; 3) plunger; 4) and 7) flanges; 5) membrane; 6) shell; 8) tube; 9) capillary; 10) valve; 11) rigid centre.

Monel metal and nickel columns are used as a rule in the chromatographic analysis of halogen and interhalogen compounds as well as metal fluorides and chlorides[40,181,184,193,194]. However, in most cases the columns are made of stainless steel in view of its ready availability and lower cost compared with nickel and Monel metal. In particular, stainless steel columns have been used in the analysis of arsenic and phosphorus hydrides, organic chloro- and bromo-compounds, and organic compounds of phosphorus, tin, and many other elements[170].

In view of the great inertness of zirconium oxides, they have been suggested as coatings for the inner walls of gas connectors and chromatographic columns to be used in the analysis of corrosive substances. For this purpose, the zirconium components are etched with oxidising solutions and kept in moist $CO_2$ at 450°C. The last process can be carried out directly in the chromatograph by passing

†See the NIITEKhIM Information Bulletin No. 2, Moscow, 1972.

through it moist $CO_2$ instead of the carrier gas [195]. The high stability and complete chemical inertness of the resulting protective film have been noted. Teflon is widely used as a material for chromatographic columns, particularly for the analysis of xenon fluoride [183], the halogens and their binary compounds [196], inorganic halogen compounds [185], hydrogen sulphides, and many sulphur compounds [187].

The problems of the detection of reactive compounds have been partly considered by Brazhnikov [197], who noted that, when the application of gas chromatography is extended from the analysis of hydrocarbons to the analysis of inorganic and organic compounds with a high reactivity, a new approach is needed for the solution of the problem of the detection of these compounds, particularly when a high sensitivity must be ensured. The detection of such compounds frequently requires both universal and selective detectors, which must be made of corrosion-resistant materials. The protection of sensor elements requires particular attention.

The thermal conductivity detector was one of the first to be used for the analysis of reactive gaseous mixtures. Many corrosive inorganic acids, certain alkylated compounds, metal chlorides, etc, have been analysed with its aid. Thus the concentration of nitrogen dioxide in air with a detection threshold of $10^{-4}$ vol. % [189] and MeGaCl, $Me_2AlCl$, $H_2$, and $CH_4$ admixtures in trimethylgallium [198] have been determined and mixtures of chlorine with chlorine, uranium, bromine, and xenon fluorides (with a lower detection limit of 0.1 vol.%), halogens and their compounds [38,40,48,183,193,196,199,200], chlorosilanes and organochlorosilanes [52,201], inorganic chlorides, and organometallic compounds [160,182,202] have been analysed using a katharometer. In order to achieve the maximum sensitivity of the katharometer, helium or hydrogen are used as the carrier gas [202], although some investigators prefer air or Freon-12. [194]

The sensor elements of the detector are mainly made of a tungsten coil with a high mechanical strength. However, tungsten is readily oxidised by traces of oxygen at high filament temperatures and is susceptible to the influence of corrosive media. To improve the stability of the sensor elements, they are gold-plated or coated with Teflon [40,181,182,200]. Although the coating of the filament with Teflon lowers the sensitivity of the detector by a factor of approximately four, its high stability in corrosive media is thereby ensured. Gold plating does not have a significant influence on the sensitivity of the detector. Platinum coils react with fluorides and are also decomposed in the presence of aluminium, gallium, and zirconium chlorides [18]. Nickel wire sensor elements have been used in the detection of chlorine and bromine chlorides, hydrogen fluoride, and fluorine, the shell of the katharometer being made of stainless steel or glass [38,183,193,196,199]. In the determination of microimpurities in $Me_3Ga$ at concentrations of $2 \times 10^{-3}$ wt.%, the detector shell was made of tantalum [198]. Thus the use of the katharometer as a rule permits the chromatographic analysis of a wide variety of reactive compounds over a wide range of concentrations, provided that materials are suitably chosen for the manufacture of its elements and special protective precautions are taken.

However, the use of extremely expensive and scarce helium and the permanent contact between the sensor element and the compounds analysed preclude the improvement of the sensitivity of the analysis when the katharometer is employed. The density detector, in which nitrogen or argon are used as the carrier gas, is free from these disadvantages. Furthermore in the analysis of substances containing components with known molecular weights, the calibration plot for the chromatograph can be calculated, which greatly facilitates work with unstable compounds. According to the literature, the density detector has been used most successfully for the analysis of organochlorosilanes [180,203-205], a sensitivity of $3.1 \times 10^3$ mV ml $mg^{-1}$ being achieved, which is approximately two orders of magnitude higher than the sensitivity of the katharometer using nitrogen as the carrier gas and an order of magnitude lower than for the katharometer with helium as the carrier gas. This detector is recommended as the most suitable for the analysis of organosilicon monomers [205].

An industrial chromatograph with a density detector has been developed [180] and used for the analysis of admixtures in a stream of organochlorosilanes at concentrations of 0.1%, the detection threshold being $10^{-3}$–$10^{-4}$ vol.%. A densitometer with argon as the carrier gas has also been used to detect HF, $H_2O$, and $SiF_4$,[206] $ClF_3$, $AsF_5$, $Cl_2$, $Br_2F_5$, etc. and in the determination of molecular weights of a number of compounds [186,193,207]; it has been employed [193] together with the katharometer [193], and in the analysis of mixtures of aluminium, gallium, niobium, and zirconium chlorides it replaced successfully the katharometer, the platinum coils of which disintegrated in the substances analysed [18].

Organochlorine and organofluorine compounds, alkylchlorosilanes, organometallic compounds, and other extremely reactive compounds [52,208-212] have been analysed with the aid of the flame-ionisation detector (FID), this type of detector being used in many instances in conjunction with selective detectors—thermionic and flame-photometric [170,213,214] (in the analysis of organometallic compounds and arsenic and phosphorus hydrides). For example, organochlorine impurities in HCl at concentrations of $(1–1.5) \times 10^{-4}$ wt.% have been determined with the aid of the flame-ionisation detector [172]; alkylchlorosilanes have been detected with a sensitivity threshold of $10^{-3}$ vol.%, which is lower by a factor of 40–50 than the sensitivity threshold of the katharometer with helium as a carrier gas in relation to these compounds [52]. However, it has been noted that the operation of the flame-ionisation detector in the analysis of alkylchlorosilanes is unreliable owing to the deposition of the decomposition products ($SiO_2$ and rust) on the electrodes.

Analysis of inorganic halogen compounds with the aid of the flame-ionisation detector is of definite interest [185]. The detector was designed in such a way that the carrier gas was introduced directly into the hydrogen flame, which significantly enhanced ionisation. The choice of the design and the selection of the positions of the electrodes ensured the optimum stability and sensitivity of the detector under the given conditions, amounting to 40.8–77.2 ml mV$\mu$ $g^{-1}$ for halogens, which is much superior to the sensitivity with respect to benzene (1310 ml mV$\mu$ $g^{-1}$) but considerably inferior to the sensitivity of the densitometer (approximately 3 ml mV$\mu$ $g^{-1}$). The authors preferred the flame-ionisation detector to the katharometer and the densitometer because the latter could not be used in combination with capillary columns. Experience gained in use showed the high stability of the platinum electrodes of the flame-ionisation detector with respect to corrosion, while the burner was corroded after prolonged use. The high linear dynamic detection range ($10^7$–$10^8$), the low sensitivity to variations in the carrier gas flow rate, pressure, and temperature, the possibility of detecting many classes of compounds, the degradation of highly toxic substances on

combustion, and other advantages have to a large extent favoured the wide-scale employment of the flame-ionisation detector in chromatographic analysis. However, the deposition of degradation products in the detector in the analysis of unstable compounds, which increase the detector noise, and the lack of sensitivity to certain compounds (chlorosilanes, nitrogen oxides, ammonia, and other compounds without carbon or with a low carbon content) hinder its use for the analysis of the compounds considered in the present review.

In contrast to the katharometer, the densitometer, and the flame ionisation detector, the electron capture detector (ECD) and the thermionic detector are selective. For example, the electron capture detector has proved to be the most suitable for the analysis of organometallic compounds in small amounts ($3 \times 10^{-4}$ mole $s^{-1}$), inorganic chlorides[181], and volatile fluorine compounds[184]. $1.5 \times 10^{-6}$% $SiCl_4$, $10^{-7}$% $PCl_3$ in $POCl_3$, and $10^{-4}$% of $PSCl_3$ in $PCl_3$ have been determined with the aid of the electron capture detector. In the analysis of admixtures in compounds which do not capture electrons, the electron capture detector is combined with the katharometer[181]. Analysis of reactive gases requires the protection of radioactive sources. The source may be exposed to an additional stream of an inert gas[181] or a special closed source may be used[184].

The thermionic detector (TID) has been known mainly as the detector most sensitive to compounds containing halogens and (particularly) phosphorus. Organochlorine impurities in germanium tetrachloride have been determined with its aid, the sensitivity being $8 \times 10^{-6}$–$5 \times 10^{-4}$ mole %, which exceeds by 1–2 orders of magnitude the sensitivity of the flame-ionisation detector[50], and the impurities in trichlorosilane have been determined with a sensitivity of $1 \times 10^{-4}$–$5 \times 10^{-2}$ mole %[43]; the possibility of the chromatographic determination of organochlorosilanes with a sensitivity threshold of $10^{-5}$% has been demonstrated[215]. Studies on the sensitivity of the thermionic detector, fitted in a "Khrom-35" chromatograph, to organochlorosilanes and alkylated tin and lead compounds showed that the sensitivity is a maximum when caesium salts are used as the ion source[216]. The detector readings are then positive in relation to silicon compounds and negative in relation to tin and lead compounds. The sensitivity of the thermionic detector giving positive readings diminishes in the sequence P > Si > Br > Cl, while for negative readings it increases in the sequence Pb < S < Sn. The thermionic detector has been used also in the analysis of boron compounds[217]. It has been established that, in order to achieve the stable operation of the detector, it is necessary to increase the temperature of the flame, which led to the employment of the refractory PbCl salt, since, under the conditions used in the analysis of boron compounds, the sensitivity of the detector depends much more on the hydrogen flow rate than, for example, in the case of phosphorus compounds.

The thermionic detector has been used in many cases in combination with other types of detector. When it was combined with the flame-ionisation detector, a sensitivity of $8 \times 10^{-7}$–$2 \times 10^{-10}$ g $s^{-1}$ was achieved in the analysis of phosphorus and arsenic hydrides, organochlorine and organoboron compounds, and organic derivatives of tin and phosphorus[170]. Both detectors were mounted in the same shell made of glass. In the analysis of phosphates and nitrogen-containing phosphorus compounds, the joint employment of the thermionic and thermal conductivity detectors is recommended[191].

However, together with its high selectivity, mention must be made of the comparatively short linear range of the response of the thermionic detector (up to $10^3$), which limits its scope for the determination of concentrations over a wide range. The most serious disadvantage of the sodium thermionic detector is its low stability, caused largely by the quality of the alkali metal salt, which evaporates in the burner flame; for this reason, surface ionisation thermionic detectors are preferable, despite their somewhat lower sensitivity.

The flame-photometric emission detector (PPD) is also selective, and its selectivity may be varied within fairly wide limits by altering the wavelength and the width of the transmission band. The problems of the application of such a detector in the detection of a wide variety of corrosive organic and inorganic compounds have been examined[197]. Mention may be made of the use of the flame-photometric detector for the analysis of boron hydrides with a detection limit of 0.7 ng[13,156] and also the possibility of determining sulphur compounds in amounts of $10^{-7}$%.[187] Like other selective detectors, the flame-photometric detector can be usefully employed in combination with, for example, the flame-ionisation detector in the analysis of organic compounds of phosphorus, tin, lead, and certain nitrogen compounds[213,214,218].

The examples considered above demonstrate the wide scope of the applications of various detectors for the chromatographic analysis of a wide range of organic and inorganic compounds with high reactivities. The wide variety of requirements which must be met by the analytical method and the sensitivity of the analysis, the operational and design features of the apparatus, the wide variety of classes of compounds analysed, and the conditions used in the analyses preclude unambiguous recommendations in the present review concerning the usefulness of a particular detector in the analysis of a specific compound. The necessary choice and combination of the optimum separation and detection systems in each individual case enable the investigator to make the correct choice of the method for the solution of the problem facing him; this is possible only after a careful preliminary study of the apparatus and of the mechanisms of the reactions occurring during separation and possible side processes.

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# Kinetics of Chemical Reactions Initiated by Hot Atoms

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A general account is given of modern ideas on the kinetics of hot-atom reactions and the fundamental postulates of the phenomenological theories, namely the Wolfgang-Estrup "kinetic theory" of hot-atom reactions and Porter's theory of the "integral reaction probability" are described. The physicochemical models of elastic and non-elastic collisions used for the solution of the Boltzmann integrodifferential equations and of the stochastic equations in Porter's theory are examined. The fundamental formulae describing the probabilities or yields of chemical reactions initiated by hot atoms in relation to the energy distribution functions of hot species are presented and a brief account is given of the methods and the results of the application of the phenomenological theories in the interpretation of the results of experiments involving hot atoms in nuclear reactions, photochemical studies, etc.
The bibliography includes 96 references.

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## I. KINETIC EQUATIONS IN THE CHEMISTRY OF HOT ATOMS

Chemical processes involving high-energy atoms or ions under the conditions of a non-uniform distribution of these species in time and space and a non-Maxwellian energy distribution of "hot" atoms or ions are widely investigated at the present time. The chemical reactions of hot atoms are of interest in connection with the high efficiency of the collisions, the dominant role of high-energy processes, and the possibility of carrying out new types of reactions. Hot atoms or ions are obtained as a result of radiation-chemical, plasma-chemical, or nuclear transformations in chemical accelerators, in photochemical reactions, in shock waves, and in cold flames. Extensive experimental data have accumulated on the yield of products in processes involving hot atoms[1-3]. During the last decade, there has been intense development of theoretical ideas about the kinetics of reactions of hot species, mainly in two directions, the first of which is associated with the study of the dynamics of the collisions of hot atoms leading to their cooling and chemical capture[4]. The second led to the establishment of phenomenological theories describing the yield of products as a function of the cross-sections of various elastic and non-elastic collisions and also the energy distribution functions of hot atoms[5,6]. Among these, the most productive have been the "kinetic theory" of hot-atom reactions proposed by Wolfgang and Estrup[7,8] and the theory of the "integral reaction probability" developed by Porter[9]. In the present review, attention has been concentrated on the fundamental postulates of the above phenomenological theories and on the results of their application in the analysis of numerous experimental data on the chemistry of recoil atoms.

## 1. Transport Equations in the Kinetics of Hot-atom Reactions

The nature of the chemical reaction of a species (atom or ion) with the target material depends on the parameters for the species at the instant of reaction and on the properties of the medium at the point of interaction, which depend in their turn on the previous history of both the given hot species and the entire set of species bombarding the target as well as the previous history of the target material. In systems where high-energy species are introduced, relaxation processes and chemical reactions are indissolubly linked. In a rigorous study of kinetic relations, it is therefore necessary to take into account the set of processes involving high-energy species:

(1) elastic and non-elastic scattering of the species and the penetration, caused by these processes, of the species into the bulk of the target with establishment of a definite spatial distribution and retardation of the species accompanied by the establishment of a definite energy distribution (taking into account both the kinetic energy and the energies of vibrational, rotational, electronic, etc. excitation);

(2) the escape of species from the boundaries of the target and their absorption by the material of the target owing to chemical reactions or retention in various types of traps;

(3) the recombination reactions of the bombarding species.

The relaxation processes of hot species are accompanied by the transfer of their excess energy to the target material with subsequent microscopic and macroscopic transformations. Such transformations include the change in the internal state of the target molecules and in their chemical energy, ionisation, dissociation, and other chemical reactions, as well as the atomisation of the surface layers, heating, and other primary radiation effects. The primary radiation processes also include the displacement and dislodgement of atoms from the crystal lattice; the dislodgement of secondary high-energy species in a system where the target contains atoms equivalent to those used in the bombardment may be regarded as the development of a cascade process. Together with the primary radiation-induced transformations, there is a possibility of secondary transformations, in particular chemical reactions of the bombarding species with the product of the radiation-induced decomposition and reactions of unstable primary products with one another or with the molecules of the target material.

The distribution of the bombarding species in space, time, and with respect to energy and their absorption are determined by the large number of random collisions leading to the above processes. The macroscopic effects, for example the release of the products of the capture of hot species or their retention in the bombarded target, are treated in hot-atom chemistry on the basis of the study of single collisions and their properties. The main task in theoretical hot-atom chemistry involves the determination of the probabilities of reactions involving hot atoms and of the reaction rates or rate constants with the aid of one of the equivalent kinetic equations, for example:

$$P = \int p_r(E) \cdot n(E)\,\mathrm{d}E\,,$$
$$k = \int \sigma_r(E) n(E) v\,\mathrm{d}E \Big/ \int n(E)\,\mathrm{d}E\,, \qquad (I.1)$$
$$R = \int \Sigma_r(E) \cdot \varphi(E)\,\mathrm{d}E,$$

where $P$, $k$, and $R$ are the probability, rate constant, and the rate of the chemical reaction respectively, $p_r(E)$ the probability of reaction on collision of an atom having the energy $E$ with the target, $n(E)\mathrm{d}E$ the number of collisions of hot atoms in the range $E-E+\mathrm{d}E$, $\Sigma_r(E)$ the reaction cross-section of the species for the energy $E$ or velocity $v(E)$, $\sigma_r(E)$ the reaction microsection, and $\varphi(E)$ the flux of species with the energy $E$.

In contrast to traditional kinetics, in hot-atom chemistry the above problems have to be solved for species having a non-equilibrium non-Maxwellian distribution, determined by their initial energy, their mass, the retarding capacity of the medium, its reactivity, etc. One of the fundamental problems in the theory of chemical reactions initiated by hot atoms is therefore associated with the search for the distribution functions of the reacting species with respect to energies or velocities and internal states, or their distribution functions within the bulk of the target. In theoretical models describing the chemical effects of hot atoms, particular attention has been concentrated at the present time on the energy distribution of the retarding species in spatially homogeneous cases[5-9], and in addition on the spatial distribution of species under spatially inhomogeneous conditions.

Models used to describe the chemical effects of recoil atoms are described in the first place in the present review, since this field has now been developed fairly extensively. A characteristic feature of the models is their spatial restriction by independent factors with a homogeneous distribution of the sources of hot species in an infinite medium, account being taken only of the energy distribution of the recoil atoms or, more precisely, of their distribution with respect to kinetic energy.

The kinetics of non-equilibrium chemical hot-atom processes may be based on the Boltzmann, Pauli, or Liouville equations[11,12]. It has been pointed out that[11] the difficulty of the solution of the Liouville equations, the inapplicability of the Boltzmann equations to three-particle processes, and the obscure nature of the problem of the uniqueness of the solutions of these equations in the general case necessitate the hypothesis that the Pauli equation is the most promising for the description of the kinetics of non-equilibrium processes; this equation is particularly convenient in numerical methods of calculation.

However, mainly the Boltzmann integrodifferential equations have been used hitherto in hot-atom chemistry. A rigorous treatment taking into account the various effects accompanying the bombardment of targets by high-energy species requires the solution of integrodifferential transport equations with many independent variables (three spatial coordinates, two variables defining the direction of motion, and the energy and time variables). The problem is complicated by the fact that, if it is necessary to take into account secondary effects, the equations become non-linear.

The neglect of secondary processes is quite valid for low flux intensities of the bombarding species and small integral fluxes. If, in addition, one disregards the internal degrees of freedom, i.e. the colliding species are assumed to be material points, or the collision cross-sections and other quantities are averaged with respect to internal states (taking into account the statistical weights), then the behaviour of the entire set of species in a scattering and absorbing medium can be described on the basis of the laws of conservation of matter and energy by linear equations with independent variables: the radius-vector $\boldsymbol{r}$, the time $t$, the solid angle $\Omega$, the energy $E$, or the velocity $v$.

The set of bombarding species may be characterised by the differential density or the differential vector flux; these quantities are linked by the equation $\rho(r, \Omega, E)v = \varphi(r, \Omega, E)$. The change in differential density or flux must depend on the ratio of the supply and loss of species in the region of phase space characterised by the quantities $r$, $\Omega$, $E$. The supply is determined by independent sources, atom migration chain processes, and the scattering of species from neighbouring regions. The loss may occur as a result of slipping of the species from the external boundaries of the target, scattering, and capture by chemical or physical traps.

In many instances, one can disregard atom migration chain processes, whereupon the change in the differential density of species or the differential vector flux in the volume element $dV$ with the energy of the species in the range $dE$ and the direction of motion in the solid angle $d\Omega$ is defined by the following factors:

(1) the density of the sources $S(r, \Omega, E)$;

(2) the loss of species from the given volume element $\Omega \cdot \mathrm{grad}\varphi(r, \Omega, E)dV d\Omega dE$;

(3) the losses on scattering and absorption $\Sigma_t \cdot \varphi(r, \Omega, E)dV d\Omega dE$ ($\Sigma_t = \Sigma_S + \Sigma_r$, where $\Sigma_r$ is the absorption cross-section and $\Sigma_S$ the scattering cross-section);

(4) the increment in the number of species as a result of displacement or scattering from neighbouring regions of phase space with the coordinates $(r, \Omega', E')$:

$$\int_{4\pi}\int_{0}^{\infty} \Sigma_s(\Omega', \Omega; E', E) \cdot \varphi(r, \Omega', E')\, d\Omega\, dE\, dV\, d\Omega'\, dE',$$

where $\Sigma_S(\Omega', \Omega; E', E)d\Omega\, dE$ is the scattering cross-section of the species with the energy $E'$ and the direction of motion $\Omega'$, the direction of motion becoming $\Omega$ (in the range $\Omega - \Omega + d\Omega$) and the energy becoming $E$ (in the range $E - E + dE$) after the collision. Hence the change in the differential density or the differential flux of the species must obey the equation

$$\frac{\partial \rho(r, \Omega, E)}{\partial t} = \frac{1}{v}\frac{\partial \varphi(r, \Omega, E)}{\partial t} = S(r, \Omega, E) - \Omega \cdot \mathrm{grad}\varphi(r, \Omega, E) + \int_{4\pi}\int_{0}^{\infty} \Sigma_s(\Omega', \Omega, E', E) \times \varphi(r, \Omega', E')\, d\Omega'\, dE' - \Sigma_t(E) \cdot \varphi(r, \Omega, E). \quad (I.2)$$

The rate of formation of recoil atoms may be assumed to be constant, except over long periods, where the loss of parent nuclei as a result of the reactions involving the formation of recoil atoms becomes significant. The constancy of the strength of the source of hot species makes it possible to treat the problem of the determination of $\rho(r, \Omega, E)$ or $\varphi(r, \Omega, E)$ as stationary, if one excludes from consideration also the region of very short times during which nearly stationary energy or spatial distributions of the species are established. This makes it possible to formulate the transport equation for hot species in the following way:

$$\Omega \cdot \mathrm{grad}\varphi(r, \Omega, E) + \Sigma_t(E) \cdot \varphi(r, \Omega, E) = S(r, \Omega, E) + \int_{4\pi}\int_{0}^{\infty} \Sigma_s(\Omega', \Omega; E', E)\varphi(r, \Omega', E')\, d\Omega'\, dE'. \quad (I.3)$$

If the target is isotropic and is so large compared with the paths traversed by the hot species before retardation in the region of chemical interaction and compared with the diffusion paths that it can be regarded as infinite and the boundary effects may be neglected, in particular the loss of species as a result of recoil or diffusion, one may eliminate from Eqn.(I.3) all spatial variables and average with respect to directions of motions quantities such as, for example, the scattering cross-sections. Under these conditions, the transport equation (I.3) may be reduced to the form:

$$\Sigma_t(E) \cdot \varphi(E) = S(E) + \int_{0}^{\infty} \Sigma_s(E', E) \cdot \varphi(E')\, dE', \quad (I.4)$$

where $\varphi(E)$ is the flux of species with the energy $E$ and $\Sigma_S(E', E)$ the scattering cross-section with a change of energy from $E'$ to a value in the range $E - E + dE$. Eqn. (I.4) is the initial equation for many specific forms of kinetic expressions in the chemistry of recoil atoms uniformly distributed within the space of infinite isotropic targets. In the case of recoil atoms, one usually operates with the density of the collisions of hot atoms with the atoms or molecules of the target and not with the fluxes of hot species. The collision density $\psi(E)$, i.e. the number of species colliding per unit volume per unit time, is related to the flux by the expression $\psi(E) = \varphi(E) \cdot \Sigma_t(E)$.

Evidently Eqn.(I.4) for the density of collisions can be written in the form:

$$\psi(E) = S(E) + \int_{0}^{\infty} \frac{\Sigma_s(E', E)}{\Sigma_s(E') + \Sigma_r(E')} \psi(E')\, dE'. \quad (I.5)$$

The applicability of Eqn.(I.5) is based not only on the stationary nature of the sources and $\psi(E)$, but also on the absence of non-uniformity in the spatial distribution of hot species due to the homogeneity of the distribution of the sources, the isotropic nature of the medium, and the large size of the target.

In order to obtain analytical solutions of equations of type (I.5), additional conditions are introduced in the chemistry of recoil atoms which vary as a function of the characteristics of the models proposed by a particular investigator. It is usually assumed that elastic collisions with the free atoms of the target at rest are of fundamental importance. For fairly high energies of hot atoms (recoil atoms usually have identical initial energies greatly exceeding the upper limit of the energy range of the chemical reactions), neglect of the thermal motions of the target atoms and the effects due to their chemical bonds cannot give rise to significant errors, but neglect of inelastic scattering can entail appreciable errors. However, in the range of energies not exceeding $E = (m_1/8m_e)I^*$ (where $I^*$ is the ionisation potential and $m_e$ and $m_1$ are the masses of the electron and the hot atom), the energy losses in inelastic collisions, particularly in electronic excitation and ionisation, are small. The above hypotheses make it possible to simplify the expression relating $\Sigma_S(E')$ and $\Sigma_S(E', E)$.

Suppose that $g(E', E)dE$ is the probability that the species with the energy $E'$ acquires after collision an energy in the range $E - E + dE$. Evidently $\Sigma_S(E', E) = \Sigma_S(E') \cdot g(E', E)$. Substitution of $\Sigma_S(E', E)$ in Eqn.(I.5) leads to the expression

$$\psi(E) = S(E) + \int_{E}^{E/\alpha} \frac{\Sigma_s(E')}{\Sigma_s(E') + \Sigma_r(E')} \psi(E')\, g(E', E)\, dE'. \quad (I.6)$$

The integration limits are determined by the quantities $\alpha = [(m - m_1)/(m + m_1)]^2$ which depend on the masses of the hot atom ($m$) and the target atoms ($m_1$). If $\alpha = 0$ or $\alpha \neq 0$ but $\alpha E_0 < E$, then the upper integration limit may be assumed equal to $E_0$; in other instances, the upper limit is $E/\alpha$. Eqn.(I.6) makes it possible to take into account the change in collision density as a result of the "erosion" of the species from the energy spectrum in chemical processes, since it includes the reaction cross-sections $\Sigma_r(E)$. If the ratio $\Sigma_S(E')/[\Sigma_S(E') + \Sigma_r(E')]$ is expressed in the form $1 - \Sigma_r(E')/[\Sigma_S(E') + \Sigma_r(E')] = 1 - p_r(E')$,

where $p_r(E)$ is the probability of chemical reaction on collision of the recoil atom having the energy $E$, then it follows from Eqn.(I.6) that

$$\psi(E)=S(E)+\int_{E}^{E/\alpha}[1-p_r(E')]\cdot\psi(E')\cdot g(E', E)\,dE'. \quad (I.7)$$

For identical initial energies of all the recoil atoms, the source function of the hot species $S(E)$ can be written in the form $S(E)=S_0\delta(E_0, E)$, where $\delta(E_0, E)$ is the delta-function. Thus, for all $E\neq E_0$, the function $S(E)$ is zero. When $\Sigma_r(E)=0$, we have $p_r(E)=0$ and Eqn.(I.7) becomes

$$\psi(E)=S(E)+\int_{E}^{E/\alpha}\psi(E')\cdot g(E', E)\,dE'. \quad (I.8)$$

The quantities $g(E', E)$ may be estimated on the basis of the laws of mechanics[13-15]. The quantities $G(E', E)=\int_{\alpha E'}^{E} g(E', E'')dE''$, characterising the probability that the species having the energy $E'$ before collision have an energy in the range $E-0$ after collision, are estimated similarly. If the scattering is isotropic, then we have for $E'>E>\alpha E'$

$$g(E', E)=\frac{1}{E'(1-\alpha)} \quad (I.9)$$

$$G(E', E)=\frac{E-\alpha E'}{E'(1-\alpha)}. \quad (I.10)$$

Using the value of $g(E', E)$ obtained, Eqns.(I.7) and (I.8) for elastic isotropic collisions may be transformed into

$$\psi(E)=S(E)+\frac{1}{1-\alpha}\int_{E}^{E/\alpha}\psi(E')\frac{dE'}{E'} \quad (I.11)$$

$$\psi(E)=S(E)+\frac{1}{1-\alpha}\int_{E}^{E/\alpha}[1-p_r(E')]\psi(E')\frac{dE'}{E'}. \quad (I.12)$$

Eqn.(I.11) has a simple asymptotic solution. The collision densities for energies less then $E_0$ are defined by the approximate expression

$$\psi_0(E)=S_0/\xi E, \quad (I.13)$$

where $\xi$ is the average logarithmic energy loss in the collision. $\psi_0(E)$ can be regarded as the asymptotic solution of Eqn.(I.11) not only for billiard collisions but also for any elastic collisions, provided that account it taken of the dependence of $g(E', E)$, $G(E', E)$, and $\xi$ on the form of the interaction potential. The asymptotic solution shows that, for any elastic collisions characterised by a spherically symmetrical potential, the collision density function decreases with increase of $E$; the nature of $\psi_0(E)$ depends on the form of the interaction potential through the function $\xi(E, \alpha)$.[16-21] In the general case, the average logarithmic energy loss in the collision can be represented by the formula

$$\xi=\overline{\ln\frac{E'}{E}}=\int_{\alpha E'}^{E'}\ln\frac{E'}{E}\cdot g(E', E)\,dE. \quad (I.14)$$

For the hard-core interaction potential, we have

$$\xi_{hs}=1+\frac{\alpha}{1-\alpha}\ln\alpha. \quad (I.15)$$

In a mixture of moderators, $\bar{\xi}=\sum_i f_i\xi_i$, where $f_i=\sigma_{si}N_i/\sum_j\sigma_{sj}N_j$ ($N_j$ is the mole fraction of the component $j$) is the fraction of the collisions of the hot atoms with the component $i$ and $\xi_i$ is determined by the potential of the interaction of the hot atoms with the atoms $i$.

In non-absorbing systems, the asymptotic solution of equations of type (I.8) for sources with an arbitrary distribution spectrum (for example in $\beta$-decomposition) in terms of collision density is

$$\psi_0(E)=S(E)+\frac{1}{\xi E}\int_{E_{min}}^{E_{max}}S(E')\,dE', \quad (I.16)$$

where $E_{max}$ is the maximum energy of the recoil atoms in the spectrum. For energies less than the minimum value, we have in the spectrum

$$\psi_0(E)=S_0/\zeta E, \quad (I.17)$$

where $S_0=\int_{E_{min}}^{E_{max}}S(E')dE'$. If the non-absorbing medium contains a mixture of moderating atoms, then Eqn.(I.11) can be written as follows:

$$\psi(E)=S(E)+\sum_i\int_{E}^{E/\alpha_i}f_i\psi(E')\frac{dE'}{E'(1-\alpha_i)}. \quad (I.18)$$

If the ratio $\sigma_{si}/\sum_j\sigma_{sj}$ is independent of the energy, the asymptotic solution of Eqn.(I.18) for a monochromatic source is

$$\psi_0(E)=S_0/\bar{\xi}E. \quad (I.19)$$

In the general case, considerable mathematical difficulties arise in the solution of Eqn.(I.7) for absorbing systems. An exact and fairly simple analytical solution is available only for $\alpha=0$, when there are no oscillations in the collision density near the sources and the upper integration limit, involving in the general case the variable $E$, is replaced by $E_0$. For a monochromatic source and $E\ll E_0$, the asymptotic solution is

$$\psi_0(E)=\frac{S_0}{E}[1-p_r(E_0)]\exp\left[-\int_{E}^{E_0}\frac{p_r(E')}{E'}dE'\right]. \quad (I.20)$$

In the $\beta$-decomposition, where the recoil atoms have a definite distribution with respect to $E_0$, it is particularly important to obtain a solution of Eqn.(I.7) for an arbitrary source $S(E)$. The solution is

$$\psi_0(E)=S(E)+\frac{1}{E}\int_{E}^{E_{max}}[1-p_r(E')]S(E')\cdot\exp\left[-\int_{E}^{E'}p_r(E'')\frac{dE''}{E''}\right]dE. \quad (I.21)$$

Solutions (I.20) and (I.21) show that, owing to "erosion" during absorption, the flux of hot species increases more slowly with decrease of the energy than would be expected from the $1/E$ law. In particular, if the ratio $\Sigma_s(E)/\Sigma_r(E)$ is independent of the energy and close to $C$, the flux for low energies is proportional to $E^{-C/(1+C)}$; the corresponding collision density is

$$\psi(E)\propto\frac{S_0}{\xi E^{\frac{C}{1+C}}}. \quad (I.22)$$

In those cases where $\alpha\neq 0$, fairly complex relations were obtained in the solution of equations (I.7) and (I.12).[22] Instead of complex solutions, one can employ in many instances simple Wigner and Fermi approximations[23].

Their use is possible, firstly, when the initial energy of the species is fairly high and the absorption region with the boundaries $E_1$ and $E_2$ lies considerably lower and, secondly, when absorption leads to a weak perturbation of the spectrum of hot species. This corresponds to a very weak absorption when $\Sigma_r < \Sigma_s$ or to absorption due to strong but well resolved resonances; the width of the resonances should then be small compared with the values of $\ln(1/\alpha)$ and the distances between the individual resonances should greatly exceed $\ln(1/\alpha)$. When the above conditions are fulfilled, one can neglect non-asymptotic oscillations near the sources of hot species and also near the absorption zone, which may be regarded as a negative source with possible non-asymptotic oscillations, and an approximate solution may be used. The solution is of the form

$$\psi_0(E) = q(E)/\xi E, \tag{I.23}$$

where $q(E)$ is the retardation density, i.e. the number of species retarded per $cm^3$ per second down to energies below $E$. In the general case, the following expression is valid for $q(E)$:

$$q(E) = \int_E^{E/\alpha} [1 - p_r(E')] \cdot \psi(E') \cdot G(E', E)\, dE'. \tag{I.24}$$

In non-absorbing media, $q(E) = S_0$ for a monochromatic source and $q(E) = \int_E^{E_{max}} S(E')dE'$ for an arbitrary source. In absorbing media with $\alpha = 0$, we have

$$q(E) = S_0[1 - p_r(E_0)] \exp\left[-\int_E^{E_0} \frac{p_r(E')}{E'} dE'\right] = S_0 p(E) \tag{I.25}$$

for a monochromatic source and

$$q(E) = \int_E^{E_0} S(E')[1 - p_r(E')] \exp\left[-\int_E^{E'} \frac{p_r(E'')}{E''} dE''\right] dE' \tag{I.26}$$

for an arbitrary source. Here $p(E)$ is the probability of avoiding capture in the retardation process until the attainment of the specified energy. In terms of the Wigner–Fermi approximation, we obtain the following expression for absorbing systems with $\alpha \neq 0$ and a monochromatic source when $p_r(E_0) \simeq 0$:

$$q(E) = S_0 p(E) = S_0 \exp\left[-\int_E^{E_0} \frac{p_r(E')}{\xi E'} dE'\right]. \tag{I.27}$$

The chemical effects of the recoil atoms can be described also in terms of other approximations obtained in neutron physics. In particular, for a flux subjected to only a slight perturbation under conditions where the cross-section $\Sigma_r$ varies only slightly with the energy, one can probably employ the Goertzel–Greuling approximation[24], according to which the following expression is valid for $p(E)$:

$$p(E) = \exp\left[-\int_E^{E_0} \frac{\Sigma_r}{\xi\Sigma_s + \gamma\Sigma_r} \frac{dE'}{E'}\right], \tag{I.28}$$

where $\gamma = 1 - \alpha \ln^2(1/\alpha)/2(1-\alpha)\xi$; for example, when $\Sigma_r(E) \sim E^{1/2}$, $\Sigma_s(E) = \text{const.}$, and $E_0 \to \infty$, we have

$$p(E) = \left[1 + \frac{\gamma}{\xi} \frac{\Sigma_r(E)}{\Sigma_s}\right]^{-2/\gamma}.$$

For an absorbing medium containing the components $j$, each of which may be involved in chemical reactions, the solutions of equations of type (I.7) for $\psi(E)$ are formulated as follows in terms of the Wigner–Fermi approximation:

$$\psi_0(E) = \frac{S_0}{\xi E} \exp\left[-\sum_j \int_E^{E_0} \frac{f_j p_{rj}(E')}{\xi E'} dE'\right]. \tag{I.29}$$

Many investigators of hot-atom chemistry also use the quantities $n(E)$ as functions characterising the distribution of species with respect to energy, together with the collision density $\psi(E)$ and the flux of the species $\varphi(E) = [1/\Sigma_t(E)]\psi(E)$; $n(E)dE$ is the number of collisions of the hot atom in the range from $E$ to $E + dE$. If the source of recoil atoms is monochromatic, then $n(E) = \psi(E)/S_0$. Transport equations and their solutions of the same types as those quoted previously for $\psi(E)$ and $\varphi(E)$ are valid for $n(E)$. One may also note that the velocity $v$ or the lethargy $\ln(E_0/E)$ may be used as variables instead of $E$.

## 2. Porter's Equations for the Integral Probability of Hot-atom Reactions

Equations analogous to Eqns. (I.7) or (I.8) can be obtained by the direct determination of the probability of the transfer of a specified energy in the elementary collision step[9,25]. The method led to the creation of Porter's phenomenological theory of the "integral reaction probability"[9,26], which is particularly interesting because it makes it possible to take into account the thermal motion of the molecules or atoms of the bombarded targets, at least in numerical computer calculations. Evidently the probability that a hot atom with the energy $E'$ retains the energy $E$ after the first collision can be represented as the ratio of the differential cross-section $\Sigma_s(E', E)$ to the sum of the average cross-sections $\Sigma_s(E')$ and $\Sigma_r(E')$; the cross-sections are averaged taking into account the distribution functions for the relative velocities of the colliding species $v_{rel}$; they can also be averaged taking into account the energy (for example Maxwellian) distribution of the target species. Then, for a particular angle $\gamma$ between the vectors of the velocities $v_1$ and $v$, we have

$$g_1(E', E) = \frac{\int \Sigma_s(E', E, v_1, \gamma) \cdot v_{rel} \cdot \Omega(E', v_{rel})\, dv_{rel}}{\int [\Sigma_s(v_{rel}) + \Sigma_r(v_{rel})]\, v_{rel} \cdot \Omega(E', v_{rel})\, dv_{rel}}, \tag{I.30}$$

where $\Omega(E', v_{rel})$ can be determined in terms of Eqn. (II.35) (see below) when the target has a Maxwellian spectrum. For arbitrary cross-sections, $g_1(E', E)$ may be calculated numerically; in the case of an elastic isotropic collision with species at rest and in many other specific instances, an analytical determination of $g_1(E', E)$ is possible (see subsection 1 of this Section)

It is also evident that the following expressions are valid for the analogous probabilities for two, three, and $n$ collisions:

$$g_n(E', E) = \int_0^{\infty} g_{n-1}(E', E') \cdot g_1(E'', E)\, dE''. \tag{I.30a}$$

For a monoenergetic source, we have

$$g_0(E', E) = \delta(E', E). \tag{I.30b}$$

The average number of collisions of the species in the energy range $E - E + dE$, when the first collision occurs for the energy $E'$, can be determined in terms of $g_n(E', E)$ as follows:

$$n(E', E)\, dE = \sum_n g_n(E', E)\, dE. \tag{I.31}$$

Substitution of Eqns. (I.30a) and (I.30b) in (I.31) yields

$$n(E', E)=\delta(E', E)+\int_0^\infty n(E', E'')g_1(E'', E)\,dE''. \quad (I.32)$$

If it is assumed that $p_r(E) = \Sigma_r(E)/\Sigma_t(E)$ and $g(E', E) = \Sigma_s(E', E)/\Sigma_s(E')$, it follows from Eqn. (I.30) that

$$g_1(E', E)=[1-p_r(E')]\cdot g(E', E). \quad (I.33)$$

Then

$$n(E', E)=\delta(E', E)+\int_0^\infty [1-p_r(E'')]\cdot g(E'', E)\cdot n(E', E')\,dE''. \quad (I.34)$$

Thus an expression analogous to Eqn. (I.7) is obtained for the function $n(E', E)$.

The solution of transport equations for the flux of the species, the collision density, the retardation density, or another equivalent distribution function of hot species opens a pathway for solving the problem of the determination for the rates and probabilities of the reactions or their yields and also to the analysis of parametric relations governing the above quantities. However, the estimation of the distribution function of hot species with respect to energy is not obligatory for the determination of the probability of the chemical reaction [9,27-30].

If the probability of the chemical interaction in the $n$th collision of the hot atom $P_n(E')$ is introduced, then evidently the probability of chemical stabilisation is defined as follows when account is taken of all the collisions for $E'$:

$$P(E')=\sum_n P_n(E'). \quad (I.35)$$

However, it is also evident that

$$P_n(E')=\int_{E_1}^{E_0} g_{n-1}(E', E)\,p_r(E)\,dE. \quad (I.36)$$

Substitution of Eqn. (I.36) in Eqn. (I.35) and transformations of $P_n(E)$ analogous to those performed for $g_n(E', E)$ (see above) lead to the expression

$$P(E')=p_r(E')+[1-p_r(E')]\int_{E_1}^{E'} g(E', E)P(E)\,dE. \quad (I.37)$$

For isotropic scattering and $\alpha = 0$, Eqn. (I.37) becomes

$$P(E')=\bar{p}_r(E)+\frac{1-p_r(E')}{E'}\int_{E_1}^{E'} P(E)\,dE. \quad (I.38)$$

The solution of Eqn. (I.38) yields

$$P(E')=1-[1-p_r(E')]\exp\left[-\int_{E_1}^{E'} p_r(E)\frac{dE}{E}\right]. \quad (I.39)$$

For anisotropic scattering, mainly at small angles, or for isotropic scattering and $\alpha$ close to unity, one obtains

$$P(E')=1-\exp\left\{-\int_{E_1}^{E'}\frac{p_r(E')\,dE'}{E'[1-p_r(E')]\int_0^{E'} g(E', E)(1-E/E')\,dE}\right\}. \quad (I.40)$$

The solution (I.39) is the same as the value obtained under analogous conditions in the determination of $P$ in terms of the distribution functions with respect to energy. In the general case, Eqn. (I.37) can be solved for $P$ by numerical, in particular iterative, methods, and $p_r(E)$ constitutes the first approximation [9,26,31].

For systems containing several components ($i$, $z$) involved in several types of reactions ($j$, $x$), $P(E)$ is defined by the equation

$$P_{ix}(E')=f_i(E')p_{rix}(E')+\int_0^\infty H(E', E)\cdot P_{ix}(E)\,dE, \quad (I.41)$$

where

$$H(E', E)=\sum_{z=1}^{N_r} f_z(E')\left[1-\sum_{j=1}^{\rho_z} p_{rzj}(E')\right]g_z(E', E)+\sum_{z=1}^{N_m} f_z(E')g_z(E', E),$$

$N_m$ is the number of moderators, $N_r$ the number of reactants, $\rho_z$ the number of reaction channels for the component $z$, and $p_{rix}$ the probability of a reaction of type $x$ with the component $i$. The method for the numerical solution of Eqns. (I.37) and (I.41) has been examined [31] with a quantum-mechanical description of elastic scattering.

Thus, without resorting to a preliminary determination of the distribution functions for the energy in terms of Boltzmann equations, one can obtain from the equations for the integral reaction probability in terms of analogous approximations (at least the simplest approximations) expressions relating the probability of chemical reactions to functions and parameters such as $p_r(E)$, $g(E', E)$, and $E_0$. However, this does not imply that the energy distribution functions of different species are no longer of any interest in hot-atom chemistry. Their determination is important, since, firstly, fairly well developed methods are now available for the solution of the Boltzmann equations, i.e. for the determination of the corresponding distribution functions and, secondly, the parametric relations found from the distribution functions, in particular the variation of $n(E)$ and $\psi(E)$ with the initial recoil energy and with the concentration of moderators, may reflect the corresponding parametric relations for the probability of chemical reactions.

The application of the stochastic method to the solution of non-stationary problems made it possible to obtain a number of kinetic equations describing the behaviour in time of the energy distribution function of the hot atoms [32]. For a stochastic description of time variations, it is important that the lifetime of the hot atom ($t$) is proportional to the number of its collisions ($n$) and the average time interval between them ($\tau$): $t = n\tau$; $dt \simeq (n+1)\tau - n\tau = \tau$. In the general case, Keizer [33] describes the variation of the density of hot atoms involved in the reactions by kinetic equations with a quasi-rate constant $k(t)$. If only a small proportion of the collisions lead to chemical absorption and $k(t) < \tau^{-1}$, the distribution is stationary. Under stationary conditions, the change in the number of hot atoms ($n$) and the yield of products ($R_i$) are described by the simple equation $R_i = k_i n/\sum_i k_i$ and $dn/dt = \sum_i k_i n$, where $k_i$ is inversely proportional to $\tau$. Thus, in the case of stationary distributions, the absorption of hot species is described by pseudofirst-order equations and the reaction rate constants have been shown [33] to correspond to an effective temperature $T^*$ determined by the parameters of the energy distributions of the hot species. The following expression has been obtained for light atoms ($m \ll m_i$) and the average energy of chemical reactions $\langle\epsilon\rangle_r$:

$$k=C(T^*)^{-3/2}\exp\left[\frac{\langle\epsilon\rangle_r}{k_B T^*}\right], \quad (I.42)$$

where the constant $C$ may depend on the temperature of the surrounding medium. It is significant that, depending on the reactivity of the system, the effective temperature $T^*$ may be close to the temperature of the target or higher.

## II. THE APPLICATION OF KINETIC EQUATIONS IN THE CHEMISTRY OF RECOIL ATOMS

### 1. Kinetic Relations for Elastic Isotropic Scattering

The kinetics of recoil atoms were first described by Libby [34] and Miller and Dodson [35,36]. Apart from the hypotheses about the isotropic nature of the medium, the elastic billiard collisions with atoms at rest, etc., the hypothesis of a definite role of the energy of the reaction cell or the liquid cage ($\epsilon$) in chemical stabilisation has been used to estimate the probability of the retention of hot atoms. The model postulates additional conditions for the formation of a stable chemical bond in reactions involving substitution by recoil atoms: the energy transmitted to the atom displaced from the molecule must exceed the energy of its chemical bond ($\nu$); the recoil atom must then have an energy $E < \epsilon$. Under these conditions, the probability of retention is defined as follows:

$$P = \frac{\int_{\nu}^{E_0} f_i \psi(E) \frac{\varepsilon}{E} \mathrm{d}E}{\sum_i \int_{\nu/\alpha_i}^{E_0} f_i \psi(E) \frac{\nu - \alpha_i E}{E(1-\alpha_i)} \mathrm{d}E} . \qquad \text{(II.1)}$$

In order to determine $\psi(E)$, one can employ methods examined previously. The form of the solution (II.1) depends on $\nu$, $\alpha$, and $E_0$. Analysis of the solutions obtained led to the conclusion that the probability of the chemical stabilisation of hot atoms is independent of their initial energy in all cases except those where account must be taken of collisions for $\alpha \neq 0$ when $\alpha E_0 < \nu$. The expressions obtained by Miller and Dodson also define the form of the dependence of the retention of hot atoms on the composition of two-component systems. It is significant that $P(E) \propto R$ increases in the presence of a second component having atoms with masses different from $m$ (Fig.1).

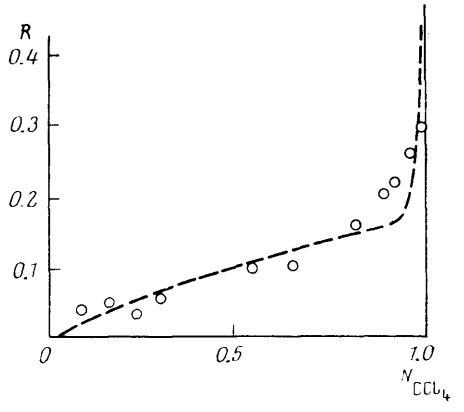



Figure 1. Variation of the yield of labelled $CCl_4$ with its mole fraction in a mixture with benzene; dashed curve—calculation; circles—experiment.

The characteristic features of the Miller–Dodson model are its applicability for relatively low recoil energies; their are no limitations on $E_0$ of the kind which occur in other models.

Postulates analogous to those put forward by Miller and coworkers [35,36] have been used by Capron and Oshima [37]. Analysis of the probability of retention for different ratios of $E_0$, $\epsilon$, and $\nu$ led them to the conclusion that the dependence of $R$ on $E_0$ may be manifested only for low initial energies and $\alpha \neq 0$ (Fig. 2). A similar method for the estimation of $R$ was subsequently developed by Nesmeyanov and Borisov [38].

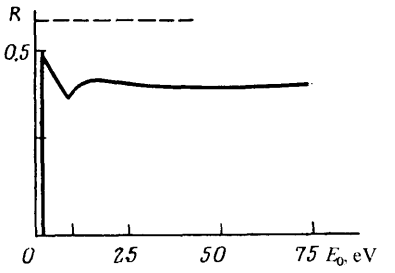



Figure 2. Variation of the yields of substitution products with the initial energy of hot atoms; continuous curve—$\alpha = 0.5$; dashed line—$\alpha = 0$.

Considerable progress in the theoretical interpretation of experimental results in the chemistry of recoil atoms has been achieved as a result of studies by Wolfgang and Estrup [7,8]. The "kinetic theory" of hot-atom reactions developed by these investigators is based mainly on the hypotheses used previously [35,36], but only instances with fairly high initial energies (exceeding the upper threshold for chemical reactions) were considered for a weak perturbation of the particle flux by chemical "erosion" [23]. It was assumed that, without reacting chemically, the recoil atoms undergo repeated elastic scattering and are retarded to energies below $\alpha^3 E_0$ or $E_2$. When the above conditions are fulfilled for weakly absorbing media, one can adopt the Wigner–Fermi approximation, according to which the solution of the transport equation for the values of $n(E)$ used by Wolfgang and Estrup can be formulated as follows:

$$n(E) = \frac{1}{\xi E} \exp\left[ -\sum_I \int_E^{E_2} f_I \frac{p_{rI}(E')}{\xi E'} \mathrm{d}E' \right] . \qquad \text{(II.2)}$$

Substitution of the values of $n(E)$ obtained in equations of type (I.1) yields

$$P = \sum_I \int_{E_1}^{E_2} f_I \frac{p_{rI}(E)}{\xi E} \cdot \exp\left[ -\sum_I \int_E^{E_2} \frac{f_I p_{rI}(E')}{\xi E'} \mathrm{d}E' \right] \mathrm{d}E . \qquad \text{(II.3)}$$

The Wolfgang–Estrup approximation, corresponding to small perturbations of the flux of hot atoms as a result of chemical absorption or the presence of sources, holds more exactly the lower the value of $E$ compared with $E_0$ and the greater the difference between $E$ and the resonance absorption energies. The accuracy of the determination of $P$ increases with decreased reactivity of the medium, characterised by the quantity $\int f p_r(E) n(E) \mathrm{d}E$. In the derivation of Eqn. (II.3), it was assumed that $f$ and $\xi$ are independent of energy; this condition is fulfilled fairly reliably for $f$. Although $\sigma_{sj}$ is a function of energy, the

variation of the ratio $\sigma_{sj}N_j/\sum_j \sigma_{sj}N_j = f_j$ with the energy may be neglected. The hypothesis of the constancy of $\xi$ is fulfilled only in specific instances, for example for isotropic scattering or when $g(E', E) \propto (1/E').\Phi(E/E')$. This limits the region of applicability of the kinetic theory and can lead to significant errors in the determination of the probability of chemical reactions when the methods of kinetic analysis based on this model are used.

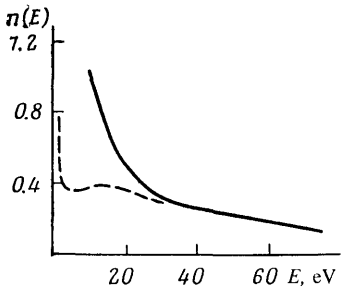



Figure 3. Variation of the number of collisions $n(E)$ in inert systems (continuous curve) and in chemical absorption of hot atoms (dashed curve).

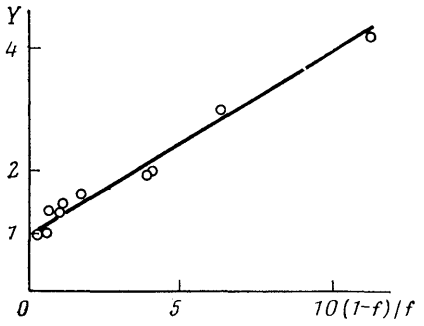



Figure 4. Variation of $y = [-1/\ln(1 - P)]$ in the $He-C_3H_8$ system with $(1 - f)/f$.

It follows from Eqn. (II.2) that, in the range of energies $E_2 \geqslant E$, the collision density corresponding to the specified energy $E$ decreases owing to the chemical reactions and the curves describing the collision density may have extrema, which are particularly distinct in the absence of moderators (Fig. 3).[39] In the Wolfgang–Estrup approximation for systems where the values of $p_r(E)$ or $f$ are significant for only one component (for example, in mixtures with an inert moderator or in the presence of small amounts of added scavengers), the probability of the retention of hot atoms is described by the equation

$$P = 1 - \exp\left[-\frac{fI}{\xi}\right] = \frac{f}{\xi}I - \frac{f^2}{\xi^2}K + \frac{f^3}{\xi^3}L - \ldots \qquad \text{(II.4)}$$

Similar equations can be obtained for the probabilities of the formation of the individual products $P_i$. The terms of the series (II.4) have the coefficients

$$A_{nl} = \frac{1}{n!}\int_{E_1}^{E_2} \frac{p_{rj}(E)}{E}\left[\int_{E}^{E_2} \frac{\sum_j p_{rj}(E')}{E'}\,dE'\right]^n dE, \qquad \text{(II.5)}$$

where $A_{0i} = I_i$, $A_{1i} = K_i$, $A_{2i} = L_i$, etc.[40] Since the series converges rapidly, primarily because of the smallness of $(f/\xi)^{n+1}$, there is no necessity to take into account more than two–three terms of the expansion.

The quantity $I_j$ characterises the integral probability of the formation of the product $j$ in the range of energies $E_2 - E_1$ and reflects the form of the excitation function $p_{rj}(E)$. In the simplest case with a weak energy dependence of $p_r(E)$ we have $\bar{p}_r = I/\ln(E_2/E_1)$ over the entire $E_2 - E_1$ range. The yield of the chemical reaction is not only a function of the probability of the reaction on collision with the species having the energy $E$, but is also determined by the probability that the hot atom is not absorbed in the process involving retardation until the attainment of the energy $E$. The terms of the series (II.5) containing $K$, $L$, etc. take into account the weakening of the flux of hot atoms owing to their absorption in the range $E_2 - E$. The role of such correction terms is particularly marked in the estimation of the yield of products formed in the lower range of the energy spectrum. The quantities $K$ or $L$ yield information about the energy ranges where the values of $p_r(E)$ are non-zero (see below).

Equations of type (II.1)–(II.5) constitute the basis of the kinetic analysis (of the first and second kind) of the experimental data whereby a systematic treatment of a wide range of results can be achieved using several simple parameters ($I$, $K$, and $\xi_r$), measured in units of $\xi_m$ (the subscripts $r$ and $m$ refer to the reactant and the moderator). For mixtures containing an inert moderator in addition to the reacting component, where $\xi = f_r\xi_r + (1 - f_r).\xi_m$, it follows from Eqn. (II.4) that

$$-\frac{1}{\ln(1-P)} = \frac{\xi_r}{I} + \frac{\xi_m}{I}\frac{1-f_r}{f_r}. \qquad \text{(II.6)}$$

When the relation between $-[1/\ln(1 - P)]$ and $(1 - f_r)/f_r$ (Fig. 4), involving the experimental yields of hot-atom reactions, is linear, Eqn. (II.6) can be used to estimate $I$ and $\xi_r$, as well as $\xi_{m_1}/\xi_{m_2}$.[8,41,42] According to the kinetic theory, in mixtures with different moderators the following expression is valid for the ratio of the yields of products $i$ and $j$:

$$\frac{I_i/\xi_{m_1}}{I_j/\xi_{m_1}} = \frac{I_i/\xi_{m_2}}{I_j/\xi_{m_2}} \qquad \text{(II.7)}$$

although the quantities $I_i$, expressed in units of $\xi_{m_1}$ or $\xi_{m_2}$, are different. The equation

$$\frac{\xi P_i}{f_r} = I_i - \frac{f_r}{\xi}K_i, \qquad \text{(II.8)}$$

which is a corollary of Eqn. (II.4), makes it possible to determine $I_i$ and $K_i$ from the corresponding experimental linear relations (Fig. 5). Estimates of the $K_i$ in individual cases[40,43,44] permit conclusions concerning the energy ranges within which various products are formed. According to Baker et al.[43], $F_i = 1 + (\frac{1}{2}I_i^2 - K_i)/[I_i(I - I_i)]$ is a criterion for the estimation of the energy ranges. If reactions (A) have a non-zero value of $p_r(E)$ in the energy range wholly above the corresponding range for reactions (B), then $K_{A,min} = \frac{1}{2}I_A^2$ and $F_A = 1$. When the energy

ranges are the same, $K_A = \frac{1}{2}I_A(I_A + I_B)$ and $F_A = 0.5$. If the energy range for reactions (A) is below that for reactions (B), then $K_{A,max} = I_A I_B + \frac{1}{2}I_A^2$ and $F_A = 0$. Methods for the comparison of the energy ranges for competing processes have been developed by Urch and coworkers[40, 44,45]. The quantities $F^* = (K - I^2/2)/(K_{max} - I^2/2)$, where $F_i^* = (K_i - I_i^2/2)/(K_{i,max} - I_i^2/2)$, varying in the range from 0 to 1, may be used as the principal criterion; all the intermediate values should correspond to overlapping energy ranges; when $F_A^* = 0$, the energy range for reactions (A) is higher than for reactions (B); when $F_A^* = 1$, the energies for which $p_{rA}(E) > 0$ lie below the corresponding energies for reactions (B).

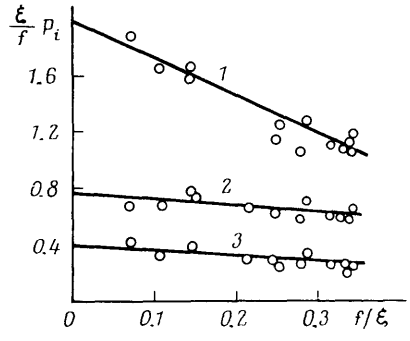



Figure 5. Variation of the probability functions for the formation of labelled products ($\xi/fP_i$) with the composition of the $He-C_3H_8$ mixture ($f/\xi$): 1) HT; 2) $C_3H_7T$; 3) remaining products.

The development of methods for kinetic analysis has led to a number of important conclusions for the interpretation of the results of experiments on the stabilisation of recoil atoms in binary and more complex systems. The prospects for the application of the first approximations of the kinetic theory in the analysis of experimental data for binary mixtures of weak or strong absorbers with $p_{rz}(E) = Cp_{ry}(E)$ and $P_y/P_z = f_y/C.f_z$ were examined by Wolfgang[8], who demonstrated the possibility of estimating $\xi_y/I_y$, $\xi_z/I_z$, and $\xi_y/\xi_z$. Differentiation of the equations obtained by Wolfgang with respect to $N$ ($N$ is the mole fraction of component $y$), assuming that $\bar{p}_r = I/\ln(E_2/E_1)$, showed that the second derivatives $\partial^2 P_z/\partial N^2$ and $\partial^2 P_y/\partial N^2$ may be non-zero.[46-49] Thus the possibility of the deviation of the yields in binary systems from additivity when $\xi_z \neq \xi_y$ or $p_{ry} \neq p_{rz}$ has been established by the analysis of the second derivatives. The causes of the deviations from additivity are evident; for example, the introduction of component $z$ with $\xi_z < \xi_y$ causes an increase of the number of collisions in the range $E_2-E_1$, which leads to an increase of $P_y$.

Since systems containing an inert moderator and a radical acceptor in addition to the reactant are most frequently investigated experimentally in hot-atom chemistry, kinetic analysis of three-component systems is of greatest interest. Methods have now been developed for correcting the results of kinetic analysis to allow for the characteristics of the third component (R).[50-54] For mixtures where this component also fulfills effectively the functions of a moderator, the kinetic analysis can be performed using equations of the type

$$-\frac{1}{\ln(1-P)} = \frac{\xi_r}{I} + \frac{\xi_m}{I}\,\frac{f_m + \frac{\xi_R}{\xi_m}f_R}{f_r}. \qquad (II.9)$$

The presence of a scavenger may also affect the results of the kinetic analysis if the scavenger interacts chemically with the recoil atoms in the hot region[51-54]. Under these conditions, the role of the scavenger is determined by the derivatives $dP/df_R = -f_r K'/\xi^2$, $dP_i/df_R = -f_r K_i'/\xi^2$, or $Y_i = (1/\xi)(df_R/dN_R)(K_i'/I_i)$. $Y_i$ characterises the overlapping of the excitation functions for reactions with the scavenger and the reactant, leading to the formation of the product $i$. The role of the competing scavenger is particularly marked when it is present in large amounts or in the presence of large amounts of a relatively ineffective moderator, where the number of collisions in the hot region is large[51,53]. It follows from Malcolme-Lawes' results[53] that in such cases one can write for $f_r \ll 1$

$$P = 1 - \exp\left(-\frac{f_r}{\xi}I - \frac{f_r f_R K'}{\xi^2}\right),$$
$$P_i = \frac{f_r}{\xi}I_i\left(1 - \frac{f_R}{f_r}K_i'\right), \qquad (II.10)$$

where

$$K' = \int_{E_1}^{E_2} p_r(E)\left(\int_{E'}^{E_2}\frac{p_R(E'')}{E''}dE''\right)dE';$$
$$K_i' = \int_{E_1}^{E_2}\frac{p_r(E')}{E'}\left(\int_{E'}^{E_2}\frac{p_{Ri}(E'')}{E''}dE''\right)dE'.$$

The equations obtained may be used to correct the results of a kinetic analysis which does not allow for the influence of radical acceptors on the yields of hot-atom reactions:

$$I_i = I_{i0} + f_R K_i',$$
$$K_i = K_{i0} + (\xi_r - 1)f_R K_i', \qquad (II.11)$$
$$\frac{\xi_r}{I} = \frac{\xi_{r0}}{I_0}$$

(the subscript zero refers to the results before correction).

Analysis of experimental data based on the kinetic theory led to a deeper understanding of the specific features of hot-atom reactions, their parameters, mechanisms, and kinetics. Without considering in detail the results thus obtained, which have been discussed in a number of reviews[1,2,5,55], we may note that kinetic analysis has yielded proof of the dependence of the quantities $\xi_r$ and $\xi_r/\xi_m$ on the energies of hot species and molecular structure[56]; evidence has also been obtained for a complex mechanism of the action of inert gas moderators, which are involved not only in the relaxation processes of hot atoms, but also in the deactivation of the excited products and their dissociation in collisions[57-60]. Interpretation of the experimental data on the basis of the kinetic theory yielded information about the nature of the excitation functions, about the relation between the energy ranges where the excitation functions for various reactions are significant[44,45], and about the relative widths of the energy ranges for reactions in the presence of various moderators[51]. The problem of the involvement of radical acceptors in hot-atom reactions[53,54] and a number of problems concerning the mechanisms of such reactions and the reactivity of various compounds[45] have been solved using the methods of kinetic analysis.

Thus the possibility of employing the approximate Wolfgang–Estrup model and the fruitfulness of methods of kinetic analysis in the interpretation of experimental results, obtained in the first place for gaseous systems, have thus been confirmed. At the same time, the limits of the applicability of the kinetic theory and its disadvantages were discovered in the course of developing methods for kinetic analysis and their employment. Thus it has been shown that the linear relations between $1/\ln(1-P)$ and $(1-f_r)/f_r$ or between $\xi P_i/f_r$ and $f_r/\xi$ do not constitute a reliable criterion of the correspondence of the model to real systems. According to Malcolme-Lawes and Urch[61], the above relations hold even if the fundamental conditions for the applicability of the Wolfgang–Estrup theory are not fulfilled. Not all the *a priori* conclusions of the theory have been confirmed experimentally. In particular, in contrast to the expected Eqn. (II.7), the following experimental relation has been found for the reactions involving the abstraction and substitution of hydrogen by hot tritium atoms[62–64]:

$$\frac{I_{HT}/\xi_{He}}{I_{RT}/\xi_{He}} > \frac{I_{HT}/\xi_{Ne}}{I_{RT}/\xi_{Ne}}.$$

The majority of the above contradictions arise because the Wolfgang–Estrup model does not take into account the anisotropic scattering and the corresponding $\xi(E)$ relation or the complexity and the many-sided nature of the action of moderators and scavengers and the influence of secondary processes.

Model calculations using the Monte Carlo method and computers have been very important in determining the limits of the applicability of the kinetic theory and of the physical significance of the kinetic parameters obtained in kinetic analysis ($I$, $K$, $\xi_r$).[54,61,65,66]. The simulation of the behaviour of recoil atoms is based on the hypothesis put forward by Wolfgang and Estrup concerning elastic scattering, which makes it possible to assume an equal-probability distribution of energy losses in the range from zero to $E_0[1-\exp(-2\xi)]$. Thus, by selecting the random numbers $u_i$, it is possible to determine the energy of the hot atom after the $i$th elastic collision: $E_i = E_{i-1} \cdot \exp(-2\xi u_i)$. On the other hand, simulation by the Monte Carlo method makes it possible to introduce into computational schemes new postulates concerning the nature of not only the $p_r(E)$ relation but also $\xi_m(E)$ or $\xi_r(E)$; in particular, a Gaussian function has been used: $p_{ri}(E) = h_i \exp[-(E-a_i)^2/c_i^2]$. Methods of kinetic analysis, whereby the quantities $P$, $I$, and $K$ can be estimated for the specified parameters $p_r(E)$, $\xi_r(E)$, $\xi_m(E)$, etc. were subsequently applied to the results of the numerical calculation of the probability of chemical reactions in terms of the fraction of absorbed species[61]. The calculations showed that, for low and even considerable reactivities of the components but with values of $\xi$ which are constant in the energy range investigated, the kinetic analysis based on the Wolfgang system is justified. The parameters $\xi_r$, $I$, and $K$ obtained by this procedure reflect (the first two less satisfactorily) the physical properties of the test objects, in particular the excitation functions. If $\xi_r$ and $\xi_m$ vary but their ratio remains constant in the experimental energy range, the results of the kinetic analysis require a complex interpretation. If $\xi_m/\xi_r$ varies in the energy zone of hot-atom reactions, the employment of the Wolfgang methods leads to erroneous results. The reliability of the estimates of the kinetic parameters depends also on the degree of overlapping of the energy ranges of different chemical reactions. The overlapping of the function $p_{ri}(E)$ has a particularly strong effect on the values of $K_i$; the distortion of the $K_i$ data becomes more pronounced with increase of $\xi_r$. The simulation data showed that one of the fundamental conditions for the improvement of the kinetic theory is allowance for the variation of $\xi$ with the energy $E$.

Summarising the discussion of the application of methods of kinetic analysis, one must consider several of the most significant factors which are bound to determine the further development of theoretical studies in hot-atom chemistry.

1. The Wolfgang–Estrup model does not take into account the thermal motion of the species of the medium and is valid only for atoms with a high initial energy ($E_0 > E_2$); the extension of the application of kinetic analysis to the description of photochemical, radiation-chemical, etc. phenomena requires the removal of the above limitations.

2. The improvement of the kinetic theory and of kinetic analysis should lead to the description of the relaxation processes of the excited products of hot-atom reactions, which were not considered in the Wolfgang–Estrup theory.

3. The results of kinetic analysis depend greatly on the values of $\xi$. The postulate of isotropic scattering, characterised by the quantity $\xi_{is}$, which is independent of the energy of the hot species, does not satisfy the conditions in real systems. The Wolfgang–Estrup model does not take into account two factors, namely the occurrence of non-elastic relaxing collisions and elastic but anisotropic collisions with small energy losses per collision. The role of the non-elastic scattering component is particularly marked for polyatomic molecules, since to a first approximation the contribution of non-elastic collisions is determined by the ratio $M/(M+m)$ ($M$ is the mass of the molecule). However at the present time there is no adequately developed theory whereby one could take into account non-elastic collisions in analytical solutions of transport equations for hot atoms; the yield of the products of hot-atom reactions has not been analysed taking into account the non-elastic scattering component. The attempts to estimate the values of $\xi$ for complex polyatomic molecules have not been successful either. When two polar postulates are adopted, namely that the molecules can be regarded as collections of individual atoms or that the molecules are involved in collisions as simple particles with mass $M$, the calculated values of $\xi$ do not agree with experimental data. For *a priori* estimates of the energy loss in non-elastic collisions of hot atoms, one of the most promising procedures is the method of statistical tests[61,66] and the analytical approach via estimates of the stopping power of the medium has also proved useful[67]. Considerable difficulties still arise also when an attempt is made to take into account the scattering anisotropy; they are associated both with the determination of the form of the functions $\xi(E)$ and with the solution of transport equations for arbitrary $\xi(E)$.

## 2. Kinetic Relations in the Anisotropic Scattering of Hot Atoms

It is known from the physics of atomic collisions[18] that the degree of asymmetry of scattering depends on the energy of the colliding species. Thus in the region of high energies, atomic collisions are of the strongly anisotropic Rutherford type but, as the energy falls below $E_A = (13.6)^2[(m+m_1)/m]Z_1Z\sqrt{Z_1^{2/3}+Z^{2/3}}$, they can be described approximately in terms of the hard-core potential and $\xi_{is}$. In the region of low energies of the chemical interaction, the elastic component of scattering is

again characterised by an appreciable anisotropy and "soft" potentials. The change in interaction potential should lead to the corresponding changes in $g(E', E)$ and $\xi(E)$. The softer the potential, the lower the value of $\xi$. As a consequence of this, an increase in anisotropy increases the number of collisions of the atom in the specified energy range and a change in the energy spectrum of the species and in the yield of the hot-atom reactions. Thus the necessity to take into account the anisotropy of scattering in hot-atom chemistry is evident.

The main tasks in hot-atom chemistry are as follows: 1. The search for the form of the functions $\xi(E)$. Since there are reliable methods for estimating $\xi_{is}$, it is important for hot-atom chemistry to find relations between $\xi$ and $\xi_{is}$. 2. Determination of the nature of the variation of the ratio $\xi_i(E)/\xi_j(E)$ with the energy, since simulation by the method of statistical tests has shown that, when $\xi_m/\xi_r$ varies with the energy, kinetic analysis leads to considerable errors in the determination of the kinetic parameters[68,69]. 3. Solution of the transport equations and the equations for the probability of chemical reactions for specified $\xi(E)$ or $g(E', E)$. 4. Determination of the nature of the variation with the energy of $\varphi(E)$, $n(E)$, or $\Lambda(E) = E.n(E)$ for specified $\xi(E)$. In particular, the test of the possibility of using for non-absorbing or weakly absorbing media asymptotic values of distribution functions of the species energy and the functions $\Lambda(E)$, which are characterised by the strongest dependence on $\xi(E)$, since $\Lambda_0 \propto 1/\xi$.[70,71]

The nature of the variation of $\xi$ with the energy is determined by the form of the interaction potential between the colliding species. For example, the level of anisotropy for the potential $U(r) = ar^{-s}$ depends on the value of $s$:[68]

$$\xi(E) = C(1-\alpha)\left[E\frac{m_1}{m_1+m}\right]^{\frac{2-s}{s(s-1)}},$$

where

$$C \propto A^{2/s}\int_0^\infty \sin^2\frac{1}{2}\,[\sigma(\rho)]\,\rho\,d\rho$$

($\rho$ is the target parameter and $\sigma$ the scattering micro-cross-section). When $s \to \infty$, the scattering is isotropic; the case where $s = 1$ corresponds to Coulombic scattering with maximum anisotropy; for many types of interaction with not unduly large or not unduly small energies, the values of $s$ are in the range 9–12; when $s \gg 2$, the $\xi$ depend relatively little on the energy. It is significant that the ratios $\xi_{m_1}/\xi_{m_2}$ depend little on the energy and are determined mainly by the ratio of the masses of the colliding species. Thus, for $U(r) = Ar^{-s}$ and the combined potential $U(r) = A_1r^{-s_1} + A_2r^{-s_2}$ under the conditions of preferential forward scattering, i.e. for low values of $s$, we have $\xi_{m_1}/\xi_{m_2} \simeq (1-\alpha_1)/(1-\alpha_2)$; when $s \to \infty$, i.e. for the hard-core-potential, we have

$$\xi_{m_1}/\xi_{m_2} = (1-\alpha_2)(1-\alpha_1+\alpha_1\ln\alpha_1)/(1-\alpha_1)(1-\alpha_2+\alpha_2\ln\alpha_2).$$

Estrup[72] was one of the first to draw attention to the necessity to consider the anisotropy of scattering in kinetic analysis. He found[72] that, when $(1-\alpha)/(1+\alpha) < 1$, then $\xi \simeq \xi_{is}.\pi r_0^2/\sigma_S(E)$, where $r_0$ is the distance of closest approach of the species in head-on collisions and $\sigma_S$ is the scattering cross-section; for $\alpha$ close to zero, the best approximation is $\xi \simeq [\pi r_0^2/\sigma_S(E)][\xi_{is} - \kappa(\alpha)\gamma^{-1} + c(\gamma)]$. Special methods were developed for estimating $\gamma$, $\kappa$, $c$, and $\sigma_S$. Calculations and analysis of the dependence of the quantities determining $\xi$ on the energy led Estrup to the conclusion that the energy variation of $\xi$ becomes weaker with increase of the kinetic energy of hot atoms (Fig. 6). Numerical calculations showed that, for collisions of T atoms with He, $D_2$, and $CH_4$, the ratios $\xi/\xi_{is}$ are respectively 0.09, 0.12, and 0.33. In the T + He + $CH_4$ system, the values of $I$ proved to be an order of magnitude smaller than those of $I_{is}$.

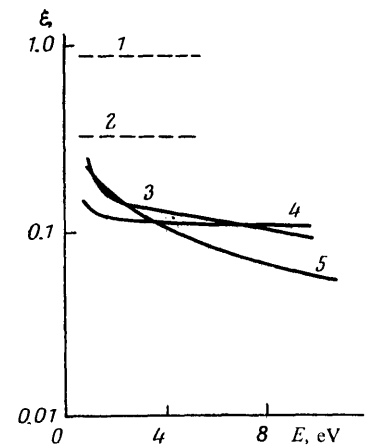



Figure 6. Variation of $\xi = \ln(E/E_0)$ with the kinetic energy of the recoil tritium atoms for isotropic ($\xi_{is}$) and anisotropic ($\xi$) elastic scattering: 1) $\xi_{is}$ in the He–$D_2$ system; 2) $\xi_{is}$ in $CH_4$; 3) $\xi$ in $D_2$; 4) $\xi$ in $CH_4$; 5) $\xi$ in He.

Gordus and coworkers[70,71] also examined elastic anisotropic scattering under the conditions of spherically symmetrical soft potentials, for which one can assume that $\xi = \xi_{is} - b([1-\alpha^2)/2 + \alpha\ln\alpha]$. If the coefficients $b$ are independent of the energy, i.e. $b = 1/(1-\alpha)^2$, then in all cases with $g(E', E) \propto (1/E')\Phi(E/E')$ the values of $\xi$ remain unchanged as $E$ is varied and are determined only by the values of $\alpha$ and $b$. If $b = 1/E(1-\alpha)^2$, the anisotropy is appreciable only for low values of $E$, and $\xi$ increases with increase of the kinetic energy of hot atoms, approaching $\xi_{is}$.

Numerical calculations have been made of $n(E)$ and $\Lambda(E)$ under the conditions of weak absorption. They showed that the greatest differences between the calculated values of $\Lambda(E)$ and the asymptotic values of $\Lambda_0(E) = 1/\xi$ for a constant $b$ correspond to the region where $E/E_0 > \alpha$. With decrease of $\alpha$, the difference between the asymptotic values and the results of the numerical solution of transport equations taking into account the scattering anisotropy becomes smoothed out; when $\alpha = 0$, the values of $\Lambda(E)$ are close to the asymptotic values for any $E$. According to Gordus and coworkers[70,71], the use of the asymptotic values of $n(E)$ or $\psi(E)$ in calculations of the probability of chemical reactions should not lead to appreciable errors; for tritium atoms, the errors should not exceed 50% (Fig. 7).

Analytical solutions have been obtained[73-79] to transport equations for soft potentials of the type $U(r) = Ar^{-s}$ and the following values of $g(E', E)$:

$$g(E', E) = \frac{1}{E'} b\left(E', \frac{E}{E'}\right) \text{ when } E' \geqslant E \geqslant \gamma E';$$

$$g(E', E) = [a(E')/E'] \Phi\left(\frac{E}{E'}\right) \text{ when } \gamma E' \geqslant E \geqslant \alpha E';$$

$g(E', E) = 0$ in the remainder of the energy range; here $\gamma = (1 + \mu^2 + 2\mu \cos\theta_c)/(1 + \mu)^2$, $\mu = m_1/m$, and $\theta_c$ is the critical scattering angle.

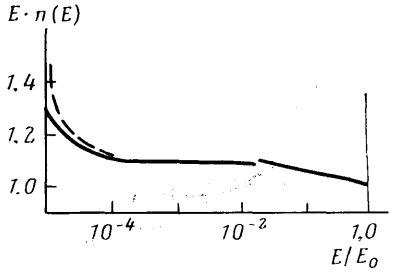



Figure 7. Variation of $E.n(E)$ with $E/E_0$ for $E_0 = 2.5 \times 10^5$ eV; $\alpha = 0.02$; $b = 1/E.(1 - \alpha)^2$; continuous curve—$E.n(E) = \Lambda(E)$; dashed curve—$E.n(E) = 1/\xi = \Lambda_0$.

In non-absorbing systems where $\gamma = 1$ and $a(E) = 1$ and the differential cross-sections are independent of $E$ for any scattering angle, Eqn.(I.8) has the solution $\psi(E') = S_0/E'\zeta$; when $\gamma \neq 1$, the solution is $\psi(E') = S_0/E'\zeta a(E')$, where

$$\zeta = \int_{\gamma}^{1} \ln\frac{E}{E'} \cdot \frac{b(E, E'/E)}{a(E)} d\left(\frac{E'}{E}\right) + \int_{\alpha}^{\gamma} \ln\frac{E}{E'} \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right).$$

Comparison of the solution obtained with the asymptotic solution showed that $\xi \simeq \zeta a(E')$. Taking into account the nature of the variation of $a(E)$ with the energy for $\Sigma_s(E) = CE^{-1(s^{-1})}$, Felder and Kostin[73] found that $\psi(E) = S_0/\zeta E^{\beta}$, where $\beta = 1 - 2/s + 1/(s - 1)$.

For reactive systems, where $\Sigma_s(E) > \Sigma_r(E) > 0$ and $\Sigma_r(E)/\Sigma_s(E) = B$, Felder and Kostin[73] examined a solution of a transport equation of type (I.7) with $g(E', E) = (1/E').\Phi(E/E')$. In this case, they used as the solution the expression $\psi(E') = C(E')^{\beta}$, the values of $\beta$ being found from the equation

$$B = \int_0^1 \Phi\left(\frac{E'}{E}\right)[(E'/E)^{\beta-1} - 1] d\left(\frac{E'}{E}\right). \qquad \text{(II.12)}$$

For an arbitrary form of $\Phi(E'/E)$, the values of $\beta$ are found numerically; when $\Phi(E'/E) = (n + 1)(E'/E)^n$, the analytical solution $\beta = [B + 1/(n - 1)]^{-1} - n$ was obtained. For isotropic scattering, $n$ should be zero, an increase of $n$ corresponding to an increase of the scattering anisotropy.

According to Felder and Kostin[73], $\psi(E) = C/E^{1/(B+1)}$ is obtained for isotropic scattering in absorbing media when $\Sigma_r(E)/\Sigma_s(E) = B > 0$. Consequently in absorbing media $\psi(E)$ varies with energy less markedly than in the absence of chemical capture. The energy spectrum is smoothed out as a result of the "erosion" of low-energy species in chemical reactions. In the most general case, where $n \neq 0$ and $B \neq 0$, an increase of $n$, corresponding to an increase of anisotropy, leads to a decrease of $\beta$ compared with its values in isotropic scattering; this promotes the smoothing of the species distribution functions with respect to energy. This conclusion has a simple physical interpretation. When energy transfer in small portions predominates, the hot atom undergoes a greater number of collisions in the specified energy range, which leads to an increased probability of its absorption in this range before it is retarded with attainment of lower energies.

Asymptotic solutions for $\psi(E)$ have been obtained[74-76,79] in the most general cases of multicomponent absorbing systems, taking into account the influence of secondary high-energy species on the yield of hot-atom reactions. When account is taken of secondary displaced atoms in isotropic scattering in chemically inert systems, we have $\psi(E) \propto 1/E^2$ [instead of $\psi(E) \propto 1/E$].[75]

When absorbing systems were considered and a number of additional conditions were introduced {the potential is not unduly soft, $s > 6$, $\Sigma_r(E)/\Sigma_s(E) = B(E)$, $B(E)/a(E) = D$, $p_r(E) = B(E)/[1 + B(E)]$ and $E < E_2 < E_0$}, Felder[77] obtained the following solutions:

$$P_0 = D^2\left[1 - \left(\frac{E_1}{E_2}\right)^{1-\beta}\right] \Big/ \zeta\zeta_\beta(1 - \beta)^2; \qquad \text{(II.13)}$$

$$P_1 = 1 - \left(\frac{E_1}{E_2}\right)^{D/\zeta} \text{ when } \mu \gg 1 \text{ or } \mu \ll 1; \qquad \text{(II.14)}$$

$$P_2 = 1 - \left(\frac{E_1}{E_2}\right)^{D/\zeta} \cdot \left(\frac{1 + CDE_2^n}{1 + CDE_1^n}\right)^{D/n\zeta} \text{ when } a(E) = CE^n;\ n = \frac{1}{s-1} - \frac{2}{s}; \qquad \text{(II.15)}$$

$$P_3 = 1 - \left(\frac{E_1}{E_2}\right)^{D/\zeta(1+CD)} \text{ when } a(E) = C, \qquad \text{(II.16)}$$

where the quantities $\beta$, $\zeta$, and $\zeta_\beta$ are defined as follows:

$$\zeta = \int_0^1 \lg\frac{E}{E'} \cdot \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right); \quad \zeta_\beta = -\int_0^1 \left(\frac{E'}{E}\right)^{\beta-1} \lg\frac{E'}{E} \cdot \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right); \qquad \text{(II.17)}$$

$$\int_0^1 \left(\frac{E'}{F}\right)^{\beta-1} \cdot \Phi\left(\frac{E'}{E}\right) d\left(\frac{E'}{E}\right) = 1 + D.$$

Together with calculations based on Eqns.(II.13)–(II.16), numerical solutions were also obtained to transport equations for Felder's model taking into account the scattering anisotropy. Comparison of the results of the numerical calculation ($P$) with the calculations by Eqns.(II.13)–(II.16) did not reveal significant differences between $P$ and $P_0$. Thus, for $\mu = 1$, $E_2 = 100$, $E_1 = 25$ eV, $s = 12$, and $D = 0.2$, the values of $P$ and $P_0$ differed by 2.8%; for $\mu = 0.01$, they were indistinguishable. The maximum differences between $P$ and $P_1$ were of the order of 0.5% for $\mu = 0.01$ and approximately 10–15% for $\mu = 0.2$. Comparison of the values of $P$ with $P_2$ and $P_3$ revealed a satisfactory agreement, particularly for $P$ and $P_3$. The differences did not exceed 3–4% for $\mu = 0.01$, 10–15% for $\mu = 0.2$, and 20–25% for $\mu = 1$.

The results of the calculations were also compared with those obtained in terms of the Wolfgang–Estrup approximation. The comparison showed that the accuracy of the simple kinetic approximation increases with increase in the difference between the masses of hot and thermal atoms and with increase in the "hardness" of the potential for low values of $p_r(E)$ or for narrow well resolved resonances in absorption.

Interesting results, characterising the influence of the scattering asymmetry on $\psi$ and $P$, were obtained by Porter

and Kunt [80]. Numerical calculations using stochastic equations yielded the values of $P$ for three different elastic particle scattering models. Model A corresponds to isotropic collisions and model B presupposes anisotropic scattering with $g(E', E) = 2(\zeta - \alpha)/E'(1 - \alpha)^2$. Model C corresponds to anisotropic scattering with $g(E', E) = a/E'(1 - \alpha)$ for $bE' > E > \alpha E'$ or $g(E', E) = [a/E'(1-\alpha)] + 2(1 - a).(\zeta - b)/E'(1 - b)^2$ for $bE' < E < E'$, where $\zeta = E/E'$. The coefficients $a$ and $b$ were fitted by quantum-mechanical calculations. For all the models $g(E', E) \propto \Phi(E/E')/E'$, where $\xi$ is independent of the energy of hot atoms, and $\xi(C) < \xi(B) < \xi(A)$.

Numerical calculations have shown that model C gives the optimum values of $P$, in good agreement with the experimental yields of the stabilisation products of tritium recoil atoms in hydrogen or deuterium. For all the models investigated, an increase is observed in the probability of reactions as a result of an increase in $\Sigma_r(E)$ in the range 0–20 eV; in the range 20–100 eV, the values of $P$ varied only slightly, broad maxima being observed in the vicinity of 20 eV. Porter and Kunt [80] showed that calculation by Eqn. (I.41) and by the Wolfgang–Estrup formulae yields different results; $P_C < P_{W-E}$ for model C and $P_{A,B} > P_{W-E}$ for models A and B. In calculations for mixtures, the deviations were proportional to the content of the reactive component. The errors for $H_2$ are greater then for $D_2$, which is consistent with $\Sigma_r$; it is known that $p_r(H_2) > p_r(D_2)$. However, one must note that the discrepancies between the results are small and comparable to the experimental errors in the determination of the yields of reactions initiated by hot atoms; they do not exceed several per cent.

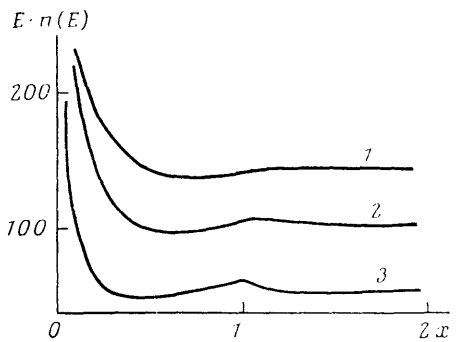



**Figure 8.** Variation of $E.n(E)$ with $x = \ln(E/E_0)/\ln\alpha$ for $E_0 = 10^5$ eV, $\alpha = 0.8882$, and different interaction potentials: 1) $U(r) = 10^2/r^6$; 2) $U(r) = 10^2/r^{12} \pm 10^2/r^6$; 3) $U(r) = 10^2/r^{12}$.

The series of studies designed to improve the kinetic models in hot-atom chemistry was continued by Baer and Amiel [16,17,27,28,41,69]. In the main, they used the postulates discussed previously, but, in the description of elastic scattering processes, they used the combined Lennard–Jones potential $U(r) = A_1/r^{s_1} + A_2/r^{s_2}$ (where $s_1 > s_2$) in addition to the hard-core potential and $U(r) = Ar^{-s}$. The combined potential makes it possible to describe both the short-range forces of the Coulombic repulsion of the nuclei of the colliding species and the long-range polarisation forces giving rise to repulsion or attraction. The Lennard–Jones potential also ensures flexibility in the description of the elastic scattering of species over a wide range of energies. However, methods have not yet been found whereby one can obtain an analytical solution for $g(E', E)$ or equivalent functions for a two-term potential. Numerical computer calculations were therefore made [16,17] of the quantities $g(E', E)$, $n(E)$, and $\Lambda(E)$.

The numerical calculations for $n(E)$ and $\Lambda(x)$, where $x = \ln(E/E_0)/\ln\alpha$ for one-term and two-term potentials, showed that $n(E)$ increases with decrease of the energy; the asymptotic values of $\Lambda_0(E)$ and $n_0(E)$ are attained rapidly, particularly for small $\alpha$ and $s$. For high energies ($E_0 > 1$ KeV), different values of $\Lambda(x)$ were obtained for one- and two-term potentials, the values of $\Lambda(x)$ for the two-term potential depending only slightly on the sign of $A_2$, i.e. on whether the second long-range term characterises repulsion or attraction. For low initial energies, the long-range terms with $A_2 > 0$ completely swamps the short-range term; when $A_2 < 0$, the values of $\Lambda(x)$ are lower than for the one-term potential or the potential with $A_2 > 0$ (Fig. 8).

The results of Amiel and Baer's calculations [16,17] indicate also a series of regularities in the variation of $\Lambda(x)$. It was shown that the variation of $\Lambda(x)$ with the coefficients $A$ and $E_0$ is characterised by the equation

$$\frac{\Lambda^{(2)}(x)}{\Lambda^{(1)}(x)} = \left[\frac{A^{(2)}}{A^{(1)}}\right]^{\frac{2}{s(s-1)}} \left[\frac{E_0^{(2)}}{E_0^{(1)}}\right]^{\frac{s-2}{s(s-1)}}. \qquad \text{(II.18)}$$

Thus the variation of $\Lambda(x)$ with $A$ and $E_0$ becomes weaker as $s$ increases. The greater the difference between the masses of the colliding species the greater the value of $\alpha$ and the greater the sensitivity of $\Lambda(x)$ to changes in any scattering parameters.

The problem of the analytical description of $\Lambda(E)$ was solved by Baer [17] for a modified two-term potential $U + \Delta U$, where $U(r) = A'/r^s$ for $R < r < \infty$ and $U(r) \to \infty$ for $0 < r < R$. These conditions reflect the swamping of the short-range term by the long-range term for low energies, i.e. make it possible to retain the principal advantages of the combined potentials but at the same time significantly simplify the analytical solutions for $G(E', E)$, $\Lambda(E)$, or $\psi(E)$. Without considering their derivation in detail, we shall merely quote Baer's expressions:

$$\psi(E) = \frac{C}{E}\left(\frac{E_{1,2}}{E}\right)^{\frac{1}{s-1}} \left\{1 + \frac{E_1}{E}\sum_{l=0}^{\infty}\frac{4(s-1)}{(2l+3)\cdot[(2l+s)^2-1]} - \right.$$

$$\left. - \frac{2(s+1)}{s(s-1)}\cdot\left(\frac{\gamma_s^2\pi}{2}\right)^{\frac{1}{s}}\cdot\frac{(1-\alpha)\cdot(E_1/E)^{\frac{s+1}{s}}}{1 - s(1-\alpha^{\frac{2s+1}{s}})/[(2s+1)\cdot(1-\alpha)]}\cdot\left(\frac{E_1}{E}\right)^{\frac{s+1}{s}}\right\}, \qquad \text{(II.19)}$$

where $R$ is the sum of the radii of the colliding species and $C = S_0/\xi$ is;

$$E_1 = AR^{-s};\quad E_{1,2} = \frac{m\pi}{2\hbar^2}\lambda_s^{s-1}\left(\frac{A'}{R^{s-1}}\right)^2;$$

$$A' = A\frac{m_1}{m_1 + m};\quad \gamma_s = \frac{\Gamma(s/2 + 1/2)}{\Gamma(s/2)};$$

$$\lambda_s = \sin\left(\frac{\pi}{2}\frac{s-3}{s-1}\right)\cdot\Gamma\left(\frac{s-3}{s-1}\right)\cdot\left[\frac{\Gamma(s/2-1/2)}{\Gamma(s/2)}\right]^{\frac{2}{s-1}};\quad \Gamma\left(\frac{s}{2}\right)\ldots\text{— gamma functions.}$$

It is noteworthy that the above expression is an asymptotic solution valid to within $E_1/E$.

Baer's treatment corresponds to the subdivision of the entire energy range into three sections: $0 < E < E_1$, where the interaction is described by the soft potential $U(r) = A/r^s$, $E_1 < E < E_{1,2}$, where a soft two-term potential also operates, and $E < E_{1,2}$, where the interaction is described by a hard-core potential.

3. Kinetic Equations Taking into Account Non-elastic Scattering and the Stopping Power of the Medium

Apart from those already discussed, Thomsen's model [67] is applicable in the case of a marked scattering anisotropy with small angles predominating. In this model, as in those already examined, no account is taken of thermal motion and the chemical bonds formed by the atoms in the target, the model being restricted to stationary conditions. Limitations are also imposed on the reactivity of the target, but, in contrast to other workers, Thomsen postulates a model whereby one can take into account, together with elastic anisotropic scattering by the nuclei, also electronic retardation, which is particularly significant for high energies. The relaxation processes are characterised in Thomsen's model by the stopping powers $-\mathrm{d}E/\mathrm{d}l$ and not the quantities $g(E', E)$ or $G(E', E)$. This is fairly correct if the moderation process can be regarded as continuous, if the energy losses in the collision $\Delta E$ are small compared with the energies of the hot species, if small scattering angles predominate, and if the masses of the colliding species differ markedly. The introduction of the stopping power as the main characteristic of the moderation processes has many other advantages. Firstly, satisfactory approximations are now available for estimates of $-\mathrm{d}E/\mathrm{d}l$ corresponding to different scattering mechanisms. Secondly, the introduction of the stopping power makes it possible to include the loss of bombarding species from targets with limited volumes, which extends the scope of the model.

Thomsen defines the probability of hot-atom reactions over the entire energy range by the formula

$$P = 1 - \exp \int_0^{E_0} \frac{\Sigma_r(E)\,\mathrm{d}E}{\mathrm{d}E/\mathrm{d}l}, \qquad \text{(II.20)}$$

which permits the determination of $\Sigma_r$ from the known yield of the chemical reaction and the stopping power of the medium. For low absorption cross-sections, when $P(E_0) \ll 1$, it follows from Eqn. (II.20) that

$$P \simeq -\int_0^{E_0} \frac{\Sigma_r(E)\,\mathrm{d}E}{\mathrm{d}E/\mathrm{d}l}. \qquad \text{(II.21)}$$

Thomsen expresses the energy distribution function $\rho(E)\mathrm{d}E$, the number of species per unit volume with the energy $E$ in the range $\mathrm{d}E$, by the product of the function of the source $S(E_0)$, the residence time of the species in the given energy range $\mathrm{d}E$, and the probability of the attainment of this range without absorption. Then

$$\rho(E_0, E)\,\mathrm{d}E = S_0(E_0) \exp\left[\int_0^{E_0} \frac{\Sigma_r(E')\,\mathrm{d}E'}{\mathrm{d}E'/\mathrm{d}l}\right] \mathrm{d}t, \qquad \text{(II.22)}$$

where $\mathrm{d}E$ and $\mathrm{d}t$ are related by the equation

$$-\mathrm{d}E = \left(\frac{\mathrm{d}E}{\mathrm{d}l}\right) \sqrt{\frac{2E}{m}}\,\mathrm{d}t.$$

It also follows from Eqn. (II.22) that, for a monochromatic source in weakly absorbing media, we have

$$\rho(E_0, E) = -\frac{S_0}{\mathrm{d}E/\mathrm{d}l} \sqrt{\frac{m}{2E}} \exp\left[\int_E^{E_0} \frac{\Sigma_r(E')\,\mathrm{d}E'}{\mathrm{d}E'/\mathrm{d}l}\right]. \qquad \text{(II.23)}$$

The functions $\rho(E)$ are related in the following way to the density of chemically active collisions:

$$\psi_r(E) = S_0 \frac{\Sigma_r(E)}{-\mathrm{d}E/\mathrm{d}l} = \rho(E)\,\Sigma_r(E) \sqrt{\frac{2E}{m}}. \qquad \text{(II.24)}$$

It is significant that the stopping powers are additive quantities and $-\mathrm{d}E/\mathrm{d}l = \sum_i N_i \Sigma_{\mathrm{st},i}(E)$, $\Sigma_{\mathrm{st}}$ being the stopping cross-section equal to the sum of the stopping cross-sections in collisions with electrons ($\Sigma_{s,e}$) and with atomic nuclei ($\Sigma_{s,n}$). Thus the introduction of $-\mathrm{d}E/\mathrm{d}l$ facilitates allowance for non-elastic collisions in estimating the quantities $\psi_r(E)$. Thomsen also examined the cases where moderation cannot be described as a continuous process and account must be taken of the discrete nature of the energy transfer, but $\Delta E \ll E$.

Comparison of the expressions obtained for the energy distribution functions and the probabilities of chemical reactions with the solutions of the transport equations for hard-core collisions and anisotropic scattering with $U(r) = Ar^{-s}$, which were discussed previously, led Thomsen to the conclusion that the formulae which he recommended give a fairly correct description of the characteristics of the distribution of hot species with respect to energy in weakly absorbing systems, but the values of $\psi(E)$ obtained from Thomsen's approximate formulae differ from the earlier asympotic solutions of the transport equations. For isotropic collisions, Eqn. (II.24) leads to $\psi_0(E) = 2S_0/(1-\alpha)E$, in contrast to $\psi_0(E) = S_0/\xi E$. The ratio of Thomsen's solution ($\nu$) to the asymptotic solution for a hard-core potential is $2\xi/(1-\alpha)$; for $U(r) = Ar^{-s}$, the following expression is valid for $\nu$:

$$\nu(s, \alpha) = s + [(s-1)/(1-\alpha)] \lg \alpha + (s-1)\cdot(1-\alpha)^{1/s-1} \cdot \int_0^{(1-\alpha)} \chi^{1-1/s} \frac{\mathrm{d}\chi}{1-\chi},$$

where $\chi = N_1\Sigma_{\mathrm{st},1}(N_1\Sigma_{\mathrm{st},1} + N_2\Sigma_{\mathrm{st},2})^{-1}$ for a mixture of two components.

Evidently the values of $\nu$ depend on the ratio of the masses of the colliding species and on the parameters of the potential ($s$) (Fig. 9).

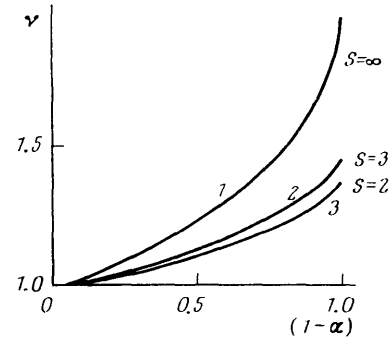



Figure 9. Variation with $\alpha$ of the ratio of the approximate and asymptotic solutions ($\nu$) for the interaction potential $U(r) \propto r^{-s}$: 1) for isotropic scattering; 2) for $s = 3$; 3) for $s = 2$.

In describing relaxation processes, Malerich and Spicer [81] took into account the energy losses in non-elastic collisions accompanied by the dissociation of the molecules of the medium. As a result of such collisions, hot atoms can lose a considerable fraction of their energy in the region of relatively low energies close to the range $E_2 - E_1$.

If the collisions with hot atoms lead to a transition of the molecules of component $z$ from the internal state $i$ to the state $f$ with $\Delta E_{zi\to f}$, then

$$g_z(E', E) = \frac{2\int_0^{2\pi} \sigma_{zi\to f}(V, \zeta, \eta)\, d\eta}{(1-\alpha_z)E'\left[1-\left(\frac{m+m_z}{m_z E'}\right)\Delta E_{zi\to f}\right]^{1/2}\Sigma_{sz}(E')} + \frac{4\pi\sigma_{zi=f}(V, \zeta)}{(1-\alpha_z)E'\Sigma_{sz}(E')}, \quad \text{(II.25)}$$

where $V$ is the relative velocity, $\eta$ and $\zeta$ are scattering angles, and

$$E = E' - \frac{1-\alpha_z}{2}E'\left[1-\left(1-\frac{m+m_z}{m_z E'}\Delta E_{zi\to f}\right)^{1/2}\cos\zeta\right] - \frac{m_z}{m+m_z}\Delta E_{zi\to f}. \quad \text{(II.26)}$$

For the non-elastic scattering component, $g_{zi\to f} = 0$ over the entire energy range, except

$$\frac{1}{2\alpha}(t - \sqrt{t^2-4\alpha s^2}) \leqslant E' \leqslant \frac{1}{2\alpha}(t + \sqrt{t^2-4\alpha s^2}),$$

where

$$s = E + \frac{m_z}{m_z+m}\Delta E_{dis}; \quad t = (1+\alpha_z)s - \frac{(1-\alpha_z)^2}{4}\cdot\frac{m_z+m}{m_z}\cdot\Delta E_{dis}.$$

For the non-elastic scattering component in the energy range of non-zero values, $g_{zi\to f}$, is described by the formula

$$g_{zi\to f}(E', E) = \frac{\Sigma_{z\,dis}(E')}{\Sigma_{sz}(E')(1-\alpha_z)E'\left[1-\frac{m_z+m}{m_z E'}\Delta E_{dis}\right]^{1/2}}. \quad \text{(II.27)}$$

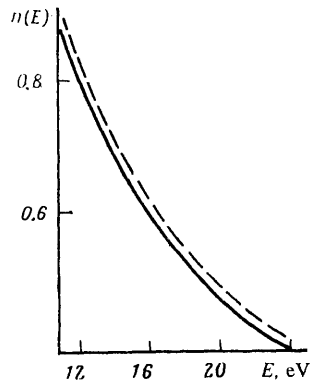



Figure 10. Variation of the asymptotic value of $n_0(E)$ with the energy; dashed curve—with allowance for dissociation; continuous curve—without allowance for dissociation (for isotropic scattering of tritium atoms by deuterium).

The limits of the energy range of non-zero values $g_{zi\to f}$ are determined by the solution of Eqn. (II.26) for the limiting scattering angles $\zeta = 0$ and $\zeta = \pi$. The minimum energy transferred in a non-elastic collision is determined by the value of $\Delta E_{dis}$ which has been set equal [81] to $E_b$; the quantity $\Delta E_{z,dis}$ was calculated by the method of trajectories. For the elastic scattering component, it was assumed [81] that $g_{zi=f}(E', E)$ in the range $E \leqslant E' \leqslant E/\alpha$ is given by the expression $g_{zi=f} = \Sigma_{s,is}/[(1-\alpha_z)\cdot\Sigma_{sz}(E')\cdot E']$. Numerical calculations of $\psi(E)$ and $P$ using the above equations for $g_{zi=f}$ and $g_{zi\to f}$ showed that, for non-elastic energy losses in dissociation, the density of collisions in the region of chemical interaction is lower than for elastic isotropic scattering (Fig. 10). In the region of low energies close to the dissociation threshold, the energy losses in the non-elastic collisions considered have a smaller effect.

## 4. Kinetic Relations Taking Account of the Relaxation of Hot Products

In the solution of transport equations, the relaxation of the hot molecules formed on chemical capture of hot atoms and having an excess kinetic or internal energy ($E_t$ or $E_i$), which makes possible dissociation and other reactions of the primary products, may be taken into account if the probability of the formation of the stable product $p_r(E)$ is represented as follows [68]:

$$p_r(E) = p_c(E) - f'q_r(E) - (1-f')q_m(E), \quad \text{(II.28)}$$

where $p_c(E)$ is the probability of the formation of the product with different sets of $E_t$ and $E_i$, $q_m(E)$ and $q_r(E)$ are the probabilities of the decomposition of the hot molecules in collisions with the moderator or the reactant respectively, and $f'$ is the fraction of the collisions of hot product molecules with reactant molecules. Then, in solutions of type (II.4), we have

$$I(E) = I_0(E) - f'I_r(E) - (1-f')I_m(E); \quad \text{(II.29)}$$

$$\text{when } I_0(E') = \int_0^{E'} p_c(E)\frac{dE}{E} \text{ we have } I_r(E') = \int_0^{E'} q_r(E)\frac{dE}{E};$$

$$I_m(E') = \int_0^{E'} q_m(E)\frac{dE}{E}.$$

Hence

$$P(E) = 1 - \exp\left\{-\frac{f}{\xi}[I_0 - f'I_r - (1-f')I_m]\right\}$$

$$[-\ln(1-P)]^{-1} = \left(\xi_r + \xi_m\frac{1-f}{f}\right)\Big/[I_0 - f'I_r + (1-f')I_m]. \quad \text{(II.30)}$$

The results obtained are important for the interpretation of the experimental data on the non-additivity of the yields in mixtures when the deviations from additivity may be caused by processes involving energy transfer from the primary excited products to the surrounding medium. In particular, it has been shown that, when the probability of the decomposition of the primary products depends on the medium, the variation of $[-\ln(1-P)]^{-1}$ with $(1-f)/f$ when $I_r \neq I_m$ may be non-linear (Fig. 11). However, for low values of $P(E)$, $f$, and $f'$, it follows from Eqn. (II.30) that

$$P^{-1} = I_0^{-1}\frac{\xi_r + \xi_m[(1-f)/f]}{1 - I_m/I_0}. \quad \text{(II.31)}$$

Eqns. (II.31) permit the estimation of the lifetimes of the hot products, since the ratios $(\xi_{m_1}/\xi_{m_2})(I_0 - I_{m_2})/(I_0 - I_{m_1})$ or $(I_0 - I_{m_2})/(I_0 - I_{m_1})$ may be determined from the experimental data for different energy acceptors.

The application of the Monte Carlo method in combination with a novel approach to the problem of describing the relaxation of hot products by binary collisions in the presence of a fraction of stabilised molecules varied by the pressure in the gas system enabled Smith et al. [82] to propose a new method for estimating the parameters of the energy distribution functions of species.

## 5. Kinetic Equations and Their Solutions taking into Account the Thermal Motion of the Molecules of the Target

In the studies examined previously, it was postulated that the thermal motion of the species of the target may be neglected, which is valid only for $E \gg k_B T$. In a series of studies by Kostin and coworkers [83-86] an attempt was made to take into account thermal motion under conditions where the initial energy of the epithermal species is low. Such conditions are encountered in plasma-chemical, radiation-chemical, and photo-chemical studies and in the investigation of chemical reactions in chemical accelerators, in flames, and with recoil atoms in many nuclear decomposition schemes. When account is taken of thermal effects in systems with non-Maxwellised atoms, the conservation equation should contain terms describing elastic collisions involving both a decrease and an increase of the energy of the atom. Under stationary conditions in the source of epithermal species $S(E)$, the conservation equation can be written similarly to Eqn. (I.5). Evidently, when $\Sigma_r \gg \Sigma_s$, the atoms react until there is a significant change in the energy and density of the hot species $\rho(E) \propto S(E)/p_r(E)$. If the medium is chemically inert and the power of the source is low, the species entering from outside attain equilibrium with the surrounding medium, acquiring a Maxwellian distribution corresponding to the target temperature; then

$$n(E) \propto M(E) = \frac{E^{1/2}}{(k_B T)^{3/2}} \exp\left(-\frac{E}{k_B T}\right).$$

When $p_r(E) \neq 0$, the distribution of the bombarding atoms with respect to energy is non-Maxwellian: $\rho(E) \propto M(E) \cdot L(E)$, where $L(E)$ is a correction factor.

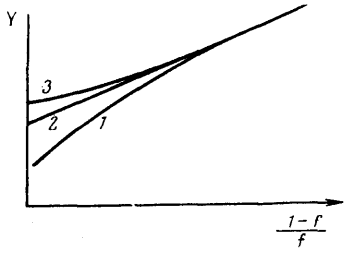



Figure 11. Variation of $Y = -[\ln(1-P)]^{-1}$ with $(1-f)/f$: 1) $I_m > I_r$; 2) $I_m = I_r$; 3) $I_m < I_r$.

The following equation was obtained for this factor on the basis of the principle of detailed balance:

$$[p_s^*(E') + p_r^*(E')] \cdot L(E') = \int_0^\infty g^*(E', E) \cdot L(E)\,dE + S(E')/M(E'), \quad \text{(II.32)}$$

where $p_s^*(E')$, $g^*(E', E)$, and $p_r^*(E')$ are the corresponding probabilities that the atom with the energy $E'$ will be scattered in unit time, will have energy in the range $E-(E+dE)$, and will react chemically.

In a few instances it is possible to convert the integral equation (II.32) into a differential form, which has a solution, by expanding $L(E)$ in Taylor's series. Thus, for small energy changes during scattering, when the scattering anisotropy is marked and there is a large difference between the masses of the colliding species, Eqn. (II.32) gave

$$\frac{1}{2} R_2(E') \frac{d^2 L}{(dE')^2} + R_1(E') \frac{dL}{dE'} + \frac{S(E')}{M(E')} = p_r^*(E') \cdot L(E'), \quad \text{(II.33)}$$

where

$$R_1(E') = \int_0^\infty (E-E') \cdot g^*(E', E)\,dE \text{ and } R_2(E') = \int_0^\infty (E-E')^2 \cdot g^*(E', E)\,dE$$

characterise the average and mean square energies transferred. For reactions with low activation energies, where $\Sigma_r$, $\Sigma_r/\Sigma_s$, and the mean cosine of the scattering angle depend little on the energy, the solution of Eqn. (II.33) assumes the following form for $\epsilon_T^{-1}(m/m_1) < 1$:

$$L(\varepsilon_T) = \text{const}\left[1 + \frac{1}{2} a\varepsilon_T + \ldots + \frac{(a)_n \varepsilon_T^n}{(2)_n \cdot n!}\right], \quad \text{(II.34)}$$

where

$$\varepsilon_T = E/k_B T; \quad a = \Sigma_r \Big/ \left[2\frac{m}{m_1}\Sigma_s(1-\langle\cos\theta\rangle)\right] \text{ and } (a)_n = a(a+1) \times (a+2)\ldots(a+n-1).$$

The solution is valid for $\epsilon_0 > 1$. If, $\epsilon_0 > \epsilon_T > 1$, then

$$L(\varepsilon_T) \propto e^{\varepsilon_T} \varepsilon_T^{a-2}; \quad \psi(\varepsilon_T) = \varepsilon_T e^{-\varepsilon_T} L(\varepsilon_T) \sim \varepsilon_T^{a-1}$$

Thus the greater the value of $a$ for a higher reactivity of the material of the target, the slower the decrease of the collision density with increase of $E$. In non-absorbing systems with $a = 0$, we obtain $\psi(E) \propto 1/\epsilon_T$. Analysis of the solutions leads to the conclusion that, in specimens containing a moderator and a radical acceptor in addition to the reactant and when the reactions have different activation energies, the ratio of the yields of the products of different chemical processes can vary with target temperature (Fig. 12), but only slightly—in the region of very low or very high temperatures.

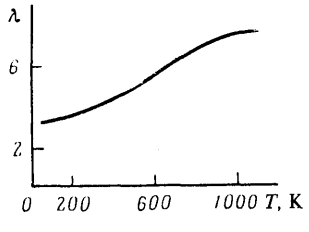



Figure 12. Variation of the ratio of the yields of the primary hot reactions to the yields of the reactions with radical acceptors ($\lambda$) as a function of target temperature ($E_0 = 2.5$ eV; $E_{thresh} = 0.3$ eV; $m_2/m_1 = 1$).

When account is taken of thermal effects, difficulties arise in many instances also in the numerical solution of Eqn. (II.32). In order to facilitate the solution, the function $g^*(E', E)$ is written in the form of a sum of $g_a$ and $g_b$, where $g_a(E', E) > g_b(E', E)$ for small energy transfers and $g_a(E', E) < g_b(E', E)$ for large transfers. This procedure makes it possible to employ instead of Eqn. (II.32) approximate equations which can be solved numerically [86].

The non-stationary problem with allowance for thermal effects has also been solved numerically [87]. For this

purpose, use was made of the transport equation with the correction factors $L(E, t)$ or $L(\epsilon, \tau)$, where $\tau = v_p t/l_s$, $\epsilon = \sqrt{E/k_B T}$, $v_p = \sqrt{2k_B T/m}$, and $l_s$ is the length of the free path of hot atoms before collision with the moderator. Calculation showed that the values of $L(\epsilon, \tau)$ are almost constant over a wide range of thermal velocities already for $\tau > 2$ (Fig. 13).

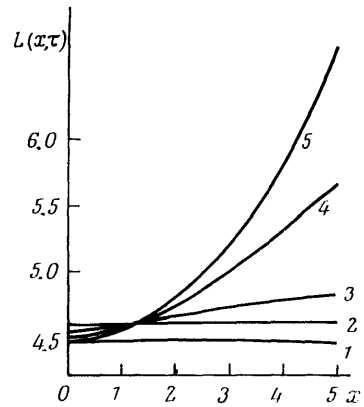



Figure 13. Variation of the correction factor $L(x, \tau)$ with the dimensionless velocity of thermalised species $x = (E/k_B T)^{1/2}$: 1) $\tau \to \infty$; 2) $\tau = 6.0$; 3) $\tau = 2.0$; 4) $\tau = 0.5$; 6) $\tau = 0$.

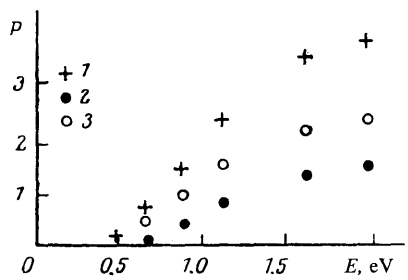



Figure 14. Variation with the energy of the integral probability $P$ of reactions involving the abstraction of deuterium atoms by photolytic H atoms: 1) $C_4D_{10}$; 2) $C_4D_6H_4$; 3) $C_4D_{10}-C_4D_6H_4$).

The kinetic theory of hot-atom reactions has been used successfully to interpret experimental data in photochemistry [88-95]. Thus the variation of the integral probabilities with energy, the threshold energies, and reaction cross-sections have been determined [92] for processes involving the abstraction of deuterium atoms from primary and secondary C–D bonds in deuterobutanes by hot photolytic hydrogen atoms (Figs. 14 and 15). Similar data were obtained from the analysis of the yields of $H_2$ in the interaction of photolytic H atoms with HBr. [93] The kinetic analysis of the photochemical data was performed taking into account the thermal motion of the target molecules; for this purpose, a function (Fig. 16) [92] characterising the kinetic energy distribution ($E_{rel}$) of colliding target species, having a Maxwellian distribution with respect to velocity at the temperature $T$, and of hot atoms with the energy $E$ [90] was introduced into the equations for the estimation of the integral reaction probabilities and the density or number of collisions:

$$\Omega(E_{rel}, E)\,dE_{rel} = \frac{1}{2\mu}\sqrt{\frac{mm_1}{\pi k_B TE}}\cdot\left\{\exp\left[-\frac{m_1}{2k_B T}\left(\sqrt{\frac{2E}{m}}-\sqrt{\frac{2E}{\mu}}\right)^2\right]-\right.$$
$$\left.-\exp\left[-\frac{m_1}{2k_B T}\left(\sqrt{\frac{2E}{m}}+\sqrt{\frac{2E}{\mu}}\right)^2\right]\right\}, \qquad (II.35)$$

where $\mu$ is the reduced mass.

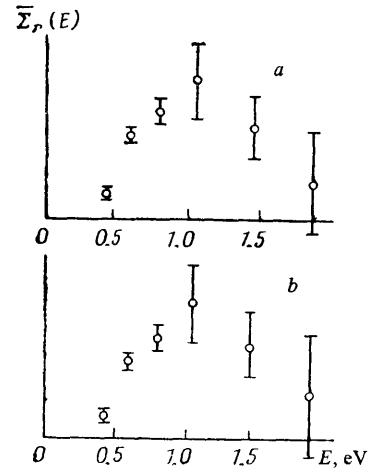



Figure 15. The cross-section of the reaction involving the abstraction of deuterium atoms by photolytic H atoms from a secondary C–D bond in $C_4D_{10}$: *a*) $U(r)_{H-Xe} \propto r^{-7}$; *b*) $U(r)_{H-Xe} \propto r^{-4}$.

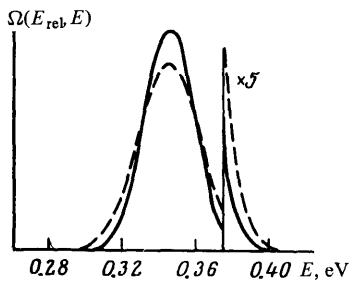



Figure 16. Variation with the energy of the function $\Omega(E_{rel}, E)$ for photolytic H atoms with $E_0 = 0.35$ eV in $C_4D_{10}$; continuous curve—at 229 K; dashed curve—at 323 K.

In systems where allowance for the thermal motion of molecules is necessary, i.e. for small initial energies of the hot atoms, close to non-zero values of $p_r(E)$ and $T > 0$ K, the following equations are valid:

$$n(E_{rel})\,dE_{rel} = \left[\int_0^\infty n(E)\cdot\Omega(E, E_{rel})\,dE\right]dE_{rel}, \qquad (II.36)$$

$$\Sigma_t(E) = \int_0^\infty \Sigma_t(E_{rel})\cdot\Omega(E_{rel}, E)\,dE_{rel}.$$

In this case, equations of type (I.1) for the probabilities of chemical reactions in mixtures containing considerable amounts of the moderator can be written in the form

$$P = \int_{E_1}^{E_2} \frac{\Sigma_r(E_{rel})}{\Sigma_{t,r}(E_{rel})} \int_0^\infty n_m(E) \frac{\Sigma_{t,r}(E)}{\Sigma_{t,m}(E)} \Omega(E, E_{rel})\, dE \cdot dE_{rel} \quad (II.37)$$

In estimating $n(E)$, Gann and coworkers [90-94] used different versions of the asymptotic solutions ($E \ll E_0$) where the average fractions of the transferred energy, in particular $\epsilon_{is} = \langle E' - E \rangle / E' = 2\mu/(m + m_1)$, were substituted for $\xi$ when $m_1 \gg m$. When account is taken of the thermal motion of the target molecules during isotropic scattering, we have

$$\bar{\varepsilon}_{is} = \frac{2\mu}{m + m_1}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right);$$

then

$$n_0(E) \simeq \frac{1}{\bar{\varepsilon}_{is} E} = \frac{m + m_1}{2\mu E}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right)^{-1}. \quad (II.38)$$

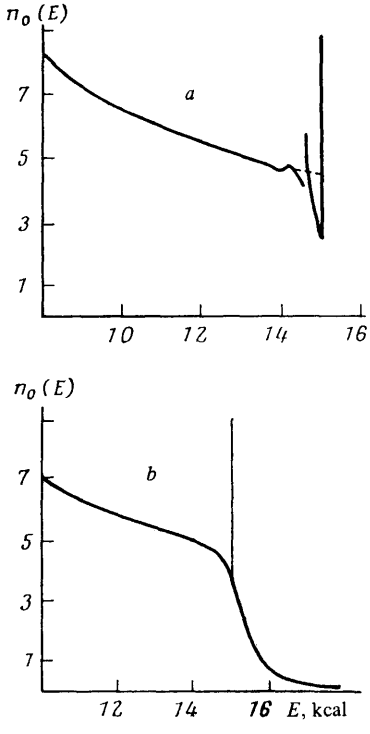



**Figure 17.** Variation with the energy of the asymptotic value of $n_0(E)$ for the hard-core potential of the scattering of photolytic H atoms ($E_0 = 15$ kcal) in xenon: *a*) at 0 K; *b*) at 273 K.

For an interaction described by potentials other than the hard-core potential, for example $U(r) = Ar^{-s}$ or the Lennard–Jones potential in the range where $E < 0.93E_0$, we have

$$\bar{\varepsilon}(E) = \frac{2\mu}{m_1 + m}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right)\frac{Q(E)}{\Sigma_t(E)},$$

where $Q(E) = \int_0^\infty Q(E_{rel})\Omega(E_{rel}, E)dE_{rel}$. In the general case, $Q(E_{rel})$, the moment of the transport cross-section, is found by graphical integration [96]. The expression

$$n_0(E) \simeq \text{const} \cdot E^{-\left(1-\frac{s}{2}+\frac{1}{s-1}\right)}\left(1 - \frac{3}{2}\frac{k_B T}{E}\right)^{-1} \quad (II.39)$$

was obtained for $U(r) = Ar^{-s}$.

Calculation of $n_0(E)$ by the above methods led to the following conclusions: (1) when $T \gg 0$ K, there are collisions in the region where $E > E_0$ (Fig. 17), the oscillations in $n(E)$ in the vicinity of $E_0$ being smoothed out under these conditions. 2. The form of the function $n_0(E)$ depends only slightly on the form of the interaction potential. 3. For the Lennard–Jones potential, the decrease of the collision density near $E_0$ is manifested less markedly than for the hard-core potential. The width at the half height level of the tail portion of the function $n_0(E)$ increases appreciably with increase of the target temperature (Figs. 18 and 19). The width of the distribution with respect to relative energy can be large even for $E_0 > k_B T$, since the relative energies are in the range $E_{max} - E_{min}$; $\Delta E \propto \mu\sqrt{k_B T E/mm_1}$.

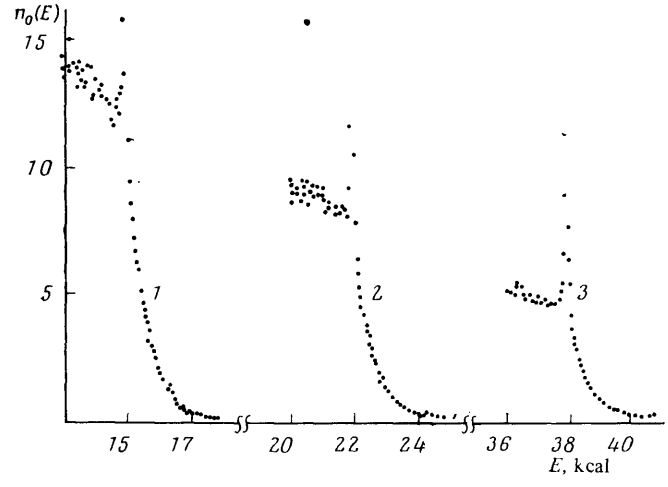



Figure 18. Variation of the asymptotic value of $n_0(E)$ for the Lennard–Jones potential in the H–Xe system ($E$ = 273 K) as a function of the energy of the photolytic H atoms (kcal): 1) 15; 2) 22; 3) 38.

Numerical solutions of the Boltzmann equation for the collision density were also obtained by Kupperman et al. [88] with the analogous function $\Omega(E, E_{rel})$ and $g(E', E)$ expressed in terms of the normalised Gaussian function. It was assumed that the flux of hot species is fairly small and does not affect the thermal distribution of the target molecules.

In conclusion of the review of data on the analytical and numerical solutions of kinetic equations in relation to the distribution functions of hot species with respect to energy or the probabilities of the chemical reactions initiated by them, we shall specify the most important of the results obtained. For energies below the initial values, the particle distribution functions with respect to energy $\psi(E)$, $n(E)$, and $\varphi(E)$, etc. attain asymptotic values. The asymptotic values increase with decrease of the energy $E$.

In the vicinity of sources, more precisely for $E = \alpha E_0$, the distribution functions undergo a discontinuity and in the vicinity of $\alpha^3 E_0 < E < E_0$ they exhibit oscillations.

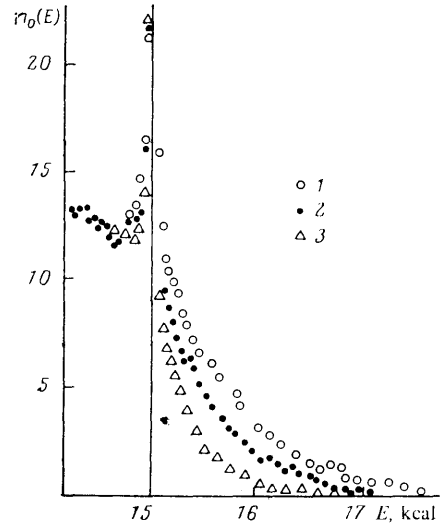



Figure 19. Variation of the asymptotic value of $n_0(E)$ for the Lennard–Jones potential of the scattering of photolytic H atoms ($E_0 = 15$ kcal) in xenon as a function of temperature (K): 1) 373; 2) 273; 3) 173.

In non-absorbing media, the asymptotic value of the collision density is inversely proportional to the energy $\psi_0(E) = S_0/E\xi(E)$. For initial energies of the species $E_0$ comparable to the energy of the thermal motion of target atoms and molecules, the asymptotic value of the collision density is inversely proportional to the energy normalised with respect to $k_B T$, i.e. $\psi_0(\epsilon_T) \propto 1/\epsilon_T$, where $\epsilon_T = E/k_B T$. The rate of attainment of asymptotic values is determined mainly by the ratio of the masses of the hot atom and target species and also by the parameters of the interaction potentials. For elastic isotropic collisions, the asymptotic value of $\psi_0(E)$ can be used in the region where $E < \xi_{is} E_0$. For elastic anisotropic scattering, for example for potentials of the type $U(r) = Ar^{-s}$ or $U(r) = A_1 r^{-s_1} + A_2 r^{-s_2}$, the rate of attainment of the asymptotic value is particularly large for small values of $s$ and $\alpha$, i.e. for similar masses of the colliding species. Analytical criteria of the applicability of $\psi_0(E)$ for arbitrary potentials are unknown. For individual types of potentials, the results of numerical calculations are available, showing that, for example, for $U(r) = Ar^{-s}$ with $s < 10$ and $\alpha < 0.8$, the asymptotic value of the collision density is attained already when $\ln(E/E_0)/\ln\alpha \geq 1$.

When hot species are retarded as a result of elastic collisions, the distribution functions show a general tendency to increase with decrease of the energy. However, the detailed variation of the change in $\psi_0(E)$ or $\psi(E)$ is determined by the average logarithmic energy losses and their variation with $E$. The values of $\xi_{is}$ are constant over the entire range of energies of the elastic isotropic collisions. For anisotropic scattering, the values of $\xi$ may remain constant as $E$ varies, for example when $g(E', E) \propto 1/E'\Phi(E, E')$, but they can also vary with the energy. Since small scattering angles predominate in elastic and anisotropic collisions, it follows that $\xi_{is} > \xi$ and $\psi_{0,is}(E) < \psi_0(E)$. The decrease of $\xi(E)$ with decrease of $E$ leads to a weakening of the dependence of the asymptotic values of the distribution functions on the energy. For example, for $U(r) = Ar^{-s}$, the collision density is inversely proportional to $E^\beta$, where $\beta = 1 - 2/s + (s-1)^{-1} \leq 1$ ($\beta = 1$ when $s = 2$, $\beta = 0.83$ when $s = 4$, etc.).

The asymptotic values of the collision densities and the equivalent distribution functions depend only slightly on the initial energy of the hot species if $E_0 \gg E$. The nature of this dependence is likewise determined by the parameters of the interaction potentials. Thus, for $U(r) = Ar^{-s}$, the ratio of the asymptotic values of $\psi_0(E, E_0^{(2)})/\psi_0(E, E_0^{(1)})$ is proportional to $[E_0^{(2)}/E_0^{(1)}]^{s - 2/s(s-1)}$; consequently, for fairly large values of $s$ and in the case of the hard-core potential, $\psi_0(E)$ is almost independent of $E_0$ for $E \ll E_0$.

In absorbing media, the distribution functions for hot particles with respect to energy have the same qualitative features as in inert moderators. They too can have discontinuities at $E = \alpha E_0$ and can exhibit oscillations in the vicinity of sources of hot species and intense chemical absorption zones, which may be regarded as negative sources. The distribution functions in the reactive systems likewise have asymptotic solutions in the regions of energies remote from the sources or the intense chemical reaction zones. The values of $\psi_0(E_0)$ in absorbing media also decrease with increase of $E$. However, those of $\psi_0(E)$ in reactive media take into account the "erosion" of the hot species from the spectrum by chemical reactions. The "erosion" has a particularly marked influence on the region of low energies. For a weak perturbation of the particle flux (see above), the asymptotic solutions of the transport equations taking into account the "erosion" have a form formally identical with that of solutions for inert moderators: $\psi_0(E) = q(E)/E\xi(E)$.

The use of asymptotic distribution functions in the calculation of the probability of chemical reactions does not lead to major errors. The results are in this case more accurate the further away is $E_0$ from the energy range of the reactions. The accuracy of the determination of $P$ in terms of asymptotic distribution functions increases with decrease of $\alpha$ and also with decrease of the reactivity of the components, i.e. with decrease of $\int f p_r(E).n(E)dE$.

In weakly absorbing systems, $q = S_0 p(E)$, i.e. it contains the correction factor $p(E)$, characterising the probability of avoiding capture during the moderation process until the attainment of the specified energy $E$. Evidently, the appearance of the correction factor dependent on $E$ may alter the variation of the distribution functions with energy in a chemically reactive medium compared with an inert medium. Interpretation of the resonance integral $p(E)$ shows that the overall tendency should be towards the smoothing out of the dependence of $\psi_0(E)$ on the energy.

Owing to "erosion" as a result of the chemical absorption of hot species, the flux or density of collisions increases more slowly with decrease of the energy than predicted by the $1/E$ law even for $\xi = \text{const}$. This is shown most clearly by the exact solutions of the transport equations for $\alpha = 0$ and for the ratio $\Sigma_s(E)/\Sigma_r(E) = c$ independent of the energy. Under these conditions, $\psi(E) \propto E^{-c/(1+c)}$; thus, with increase of the reactivity of the system owing to the decrease of $c$, the collision density changes with the energy less markedly. This general tendency persists for approximate solutions under the

conditions of appreciably different masses of the colliding species, when $\alpha \neq 0$, regardless of the potential used to describe the scattering processes and whether or not the scattering is isotropic or anisotropic. The smoothing out of the variation of the distribution functions with energy is characteristic also of the energy range where account must be taken of the thermal motion of the target species. In certain specific instances, the asymptotic value of $\psi_0(\epsilon_T)$ is inversely proportional to $\epsilon_T^{(1-a)}$. The values of $a$ are proportional to the ratio $\Sigma_r(E)/\Sigma_s(E)$ and characterise the reactivity of the medium. The higher the reactivity of the material of the target, the larger the value of $a$ and the correspondingly less marked the dependence of $\psi_0(\epsilon_T)$ on the energy.

The anisotropy of scattering for values of $\xi_{anis}$ dependent on the energy promotes, as in non-absorbing systems, a further smoothing out of the energy spectrum and a slower variation with the energy of the asymptotic values of the distribution functions. Whereas $\psi(E) \propto E^{-c/(1+c)}$ for retardation as a result of elastic isotropic scattering, we have $\psi_0(E) \propto E^{-\beta}$ for anisotropic scattering and $|\beta| < |c/(1+c)|$. The softer the potential of the elastic interaction, the smaller the value of $\xi_{anis}$ and the greater the number of collisions per unit energy. This leads to an increase of the overall probability of chemical capture owing to the large number of collisions for the same probability of a single collision.

The asymptotic values of the distribution functions in absorbing systems depend only slightly on the initial energy of the hot species if $E \ll E_0$. This is evident, since the values of $\psi_0(E)$ undistorted by chemical absorption (in non-absorbing systems) depend only slightly on $E_0$ and the probability of avoiding capture following retardation to $E$ is almost independent of $E_0$ when $E_2 < E_0$. Accordingly, the probability of chemical reactions for $E_2 < E_0$ may be expected to depend only slightly on $E_0$. This conclusion follows from the stochastic definition of the probability of chemical reactions of hot atoms in terms of Porter's formulae.

For mixtures of inert moderators, $\psi_0(E) \propto 1/\bar{\xi}E$, where $\bar{\xi} = \sum_i f_i\xi_i = \sum_i (N_i\sigma_{si}/\sum_j N_j\sigma_{sj})\xi_i$. The dependence of $\bar{\xi}$ on the mole fraction of the components determines to a large extent the nature of the corresponding variation of the collision densities and probabilities and yields of hot reactions in binary and more complex systems. The simplest linear relations, for example between $-1/\ln(1-P)$ and $(1-f_r)/f_r$, describe the yields of chemical reactions in mixtures of the reactive components with inert moderators. Similar simple relations have been obtained also for mixtures containing, apart from the moderator, two reactants with low chemical reaction cross-sections, for mixtures of the moderator and two strong absorbers with $p_{rz}(E) = \text{const.}p_{ry}(E)$, and for mixtures of two reactants. Comparison of the above relations with the experimental data for kinetic analysis made it possible to obtain much information about the nature of the processes involving hot atoms.

In conclusions, one should note that the characteristics of the parametric relations involving distribution functions with respect to energy and the probabilities of chemical reactions, obtained by solving Boltzmann equations, agree with the results of calculations based on stochastic schemes.

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# Niobates and Tantalates of Tervalent Elements

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The types of compounds in the $A_2O_3$–$B_2O_5$ systems, where A = the *p*-, *d*-, and *f*-elements of Group III, the *p*-elements of Group V, and the *d*-elements of the fourth period in the tervalent state and B = Nb or Ta, are considered. An analysis of the methods of making the niobates and tantalates is given, their structure is described, and their physicochemical and electrophysical properties are reviewed. Special attention has been paid to the description of the rare-earth element metaniobates, which exhibit the properties of electrets, and of the compounds of composition $ABO_4$ (A = Sb, Bi; and B = Nb, Ta), which belong to a new group of ferroelectrics. Bibliography of 147 references.

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## I. INTRODUCTION

Niobates and tantalates of various metals are widely used in contemporary technology. They are usually used as the pure compounds or as components of solid solutions, which exhibit ferro-, piezo-, and pyro-electric, electro-optical, and other properties[1-3]. Materials based on them are employed in the production of ceramic generators of ultrasound, sound pickups, piezoelectric microphones and telephones, strain gauges, hydroacoustic collectors (receivers) of energy, laser crystals, etc.[3]

The development of the newest technology and the consequent requirement for new materials has aroused exceptional interest in the niobates and tantalates of tervalent metals. The successful combination of various physical properties with chemical inertness, high resistance to heat and moisture, and mechanical strength puts the niobates and tantalates of the tervalent metals among the most important materials of the new technology. Thus the rare-earth element (r.e.e.) orthoniobates of composition $RNbO_4$, activated with $Nd^{3+}$ ions, serve as materials for lasers[4]. Antimony and bismuth orthoniobates and orthotantalates of composition $ABO_4$ have ferroelectric properties, which are successfully combined with high pyro- and piezo-sensitivity[5]. The metaniobates $R(NbO_3)_3$ can be used as ceramic electrets[6,7]. The niobates and tantalates of composition $RBO_4$ (where R = Y, La, or Nd) with fergusonite structure are antiferroelectrics with a high Curie temperature[8,9].

The number of papers dealing with the preparation and investigation of the properties of niobates and tantalates began to increase sharply after 1960. However, the results obtained have not yet been systematically examined, although there have been monographs[1,2] which deal with a limited set of problems on the preparation and certain properties of the niobates and tantalates of tervalent elements.

The present paper systematically examines the results on the methods of preparation, crystal-chemistry, and certain physicochemical and electrophysical properties of the niobates and tantalates of tervalent elements. Of the many types of compound among the niobates and tantalates we will consider only the simple compounds of the $A_2O_3$–$B_2O_5$ binary systems, where B is Nb or Ta, and will not deal in detail with mixed niobates and tantalates, that is, the compounds formed in the $M_2O$–$A_2O_3$–$B_2O_5$ systems and also the so-called aquoniobates and aquotantalates formed in the $A_2O_3$–$B_2O_5$–$H_2O$ system. Special attention is paid to the most important inorganic materials of contemporary technology, the r.e.e., Sb, and Bi niobates and tantalates.

The niobates and tantalates of tervalent metals can be regarded as salts of hypothetical niobic and tantalic acids, namely, the ortho-salts $ABO_4$ as derivatives of the ortho-acids $H_3BO_4$ ($3H_2O.B_2O_5$), the meta-salts $A(BO_3)_3$ as derivatives of the meta-acids $HBO_3$ ($H_2O.B_2O_5$), and finally, many polyniobates and polytantalates $A_nB_mO_{2.5m+1.5n}$ (for example, $ANb_5O_{14}$, $ANb_{11}O_{29}$, $A_2Nb_{12}O_{33}$, $A_2Ta_{12}O_{33}$) as salts of the acids $nH_2O.mB_2O_5$.

Depending on the chemical nature of element A, it is desirable to consider the niobates and tantalates by dividing them into the following classes: (a) the niobates and tantalates of the Group III *p*-elements (Al, Ga, In, Tl); (b) the niobates and tantalates of the Group III *d*- and *f*-elements (r.e.e.); (c) the niobates and tantalates of the Group V *p*-elements (Sb and Bi); (d) the niobates and tantalates of the fourth period *d*-elements (Ti, V, Cr, and Fe).

## II. TYPES OF COMPOUND

### 1. ALUMINIUM, GALLIUM, INDIUM, AND THALLIUM NIOBATES AND TANTALATES

Table 1 shows the niobates and tantalates of the metals of the aluminium subgroup known at present. The orthoniobates and orthotantalates of composition $ABO_4$ (known for all the elements except thallium) are characteristic. Aluminium orthotantalate $AlTaO_4$ is encountered in nature as the mineral simpsonite[28]. The existence of metaniobates and metatantalates of composition $A(BO_3)_3$ has been established reliably only for thallium[26,27]. There are reports of the preparation of the aquometaniobates $Al(NbO_3)_3.nH_2O$[20,29,30] and $In(NbO_3)_3.nH_2O$.[25]

The compounds in the $Al_2O_3$–$Nb_2O_5$ system (Fig. 1) have been studied most completely; apart from $AlNbO_4$, the existence of the polyniobates $AlNb_{11}O_{29}$ and $AlNb_{49}O_{124}$ has been found[12,21]. There have also been reports of the existence in this system of the compounds $AlNb_9O_{24}$,[14] $AlNb_{25}O_{64}$,[14] and $AlNb_{29}O_{74}$.[16]

**Table 1.** Niobates and tantalates of the *p*-elements of Group III and methods of making them.

| B | Al | | Ga | | In | | Tl | |
|---|---|---|---|---|---|---|---|---|
| | composition | method of preparation* | composition | method of preparation* | composition | method of preparation* | method | method of preparation* |
| Nb | $AlNbO_4$ [10–13] | T[10–13,18], CO[20] | $GaNbO_4$ [13,21,22] | T[13,21,22] | $InNbO_4$ [13,22,24] | T[13,22,24], CO[25] | — | — |
| | $AlNb_9O_{24}$ [14] | T[14] | $GaNb_5O_{14}$ [22] | T[22] | | | $TlNb_3O_{19}$ [26] | T[26] |
| | $AlNb_{11}O_{29}$ [11–17] | T[11–17] | $GaNb_{11}O_{29}$ [21] | T[21] | | | $Tl_4Nb_6O_{21}$ [26] | T[26] |
| | $AlNb_{25}O_{64}$ [14] | T[14] | — | — | | | | |
| | $AlNb_{29}O_{74}$ [16] | T[16] | $GaNb_{29}O_{74}$ [16] | T[16] | | | | |
| | $AlNb_{49}O_{124}$ [13,17] | T[13,17] | $GaNb_{49}O_{124}$ [21] | T[21] | | | | |
| Ta | $AlTaO_4$ [11,13] | T[11,13,19] | $GaTaO_4$ [13,23] | T[13,19,23] | $InTaO_4$ [13,24] | T[13,24] | — | — |
| | | | | | | | $TlTa_3O_9$ [27] | CO[27] |
| | | | | | | | $Tl_4Ta_6O_{21}$ [27] | CO[27] |

T = solid-phase preparation by heating mixture of oxides; CO = coprecipitation of the components from solutions.

Note. In this table and in subsequent tables all superscripts are reference numbers.

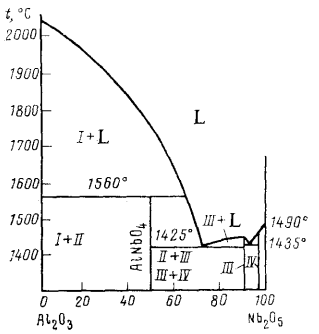



**Figure 1.** Equilibrium diagram of the $Al_2O_3$–$Nb_2O_5$ system[12]: *I* = $Al_2O_3$; *II* = $AlNbO_4$; *III* = $AlNb_{11}O_{29}$; *IV* = $Nb_2O_5$.

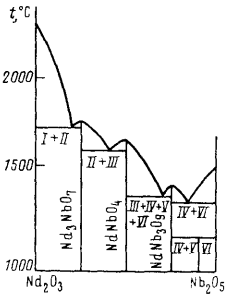



**Figure 2.** Equilibrium diagram of the $Nd_2O_3$–$Nb_2O_5$ system[59]. *I* = $Nd_2O_3$; *II* = $Nd_3NbO_7$; *III* = $NdNbO_4$; *IV* = $NdNb_3O_9$; *V* = $Nd_2Nb_{12}O_{33}$; *VI* = $Nb_2O_5$.

## 2. R.E.E. NIOBATES AND TANTALATES

In considering the niobates and tantalates of the Group III *d*- and *f*-elements it is desirable to isolate into separate groups Sc and Y compounds, compounds of the cerium-subgroup lanthanides (La, Ce, Pr, Nd, Sm, and Eu), and those of the yttrium-subgroup lanthanides (Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). The many types of niobates and tantalates of these subgroups of metals are shown in Table 2, from which it is clear that compounds $ABO_4$ are known for all the r.e.e. Compounds of this composition are widely encountered in nature as the minerals fergusonite[83] ($YNbO_4$) and formanite ($YTaO_4$).

The compounds $A_3NbO_7$ and $A_3TaO_7$ are also known for all the r.e.e. However, the niobates $A_3NbO_7$ of the yttrium-subgroup elements have been obtained only for Gd,[38] Dy,[38] and Ho,[78] whereas tantalates of analogous composition are known for all the elements. The metaniobates $RNb_3O_9$ have been described only for the lanthanides of the cerium subgroup. The elements with ionic radius < 0.80 Å apparently cannot form compounds of this type. However, metatitanates $RTa_3O_9$ have been obtained for almost all the r.e.e. Since the r.e.e. metaniobates and metatantalates have the structure of perovskite $ABO_3$, their formula is best represented as $Ln_{1/3}NbO_3$ and $R_{1/3}TaO_3$.

The formation of pentaniobates of composition $LnNb_5O_{14}$ has been shown for La, Ce, Pr, Nd, and Eu[56–58] but such compounds are not formed for the other elements. There is no information about r.e.e. pentatantalates. Dodecaniobates $Ln_2Nb_{12}O_{33}$ (Ln = La, Ce, Pr, and Nd)[45,59] and dodecatantalates $Ln_2Ta_{12}O_{33}$ (Ln = La, Nd)[37,61] have been described only for the elements of the cerium subgroup.

For tantalum, the compounds $LnTa_7O_{19}$ are also known[38,41], being formed throughout the entire series of lanthanides except for Yb and Lu.[41] The equilibrium diagrams in the $Ln_2O_3$–$Nb_2O_5$ and $Ln_2O_3$–$Ta_2O_5$ systems have not been studied systematically. As an example, Fig. 2 gives the equilibrium diagram of the $Nb_2O_5$–$Nd_2O_3$ system as an example. The existence of the compounds $Nd_3NbO_7$, $NdNbO_4$, $NdNb_3O_9$, and $Nd_2Nb_{12}O_{33}$ has been observed.

**Table 2.** Rare-earth element niobates and tantalates and methods for making them.

| B | Sc, Y | | La—Eu | | Gd—Lu | |
|---|---|---|---|---|---|---|
| | composition | method of preparation* | composition | method of preparation* | composition | method of preparation* |
| Nb | $ANbO_4$ [13,31—37] | T[13,31—35], CO[36,42,43], Kp[37,44] | $LnNbO_4$ [13,30,45—53] | T[13,31,45—53], CO[6,51,67,68,73,74], Ch[69], Kp[44] | $LnNbO_4$ [21,31,53,77—79] | T[13,31,53,71,72], CO[68,77] |
| | $A_3NbO_7$ [38] | T[38] | $Ln_3NbO_7$ [31,38,48—50,54] | T[31,38,48,49], CO[54] | $Ln_3NbO_7$ [38,78] | T[38,78] |
| | — | — | $LnNb_9O_9$ [40,48—50,55] | T[48,49,58,55], CO[6,51,70] | — | — |
| | — | — | $LnNb_5O_{14}$ [50,56—58] | T[57] | — | — |
| | — | — | $Ln_2Nb_{12}O_{33}$ [49,59] | T[49,59], CO[59] | — | — |
| Ta | $ATaO_4$ [13,31,34,35,39] | T[13,31,34,35,39] | $LnTaO_4$ [13,31,53,60—66] | T[13,31,49,53,60—63], CO[65,66] | $LnTaO_4$ [13,62,63,80—82] | T[13,62,80—82], CO[63] |
| | $A_3TaO_7$ [38] | T[38] | $Ln_3TaO_7$ [31,38,44,61,63] | T[31,38,49,61,63] | $Ln_3TaO_7$ [38,63] | T[38,63] |
| | $ATa_3O_9$ [40] | T[40] | $LnTa_3O_9$ [40,55,61,63,66] | T[41,40,55,61,63] | $LnTa_3O_9$ [40,55,63] | T[40,55,63] |
| | — | — | $Ln_2Ta_{12}O_{33}$ [49,61] | T[49,61] | — | — |
| | $ATa_7O_{19}$ [41] | T[41], CO[41] | $LnTa_7O_{19}$ [41,57] | T[41,57], CO[41] | $LnTa_7O_{19}$ [41] | T[41], CO[41] |

*T = solid-phase preparation by heating mixtures of oxides; CO = coprecipitation of the components from solutions; Kp = crystallisation from solution in a melt; Ch = preparation of single crystals after Czochralski.

Even a simple list of the types of compounds of the elements of subgroup IIIa shows that (unlike the niobates) the tantalates exist in a large number of varieties. This is especially noticeable for Sc, Y, and the yttrium subgroup of lanthanides.

## 3. ANTIMONY AND BISMUTH NIOBATES AND TANTALATES

The minerals stibiocolumbite $SbNbO_4$, stibiotantalite $SbTaO_4$, and bismutotantalite $BiTaO_4$,[83] are encountered in nature, and these compounds have been prepared under laboratory conditions only comparatively recently[13,84-93], evidently owing to the volatility of the oxides $Sb_2O_3$ and $Bi_2O_3$ above 650–700°C.

**Table 3.** Antimony and bismuth niobates and tantalates and methods for making them.

| B | Sb | | Bi | |
|---|---|---|---|---|
| | composition | method of preparation | composition | method of preparation |
| Nb | $SbNbO_4$ [13,84—87]; $SbNb_3O_9$ [90] | T[13,84,85], H[86,95—97], CO[87]; T[90] | $BiNbO_4$ [84,88,89] | T[84,88,89], H[98], CO[98] |
| | | | — | — |
| | | | $Bi_3Nb_3O_{15}$ [89] | T[89] |
| | | | $Bi_8Nb_{18}O_{63}$ [89] | T[89] |
| | | | $BiNb_5O_{14}$ [89] | T[89] |
| | | | $Bi_3Nb_{17}O_{47}$ [92] | T[89] |
| Ta | $SbTaO$[84—85,91] | T[84—85], H[96], CO[147] | $BiTaO_4$ [84,88] | T[84,88], H[98], CO[147] |

*T = solid-phase preparation by heating mixtures of oxides; CO = coprecipitation of the components from solutions; H = hydrothermal preparation.

Special interest in the Sb and Bi niobates and tantalates was aroused recently owing to the observation of ferroelectric properties in the mineral stibiotantalite[5] and the synthetic $ABO_4$ (where A = Sb or Bi, B = Nb or Ta)[94]. Table 3 gives the types of antimony and bismuth compounds. The most characteristic compounds are the orthoniobates and orthotantalates $ABO_4$. For antimony, the compound $SbNb_3O_9$ is also known[90].

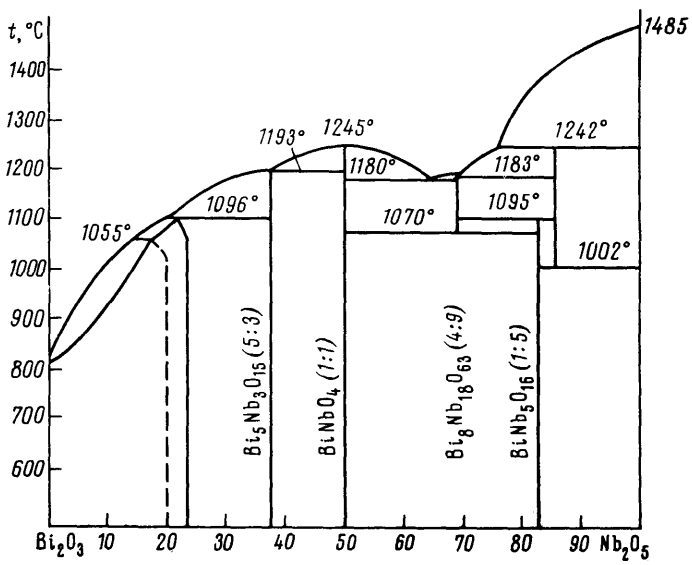



Figure 3. Equilibrium diagram of the $Bi_2O_3$–$Nb_2O_5$ system[89].

Fig. 3 gives the equilibrium diagram of the $Bi_2O_3$–$Nb_2O_5$ system. Formation of the compounds $BiNbO_4$, $Bi_5Nb_3O_{15}$, $Bi_8Nb_{18}O_{63}$, and $BiNb_5O_{14}$ has been reported[89].

Nothing has been published on the existence of Sb and Bi tantalates of a composition other than $ABO_4$.

## 4. NIOBATES AND TANTALATES OF THE *d*-METALS OF GROUPS IV–VIII

Of all the *d*-elements of periods IV and V which can exist in the tervalent state, only Ti, V, Cr, Mn, Fe, and Rh are known to have niobates and tantalates. Table 4 shows that in addition to the compounds of type $ABO_4$ several polyniobates have also been described[17,103].

Information is also available about the existence of the orthoniobates $TiNbO_4$,[13] $VNbO_4$,[13] $MnNbO_4$,[81] $RhNbO_4$,[13,18] and the orthotantalates $TiTaO_4$,[13] $VTaO_4$,[13] and $RhTaO_4$.[13,18] The possibility of the formation of iron hexatantalate $Fe_8(Ta_6O_{19})_3.44H_2O$ has also been suggested[105].

Table 4. Chromium and iron niobates and tantalates and methods for making them.

| B | Cr | | Fe | |
|---|---|---|---|---|
| | composition | method of preparation* | composition | method of preparation |
| Nb | $CrNbO_4$ [13,99–102] | T[13,19,99–101], TRG[102] | $FeNbO_4$ [100–104] | T[19,100,103,104], TRG[102] |
| | — | — | $FeNb_9O_{24}$ [103] | T[103] |
| | $CrNb_{11}O_{29}$ [17] | T[17] | $FeNb_{11}O_{29}$ [17] | T[17] |
| | — | — | $Fe_2Nb_{50}O_{93}$ [103] | T[103] |
| | $CrNb_{49}O_{129}$ [17] | T[17] | $FeNb_{49}O_{124}$ [17,103] | T[17,103] |
| Ta | $CrTaO_4$ [13,99] | T[13,19,99] | $FeTaO_4$ [18] | T[18,19] |

*T = solid-phase preparation by heating mixtures of oxides; TRG = transport reactions from the gas phase with formation of single crystals.

## III. PREPARATION OF NIOBATES AND TANTALATES OF TERVALENT ELEMENTS

Almost all the methods of making inorganic materials are used for obtaining niobates and tantalates of tervalent elements but the following are those used most widely: (1) solid-phase synthesis (T); (2) coprecipitation of the components from solutions followed by heating of the precipitate (CO); (3) hydrothermal synthesis (H). Tables 1–4 give information about the use of the various methods for making the niobates and tantalates.

### 1. SOLID-PHASE SYNTHESIS

Solid-phase synthesis (in other words, the ceramic method) which consists in the high-temperature heating of a mechanical mixture of the components, has been widely used for every niobate and tantalate of a tervalent element (Tables 1–4).

The starting materials in the solid-phase synthesis of niobates and tantalates are usually mixtures of the corresponding oxides. Much more rarely, a mixture of the oxides $Nb_2O_5$ ($Ta_2O_5$) with the carbonates, oxalates, nitrates, or other thermally unstable salts of the tervalent metal is used. Since the mechanism of solid-phase reactions depends mainly on the phase composition of the initial mixture, the latter also determines the temperature at which the mixture is heated.

We give below some examples of solid-phase synthesis. Thus for the preparation of $R_3NbO_7$, where R = La, Nd, Sm, Gd, Dy, Sc, and Y the oxides $R_2O_3$ and $Nb_2O_5$ are mixed in the necessary ratio and heated as tablets for 2 h at 1000°C. Then the mixture was pressed again and heated for 2 h at 1400°C. The tablets were then homogenised by being heated rapidly to 1800°C.[38] The r.e.e. and also V, Cr, Fe, and Rh orthoniobates were made analogously at 1250°C and the orthotantalates of the same elements at 1350°C.[13] The La, Ce, Pr, and Nd metaniobates and also the La, Ce, Pr, Nd, Sm, Gd, Dy, and Y metatantalates are obtained by heating mixtures of the oxides to 1450–1500°C.[40] Afonskii and Neiman[61] obtained the tantalates $LaTaO_4$, $La_3TaO_7$, $LaTa_3O_9$, and $La_2Ta_{12}O_{33}$ at lower temperatures (1300–1500°C).

A comparison of the results shows that different investigators give different temperatures for the preparation of the same compound. This is because the solid-phase reaction can be carried out over some range of temperatures higher than the temperature for the start of interaction between the initial oxides. Actually, in an investigation[72] of the interaction of a mixture of the oxides $La_2O_3$ and $Nb_2O_5$ the effect due to the formation of lanthanum orthoniobate $LaNbO_4$ is observed at 1190°C. $LaNbO_4$ has been prepared by various investigators at 1250–1300°C[52] and even 1600°C.[71] It seems that the reaction temperature depends on the duration of the sintering, which determines the completeness of the interaction of the initial substances. The tervalent metal tantalates are almost always prepared at higher temperatures than the niobates.

When one of the oxides in the solid-phase synthesis is volatile (for example, $Sb_2O_3$ and $Bi_2O_3$), then the niobates and tantalates are prepared in a closed volume. For example, to make antimony orthoniobate the mixture of oxides was first heated at 820°C for 2 h. After this, the material was sealed in a platinum tube and heated at 905°C for 16 h, then at 1000°C for 1 h, and at 1103°C for 14 h.[84]

The mechanism of the solid-phase processes has been studied repeatedly. The simplest compounds $ABO_4$ are evidently formed in a single stage[50,60]. The compounds $Ln_3NbO_7$ are formed in stages. The example of $Eu_3NbO_7$ showed[50] that initially (in the temperature range up to 1100°C) $EuNbO_4$ is formed and then further addition of $Eu_2O_3$ is observed at 1300°C.

The mechanism of formation of cerium metaniobate $CeNb_3O_9$ can, according to Godina and coworkers[51], be represented by the following processes:

$$Ce_2O_3 \cdot n\,H_2O + Nb_2O_5 \cdot n\,H_2O \xrightarrow{850^\circ} CeNbO_4\ (\text{cub.}) + Nb_2O_5\ (T\text{-form}),$$
$$CeNbO_4 + Nb_2O_5 \xrightarrow{1000\text{–}1100^\circ} CeNb_3O_9.$$

Kiparisov and coworkers[50] think that the formation of europium metaniobate $EuNb_3O_9$ takes place by the reaction:

$$EuNb_5O_{14} \xrightarrow{1500^\circ} EuNb_3O_9 + Nb_2O_5.$$

The scheme of formation of dodecaniobates (for example, $Ce_2Nb_{12}O_{33}$) postulates the formation of the intermediate phases $CeNbO_4$ and $CeNb_3O_9$.[51]

The kinetics of interaction of $Sc_2O_3$ and $Y_2O_3$ with $Nb_2O_5$ have been studied[32,35], also those of $Y_2O_3$, $Sm_2O_3$, $Eu_2O_3$, and $Gd_2O_3$ with $Ta_2O_5$.[35,62] The activation energy is 48.3 kcal mole$^{-1}$ for the formation of $ScNbO_4$,[32] 56.8 kcal mole$^{-1}$ for $YNbO_4$,[35] and 42.3 kcal mole$^{-1}$ for $YTaO_4$.[35]

As noted above, the solid-phase synthesis can be carried out over a rather wide range of temperatures, which allows the various polymorphic configurations of the niobates and tantalates to be investigated[53,71]. However, the ceramic method has significant drawbacks, which reduce the effectiveness and make it unpromising in practice. These drawbacks are: (a) the heterogeneity of the product; (b) the purity of the product being inadequate; (c) the low stoichiometry of the components; (d) the comparatively high synthesis temperatures. The duration of the process is also characteristic of this method, several days sometimes being required for homogeneity to be attained and the reaction to be complete; higher synthesis temperatures lead to the high energy capacity of the method.

## 2. COPRECIPITATION OF THE COMPONENTS FROM SOLUTIONS

The precipitation of the components from solutions can be brought about by mixing aqueous solutions of the niobates $KNbO_3$, $K_3NbO_4$, and $K_8Nb_6O_{19}$ or tantalates $K_8Ta_6O_{19}$ with solutions of tervalent metal salts. In addition, a version of the preparation in which hydroxides are precipitated by the action of ammonia on a mixture of a solution of $NbCl_5$ ($TaCl_5$) and a salt of the metal, the compound of which is being made. $(NH_4)_2CO_3$ can also be used as precipitant. In both instances the precipitate was heated to the crystallisation temperature of the corresponding niobate or tantalate.

Soluble orthoniobates were used as starting materials for obtaining the orthoniobates $AlNbO_4$,[20] $InNbO_4$,[25] $YNbO_4$,[42] and $ScNbO_4$.[43] Aluminium[20,29,30] and indium[25] aquometaniobates have been made by this method.

The mechanism of the precipitation of Al, In, Y, and Sc ortho- and meta-niobates when aqueous solutions of the corresponding potassium niobates and salts of the metals being precipitated are mixed has been studied[20,25,42,43]. Orthoniobates of these metals are precipitated on reaching the ratio A : Nb = 1 : 1, which corresponds to pH 6–7. Metaniobates are precipitated when the ratio in the solution is A : Nb = 1 : 3.

Clearly, this version of the coprecipitation method requires the preliminary preparation of water-soluble niobates and tantalates, which somewhat reduces its effectiveness. A second version of the preparation, which uses the coprecipitation of the components in the form of hydroxides is evidently more effective, since it can be used for making the niobates and tantalates of any composition and it employs readily available reagents.

R.e.e. orthoniobates[36] and the tantalates $Tl_4Ta_6O_{21}$ and $TlTa_3O_9$[27] were obtained by using aqueous solutions. Since aqueous solutions of niobium and tantalum are unstable, a method using precipitation of the components from non-aqueous solutions is receiving greater attention. Thus, in making lanthanide orthoniobates $LnNbO_4$ (La, Ce, Pr, Nd),[67,68] the metaniobates $LnNb_3O_9$ (La, Pr, Nd, Sm),[6,51] the niobates $Ln_3NbO_7$ (La, Pr, Nd)[54] and $Ln_2Nb_{12}O_{33}$ (La, Ce, Pr, Nd),[59] and also bismuth orthoniobate $BiNbO_4$,[93] coprecipitation of the niobium and tervalent element hydroxides was carried out from alcoholic solutions.

Despite the rather wide use of coprecipitation for making niobates and tantalates, the mechanism of the process itself has still been studied insufficiently. There appear to be two possibilities: one is linked with the high dispersion of the coprecipitated components, the other, with the formation of contact compounds between the solid phases being coprecipitated[106]. Whereas the heat treatment of the material formed in the first instance gives some reduction of the crystallisation temperature of the final products as compared with the ceramic method, in the second instance the formation of crystalline compounds takes place at an appreciably lower temperature than in the sintering of the oxides.

The mechanism of the formation of the compounds during coprecipitation has been studied for only certain examples[6,67,87,93]. Chemical interaction of the components has been observed in the coprecipitation of Nd and Nb from aqueous alcoholic solutions. The precipitate obtained contained up to 60% combined Nd. In this instance hydroxoniobates of the type

$$Ln[NbO_{3-x/2}(OH)_x]_3 \cdot nH_2O,$$

where $x = 0–6$, are probably formed. Analogous results were obtained in studies of the formation of Ce, Pr, Nd,[67] Sb,[87] and Bi[93] orthoniobates.

There have been considerably more papers on the chemical reaction of the coprecipitated hydroxides of niobium or tantalum and a tervalent element during heating. However, they relate mainly to the processes taking place with participation of r.e.e. hydroxides[51,54,59,65,73,74,77] and, as noted above, only two studies concern the reaction of coprecipitated niobium and antimony or bismuth hydroxides[87,93]. In all these investigations it was found that when coprecipitated hydroxides are heated niobates (or tantalates) are formed without the intermediate production of the free oxides[6,51,59,93]. Usually, the crystallisation temperature is 300–500 K below the synthesis temperature in ceramic technology. This reduction in the temperature of preparation of the compounds is a principal advantage of the method of coprecipitation of the components from solution.

The observed decrease in the temperature of formation of niobates and tantalates when the coprecipitation method is used is often explained by the Hedvall effect, that is, the increase in the activity of the components during the thermal decomposition (dehydration) of hydroxides or salts. However, on taking into account the fact of chemical interaction between the components even at the moment of precipitation, it is thought[6,93,106] that the formation of intermediate compounds of the hydroxoniobate type, which are converted into niobates at comparatively low temperatures can also be responsible for the reduction in the synthesis temperature. The absence of individual oxides during the heating of the coprecipitated components suggests the impossibility of relating the mechanism of formation of the niobates and tantalates to simple interaction of oxides of increased activity.

In conclusion, it must be mentioned that in addition to the decrease in the synthesis temperature the coprecipitation method allows products of high homogeneity to be obtained. The purity of the compounds prepared by this method is usually higher than the purity of the initial solutions. These advantages make the method irreplaceable in the need to obtain homogeneous, high-purity materials with well reproducible properties.

## 3. HYDROTHERMAL SYNTHESIS

Crystallisation from solution at elevated pressures and temperatures has been used as a method of preparation only for antimony[86,96] and bismuth[98] orthoniobates and orthotantalates of composition $ABO_4$. The crystallisation was carried out in batch autoclaves. The starting materials were $Sb_2O_3$, $Bi_2O_3$, $Nb_2O_5$, and $Ta_2O_5$. The main parameters of the crystallisation process are: temperature 500–650°C, temperature rise up the height of the autoclave 15–65 K, coefficient of filling 0.6–0.65. Sych and coworkers[87,93] started from polycrystalline $SbNbO_4$ and $BiNbO_4$ with the aim of increasing the yield of single crystals; the recrystallisation of $SbNbO_4$ and $BiNbO_4$ took place at 500–560°C and a temperature gradient of 1.0–2.5 K $cm^{-1}$ up the height of the autoclave.

## IV. CRYSTAL-CHEMISTRY OF NIOBATES AND TANTALATES OF TERVALENT ELEMENTS

The structures of tantalates and niobates of the same composition type are usually similar, but in certain instances they are not completely isostructural.

1. NIOBATES AND TANTALATES OF THE GROUP III *p*-ELEMENTS

Little is known about the crystal-chemistry of the aluminium, gallium, indium, and thallium niobates and tantalates. Only the $ANbO_4$ (A = Al, Ga, In), $InTaO_4$, and $ANb_{11}O_{29}$ have been investigated by X-ray diffraction. According to Pedersen[75], $AlNbO_4$ is monoclinic, space group $C2/m$. The number of formula units $AlNbO_4$ in the unit cell is $Z = 4$. The monoclinic lattice parameters are: $a = 12.13$, $b = 3.726$, $c = 6.46$ Å, $\beta = 107.2°$. However, Burdese and Lucco[76] state that $AlNbO_4$ is orthorhombic with $a = 6.17$, $b = 7.38$, $c = 8.4$ Å, $Z = 6$, $\rho_{expt} = 4.5$, $\rho_{X\text{-ray}} = 4.15$ g cm$^{-3}$.

Gallium orthoniobate $GaNbO_4$ is monoclinic[21,107] with $a = 15.22$, $b = 3.75$, $c = 8.07$ Å, $\beta = 141.5°$;[21] it does not undergo any polymorphic transformations up to the melting point (1480°C).[22]

The compounds $InNbO_4$ and $InTaO_4$ are isostructural and of the wolframite type[13,24], space group $P2/c$, $Z = 2$. The $InNbO_4$ monoclinic lattice parameters[13] are: $a = 4.843$, $b = 5.773$, $c = 5.140$ Å, $\beta = 91.140°$, $\rho_{expt} = 6.22$, $\rho_{X\text{-ray}} = 6.28$ g cm$^{-3}$.

The compounds $AlNb_{11}O_{29}$ and $GaNb_{11}O_{29}$ are monoclinic[15,16]. The lattice parameters of $GaNb_{11}O_{29}$ are[16]: $a = 15.35$, $b = 3.82$, $c = 20.91$ Å, $\beta = 113°26'$. Other investigators[16,21] have reported the existence also of an orthorhombic modification of $GaNb_{11}O_{29}$ with lattice parameters: $a = 28.67$, $b = 3.813$, $c = 20.58$ Å.

Table 5. Lattice parameters of the r.e.e. orthoniobates[13].

| Compound | *a*, Å | *b*, Å | *c*, Å | β | *Z* | $\rho_{expt}$, g cm$^{-3}$ | $\rho_{X\text{-ray}}$, g cm$^{-3}$ |
|---|---|---|---|---|---|---|---|
| $LaNbO_4$ | 5.565 | 11.528 | 5.201 | 94°40′ | 4 | 5.82 | 5.909 |
| $CeNbO_4$ | 5.539 | 11.415 | 5.165 | 94°33′ | 4 | 6.04 | 6.061 |
| $PrNbO_4$ | 5.499 | 11.342 | 5.137 | 94°34′ | 4 | 6.10 | 6.170 |
| $NdNbO_4$ | 5.468 | 11.282 | 5.144 | 94°32′ | 4 | 6.31 | 6.324 |
| $SmNbO_4$ | 5.417 | 11.166 | 5.117 | 94°40′ | 4 | 6.61 | 6.616 |
| $EuNbO_4$ | 5.393 | 11.133 | 5.113 | 94°35′ | 4 | 6.67 | 6.705 |
| $GdNbO_4$ | 5.371 | 11.090 | 5.107 | 94°37′ | 4 | 6.80 | 6.882 |
| $TbNbO_4$ | 5.349 | 11.036 | 5.085 | 94°33′ | 4 | 6.93 | 7.012 |
| $DyNbO_4$ | 5.320 | 11.000 | 5.074 | 94°34′ | 4 | 7.12 | 7.168 |
| $HoNbO_4$ | 5.298 | 10.957 | 5.068 | 94°29′ | 4 | 7.15 | 7.167 |
| $ErNbO_4$ | 5.280 | 10.914 | 5.064 | 94°29′ | 4 | 7.30 | 7.400 |
| $TmNbO_4$ | 5.262 | 10.876 | 5.049 | 94°31′ | 4 | 7.51 | 7.517 |
| $YbNbO_4$ | 5.237 | 10.842 | 5.043 | 94°47′ | 4 | 7.56 | 7.677 |
| $LuNbO_4$ | 5.293 | 10.043 | 5.065 | 94°32′ | 4 | 7.69 | 7.756 |
| $YNbO_4$ | 5.293 | 10.943 | 5.065 | 94°32′ | 4 | 5.53 | 5.583 |
| $ScNbO_4$ | 4.818 | 5.655 | 5.101 | 88°25′ | 2 | 4.76 | 4.817 |

2. NIOBATES AND TANTALATES OF THE GROUP III *d*- AND *f*-ELEMENTS

This section considers the structural features of the compounds $RBO_4$, $R_{1/3}BO_3$, $R_3BO_7$, and $RB_5O_{14}$. Information about the crystal-chemistry of the other niobates and tantalates is extremely limited or completely non-existent.

A. Orthoniobates and Orthotantalates of Composition $ABO_4$

The r.e.e. (with the exception of Sc) orthoniobates of composition $RNbO_4$ have a fergusonite structure at room temperature[13,50,53,108]. As Table 5 shows, as the ionic radius of the lanthanide in $LnNbO_4$ is reduced there is a regular decrease in the monoclinic lattice parameters, the parameters *a* and *c* falling linearly from La to Eu and from Gd to Lu, with a pronounced break at $EuNbO_4$ (Fig. 4). The lattice parameters of $YNbO_4$ do not fit into this regularity. It seems that the dimensions of the $RNbO_4$ unit cell are affected not only by the ionic radius of the cation but also by the fraction of the covalent bond A–O, which decreases appreciably on going from Sc to Y and La.

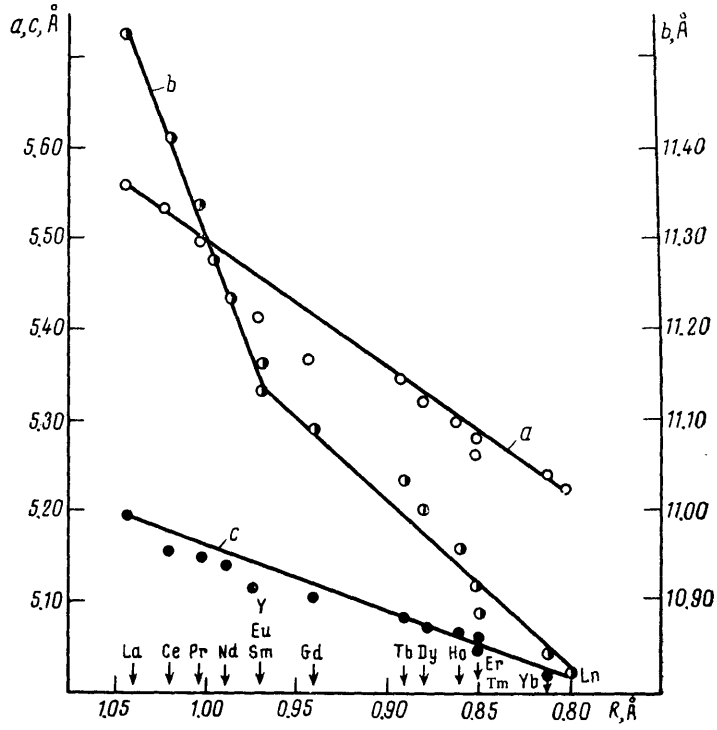



Figure 4. Variation of the lattice parameters of the r.e.e. orthoniobates[13] with the radius of the r.e.e. ion[116].

The orthotantalates $LnTaO_4$, where Ln = Nd–Lu, and $YTaO_4$ also crystallise in a monoclinic lattice of the fergusonite type[13,109,110] (Table 6). As for the orthoniobates, there is a linear increase in the size of the monoclinic cells of the $LnTaO_4$ as the ionic radius of the lanthanide is increased.

The $ABO_4$ crystal structure of fergusonite type is a distorted scheelite structure[45,111]. The Nb (or Ta) atoms are situated within several distorted tetrahedra of oxygen atoms. The r.e.e. atoms have coordination number 8 and are also surrounded by oxygen atoms[45,108,111]. All 16 oxygen atoms in the $LnNbO_4$ unit cell ($Z = 4$) occupy positions with general symmetry ($C_1$) and the Ln and Nb atoms are situated at points with site symmetry $C_2$.

It has been reported[112] that the X-ray diffraction pattern of $YTaO_4$ can be indexed in a basocentric monoclinic unit cell with $a = 6.978$, $b = 10.930$, $c = 5.323$ Å, $\beta = 133°50'$. Probable space group: $C2/c$ or $Cc$.

B. Isomorphism of the Compounds $ABO_4$ with Fergusonite Structure

When compounds of the $RNbO_4$ (R = Y, Ln) or $RTaO_4$ (R = Y, Nd–Lu) type are heated their monoclinic cell is converted into a tetragonal one (scheelite structure)[45,53]. The transformation is reversible, takes place in stages, has a "shear" nature[45], and is accompanied by a gradual change in the lattice parameters, which is accelerated close to the transformation temperature[109]. During such a transformation the parameters $a$ and $c$ of the monoclinic cell become equal to the parameter $a$ of the tetragonal, and the parameter $b$ of the monoclinic cell is changed to the parameter $c$ of the tetragonal cell[53].

Table 6. Lattice parameters of the r.e.e. orthotantalates.

| Compound | $a$, Å | $b$, Å | $c$, Å | β | $Z$ | $\rho_{expt}$, g cm$^{-3}$ | $\rho_{X\text{-ray}}$, g cm$^{-3}$ |
|---|---|---|---|---|---|---|---|
| $LaTaO_4$ [13] | 7.651 | 5.577 | 7.823 | 101°31′ | — | — | — |
| $NdTaO_4$ [13] | 5.514 | 11.237 | 5.114 | 95°42′ | 4 | 8.12 | 8.199 |
| $SmTaO_4$ [13] | 5.455 | 11.137 | 5.091 | 95°44′ | 4 | 8.47 | 8.548 |
| $EuTaO_4$ [13] | 5.428 | 11.103 | 5.087 | 95°44′ | 4 | 8.60 | 8.644 |
| $GdTaO_4$ [13] | 5.405 | 11.063 | 5.084 | 95°35′ | 4 | 8.76 | 8.830 |
| $TbTaO_4$ [13] | 5.382 | 11.022 | 5.068 | 95°40′ | 4 | 8.82 | 8.967 |
| $DyTaO_4$ [13] | 5.354 | 10.974 | 5.061 | 95°43′ | 4 | 8.97 | 9.147 |
| $HoTaO_4$ [13] | 5.329 | 10.935 | 5.056 | 95°32′ | 4 | 9.25 | 9.284 |
| $ErTaO_4$ [13] | 5.306 | 10.893 | 5.042 | 95°44′ | 4 | 9.27 | 9.443 |
| $TmTaO_4$ [86] | 5.053 | 10.82 | 5.243 | 95°11′ | 4 | — | — |
| $YbTaO_4$ [82] | 5.035 | 10.82 | 5.23 | 84°22′ | 4 | — | — |
| $LuTaO_4$ [82] | 5.03 | 10.78 | 5.25 | 84°22′ | 4 | — | — |
| $YTaO_4$ [13] | 5.239 | 10.893 | 5.056 | 95°31′ | 4 | 7.56 | 7.592 |
| $ScTaO_4$ [13] | 4.809 | 5.670 | 5.118 | 88°20′ | 4 | 6.84 | 6.802 |

The temperature of the transformation into the scheelite structure for the orthoniobates is 500–800°C. Usually the temperature for the appearance of the tetragonal phase increases with decrease in the atomic radius of the r.e.e., that is, in the order La–Lu. It is significantly higher for the tantalates than for the niobates[109]. A high-temperature form has not been observed for the Tm, Yb, and Lu tantalates[109].

During the growing of single crystals of the r.e.e. orthoniobates and orthotantalates the formation of a third polymorphic modification of the $ABO_4$ compounds was observed[113,114]. The monoclinic lattice parameters (example, $YTaO_4$)[114] are: $a = 5.292$; $b = 5.451$, $c = 5.110$ Å, $\beta = 96.44°$, $Z = 2$. In the structure of this modification of $YTaO_4$ the Ta atoms are at the centre of a distorted $TaO_4$ tetrahedron (Ta–O distance = 1.94–2.03 Å) and the Y atoms are at the centre of a distorted cube (Y–O distance = 2.25–2.42 Å).

C. The Orthotantalates $LnTaO_4$ (Ln = La, Ce, Pr)

The La, Ce, and Pr orthotantalates are not isostructural with the corresponding orthoniobates. $LaTaO_4$ is monoclinic, space group $P2_1/c$.[115] The Ta atoms are situated close to the centres of distorted octahedra, and the Ta–O distance varies within the limits 1.91–2.05 Å (mean distance 2.00 Å). The octahedra are linked at the vertices and form an infinite (in two-dimensions) corrugated layer. Each octahedron has four vertices in common with four neighbouring octahedra, the layers being separated from those similar in configuration to them by layers of La atoms, which have eightfold coordination, the eight La–O distances lying within the range 2.40–2.84 Å.[115] Fig. 5 shows a fragment of the $LaTaO_4$ structure.

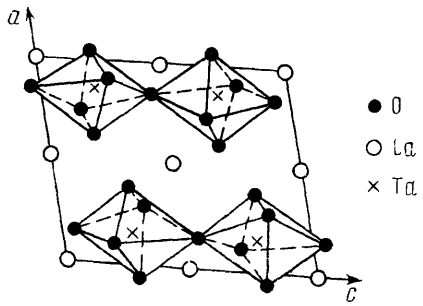



Figure 5. Fragment of the $LaTaO_4$ structure projected on [010].

Scandium orthoniobate and orthotantalate are monoclinic[53] (Tables 5 and 6). Their structure shows greater similarity with the wolframite structure[32,53] than with the fergusonite structure, which seems to be due to the appreciable difference between the size of the $Sc^{3+}$ ion and those of the other r.e.e. ions.

D. R.e.e. Metaniobates and Metatantalates

All the r.e.e. metaniobates and metatantalates have a perovskite $ABO_3$ structure[40,55,110,117] and their formulae are usually written as $R_{1/3}BO_3$. Whereas the metatantalates $R_{1/3}TaO_3$ are known for almost all the r.e.e., metaniobates have been obtained only for La, Ce, Pr, Nd, and Eu.

The lanthanide metaniobates are orthorhombic; the La, Ce, Gd, Dy, Ho, Eu, and Y metatantalates are tetragonal; Pr, Nd, and Tb metatantalates are orthorhombic, and Yb metatantalate is monoclinic (Table 7). The lattice parameters and unit-cell volume[40,55] of the metaniobates $Ln_{1/3}NbO_3$ and metatantalates $R_{1/3}TaO_3$ fall regularly with increase in the atomic number of the lanthanide.

Since the metaniobates with perovskite structure are known only for the metals of the cerium subgroup, the very existence of compounds of composition $A_{1/3}BO_3$ depends in a definite manner on the size of the r.e.e. cation. As Table 8 shows, metaniobates with the perovskite structure can exist at Goldschmidt stability factors $\leqslant 0.9$. Therefore the metaniobates of Fe, Cr, Sc, and other 3*d*- or *p*-metals with perovskite structure can hardly be obtained. Nevertheless the hitherto unknown $Bi_{1/3}TaO_3$ should be stable. The lower limit of the stability factor for the metatantalates of composition $A_{1/3}TaO_3$ should be somewhat lower than for the niobates and seems to be 0.83–0.84.

The structure for the metaniobates and metatantalates of composition $R_{1/3}BO_3$ has been determined for $La_{1/3}NbO_3$ [55] and $La_{1/3}TaO_3$, [55,117] and also $Y_{1/3}TaO_3$. [117] All the compounds have a perovskite structure, $P4/mmm$. [55,117] However, unlike the ideal structure of perovskite, for the compounds $A_{1/3}BO_3$ only one-third of the sites in the A sublattice can be occupied and the remaining two-thirds of the sites remain vacant.

Table 7. Lattice parameters of the metaniobates and metatantalates $A_{1/3}BO_3$.

| Compound | Symmetry | Lattice parameters | | | | |
|---|---|---|---|---|---|---|
| | | *a*, Å | *b*, Å | *c*, Å | *V*, Å³ | *Z* |
| $La_{1/3}NbO_3$ [55] | o-rh. | 3.911 | 3,917 | 7.908 | 121.2 | 2 |
| $Ce_{1/3}NbO_3$ [55] | o-rh. | 3.901 | 3.917 | 7.886 | 120.5 | 2 |
| $Pr_{1/3}NbO_3$ [55] | o-rh. | 3.891 | 3.915 | 7.862 | 119.8 | 2 |
| $Nd_{1/3}NbO_3$ [55] | o-rh. | 3.878 | 3.907 | 7.840 | 118.8 | 2 |
| $Eu_{1/3}NbO_3$ [50] | o-rh. | 3.624 | 3.806 | 7.90 | 108.9 | 2 |
| $La_{1/3}TaO_3$ [55] | tetr. | 3.918 | — | 7.913 | 121.5 | 2 |
| $Ce_{1/3}TaO_3$ [55] | tetr. | 3.915 | — | 7.878 | 120.7 | 2 |
| $Pr_{1/3}TaO_3$ [55] | o-rh. | 3.845 | 3.910 | 7.836 | 119.3 | 2 |
| $Nd_{1/3}TaO_3$ [55] | o-rh. | 3.876 | 3.916 | 7.829 | 118.8 | 2 |
| $Sm_{1/3}TaO_3$ [55] | o-rh. | 3.882 | 3.896 | 7.785 | 117.7 | 2 |
| $Eu_{1/3}TaO_3$ [110] | o-rh. | 3.843 | 3.854 | 7.915 | 117.0 | 2 |
| $Gd_{1/3}TaO_3$ [55] | tetr. | 3.874 | — | 7.795 | 117.0 | 2 |
| $Tb_{1/3}TaO_3$ [110] | o-rh. | 3.861 | 3.865 | 7.807 | 116.7 | 2 |
| $Dy_{1/3}TaO_3$ [55] | tetr. | 3.847 | — | 7.769 | 115.0 | 2 |
| $Ho_{1/3}TaO_3$ [55] | tetr. | 3.841 | — | 7.756 | 114.0 | 2 |
| $Er_{1/3}TaO_3$ [55] | tetr. | 3.825 | — | 7.754 | 113.5 | 2 |
| $Yb_{1/3}TaO_3$ [40*] | mon. | 3.793 | 3.805 | 7.708 | 111.2 | 2 |
| $Y_{1/3}TaO_3$ [55] | tetr. | 3.824 | — | 7.758 | 113.5 | 2 |

* $\beta = 91.6°$

An increase in the lattice parameter along the *c* axis by a factor of two in comparison with the initial perovskite cell is characteristic for all the compounds. This doubling is due to the alternation of the empty layers with the layers two-thirds filled with atoms A. The atoms A are distributed statistically in two-thirds filled cubo-octahedra. The sometimes suggested [118] doubling of the lattice parameters also along axes *a* and *b*, which for the composition $Ln_{1/3}NbO_3$ requires $Z = 8$, can hardly be correct.

The niobium and tantalum atoms are surrounded by six oxygen atoms, which are situated at the vertices of an almost regular $NbO_6$ (or $TaO_6$) octahedron. The structure and interatomic distances for $Ln_{1/3}NbO_3$ are given in Fig. 6. Clearly the distance Nb–O (or Ta–O) in the r.e.e. metaniobates and metatantalates differs from the B–O distance in the ideal perovskite. This is due to some displacement of the Nb (Ta) atom along the *c* axis. Similar structural features are characteristic for ferroelectrics of the oxygen-octahedral type, for example, $BaTiO_3$, $KNbO_3$, etc. [119]

## E. Niobates and Tantalates of Composition $A_3BO_7$

The niobates of composition $A_3BO_7$ belong to three structural groups, depending upon the nature of the r.e.e. and the temperature. The La, Nd, and Sm niobates, which form the first group, are orthorhombic, weberite structure type [38], space group $Pncm$. [120,121] $Eu_3NbO_7$ and $Gd_3NbO_7$, which belong to the second structural group, are monoclinic, space group $P2/m$. [122] All the niobates $R_3NbO_7$ (R = Dy–Lu, Y, Sc) of the third group are cubic, fluorite type [120–122]—according to other investigators [38], pyrochlore type.

Table 8. Relation between the ionic radius and stability factor for certain niobates of composition $A_{1/3}NbO_3$ with a perovskite structure.

| Element A | Ionic radius, $r_A$, Å | Stability factor, *t* | Compound |
|---|---|---|---|
| La | 1.04 | 0.924 | $La_{1/3}NbO_3$ [40,55] |
| Nd | 0.99 | 0.907 | $Nd_{1/3}NbO_3$ [40,45] |
| Sm | 0.97 | 0.900 | unknown |
| Eu | 0,97 | 0.900 | $Eu_{1/3}NbO_3$ [50] |
| Gd | 0,94 | 0.888 | unknown |
| Lu | 0,80 | 0.835 | unknown |
| Y | 0,97 | 0.900 | unknown |
| Sc | 0.83 | 0.844 | unknown |
| Bi | 1,20 | 0.988 | unknown |
| Sb | 0,90 | 0.874 | $Sb(NbO_3)_3$ structure $PbNb_2O_6$ [90] |
| Fe | 0.67 | 0.785 | unknown |
| Al | 0,57 | 0.744 | unknown |
| Ga | 0,62 | 0.765 | unknown |
| In | 0.92 | 0.883 | unknown |

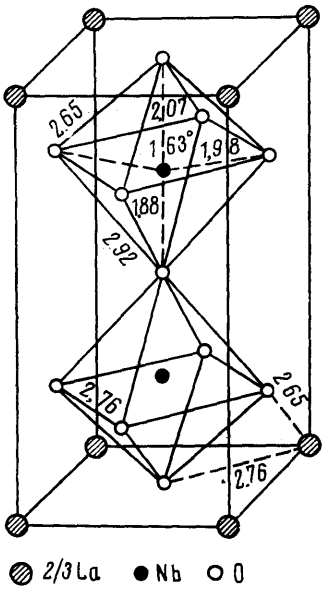



**Figure 6.** Unit cell of $La_{1/3}NbO_3$. [55]

Table 9 gives the lattice parameters of the compounds $R_3NbO_7$. With increase in the atomic radius of the r.e.e. the fluorite lattice parameter increases. The niobates $Ln_3NbO_7$ of the first and second groups undergo polymorphic transformations above 1300°C with change to a stable fluorite cubic structure [121,122] (Table 9).

The tantalates of composition $R_3TaO_7$ (where R = La, Nd, Sm, Gd, Dy, Y, and Sc) are cubic[38]. However, Rooksby and White[38] could not find any difference between the disordered fluorite structure and the ordered pyrochlore structure. According to Romashov and coworkers[110] the $R_3TaO_7$ (R varies from Sm to Lu and Y) have a pyrochlore structure. The lattice parameters change regularly along the lanthanide series.

**Table 9.** Lattice parameters of certain niobates and tantalates $R_3BO_7$.

| Compound | Symmetry | Lattice parameters | | | | Structure type* | Polymorphic transformation |
|---|---|---|---|---|---|---|---|
| | | a, Å | b, Å | c, Å | β | | |
| $La_3NbO_7$ [38] | o-rh. | 7.84 | 10.86 | 7.70 | — | | W $\xrightarrow{1300°}$ F[122] |
| $Nd_3NbO_7$ [38] | o-rh. | 7.66 | 10.98 | 7.70 | — | W | W $\xrightarrow{1300°}$ F[122] |
| $Sm_3NbO_7$ [123] | o-rh. | 7.56 | 10.81 | 7.59 | — | W | W→P2/m→F[122] |
| $Eu_3NbO_7$ [121] | mon. | 10.672 | 10.679 | 10.666 | 90°25′ | — | P2/m $\xrightarrow{1300°}$ F[121] |
| $Gd_3NbO_7$ [38] | cub. | 5.32 (F); 10.64 (P) | — | — | — | F,P | P2/m→F[121] |
| $Dy_3NbO_7$ [38] | cub. | 5.26 (F); 10.53 (P) | — | — | — | F,P | — |
| $Lu_3NbO_7$ [120] | cub. | 5.33 | — | — | — | F | — |
| $Y_3NbO_7$ [38] | cub. | 5.24 (F); 10.49 (P) | — | — | — | F,P | — |
| $Sc_3NbO_7$ | cub. | 4.88 (F); 9.99 (P) | — | — | — | F,P | — |
| $La_3TaO_7$ [38] | o-rh. | 7.84 | 10.87 | 7.70 | — | W | — |
| $Nb_3TaO_7$ [38] | o-rh. | 7.66 | 10.98 | 7.52 | — | W | — |
| $Sm_3TaO_7$ [38] | cub. | 5.36 (F); 10.75 (P) | — | — | — | F,P | — |
| $Gd_3TaO_7$ [38] | cub. | 5.32 (F); 10.64 (P) | — | — | — | F,P | — |
| $Dy_3TaO_7$ [38] | cub. | 5,26 (F); 10,58 (P) | — | — | — | F,P | — |
| $HoTaO_7$ [110] | cub. | 10.45 | — | — | — | P | — |
| $Er_3TaO_7$ [110] | cub. | 10,50 | — | — | — | P | — |
| $Tm_3TaO_7$ [110] | cub. | 10.33 | — | — | — | P | — |
| $Lu_3TaO_7$ [110] | cub. | 10.33 | — | — | — | P | — |
| $Y_3TaO_7$ [38] | cub. | 5.24 (F); 10,49 (P) | — | — | — | F,P | — |
| $Sc_3TaO_7$ [38] | cub. | 4.88 (F); 9,66 (P) | — | — | — | F,P | — |

*W = weberite; F = fluorite; P = pyrochlore.

## F. Niobates and Tantalates of Composition $LnB_5O_{14}$

According to Badiot[58] the pentaniobates $LnNb_5O_{14}$ (Ln = La, Ce, Pr, and Nd) are orthorhombic, the lattice parameters for $LaNb_5O_{14}$ being: $a = 20.12$, $b = 12.42$, $c = 7.74$ Å, $Z = 8$, space group $C_{2V}^9$. The tantalates $RTa_5O_{14}$ (R = La, Ce, Nd, Pr, Sm, Dy, Tm, and Y) have an orthorhombic basocentric lattice, corresponding to a distorted $ReO_3$ structure[124]. The lattice parameters for $LaTa_5O_{14}$ are: $a = 17.56$, $b = 16.98$, $c = 3.851$ Å. According to Ferguson[111], $LaTa_5O_{14}$ is not isostructural with $LaNb_5O_{14}$, despite Iyer and Smith's claim[55].

## 3. CRYSTAL-CHEMISTRY OF THE ANTIMONY AND BISMUTH NIOBATES AND TANTALATES

According to Roth and Waring[84] compounds of composition $ABO_4$ (A = Sb or Bi; B = Nb or Ta) at room temperature are isostructural and have the same structure as the natural mineral cervatite $SbSbO_4$,[91] stibiocolumbite (Sb, Bi)(Nb, Ta)$O_6$, or bismutotantalite (Bi, Sb)(Ta, Nb)$O_4$.[125]

Table 10 gives the orthorhombic lattice parameters. X-ray diffraction investigation of $SbTaO_4$ [13,91] and $SbNbO_4$,[13,85] as examples, indicated the space group of the $ABO_4$: $Pna2_1 = C_{2V}^9$, $Z = 4$. The $SbTaO_4$ structure is shown in Fig. 7. It is characteristic of an octahedral environment for the atoms Nb and Ta. The atoms Sb and Bi also have a coordination number of 6. Fig. 8 gives the bond lengths in the $SbNbO_4$ structure[85]. The $NbO_6$ and $TaO_6$ octahedra form toothed chains. The monolayers of $BO_6$ octahedra are separate in the $z$ direction. The ions A occupy the vacancies between the $BO_6$ octahedra.

**Table 10.** Lattice parameters of antimony and bismuth orthotantalates and orthoniobates[84].

| Compound | a, Å | b, Å | c, Å | Z | $\rho_{expt}$, g cm$^{-3}$ | $\rho_{X\text{-ray}}$, g cm$^{-3}$ |
|---|---|---|---|---|---|---|
| $SbNbO_4$ | 4.929 | 11.797 | 5.559 | 4 | 5.75[87] | 5.79 |
| $BiNbO_4$ | 4.980 | 11.709 | 5.675 | 4 | 7.37[93] | 7,34 |
| $SbTaO_4$ | 4,911 | 11.814 | 5.535 | 4 | 7,57[147] | 7.65 |
| $BiTaO_4$ | 4.957 | 11,763 | 5.633 | 4 | 9.26[147] | 9,22 |

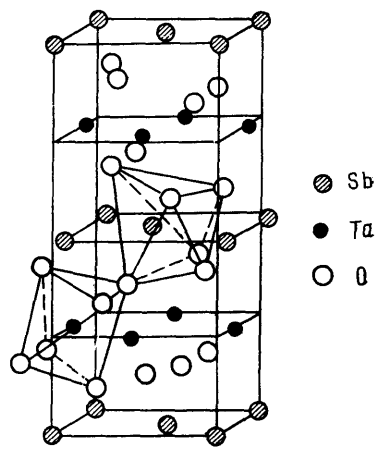



**Figure 7.** Structure of antimony orthotantalate $SbTaO_4$.[91]

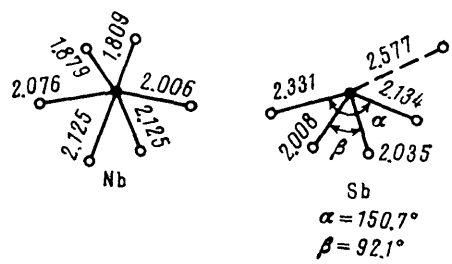



**Figure 8.** Lengths of the Nb–O and Sb–O bonds and valence angles in the $SbNbO_4$ structure[85].

According to Popolitov and coworkers[98] the orthorhombic single crystals of $BiNbO_4$ and $BiTaO_4$ prepared under hydrothermal conditions have the centrosymmetric space group $D_{2h}^6 = Pnna$.

In addition to the orthorhombic modification $\alpha$-$ABO_4$ a high-temperature modification $\beta$-$ABO_4$ is characteristic

for bismuth orthoniobate and orthotantalate. The triclinic high-temperature modification for $BiNbO_4$ and $BiTaO_4$ was first obtained by heating mixtures of $Bi_2O_3$ and $Nb_2O_5$ [or $Ta_2O_5$ (Ed. of Translation)] in air at 1100–1200°C.[88] $\alpha$-$BiNbO_4$ and $\alpha$-$BiTaO_4$ are irreversibly converted into the triclinic $\beta$-modification when heated to 1020° and 900°C respectively[84,89].

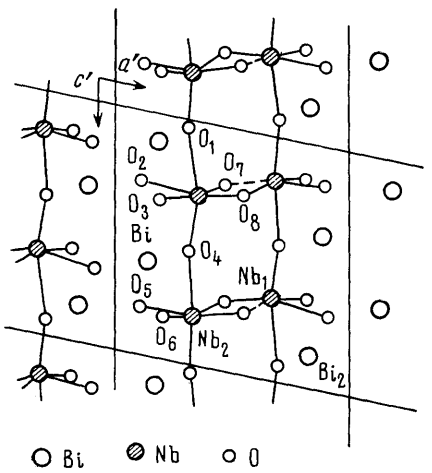



Figure 9. Projection of the $\beta$-$BiNbO_4$ structure on [010].[126]

The lattice parameters of the triclinic $\beta$-$BiBO_4$ are[88]:

| | a, Å | b, Å | c, Å | α | β | γ |
|---|---|---|---|---|---|---|
| $\beta$-$BiNbO_4$ | 7.61 | 5.53 | 7.91 | 83.99° | 74.43° | 82.15° |
| $\beta$-$BiTaO_4$ | 7.62 | 5.58 | 7.77 | 89.92° | 77.12° | 96.45° |

The space group of $\beta$-$BiNbO_4$ is[126]: $P1$, $Z = 4$.

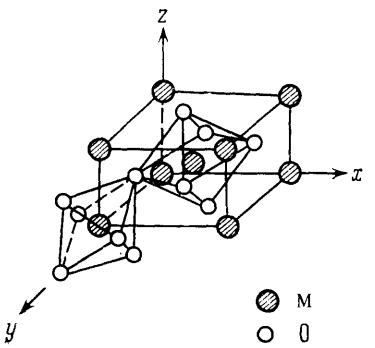



Figure 10. Rutile structure for compounds of the $ABO_4$ type (A = Ti, V, Cr, or Fe).

The structure of $\beta$-$BiNbO_4$ [126,127] (Fig. 9) consists of corrugated lattices constructed from $NbO_6$ octahedra parallel to the plane $oc$. Each octahedron is connected by vertices with four other octahedra. The $NbO_6$ lattices are maintained by Bi atoms. The Bi atoms have a coordination number of eight. The Bi polyhedron is a distorted tetragonal antiprism. The Bi–O distance is in the range 2.105–3.017 and the Nb–O distance in the range 1.803–2.313 Å.

$SbNb_3O_9$ is orthorhombic with lattice parameters $a$ = 17.635, $b$ = 3.968, $c$ = 17.219 Å. The structure is analogous with the ferroelectric $PbNb_2O_6$, $Z = 10$.[90] The compound $Bi_3Nb_{17}O_{47}$ has the structure of a tungsten "bronze".[37,128] The orthorhombic lattice parameters are: $a$ = 12.516, $b$ = 37.14, $c$ = 3.922 Å, $Z = 2$. Space group $Pba2$. Some of the niobium atoms have coordination number 7. The coordination polyhedron is a pentagonal bipyramid. The remaining 8 niobium atoms are arranged in octahedra. The Nb–O distance is 1.48–2.46 Å.[92]

## 4. CRYSTAL-CHEMISTRY OF THE *d*-ELEMENT NIOBATES AND TANTALATES

### Compounds of Composition $ABO_4$ (A = Ti, V, Cr, Fe)

The orthoniobates and orthotantalates of composition $ABO_4$ crystallise according to rutile type[13,18,129]. The $TiO_2$ rutile structure is tetragonal, space group $D_{2h}^{14}$ [$D_{4h}^{14}$? (Ed. of Translation)]. The number of formula units for $TiO_2$ is $Z = 2$; that for $ABO_4$ is $Z = 1$. The lattice parameters of the compounds of composition $ABO_4$ are $a$ = 4.6, $c$ = 3.0 Å (Table 11). Fig. 10 shows the $ABO_4$ structure. Atoms A and B are arranged randomly in the cell of the double oxide[13,129] and have coordination number 6, occupying identical positions.

Table 11. Lattice parameters of the *d*-element orthoniobates and orthotantalates with a rutile structure.

| Compound | a, Å | c, Å | $\rho_{X\text{-ray}}$, g cm$^{-3}$ | $\rho_{expt}$, g cm$^{-3}$ |
|---|---|---|---|---|
| $TiNbO_4$ [13] | 4.712 | 2.996 | 5.100 | 5.01 |
| $VNbO_4$ [13] | 4.681 | 3.033 | 5.194 | 5.13 |
| $CrNbO_4$ [18] | 4.635 | 3.005 | — | — |
| $FeNbO_4$ [18] | 4.68 | 3.05 | — | — |
| $TiTaO_4$ [129] | 4.645 | 3.020 | — | — |
| $VTaO_4$ [129] | 4.667 | 3.047 | — | — |
| $CrTaO_4$ [129] | 4.638 | 3.018 | — | — |
| $FeTaO_4$ [129] | 4.679 | 3.047 | — | — |
| $TiO_2$ [130] | 4.594 | 2.959 | — | — |

For iron orthoniobate $FeNbO_4$, in addition to the tetragonal form mentioned there are another two polymorphic modifications—monoclinic and orthorhombic[131]. Roth and Waring[132] think that the low-temperature modification, stable up to 1085°C, is monoclinic, space group $P2_1/a$. The lattice parameters are $a$ = 5.001, $b$ = 5.620, $c$ = 4.653 Å, $\beta$ = 90°16′. The orthorhombic phase ($a$ = 5.005, $b$ = 5.613, $c$ = 4.647 Å) is stable from 1085° to 1380°C. The rutile modification exists from 1380°C up to the melting point (~ 1475°C).[132] Conversion of the low-temperature rutile modification into the high-temperature orthorhombic modification, with wolframite structure, is observed for iron orthotantalate $FeTaO_4$. The lattice parameters are $a$ = 4.63, $b$ = 5.64, $c$ = 5.04 Å.[133]

The above crystallographic results show that the niobates and tantalates of tervalent elements form two structural groups: with tetrahedral and octahedral environment of the Nb or Ta. Tetrahedral coordination is encountered only in the orthoniobates and orthotantalates $ABO_4$. However, even for this composition it is not the only possibility. Isolated $BO_4^{3-}$ tetrahedra exist only in the r.e.e. orthoniobates and (in part) orthotantalates (except for La, Ce, and Pr) with the fergusonite structure, which has many features in common with the scheelite structure. The remaining tervalent metal niobates and tantalates for which structural results have been published are compounds of octahedral type.

A comparison of the available results shows that the change from tetrahedral to octahedral configuration even in the series of $ABO_4$ compounds is not determined by the increase in the ionic radius of the r.e.e. This transformation is usually due to the change in the nature of the A–O bond and the competition of the A atoms with the Nb(Ta) atoms for possession by the oxide ligands.

The niobates and tantalates of tervalent metals with an octahedral configuration crystallise according to the $LaTaO_4$ type, perovskite, cervantite, or rutile. In all these structures the $BO_6$ octahedra are usually connected by their vertices with the formation of two-dimensional or three-dimensional skeletons, unlike the fergusonite structure with isolated $BO_4^{3-}$ tetrahedra.

Table 12. Interplanar spacings (Å) in niobates and tantalates with octahedral coordination.

| Structure type | $(B-O)_{min}$ | | $(B-O)_{max}$ | | $(B-O)_{av}$ | |
|---|---|---|---|---|---|---|
| | Nb–O | Ta–O | Nb–O | Ta–O | Nb–O | Ta–O |
| $LnTaO_4$ | — | 1.91 | — | 2.05 | — | 2.00 |
| Perovskite ($La_{1/3}BO_3$) | 1.88 | 1.90 | 2.07 | 2.06 | 1.98 | 1.98 |
| Cervantite ($SbBO_4$) | 1.81 | 2.06 | 2.07 | 2.09 | 2.00 | 2.09 |
| Rutile ($ATaO_4$) | — | 1.95 | — | 2.04 | — | 2.00 |
| Mean value (B–O) | 1.85 | 1.95 | 2.07 | 2.07 | 1.99 | 2.01 |

The B–O interatomic distances in the compounds of octahedral type according to the available information are given in Table 12. A regular dependence of the B–O distances on the nature of the metal A is not observed. The Ta–O distance is somewhat greater than the Nb–O distance. The mean interatomic B–O distances in the octahedral compounds (2.00 Å) is greater than the mean B–O distance in the tetrahedral compounds (1.77–1.78 Å for scheelite). Distortion of the octahedron is observed in all the compounds of octahedral type, the shortest bond always being *trans* to the longest B–O bond (cf. Figs. 6 and 8). This fact can be due to the displacement of the Nb (Ta) atom from the centre of the octahedron along one of the fourth-order axes. These structural features are known to facilitate the production of a spontaneously polarised state in tantalates, niobates and molybdates of a series of *s*- and *p*-elements.

## V. PROPERTIES OF NIOBATES AND TANTALATES OF TERVALENT METALS

### 1. PHYSICOCHEMICAL PROPERTIES

The information about the chemical stability and solubility of the niobates and tantalates of tervalent metals is disconnected. However, the available information suggests that all the compounds considered have high chemical stability. Both the niobates and tantalates are almost insoluble in water. For example, when the r.e.e. tantalates were treated with boiling water for 10 h there was no change in the structure of the compound, and r.e.e. ions could not be detected in the water[63].

The niobates and tantalates do not react with dilute HCl, $HNO_3$, $HClO_4$, $H_3PO_4$ or solutions of alkalis. However, when heated with concentrated acids or alkalis they are partly decomposed, and in hot $H_2SO_4$ some of the niobates and tantalates[63] can decompose completely. They also dissolve in hydrofluoric acid.

Niobates and tantalates are also highly resistant towards solutions of organic acids, and to many molten salts and metals. The niobates and tantalates are stable also towards moderate heating. Thus the r.e.e. (except Eu) orthoniobates are not reduced in an atmosphere of hydrogen at 1100–1200°C.[134] Under the same conditions $EuNbO_4$ is reduced to the metaniobate with perovskite structure ($a$ = 3.95 Å)[134].

### 2. MELTING POINTS

Tables 13 and 14 give the melting points of the niobates and tantalates of some tervalent metals. As might be expected, the tantalates melt at a higher temperature than the corresponding niobates.

Table 13. Melting points of certain niobates of tervalent metals, °C.

| Element A | $ANbO_4$ | $A_{1/3}NbO_3$ | $A_3NbO_7$ | Other compounds |
|---|---|---|---|---|
| Al | 1560[12] | — | — | — |
| Ga | 1450[22] | — | — | — |
| In | 1740[22] | — | — | — |
| Sc | 1950[32] | — | — | — |
| Y | 2000[77] | — | — | — |
| La | 1620[48] | 1460[48] | 1760[48] | $La_2Nb_{12}O_{33}$—1330[59] |
| Ce | 1660[48] | 1480[48] | 1790[48] | $Ce_2Nb_{12}O_{33}$—1350[59] |
| Pr | 1720[48] | 1550[48] | 1800[48] | — |
| Sb | 1160[87] | — | — | — |
| Bi | 1245[59] | — | — | — |

Another obvious regularity is observed for the r.e.e. niobates and tantalates. With increase in the molar ratio A : B in the compounds, that is, in the series $AB_3O_9$–$ABO_4$–$A_3BO_7$, the melting points of the compounds of a single element A increase (Tables 13 and 14). The compounds of composition $A_3BO_7$, which contain the greatest possible proportion of tervalent metal, have the highest melting point. A tendency towards an increase in the melting points of the compounds in the series La–Lu is not observed. The melting points for all types of compound undergo a jump at gadolinium and they reach a maximum for the La–Lu series.

## 3. ELECTROPHYSICAL PROPERTIES

As noted above, in most of the niobates and tantalates the $NbO_6$ (or $TaO_6$) octahedra are usually distorted owing to the displacement of the B atoms from the centres of the octahedra. This is characteristic of many ferroelectrics, for example, $KNbO_3$, $KTaO_3$, $PbNb_2O_6$, the antiferroelectric $NaNbO_3$, the piezoelectrics $Sr_xBa_{1-x}Nb_2O_6$, and other commercially important niobates and tantalates[119].

**Table 14.** Melting points of certain r.e.e. tantalates[63], °C.

| Element A | $ATaO_4$ | $A_{1/3}TaO_3$ | $A_3TaO_7$ | Element A | $ATaO_4$ | $A_{1/3}TaO_3$ | $A_3TaO_7$ |
|---|---|---|---|---|---|---|---|
| Y | 2100 | 1920 | 2380 | Tb | 1980 | 1820 | 2230 |
| La | 1860 | 1780 | 1960 | Dy | 2030 | 1820 | 2270 |
| Ce | 1890 | — | — | Ho | 2010 | 1835 | 2270 |
| Pr | 1845 | 1750 | 1990 | Er | 2010 | 1810 | 2360 |
| Nd | 1825 | 1820 | 1980 | Tm | 1990 | 1770 | 2260 |
| Sm | 1930 | 1810 | 2050 | Yb | 2030 | 1780 | 2360 |
| Eu | 1830 | 1805 | 2000 | Lu | 1980 | 1760 | 2340 |
| Gd | 2050 | 1840 | 2280 | | | | |

### A. Al, Ga, and In Niobates and Tantalates

Manakov and coworkers[135] were the first to study the dielectric properties of the $Al_2O_3$–$Nb_2O_5$ system. Ionic conductivity was observed for the entire composition region. As the temperature is raised (100–1600°C) in the $Al_2O_3$–$Nb_2O_5$ system the curve of electrical conductivity $\sigma$ against temperature shows an inflection characteristic of ionic conduction, and this inflection corresponds to the melting point[135].

The curves showing the temperature dependence of $\epsilon$ and $\sigma$ for the $Al_2O_3$–$Nb_2O_5$ and $Ga_2O_3$–$Nb_2O_5$ systems have anomalies characteristic of ferroelectric materials close to the Curie point. The most pronounced maximum on the curve of $\epsilon$ against temperature is observed at the composition $Al_2O_3 : Nb_2O_5 = 1 : 5$. However, the absence of a hysteresis loop did not confirm the hypothesis of ferroelectric properties for these materials[31,107]. The dielectric properties of ceramic specimens of $AlNbO_4$ and $GaNbO_4$ have also been studied[20,136]. The variation of $\epsilon$ and tan $\delta$ with the temperature for all the specimens agrees with the temperature dependence of electrical conductivity. It is therefore thought[20] that the inflections on the above curves are due to relaxation processes.

Anomalies in the dielectric properties have not been observed for Al and Ga tantalates[31]. Their dielectric constant is much less than for the corresponding niobates in the temperature range up to 350°C.

### B. Niobates and Tantalates of Scandium Subgroup Elements

(1) Orthoniobates of composition $RNbO_4$. The electrical properties of compounds of the type $ABO_4$ have been studied only for $YNbO_4$,[9,42] $NdNbO_4$,[6,137] $GdNbO_4$,[137] and $HoNbO_4$,[9] and for $LaNbO_4$, $YbNbO_4$, $YTaO_4$, and $YbTaO_4$.[8] These r.e.e. orthoniobates are antiferroelectrics with a rather high Curie temperature (500–830°C)[8,9]. The Curie temperature is inversely proportional to the radius of cation A and lies in the range 500–730°C for $ABO_4$, where A = Y, La, Yb.[8]

The dielectric constant and slope of the dielectric loss vary slightly up to 160°C.[42] When the temperature is raised further there is an increase in $\epsilon$ and tan $\delta$;[8,137] the curves have a characteristic inflection at the Curie point (Fig. 11). The reciprocal of the dielectric constant $1/\epsilon$ is a linear function of temperature, which agrees with the Curie law[137]. The electrical conductivities $\sigma$ of the $LnNbO_4$ (Ln = Nd, Gd) also increase with the temperature[6,137]. Above 130°C for $NdNbO_4$ and 230°C for $GdNbO_4$ lg $\sigma$ varies linearly with $1/T$.[137] The $NdNbO_4$ and $GdNbO_4$ exhibit *n* type conduction.[137]

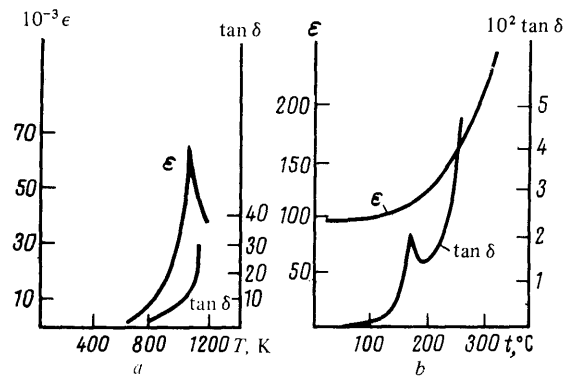



**Figure 11.** Variation of the dielectric constant $\epsilon$ and slope of the dielectric loss tan $\delta$ with temperature: *a*) $NdNbO_4$;[137] *b*) $Nd_{1/3}NbO_3$.[138]

(2) Metaniobates of composition $Ln_{1/3}NbO_3$. The niobium compounds of oxygen-octahedral type of composition $MNbO_3$ (M = K or Na) with perovskite structure usually exhibit ferroelectric or antiferroelectric properties[119]. This very feature is responsible for the more detailed study of the dielectric properties of the r.e.e. metaniobates.[6,7,133,138].

On the curves for the temperature dependence of $\epsilon$ and tan $\delta$ for $Ln_{1/3}NbO_3$ there are distinct inflections[31,138] which allow them to be associated with a phase transformation (Fig. 11). However, neither the shape nor the size of these maxima are characteristic of ferroelectrics[138] but seem to be characteristic of relaxation[6,138]. The latter is explained by the ordered alternation of filled layers and vacancies in the A sublattice[138].

The electrical conductivity $\sigma$ of the r.e.e. metaniobates is similar, as regards absolute value and temperature dependence, to that for the orthoniobates[6]. All the metaniobates exhibit an ability to accumulate a large residual charge[6,7]. The existence of residual charges capable of being retained for a long time (up to 1–5 years) and the reversal of the sign of the charge shows the $Ln_{1/3}NbO_3$ to possess electret properties, this being connected with the residual polarisation of the specimens. The residual charge of the r.e.e. metaniobates[6] (Table 15) usually exceeds that for the other known ceramic electrets, for example, those based on titanates[139], consequently materials based on r.e.e. metaniobates are interesting not only as electrets but also as low-power sources of current.

C. Antimony and Bismuth Niobates and Tantalates

The detailed study of the dielectric properties of the antimony and bismuth orthoniobates and orthotantalates of composition $ABO_4$ with cervantite structure began after the discovery in 1970 that the natural mineral stibiotantalite $(Sb,Bi)(Ta,Nb)O_4$ exhibits ferroelectric properties[5,140]. Later on, ferroelectric properties were also observed in synthetic specimens of $SbNbO_4$ [87,96,97] and $SbTaO_4$.[95,96] Phase transformations, the nature of which is still disputed, are shown clearly on the curves of $\epsilon$ and $\tan\delta$ against temperature (Fig. 12). Some investigators[86,87,97] identify the phase transformation at 410°C with the Curie temperature, that is, with a change from a spontaneously polarised state into a pyroelectric phase. These results agree with the Curie temperature of $T_C = 410°C$ for the natural mineral stibiotantalite[5].

Table 15. Residual charge of certain ceramic electrets.

| Composition | $\epsilon$ | $P$, C cm$^{-2}$ | Composition | $\epsilon$ | $P$, C cm$^{-2}$ |
|---|---|---|---|---|---|
| $La_{1/3}NbO_3$ | 200 | $(4.5-8)\cdot10^{-4}$ | $MgTiO_3$ | 15 | $1.3\cdot10^{-7}$ |
| $Pr_{1/3}NbO_3$ | 70 | $(3-5)\cdot10^{-5}$ | $CaTiO_3$ | 150 | $1.0\cdot10^{-7}$ |
| $Nd_{1/3}NbO_3$ | 50 | $(1-2.5)\cdot10^{-5}$ | | | |

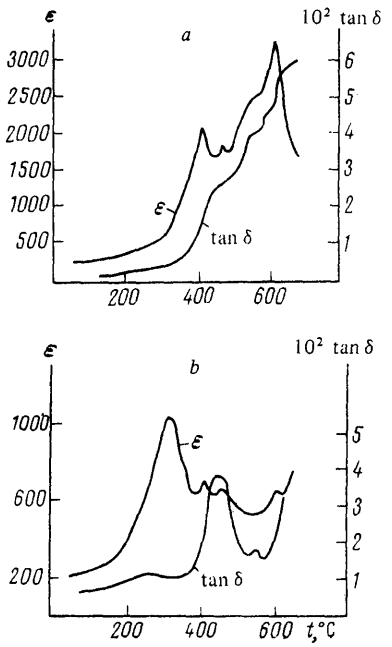



**Figure 12.** Variation of the dielectric constant $\epsilon$ and of the slope of the dielectric loss $\tan\delta$ with temperature[96]: *a*) $SbNbO_4$; *b*) $SbTaO_4$.

Combined studies of single-crystalline ceramic specimens of $ABO_4$ showed[94,96,98] that the Curie point lies at temperatures higher than thought earlier, namely $T_C = 600°C$ for $SbNbO_4$, 605°C for $SbTaO_4$. Below the Curie point they have an antiferromagnetic phase, but Ivanova and coworkers[96] think that ferroelectric properties appear at 400–410°C. The compounds $BiNbO_4$ and $BiTaO_4$ are antiferroelectrics with $T_C = 570°C$.[98]

The existence of a spontaneously-polarised state in the compounds $ABO_4$ agrees with the appearance of pyro- and piezo-electric properties. The hydrostatic piezo-modulus $d_h$ at room temperature is $8\times10^6$ cgse units for $SbNbO_4$. The combination of this $d_h$ with low dielectric constant shows the high piezoelectric sensitivity of $SbNbO_4$ in relation to omnidirectional pressure[86].

In addition, the high resistance to heat and moisture, the chemical inertness, and the mechanical strength of the antimony and bismuth niobates and tantalates will facilitate their wide use in various branches of technology.

D. Niobates and Tantalates of the 3*d*-Metals

Among the niobates and tantalates of the 3*d*-metals, the dielectric properties of the Ti, V, Cr, and Fe orthotantalates[141] and orthoniobates[142] have been studied.

The temperature dependence of the electrical conductivity of $ATaO_4$ [141,143,144] and $FeNbO_4$ [145] has been investigated. All the compounds exhibit electron conductivity. An insignificant fraction of an ionic component appears only at 1000°C. The temperature dependence of the conductivity of the $ATaO_4$ is of a semiconductor nature[144].

It has also been shown that the $ANbO_4$ (where A is Ti, V, Cr, or Fe) are semiconductors with a narrow forbidden gap[142]. The mechanism for the establishment of electrical conductivity and its nature have been discussed from the standpoint of ideas about the formation of the chemical bond in the $ATaO_4$.[141,143] Study of the temperature dependence of the dielectric constant $\epsilon$ has shown that $TiTaO_4$, $VTaO_4$, $CrTaO_4$, and $FeTaO_4$ are ferroelectrics[141,146].

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# New Advances in Catalysis by Ion-exchange Resins

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Current research on the general problems, methods and theory of catalysis by ion-exchange resins as well as new advances in its application in hydrolytic, hydration, and dehydration reactions, the synthesis of esters, alkylation, polymerisation, isomerisation, and condensation are surveyed.
The bibliography includes 276 references.

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This review is a continuation and logical development of previous publications by one of the authors[1,2], which appeared in 1962 and 1970. Reviews on the applications of ion-exchange resins as catalysts of various organic reactions[3-5] and narrowly specialist review articles on hydration[6], condensation[7,8], and esterification[9] reactions were published somewhat later; the literature references cover publications mainly after 1970. This review surveys the literature on catalysis by ion-exchange resins up to February 1976.

## I. GENERAL PROBLEMS OF CATALYSIS BY ION-EXCHANGE RESINS

The catalytic functions of ion-exchange resins and other similar substances reduce to the formation of reactive intermediate complexes either by the addition of the mobile ions (counterions) of the polymers to the molecules of one of the reactants or by the protonation of the electron-donating atoms of the active groups. Since there is no ion exchange either at this or subsequent reaction stages up to the formation of the final product, it is desirable to replace the established term "ion-exchange catalysis"[2,10] by "catalysis by ion-exchangers"[11].

Recent development of catalysis by ion exchangers in the stage under consideration, which includes the period 1969–1975, has led to numerous confirmations of their advantages as catalysts for chemical reactions involving organic substances over soluble acids and bases, which have been used for a long time in acid–base catalysis.

The simplicity of separation of the ion exchangers from the reaction products opens new effective pathways to the solution of the global problem — the protection of nature from chemical pollution by eliminating or greatly reducing the amount of waste water and harmful gases produced in various branches of chemical industry manufacturing alkylphenols[12], phenols[13], epoxy-compounds[14], and other products. In many cases this advantage confers also additional benefits such as reduction of the risk of fire and explosion in the manufacturing process, the facilitation of continuous technological processes, the simplification of the use of heat-exchange apparatus, etc. Since cation and anion exchangers constitute different phases and are immiscible with the reaction mass, the methods of catalysis by ion-exchangers makes it possible to carry out in a single stage reactions proceeding via a cationic or anionic mechanism, for example the synthesis of aminoaldehyde resin and its esterification by butanol[15]. It is noteworthy, that, as a result of the application of ion exchangers, new advances have been made in the synthesis of aminoresins with a high purity and their practical properties have been thereby improved.

In very many cases ion exchangers surpass soluble acids and bases as regards the specificity of catalytic action and this leads to a decrease in the amount of reactants wasted on side processes and improves the yield of the desired product (for example in the esterification of propylene glycol by stearic acid[16] and in the decomposition of isopropylphenyl hydroperoxides[13,17]).

Naturally, the specificity of ion exchangers as catalysts of organic reactions must not be overestimated. As an illustration, we may quote a number of reactions of different types where at least one, and sometimes a whole series, of side products are formed together with the main product. Such reactions include the thiolysis of 1,3-dioxepan by ethanethiol[18], the alkylation of cresol by indene[19], as well as numerous condensation reactions catalysed by cation exchangers (those of bicyclopentadiene[20], 4-vinylcyclohexene[21], and $\alpha$-methylstyrene[22] with formaldehyde and of methylallyl alcohol with phenol[23]) or anion exchangers (the condensation of n-butylraldehyde with formaldehyde[24]). One of the main problems of catalysis by ion exchangers is the reduction to a minimum of side reactions and the possible acceleration of the main reaction, which is achieved by the selection of the optimum ion exchanger, solvent, molar reactant ratio, and experimental temperature.

Ion exchangers are milder catalysts than soluble acids and bases, which makes it possible to prevent undesirable reactions, for example the opening of the epoxide ring on epoxidation[14] and permits the extremely delicate synthesis of fructose-1,6-diphosphate by the condensation of triosephosphates[25], which was previously achieved only by enzymatic catalysis. This feature of the catalytic action of ion exchangers will undoubtedly find many further useful applications in biochemical and fine organic syntheses.

However, one should note that such reactions catalysed by the protons of soluble acids are either not accelerated by the so called standard or gel ion exchangers or give rise to the useful products in insignificant yields. Even a brief list of such reactions, including the interaction of

acetic acid with benzyl alcohol[26], the reaction of dodecyl alcohol with sorbic acid[27] (which hardly occurs in the presence of the usual KU-2 × 8 cation-exchange resin), the reaction of t-butyl hydroperoxide with aliphatic acids[28], and the reaction of benzene with propene[29], shows that the negative result is due to steric causes, namely the inability of the large molecules of the reactants or products to penetrate the resin micropores and enter or leave the gel phase.

In very many instances, these difficulties can be overcome by means of ion exchangers with an artificially created heterogeneity, usually synthesised from macroporous styrene–divinylbenzene copolymers. Such ion exchangers have been particularly effective as catalysts of reactions in non-solvating non-aqueous media: in the absence of swelling of high-molecular-weight polyelectrolytes, the access of the reactant molecules to the active groups is assured by the large internal surface area.

Table 1 lists the most important properties of typical porous sulphonated cation exchangers synthesised from the copolymers of styrene with different amounts of divinylbenzene.

**Table 1.** Certain properties of porous sulphonated cation-exchange resins[30] with different contents of divinylbenzene (DVB).

| DVB, % | 10 | 15 | 25 | 50 | 70 |
|---|---|---|---|---|---|
| Volume capacity, mequiv. $g^{-1}$ | 5.34 | 5.28 | 3.43 | 2.68 | 2.22 |
| Specific surface, $m^2 g^{-1}$ | 0.1 | 43.0 | 77.5 | 263.2 | 266.3 |
| True density, g $cm^{-3}$ | 1.44 | 1.43 | 1.40 | 1.33 | 1.31 |
| Apparent density, g $cm^{-3}$ | 1.38 | 0.96 | 0.86 | 0.49 | 0.48 |
| Total porosity, ml $ml^{-1}$ | 0.04 | 0.329 | 0.386 | 0.632 | 0.634 |
| Average pore radius, Å | — | 148 | 147 | 101 | 77 |
| Calculated pore wall thickness, Å | — | 110 | 89 | 26 | 19 |

The most striking feature noted when the data in Table 1 are inspected is the enormous specific surface of cation exchangers containing ≥ 15% of divinylbenzene and the considerable differences between the true and apparent densities, indicating the porous nature of the ion-exchange copolymers investigated. The average pore radius in the cation-exchange resin synthesised varies in the range 77–148 Å. Depending on the conditions of synthesis of the copolymers and ion exchangers, the pores can be larger or smaller (see pp. 54 and 55 in Polyanskii's monograph[11]), but in most instances their equivalent radius amounts to hundreds of angstroms. According to Dubinin's classification[31], such sorbents should be regarded as mesoporous, but the term "macroporous ion exchangers" has become firmly established in the literature on ion exchange; to avoid confusion, this term will be used henceforth in the present text. We may point out for comparison that gel ion exchangers contain cavities with molecular dimensions, varying in the range from 8 to 20 Å for the SBS cation-exchange resin and from 7 to 13 Å for the KU-2 cation-exchange resins with different degrees of cross linking (see p. 55 in Polyanskii's monograph[11]).

A study of the polymerisation of dimethylcyclosiloxanes has shown[32] that the catalytic activity of macroporous ion exchangers can be predicted on the basis of the overall porosity of the resins, which can be determined by simpler methods than the specific surface or pore radius. In the above reaction, the maximum catalytic activity was shown by sulphonic acid cation-exchange resins with an overall porosity of 0.8 $cm^3 g^{-1}$, a specific surface not less than 60–70 $m^2$, and a pore radius not greater than 300 Å. Naturally, these characteristics are not of general significance, but depend on the chemical structure of the reactants and products. It is also clear that the optimum ion exchanger should have a fairly high porosity and not unduly small pores; for macroporous ion-exchange polymers, these conditions are usually fulfilled in the presence of 20–30% of divinylbenzene (DVB). Ion exchangers with this degree of cross linking retain their porosity after many repeated swelling and drying operations and do not lose it as a result of conversion from one ionic form to another either. On the other hand, cation exchangers with 10% DVB lose their porosity entirely and become gel resins when they are kept in water or another solvating liquid[30]. Such changes can have a decisive influence on the catalytic properties of ion exchangers.

When macroporous ion exchangers began to be used, it was possible to achieve reactions which did not occur in the presence of gel resins[27,29], to accelerate other reactions with reduction or elimination of the induction period[33], and in certain cases to raise the yield of the desired product[13]. At the same time, reactions have also been described (alkylation of phenol by isobutyl alcohol) in which the macroporous cation exchanger employed did not have kinetic or other advantages over gel resins[34]. In aqueous or mixed media, the reactions can actually take place faster in the presence of gel cation exchangers (for example the inversion of sucrose[35] or the hydrolysis of esters[36]) if the molecules of the reacting substances do not penetrate into the pore walls of macroporous ion-exchange polymers, which have a dense three-dimensional network in the presence of a high DVB content, but do penetrate into the gel phase of cation exchangers with moderate degree of cross linking. Some authors[37] do not recommend at all the use of macroporous resins for the acceleration of the Prins reaction, since these ion exchangers sorb the reaction mass with cracking of the grains, which hinders both the repeated use of the catalyst and the filtration of the reaction mass through the latter. However, one should note that this conclusion cannot be regarded as general, since the authors[37] tested only one cation-exchanger specimen and did not determine its porosity. There is no doubt that the porometric characteristics of the ion exchangers influence not only their catalytic activity but also the effects due to the blocking of the active centres by the components of the reaction mixture (see pp. 505 and 506 in Polyanskii's review[2]) on which the stability of the operation of the catalyst depends.

Both macroporous and gel ion exchangers have been used not only in hydrogen- or hydroxide-forms, but also in salt-forms, functioning as Lewis acids or bases. These catalysts are as a rule more thermostable[38,39] and in some cases surpass cation exchangers in the H-forms and anion exchangers in the OH-forms as regards the specificity of their action. The use of carboxylic cation exchangers in the Zn-forms in the condensation of urea with formaldehyde[40] and of the Zn-forms of sulphonic acid cation exchangers in the alkylation of phenol[41] has been described. A gel sulphopolystyrene resin in the Fe-form has been used as the catalyst of the conversion of *para*-hydrogen[42] and the macroporous Amberlyst 15 cation exchanger, containing $Na^+$ counterions and those of *d* (or *f*) elements, proved to be an effective catalyst of the isomerisation of but-1-ene[43]. The activity and stereo-selectivity of the catalyst depend on the electronegativity of the counterions, i.e. on their strength as Lewis acids.

Metallised cation exchangers, obtained by the reduction of the corresponding ionic forms to the free metal, have been tested as substitutes for certain catalysts used in heterogeneous catalysis[44,45]. This interesting field undoubtedly requires further development. There are no data on the use of metallised anion exchangers, but the salt-forms of these polyelectrolytes have been used successfully in a few cases. In this connection mention should be made of the use of $Cu^{2+}$ or $Co^{2+}$ complexes with bifunctional anion exchangers as catalysts of the reaction of 2- or 4-vinylalkylpyridines with amines to form N-substituted aminoethylalkylpyridines[46,47] and also of the employment of a strongly basic anion exchanger in the chloroplatinate-form in a very interesting reaction involving the hydrosilylation of alkenes, alkynes, and unsaturated acid esters[48].

Together with the modification of ion exchangers with the aim of imparting catalytic functions to them, investigators have resorted to different procedures for the promotion or stabilisation of catalysts. It has been shown[49] that treatment of the AV-17 anion-exchange resins with aqueous suspensions of calcium and magnesium oxides, forming complexes with hydroxy-compounds, accelerates the reaction between formaldehyde and ethyl methyl ketone, increasing thereby the yield of the main reaction product—3-hydroxymethylbutan-2-one. Another modification procedure, based on the esterification of the sulphogroups by mercaptoethanol, increases the stability of the Dowex-50 W cation-exchange resin and the duration of its operation without a significant decrease of activity[50].

The problems of the stability of catalysts in the course of their operation and the causes and prevention of the changes in catalytic properties as well as regeneration procedures constitute a set of inter-related problems. It has been shown[51] that their solution is possible only by a joint consideration of the thermal stability of ion exchangers, in a broad sense of this term, and of their catalytic activity.

The first possible cause of the decrease of the catalytic activity of ion exchangers is the decrease of their exchange capacity owing to reactions involving the electrolytic or nucleophilic substitution of the active groups as a result of the interaction with the components of the reaction mixture, including the moisture present initially in the catalyst itself. This concerns the desulphonation of strongly acidic cation exchangers or the deamination of anion exchangers, which determine the position of the upper temperature limit of the prolonged use of ion-exchange resins: 150° and 300°C for sulphonated styrene–divinylbenzene copolymers in the hydrogen- and salt-forms respectively; 60–70° and 100–110° for highly basic anion exchangers in the OH- and salt-forms.

Under milder conditions, excluding desulphonation or deamination, the second cause of the decrease of catalytic activity operates—the blocking of the ion-exchange groups. This phenomenon is most typical in the presence of substances reacting with the active groups (for example, as a result of the esterification of the sulpho-group by alcohols[52]) and also on formation of polymeric or crystalline products of different types, shielding the counterions from interaction with the reactant molecules (for example, the blocking of cation exchangers in condensation[53,54], thiolysis[55], and alkylation[56] reactions and of anion exchangers in the hydrosilylation reaction[48]).

The third cause of the decrease of the activity and of the duration of the useful life of ion exchangers is the possible substitution of the $H^+$ and $OH^-$ counterions by other ions with formation of salt-forms which do not catalyse the reaction under the experimental conditions. The source of the substituting ions may be impurities in the reactants or the products of the corrosion of the reactor material. By passing the reactants through an ion-exchange column, the impurities are removed and the useful life of the catalyst is greatly increased[53].

The fourth cause of the decrease of the useful life of ion-exchanger catalysts is the limited osmotic stability of the latter, i.e. the disruption of their grains following changes in swellability in different media; the resulting fine particles offer a greater resistance to the flow of reactants and the process stops. For this reason, it was necessary to abandon the KU-2 cation-exchange resin as the catalyst of the condensation of mesityl oxide with methanol and preference had to be given to the less thermostable sulphophenolformaldehyde cation-exchange resin, the grains of which did not fragment; the mild reaction conditions (20–30°C) make this change feasible[57].

The changes in ion exchangers described above frequently influence the kinetics of the reactions which they catalyse (see Polyanskii[11], pp. 20 and 21 and Fig. 2, as well as the paper of Reikhsfel'd et al.[48]), are responsible for the decreased yield of the desired products and the enhanced formation of side products[58,59], and alter the selectivity of the catalytic action in reactions involving multicomponent mixtures of related substances and the composition of the reaction mass[60].

The intensity of the changes enumerated above, leading to a decrease of the useful life of the catalysts, depends on the nature of the ion exchanger, solvent, and reaction mixture, reaction temperature, the purity of the starting materials, and the corrosion resistance of the reactor material. In various syntheses, these parameters change over a wide range and it is therefore not surprising that investigators quote extremely different useful lives of resin catalysts. Without regeneration, catalysts of the KU-type in the H-form have been used in the synthesis of peracids (150 h),[14] in the dehydration of ethylene glycol to dioxan (200 h),[61] in the alkylation of *p*-cresol by isobutene (500 h),[62] and in the decomposition of isopropylphenyl hydroperoxide (1400 h).[17] The activity of the AV-17 anion-exchange resin in the chloroplatinate-form as the catalyst of the hydrosilylation of alkenes decreased sharply, owing to their partial polymerisation, after 20–30 h. However, when the polymers are periodically dissolved in hexane, the catalyst can be employed twenty times in the course of 180 h.[48]

The examples quoted show that an increase of the lifetime of the catalysts may be achieved only on the basis of a combined approach involving a comprehensive study of all the causes of the decrease of catalytic activity; the synthesis of new thermostable ion exchangers, on which investigators have been working persistently and not without success, constitutes only part of the general problem.

Despite the difficulties enumerated above, a considerable expansion of the fields of application of ion exchanger catalysis has occurred in the last few years. The synthesis of a wide variety of compounds is no longer its only field of application. The catalytic properties of ion exchangers are used to convert isomers with very similar properties into substances capable of subsequent separation by distillation[63], for the elimination of whole series of impurities from phenol[64], and for the selective extraction of isobutene from mixtures with n-butenes, which remain unchanged under the reaction conditions[12]. Ion exchanger catalysis is finding increasing applications in biochemical synthesis[65–67] and in analysis[68]. There is a continuous growth of interest in ion exchangers as catalysts in scientific disciplines related to chemistry.

## II. EXPERIMENTAL METHODS

Granulated ion exchangers are usually employed as catalysts, but in special cases, when the kinetic studies are performed to investigate the reaction mechanism and spectroscopic measurements have to be made, film or membranes are used[69,70]. The method of preparation of ion-exchange films has been described in a paper[70] and in a monograph[71].

Before use in catalysis, technical ion exchangers must be conditioned—the three-dimensional network has to be purified and conditioned in order to stabilise its structure. The best conditioning procedure is believed to involve the treatment of cation exchangers with 1–2 *N* NaCl or NaOH solutions, water, 1–2 *N* HCl solution, and again water, while anion exchangers are treated with 1–2 *N* NaCl or HCl solutions, 1–2 *N* NaOH solution, and again water. The treatment in the Na–H or Cl–OH exchange cycles lasts approximately 12 h in each case and is repeated three–four times. Cation and anion exchangers which are weak electrolytes are conditioned with NaOH or HCl respectively instead of NaCl, since otherwise the preparation of their salt-forms requires enormous volumes of reagents. There are almost no data concerning the influence of conditioning on the catalytic properties of ion exchangers, apart from a study[50] where it was noted that there is no change in sulphonated cation exchangers based on the styrene–divinylbenzene copolymer, used as catalysts of the condensation of phenol and acetone, after alternate treatment with NaOH and $HNO_3$ solutions. More extensive systematic studies are needed in order to reach final conclusions on this problem.

The elimination of low-molecular-weight organic impurities from ion exchangers is achieved by treatment with alcohols, benzene, an alcohol–benzene mixture, or acetone in Soxhlet apparatus. Methanol has been used successfully to regenerate the spent ion exchangers by removing polar blocking impurities[53] and a sulphonated cation exchanger of the polycondensation type, used as the catalyst of the hydration of isobutene, has been regenerated by treatment with concentrated sulphuric acid at 105°C for 2 h.[72]

Ion exchangers are converted into the required ionic form by passing through them a 1–2 M solution of the appropriate reagent (a strong acid, usually hydrochloric acid, in order to obtain cation exchangers in the H-form, alkali to produce anion exchangers in the OH-form, chlorides or other soluble salts in order to obtain salt-forms) until its concentration in the filtrate is constant, or preferably until the test for the displaced ion is negative. In the preparation of salt-forms of ion exchangers, one must bear in mind that hydrolysed ions may be absorbed from salt solutions. To avoid the displacement of the hydrolytic equilibrium in such cases and also in the preparation of any salt-forms of weakly acidic cation exchangers or weakly basic anion exchangers, they must be washed with 95% ethanol and not water. A high degree of substitution of counterions is sometimes achieved in the preparation of one salt-form from another and not from the H-form of the cation exchanger or the OH-form of the anion exchanger. Such a case has been described[73], the authors having used an anion exchanger in the tetrachloropalladate(II)-form as the catalyst of the hydrogenation of olefins and allyl alcohol[74]. A high degree of substitution of counterions can be achieved by displacing the equilibrium associated with the formation of a relatively undissociated compound. This principle has been used by Reikhsfel'd et al.,[48] who obtained the AV-17 anion-exchange resin with the $PtCl_6^{2-}$ counterion by passing an aqueous solution of $H_2PtCl_6$ through the resin in the OH-form. The mechanically sorbed acid was extracted with water by treating the hydrosilylation catalyst obtained in a Soxhlet apparatus.

Metallised cation exchangers have been obtained[75] from the macroporous Amberlyst 15 resin in the Na-form, through which aqueous solutions of $Pt(NH_3)_4Cl_2$, $Pd(NH_3)_4 \cdot Cl_2$, $NiCl_2$ in the presence of an excess of $NH_4OH$, or $AgNO_3$ in the presence of an excess of $NH_4OH$ were passed. The cation exchanger was then washed with water and alcohol, dried in air and then *in vacuo* at 107°C, and the ions reduced to the free metal in a stream of hydrogen or by treatment with an aqueous hydrazine solution which had been made alkaline; the resulting catalyst was used to accelerate the oxidation of ethanol under very mild conditions.

Ion exchangers designed to accelerate reactions in non-aqueous media are usually employed in the dehydrated state. In preparative studies, they normally are dried when the water in the ion exchanger can cause undesirable reactions of the components of the reaction mixture, for example the hydrolysis of esters in transesterification reactions[76]. In kinetic studies, it is necessary to bear in mind the influence of water on the rate of the catalysed reaction (see below) and one must therefore standardise rigorously the moisture content of the resin. In some cases, the nature of the reaction occurring depends on the resin moisture content (see p. 511 in Polyanskii's review[2]).

The behaviour of various cation and anion exchangers on drying by heat has been examined in detail[38,39]. The drying is carried out at atmospheric pressure in air, in a stream of hydrogen or helium, or *in vacuo*. Unfortunately, the recommended conditions are extremely varied even for ion exchangers of the same type and in most cases have been inadequately described and by no means always justified. In addition to the procedures described in the reviews quoted above, we shall list the most characteristic conditions used in the drying of sulphonated cation exchangers based on styrene–divinylbenzene copolymers and used as catalysts of various organic reactions: at 90°C and 14 mmHg;[77] at 90°C and $10^{-6}$ mmHg;[42] at 120°C[29,43] (residual pressure not indicated); at 120°C in a stream of helium dried at the temperature of liquid nitrogen[78] and having a partial water vapour pressure of $10^{-6}$ mmHg. Some workers use two-stage drying methods—initially at the usual pressure and then *in vacuo*. Thus the Zeocarb-225 cation-exchange resin is initially dried in a thermostat at 110°C for 48 h and then for 2 h at 150°C and a residual pressure of $10^{-2}$ mmHg. The additional weight loss in the second stage amounted to 10%.[79] The same cation exchanger has been dried[80] in a thermostat at 130°C (time not indicated) and in a vacuum of $10^{-2}$ mmHg at 120°C for 2 h. As in the previous case, the additional weight loss in the second stage amounted to 10%. Within the limits of the sensitivity of infrared spectroscopy, the cation exchanger dried under the above conditions in a stream of helium did not contain water. In the remaining cases, no data are quoted for the water content in the dried cation-exchange resins.

Some workers store the dried cation exchangers in a desiccator over $P_2O_5$ (sometimes in sealed tubes), while others proceed more correctly, drying the required amount of the cation exchanger directly before each experiment. It is noteworthy that, before introducing the sample into the reactor, it is desirable to test for soluble desulphonation products, which are formed during drying as a result of thermal hydrolysis or decomposition of the matrix[38]. For this purpose, it is sufficient to introduce approxi-

mately 200 mg of the resin into 5–10 ml of water, separate the liquid after stirring for 10 min, and titrate with 0.01 *N* hydrochloric acid using Methyl Orange; the amount of titrant used should not exceed 3–4 ml.

We believe that two-stage drying is the most effective and convenient method for routine work. Before drying *in vacuo*, it is desirable to separate the resin into fractions in order to isolate grains having a specified size and eliminate the fine particles, which increase the resistance of the resin to the flow of liquid.

It is desirable to fractionate the dehydrated resins by dry screening, which may be accelerated by means of a special apparatus[81] with an electric motor and an articulated transmission. A small amount of grains of similar size, suitable for accurate kinetic studies, can be obtained by using a Kapron [Russian nylon] brush to remove the grains caught in the mesh of each sieve. The authors of this review succeeded in obtaining by this procedure fairly homogeneous fractions of a carboxylic acid cation-exchange resin with grain sizes of 0.504 ± 0.021, 0.403 ± 0.016, and 0.262 ± 0.012 mm. In view of the possible inhomogeneity of the resins, the isolated fractions must be tested in terms of fundamental physicochemical properties.

Unfortunately, one should note that, even in modern studies on catalysis by ion exchangers, the catalysts employed are frequently not characterised in terms of their fundamental physicochemical parameters. Kinetic studies are thereby made almost completely valueless. The description of any ion exchanger used as the catalyst must include the characteristics of its thermal stability in the reaction mass, exchange capacity, and the coefficient of moisture absorption capacity. In kinetic studies on reactions occurring in the resin phase, it is also necessary to quote the partition coefficients of the reactant λ, to which the resin efficiency is related (see p. 505 in Polyanskii's review[2]). Methods for the determination of these parameters have been examined in Polyanskii's monograph[11] and in reviews[38,39]. In connection with recent studies, certain additional comments must be made concerning the partition coefficient.

According to Helfferich[82], this quantity is expressed in one of two ways:

$$\lambda' \equiv \bar{c}_i/c_i, \quad (1)$$

$$\lambda \equiv \bar{m}_i/m_i, \quad (2)$$

where $c$ and $m$ are respectively the molar and molal concentrations, $\bar{c}_i$ and $\bar{m}_i$ refer to the resin phase, $\bar{c}_i$ being expressed in terms of the number of moles of the given substance retained per unit volume of the swollen resin and $\bar{m}_i$ referring to the unit mass of the absorbed solvent. For reactions in aqueous solutions, $\bar{m}_i$ is found from the degree of sorption of the reacting substance by the resin and its water content. The concentrations of the substance in aqueous solution $c_i$ and $m_i$ have the corresponding significance.

It has been suggested[35] that the partition coefficient be defined as the ratio of the mass of the sorbate to the volume of the resin divided by the content of the same substance per unit volume of the solution. This definition is most convenient for the description of the partition of the reactants between resins and non-aqueous systems.

An approximate quantitative estimate of the partition coefficient is possible by means of the familiar relation

$$q = \lambda\bar{k}/k, \quad (3)$$

where $q$ is the relative efficiency (see p. 1046 in Polyanskii's review[1]) and $\bar{k}$ and $k$ are the rate constants for the reaction catalysed by ion exchangers and solutions of acids or bases respectively at the equivalent concentration of the catalyst ions. If $\bar{k} = k$, the efficiency of the resin may be inferred from the partition coefficient and conversely. Wolf[83], who suggested this principle, made the additional assumption that the active groups are present in the reaction volume (which was calculated from the exchange capacity and the weight of the resin sample) in the form of a 0.1 *N* solution. The efficiencies of three different Wofatits as catalysts of the hydrolysis of methyl acetate, ethyl acetate, and n-butyl acetate were calculated from the rate constants, measured in the presence of the resin and the equivalent amount of 0.1 *N* HCl, and are compared in Table 2 with the experimental partition coefficients of various substances which remain unchanged in the presence of Brønsted acids.

Table 2. The efficiencies of cation-exchange resins as catalysts of the hydrolysis of methyl acetate ($q$) and ethyl acetate ($q'$) at 20°C and their comparison with the partition coefficients λ between ion-exchange resins and 2% solutions of certain organic substances[83].

| System | $q$ | $q'$ | $\lambda$ ($C_6H_5OH$) | $\lambda$ ($CH_3COOH$) | $\lambda$ ($C_6H_6OH$) | $\lambda$ (n-$C_3H_7OH$) | $\lambda$ (n-$C_4H_9OH$) |
|---|---|---|---|---|---|---|---|
| Wofatit | 1.90 | 2.12 | 5.0 | 2.2 | 1.9 | 2.0 | 2.5 |
| Wofatit P | 2.44 | 3.17 | 19.6 | 4.3 | 2.2 | 2.2 | 3.0 |
| Wofatit KPS × 8 KPS×8 | 1.31 | 1.48 | 3.3 | 1.2 | 1.5 | 1.5 | 1.3 |

Table 2 shows that there is an approximate correspondence between the resin efficiency and the partition coefficient of an indifferent substance with the same number of carbon atoms as in the ester whose hydrolysis is investigated. Similar relations have been observed in the hydrolysis of esters catalysed by macroporous ion exchangers[84]. It has been shown[84] that the partition coefficients of alcohols and ketones are almost independent of the overall porosity, but decrease rapidly with increase of the divinylbenzene content in the cation exchanger. Data concerning the effect of the degree of cross linking on the partition coefficient of 1-butanol and benzoic acid between their mixtures and the Dowex-50 W gel cation-exchange resin have been published[85].

In studies of vapour-phase processes, it is necessary to measure the sorption of vapours by ion exchangers. This problem is solved by means of the classical sorption technique based on the use of the McBain balance[86] and its modifications[30]. With macroporous resins, these methods yield the overall sorption due to adsorption and capillary condensation in the mesopores, the macropores remaining unfilled under these conditions.

On the other hand, in contact with non-solvating organic liquids, open pores of any size are completely filled, which has been used by one of the present authors and Gorbunov to determine the overall porosities of macroporous ion exchangers[87]. For this purpose, 200–300 mg of the resin dried at 120°C for 8 h was placed in a dry test tube and covered with anhydrous solvents. After 2 h, the pores were completely filled, after which the samples were transferred quantitatively to dry weighed polyethylene test tubes with holes in the bottom, closed by lids, and centrifuged: for 1 min at 130*g* in the case of n-heptane and iso-octane, and for 5 min at 1200*g* in the presence of other more viscous and less volatile liquids, for example

n-decane. The test tubes were then reweighed and the weight increment was divided by the density of the corresponding liquid at the experimental temperature and by the weight of the initial sample of the dry resin, the overall porosity being calculated in $cm^3$ per gram of the sorbent. The method described provides a simple experimental solution of the problem of the determination of porosity and yields more accurate results than the densimetric methods usually employed for this purpose[88]. As stated above, the overall porosity is an important characteristic of the catalytic properties of macroporous ion exchangers and must therefore be determined in kinetic studies.

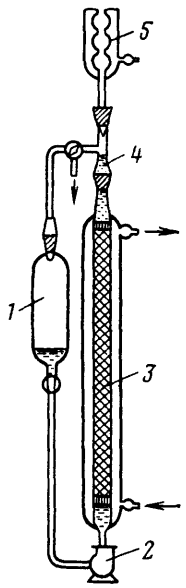



**Figure 1.** Apparatus for a catalytic process[32]: 1) collector; 2) metering micropump; 3) catalytic column; 4) packing; 5) reflux condenser.

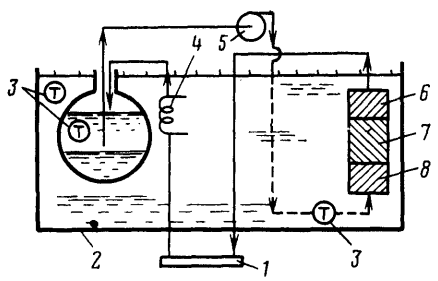



**Figure 2.** Reactor with circulation[35]: 1) polarimeter; 2) thermostat; 3) control devices; 4) heater; 5) pump; 6) glass beads or a weakly basic anion-exchange resin; 7) catalyst; 8) glass beads or a weakly acidic cation-exchange resin.

The reactions in the presence of ion exchanger catalysts are carried out in glass or metallic tubes (see pp. 81 and 82 in Polyanskii's monograph[11]), in reactors with mechanical[89] or pneumatic[90] stirring, and in various columns through which a stream of the test liquid is passed. In order to accelerate the reactions and the displacement of the equilibrium, one of the products, usually water, is removed, by separating its azeotrope with a suitable component of the reaction mixture[89] or a specially added indifferent solvent[91], for example toluene. The condensed reaction mixture is separated in a Dean–Stark trap, the organic layer being returned to the reactor. On the other hand, if the products must be separated by fractionation, the chemical reaction is carried out in an apparatus of the fractionating column type, which is filled above and below with glass packing and the resin is placed in the intervening gap. Chebotarev et al.[92] successfully carried out the hydrolysis of butyl butyrate on apparatus of this type using as the catalyst a sulphonated cation exchanger combined with a thermoplastic material and moulded in the shape of Raschig rings. Some investigators[93] recommend that a mixture of the resin and glass beads be introduced into the column in order to improve heat exchange.

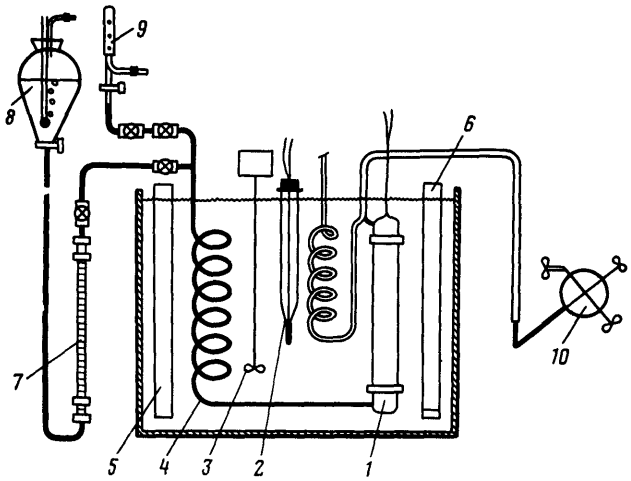



**Figure 3.** Apparatus with a tubular reactor[94]: 1) reactor; 2) thermoregulator; 3) stirrer; 4) evaporator; 5) and 6) heaters; 7) flow meter; 8) reservoir; 9) burette; 10) valve for the removal of gas.

All the above reactors are suitable for the investigation of kinetics, provided that conditions have been created in the system such that the reaction proceeds in the kinetic region, which is achieved by vigorous stirring or rapid circulation of the reactants in order to eliminate the effects of transport or film diffusion. Naturally such measurements are made with rigorous temperature control of the reaction volume and measurement of the temperature in the reactor itself.

Without going into details, Figs. 1–4 illustrate schematically several of the most interesting types of apparatus used to investigate the kinetics of liquid-phase[32,35] and vapour-phase[70,94] reactions. In the scheme shown in Fig. 2, provision is made for the continuous polarimetric monitoring of the reaction kinetics, while in the scheme illustrated in Fig. 3 the reaction kinetics are followed by a chromatographic method. Fig. 4 illustrates schematically a flow-type reactor with a membrane as the catalyst, which

combines the functions of a cell for the recording of infrared spectra. A reactor designed for the simultaneous investigation of reaction kinetics and the sorption of reactant vapour by the catalyst (from the increase in the length of a quartz coil) has been described[95].

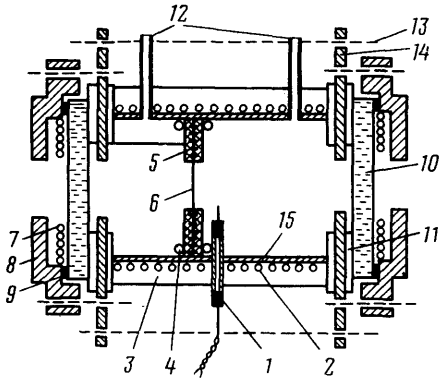



**Figure 4.** Flow-type cuvette for the investigation of dehydration[70]: 1) thermocouple; 2) heater; 3) insulation; 4) spring; 5) Teflon frame of the membrane; 6) catalytic membrane; 7) window heater; 8) brass window frame; 9) paper washer; 10) NaCl window; 11) silicone rubber seal; 12) tubes for the introduction and removal of solution; 13) supporting bolts; 14) stainless steel plates; 15) stainless steel shell.

The results of the study of the kinetics of different reactions will be examined in the next Section.

## III. KINETICS OF REACTIONS CATALYSED BY ION-EXCHANGE RESINS

During the period under consideration, the kinetics of reactions catalysed by ion exchangers have been studied at a rate higher than for research in other fields. The extensive experimental data obtained confirmed the validity of the general treatment of reactions in the presence of resins, in which Polyanskii[11] and Helfferich[82] saw the features of both homogeneous and heterogeneous catalysis.

Reactions occurring throughout the bulk of the swollen resin grain can be legitimately regarded as homophase processes, since there is no interface between the reaction mass and the catalyst itself. The kinetics of such reactions (and sometimes also the nature of the product formed) depend on the composition of the reaction mass in the catalyst pores, which is in its turn determined by the partition coefficient of each component between the resin and the external solution [see pp. 504 and 505 in Polyanskii's review[2] and Eqn. (3) in the present paper].

It is important to find the partition coefficients over a wide range of concentrations of the reactants if a different analytical expression describes the sorption isotherm of each. The isotherms can be described by the Langmuir equation for some substances and by the Freundlich equation for others, while a third group can give rise to complex saddle-shaped curves[96]. In such cases the enhancement of the absorption of one substance by the resin influences the degrees of sorption of the other components of the reaction mixture, which in its turn affects the reaction rate.

The fruitfulness of the combined study of the sorption of the reaction components by resins and of the kinetics of the catalysed reaction has been strikingly demonstrated[97,98]. According to the data of Reikhsfel'd et al.,[97] the effective rate constants for the transesterification of ethyl acrylate by butyl alcohol in the presence of different cation-exchange resins show an excellent correlation with the degrees of sorption of butanol from real reaction mixtures. The rate of this (and the reverse) reaction depends on the concentration of the intermediate complex $ROH_2^+$ formed as a result of the interaction of the alcohol molecules with the cation exchanger counterions. Naturally, there is no correlation of this kind if the intermediate complex, formed by the given reaction component (for example ethyl acetate in the study of Reikhsfel'd et al.[97]), is not reactive.

The true rate constants $k_{true}$ can be found from the sorbability by the resin of the component which forms a reactive complex and from the experimentally determined effective rate constants $k_{eff}$, using the relation

$$k_{eff} = k_{true}(\alpha_i^{rs} - \alpha_i^0), \qquad (4)$$

where $\alpha_i^{rs}$ is the sorbability of the above component calculated as the ratio of the number of moles of this substance in the catalyst phase to its overall amount in moles and $\alpha_i^0$ is the sorbability of the same component in the inactive form, determined by extrapolating the linear function $k_{eff} = f(\alpha_i^{rs})$ to the abscissa axis. In contrast to $k_{eff}$, which increases steadily and appreciably with the sorbability of the component forming the reactive complex, $k_{true}$ changes only slightly. The equilibrium constant depends on the sorbabilities of both components of the transesterification reaction; it can be easily calculated by means of the equation quoted by Reikhsfel'd et al.[98]

The difference between the compositions of the reaction mass in the resin phase and in solution is an important specific feature of catalysis by ion exchangers compared with homogeneous acid–base catalysis. A second characteristic of catalysis by ion exchangers, in terms of which it resembles heterogeneous catalysis, is that the reaction kinetics are frequently determined by adsorption processes. In such cases, the rate of reaction depends on the probability that the reactant molecules encounter fixed active centres. With increase in the concentration of the sorbed reactant, it rises initially, but reaches a limit as soon as all the active centres have been filled. This situation has been demonstrated, for example, in a study of the kinetics of the propylation of benzene in n-heptane on Amberlyst 15, the results being illustrated in Fig. 5 by a plot of the reaction rate against the concentration of the reactants. Evidently the behaviour of propene is described by the Langmuir–Hinshelwood model of an ideal adsorbed layer. The rate-limiting stage of the reaction is the electrophilic interaction of the chemisorbed propene with the benzene which has penetrated into the resin phase together with n-heptane. Since the concentrations of benzene in the inner and outer solutions vary in parallel, the rate of reaction increases continuously with increased concentration in the solution. The non-linearity of the curve describing the variation of the reaction rate with benzene concentration[29] indicates the inhibition of the reaction by n-heptane, which competes with the aromatic hydrocarbon in the swelling of the resin matrix.

The Langmuir–Hinshelwood model has been tested in studies of many other reactions catalysed by resins, for example esterification[99], transesterification[100], and

dehydration[101-104]. The authors of the above studies suggested that account be taken of the competition between the starting materials and reaction products for the active centres by introducing into the kinetic equations the adsorption equilibrium constant. For example, the kinetics of the vapour-phase dehydration of methanol and ethanol[101], in which two molecules sorbed on the active centres react, are described by the equation

$$r = \frac{k \cdot K_A^2 p_A^2}{(1 + K_A p_A + K_E p_E + K_W p_W)^2}, \qquad (5)$$

where $k$ is the reaction rate constant (mole $min^{-1}$ $mequiv.^{-1}$), $K$ the adsorption equilibrium constant ($atm^{-1}$), $p$ the partial pressure of the given component, and $r$ the rate of reaction (mole $min^{-1}$ $mequiv.^{-1}$) referred to the alcohol; the subscripts A, E, and W refer respectively to the alcohol, ester, and water. In solving equations of this type for liquid-phase reactions, it is recommended[103] that the concentrations of reactants be replaced by their activities in the condensed phase.

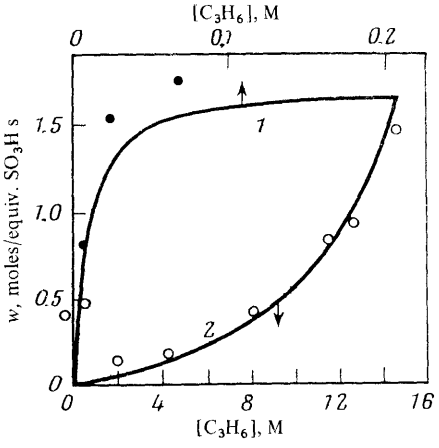



**Figure 5.** Variation of the rate of alkylation of benzene by propene with the concentrations of the components: 1) propene solution in benzene; 2) benzene–n-heptane mixture saturated with propene.

A possible cause of the inhomogeneity may also be the different states of hydration of the active groups within the bulk of each resin grain. This type of inhomogeneity, caused by the kinetics of the reaction under consideration, was taken into account by Heath and Gates[33] in terms of the "shrinking core" model which they proposed and used to account for the time variation of the efficiency of polystyrene cation exchangers with 8–12% DVB as catalysts of the dehydration of t-butyl alcohol. The anhydrous alcohol does not cause the swelling of the catalyst and the reaction, which begins only on the active surface centres, therefore proceeds very slowly (Fig. 6). Water, formed in the initial stage of the reaction, is partly transferred to the liquid phase and partly combines with the sulpho-groups via hydrogen bonds, causing swelling. This facilitates the transport of alcohol within the grain and accelerates the reaction. During the reaction, the boundary between the hydrated and non-hydrated zones in the grain is displaced inwards and, when each grain has been fully solvated, further absorption of water results in its binding to the active groups, which reduces the activity of the catalyst and hence the reaction rate. The duration of the induction period (see the left-hand branch of the curve in Fig. 6) increases appreciably with decrease of temperature and with increase of the resin grain size, owing to the influence of diffusional inhibition on the kinetics of the given reaction.

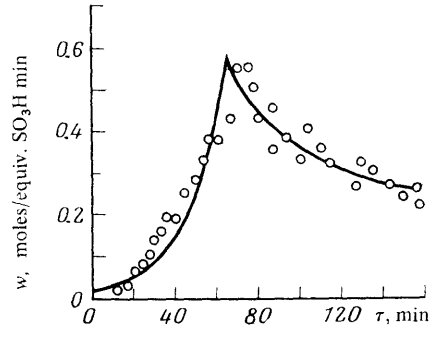



**Figure 6.** Kinetic curves for the dehydration of t-butyl alcohol.

The fact that the Langmuir–Hinshelwood model could be used to describe many reactions led to ion exchangers being considered as almost ideal catalysts with virtually equivalent active centres. Incidentally, other ideas have been frequently expressed in the literature, whose authors considered the inhomogeneity of the active groups in the steric[105], general chemical[106], and catalytic[43] sense of this term. We believe that this latter view corresponds more accurately to the present state of knowledge about the structure of ion-exchange resins[107], and the results of a direct experiment in which the non-equivalence of the active groups of Amberlyst 15 in the H-form was demonstrated by titrating it with a solution of n-butylamine in cyclohexane using Hammett indicators[108].

The third feature of catalysis by ion-exchange resins, in terms of which resins resemble non-ionogenic solid catalysts of gas- or liquid-phase processes, may be associated with the inhomogeneity of the active centres.

The role of diffusional inhibition, which constitutes a fourth feature of catalysis by ion-exchange resins, is manifested to a greater extent the larger the reactant molecules and the higher the degree of cross linking of the continuous-gel ion-exchange polymer[33,109-111]. Different workers have therefore used, in the kinetic description of catalytic reactions in the presence of ion-exchange resins, Boyd's theory of internal and external diffusion rate control (see pp. 27–30 in Polyanskii's review[11]) and the model of simultaneous diffusion and chemical reaction proposed by Wheeler and Thiele[33,35,112-114]. It is noteworthy that Boyd's theory was proposed for ion-exchange reactions and the Wheeler–Thiele model was designed for gas-phase reactions on the surfaces of solid catalysts. Nevertheless the mathematical apparatus associated with both concepts has been used successfully to investigate catalytic reactions on resins regardless of the phase state of the reactants.

One of the important features of the internal diffusion rate limitation is low activation energies, usually not exceeding 10 kcal mole$^{-1}$. Thus the activation energy for the hydrogenation of allyl alcohol is 3.4 kcal mole$^{-1}$ [74] and that for the alkylation of phenol by trimeric propene [115] amounts to 9.4 kcal mole$^{-1}$. Such low activation energies in the presence of diffusional inhibition in no way indicate a high activity of the catalyst: reactions of this kind proceed at a moderate rate. The product of the activation energy and the rate constant for the chemical reaction, which has been called [56] the "power of activation" ("aktivierungsleistung"), is of more general importance as a measure of the activity of the ion exchanger catalyst; for unimolecular reactions, this quantity is expressed in kcal litre mole$^{-1}$ s$^{-1}$. We believe that the product of the activation energy and the pre-exponential factor can serve as a criterion of catalyst activity.

Using the mathematical apparatus of the theory of absolute reaction rates, some workers [85,116] calculated the activation entropies from the activation energies and rate constants. It was shown that the entropy changes steadily, being a function of the degree of cross-linking of the resin and of the partition coefficients of the reactants between the solid and liquid phases.

The rate constants, expressed in the traditional way or their specific values referred to one milliequivalent of active groups of the ion-exchange resin, are usually employed as a direct characteristic of the reaction kinetics. In those cases where the rate constants do not remain invariant throughout the reaction owing to the influence of the blocking of the active groups or of a change in their solvation state, the kinetics are described by plots of the percentage conversion against time or by the usual kinetic curves.

The influence of various factors on the kinetics of reactions catalysed by ion exchangers has been examined in detail in Polyanskii's monograph [11] (pp. 37–62) and we shall therefore consider here only individual aspects of this problem.

The most important factors on which the reaction kinetics depend are usually thought to be the nature of the resin in a wide sense of this word, including the chemical structure of the matrix, the content of the cross-linking agent, the degree (or constant) of the electrolytic dissociation of the active groups, and the nature of the counterions. The catalytic activity of cation exchangers is correlated with their proton-donating capacity. For example, weakly acidic carboxylic acid cation exchangers hardly catalyse the Prins reaction between formaldehyde and styrene, while in the presence of sulphonated cation exchangers it does proceed [37]. Comparative data on the rates of dehydration of dimethylphenylmethanol and the transesterification of ethyl acetate by methanol in the presence of sulphonic and phosphonic acid cation-exchange resins have been published [102,117] and the considerable advantage of catalysts with strongly acidic active groups has been demonstrated. The activity of ion-exchange resins with active groups of the same type may differ markedly in the presence of matrices with different structures. For example, the KU-2 resin is less active in the dehydration of dimethylphenylmethanol than the sulphonated styrene–butadiene copolymer [117]. On the other hand, the condensation of phenol with acetone in aqueous alcoholic media [118] and the oxidation of ethylmethylphenylmethanol by hydrogen peroxide to a hydroperoxide [119] take place at a much higher rate in the presence of the KU-2 cation-exchange resin than in the presence of sulphophenol-formaldehyde resins with a dense structure of the three-dimensional network.

The problem of the effect of the degree of cross-linking on the reaction kinetics cannot be treated in isolation from the molecular size of the initial reactants and reaction products and sometimes also the degree of swelling of the catalyst on which the bulk-phase concentration of the active groups depends. If one of the components of the reaction mixture has large molecules, comparable to the diameter of the resin micropores, the rate of reaction usually decreases with increased content of the cross-linking agent in the matrix. Such relations have been established for the esterification of 1-butanol by benzoic acid [85], of pentyl alcohol by valeric acid, of isopentyl alcohol by isovaleric acid [52], and of propylene glycol by stearic acid [16], an increase in the degree of cross-linking having a particularly marked influence on the rate of formation of esters with the iso-structure [52]. In some cases even cation exchangers with a moderate DVB content (8%) do not catalyse the reaction, while in the presence of a lower degree of cross-linking it does proceed; such an example has been described in a study [50] devoted to the condensation of phenol with acetone.

If the molecular size of the reaction components is smaller than the size of the resin micropores, an increased degree of cross-linking does not enhance diffusional inhibition or steric hindrance to the formation of the active complex. The corresponding increase in the concentration of active groups or the decrease of the hydration number of the counterions [120], which become more accessible, as a result, to the reactant molecules, can then play the role of the factor accelerating the reaction with increase of the degree of cross linking. Such relations have been observed in studies on the kinetics of the decomposition of formic acid [78] and the dehydration of t-butyl alcohol [121]. However, one should note that Heath and Gates [33], who investigated a large assortment of catalysts in the same dehydration reaction, pointed out the non-monotonic variation of the rate with the degree of cross-linking: the cation exchanger containing 8% DVB proved to be the most active.

In the vapour-phase dehydration of isopropyl alcohol in the presence of homogeneous sulphonated cation-exchange membranes, the relative reaction rates depend on the partial vapour pressure of this substance diluted with nitrogen. At $p < 0.2$ atm, the membrane with 5% DVB was several times more efficient than the analogous catalyst with 2% of the cross-linking agent, but at $p \simeq 0.4$ atm the reaction rates were almost equalised. These differences have been accounted for [70] by a change in the reaction mechanism, but we believe it more likely that they are related to the state of solvation of the active groups.

Even in the presence of a high content of the cross-linking agent, macro-porous cation exchangers exhibit the same and sometimes even a higher catalytic activity [33,52,56] as weakly cross-linked ion-exchange polymers, but are much superior to the latter as regards chemical strength and osmotic stability. Fig. 7 presents the results of a comparative study of the efficiency of cation exchangers with 8% DVB and different porosities as catalysts of the dodecylation of phenol [56]. The porosity of the cation exchangers investigated is regulated by the introduction in the styrene–divinylbenzene copolymerisation stage of 20, 35, and 50% of petrol, which plays the role of an indifferent solvent. The alkylation kinetics in the presence of these catalysts are represented by curves *2*, *3*, and *4* in Fig. 7 respectively. The plots show that the activity of the macroporous ion exchangers falls with decrease in the amount of added indifferent solvent, since the porosity of the catalyst changes in the same direction. In conformity

with the general behaviour, the continuous-gel cation exchanger (curve *1* in Fig. 7) is the least efficient.

The rates of catalytic reactions are naturally influenced by the amount of ion exchanger, but the relations valid under these conditions are inconsistent with the general behaviour. For many reactions (apparently among those whose rate is limited by the chemical interaction step), for example, the esterification of ethyl acrylate[122], the hydrosilylation of unsaturated hydrocarbons[48], or the alkylation of phenols by benzyl alcohol[123], a linear relation has been established between the rate constant and the amount of catalyst. A linear relation between the logarithm of the rate constant and the amount of added catalyst has also been established for the esterification of benzoic acid by methanol[124], whose rate is limited by internal diffusion. An increase of the amount of anion exchanger from 15 to 30% in the aldol condensation of ketones with formaldehyde does not influence the rate of reaction[49]; this finding can be explained by the fact that the formation of hydroxyketones involves only a small proportion of the methylene component—its enolic form.

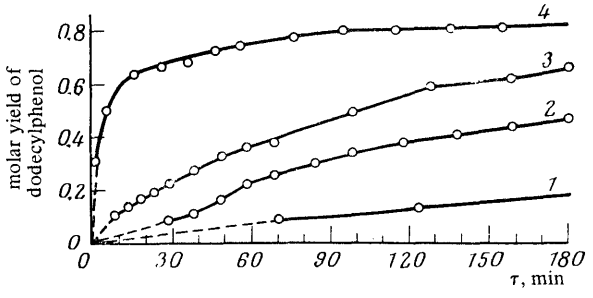



**Figure 7.** Kinetics of the dodecylation of phenol in the presence of gel (curve *1*) and macroporous (curves *2–4*) sulphonated cation-exchange resins; curves *2–4* correspond to macroporous resins obtained from a copolymer synthesised in the presence of 20, 35, and 50% of petrol respectively.

Since ion-exchange resins exhibit their catalytic functions via the counterions, the nature of the latter has a decisive influence on the reaction kinetics. It has been shown[121] that partial substitution of hydrogen atoms in sulpho-groups by alkali metal atoms leads to a decrease of not only general but also specific (i.e. referred to one milliequivalent of $H^+$ counterions) rate constants for the dehydration of t-butyl alcohol. The relative decrease of the reaction rate as a result of the substitution of $H^+$ by $Na^+$, $K^+$, or $Rb^+$ is the same, but in the mixed H–Li-form of the cation exchanger the effect is weaker. The above anomaly is explained by the fact that, in conformity with the laws of ion-exchange equilibrium, lithium substitutes a smaller number of protons in the most active groups than its electronic analogues, or by the involvement of the protons of the water molecules remaining in the cation exchanger after drying[93,121]. The study of the kinetics of the esterification of benzoic acid by 1-butanol led the authors[125] to the conclusion that, with increased degree of substitution of hydrogen ions in the sulphonated cation exchanger by alkali metal or alkaline earth metal cations, the ratio of the numerical partition coefficients changes appreciably and this affects the reaction kinetics, in conformity with Eqn. (3).

The substitution of hydrogen counterions can also lower the proton-donating activity of the sulpho-groups and can hinder the incorporation of the reactant in the three-dimensional polymer network; the change in the rate of propylation of benzene on Amberlyst 15 in accordance with a seventh-degree equation as a function of the fraction of hydrogen atoms converted into protons in relation to the overall content of counterions has been explained[29] by these effects. In reactions involving large molecules, the dependence of the rate constant on the degree of substitution of hydrogen counterions by other cations is influenced by the Thiele modulus, which is determined by the radius of the resin grain and the diffusion coefficient of the reacting substance[112]. Different kinetic relations correspond to different values of this modulus in the sucrose inversion reaction, the rate of which is controlled by internal diffusion.

The instances where the internal-diffusion limitation of the rates of reactions of large molecules and, in the case of a dense structure of the three-dimensional catalyst network, also of molecules of moderate size are fairly common in catalysis by ion exchangers. This cannot be said of external-diffusion rate limitation, since the reaction can be readily achieved in the kinetic region by increasing the rate of stirring of the reaction mixture under static conditions and the flow rates of the reactants under dynamic conditions.

The increase of the reaction rate with decrease of the catalyst grain size does not by itself demonstrate the presence of diffusional inhibition. For example, the rate of esterification of ethanol by propionic acid[126] increased with decrease of the catalyst grain size, but it was found that this was due to the inhomogeneity of the cation exchanger employed, the fine grains of which had a higher exchange capacity than the large grains. It is not therefore surprising that calculation of the specific rate constants referred to one milliequivalent of active catalyst groups yielded identical numerical values for three different fractions, showing that the reaction rate is limited by the chemical interaction step itself.

A reliable criterion of the presence of diffusional inhibition is the inverse proportionality between the reaction rate and the square of the grain radius for internal diffusion rate limitation and to the radius itself for external diffusion rate limitation. However, tests of these simple relations are frequently difficult because of the change in the size of the grains or in their physical state during the reaction itself. Thus a study of the kinetics of the esterification of stearic acid by propylene glycol[127] established for the first time the unexpected increase of the reaction rate with increase in the grain size of the KU-2 cation-exchange resin. It was found that the anomaly is due to the presence of a large number of accumulations of fine particles in the large-grain fraction, which become independent in the reaction mixture, where they act in accordance with their true size. On the other hand, if the aggregates of the cation exchanger grains are ground, screened, and redried, the normal relation is observed between the catalyst grain size and the reaction rate, corresponding to internal diffusion rate limitation.

The rate of formation of isobutene from t-butyl alcohol is higher the smaller the grain size up to the completion of the hydration of the Dowex-50W cation exchanger catalyst grains with the water produced, but, as dehydration proceeds, these differences are smoothed out, i.e. the diffusion-dependent rate limitation is replaced by chemical

rate limitation. All the foregoing considerations emphasise yet again the importance of taking into account and describing exactly the physical state of the ion-exchange resin catalysts employed.

The results of one correct series of experiments are presented in Table 3, which demonstrates the influence of the cation exchanger grain size, the method of drying the cation exchanger, and certain other factors on the kinetics of the esterification of salicylic acid by methanol[80]; analogous data for the inversion of sucrose have been published[79].

It follows from the data in Table 3 that the decrease in grain size, the elimination of water from the reaction mixture, and especially more thorough drying of the cation exchanger *in vacuo* lead to an increase of its catalytic activity. We shall consider in greater detail the last two factors. An increase of the activity of the cation exchanger catalyst with more thorough drying on raising the temperature has also been established in a study of the kinetics of the isomerisation of but-1-ene in the presence of the Na-Fe-form of Amberlyst 15.[43] The observed effects are very appreciable and are manifested by an almost twofold increase of the reaction rate constant with increase of the drying temperature of the resin from 75° to 150°C. In this reaction, they are caused by the more complete elimination of the water blocking the metal ions in the cation exchanger, which act as comparatively strong Lewis acids. The dehydration of the cation exchanger in the H-form in the above esterification reaction (Table 3) leads to the dissociation of the hydrogen bonds and increases the proton-donating activity of the sulpho-groups on formation of the intermediate complexes.

Table 3. The rate of esterification of salicylic acid ($w$ = g $h^{-1}$ per gram of cation-exchange resin) by methanol (M) in the presence of the Zeocarb-225 cation-exchange resin[80].

| Grain size, mm | −0,5+0,25 | | | | | −0,8+0,63 | |
|---|---|---|---|---|---|---|---|
| $H_2O$ in mixture with M, vol.% | 2[a] | 2 | 2[b] | 0 | 0[c] | 2 | 0 |
| $w$ | 13.39 | 13.31 | 13.36 | 16.81 | 34.09 | 10.66 | 12.66 |

Note. The amounts of cation exchanger in cases *a* and *b* were 10 and 40 g respectively and in the remaining cases 20 g; the salicylic acid : cation exchanger ratio was 6.90 and 1.73 in cases *a* and *b* and 3.45 in the remaining cases; the cation-exchange resin was usually weighed in the thermostat; it was weighed *in vacuo* only in experiment *c*.

However, cases are also known where thorough drying leads to the loss of the cation exchanger's ability to catalyse the reaction[128]. One should always remember the possible influence of water on the kinetics of the reaction, and one must therefore control rigorously the conditions in the drying of the ion exchangers and follow the changes in their grains (comminution and the formation of cracks); without this, it is impossible to expect reproducible data for the rate of the process investigated.

The purity of the reactants and solvents employed is also of great importance: it has been shown in a study of the kinetics of the dehydration of t-butyl alcohol[33,101], the condensation of phenol with acetone[50], and the esterification of n-butyl alcohol by acetic acids[129] that admixtures of proton-acceptors (water and alcohols) greatly reduce the catalytic activity of cation-exchange resins in the H-form. Admixtures of substances with proton-donating activity should influence in the same way the kinetics of reactions proceeding via intermediate anionic complexes; in both cases, the mechanism of the action of the ingredients reduces to the blocking of the active catalyst centres.

The influence of indifferent solvents on the kinetics of reactions catalysed by ion exchangers has been very little investigated despite the importance of this problem. It is clear, however, that, together with a simple change of the rate of the main process (as in the esterification of benzoic acid by 1-butanol[89]), the addition of solvents may influence the nature of the products formed (as has been noted for the Prins reaction[37]) or can retard parallel reactions (as in the hydration of isoprene[130]). In the esterification of benzoic acid by 1-butanol in n-heptane, benzene, and toluene[89], the logarithm of the reaction rate constant is a linear function of the reciprocal of the dielectric constant. However, one should note that the experimental points exhibit a marked statistical scatter, which may be caused by errors in the estimation of the partition coefficients used for kinetic calculations by Eqn. (3). The influence of the partition of the components of the reaction mixture on the kinetics of the transesterification of ethyl acrylate by 1-butanol in the presence of the KU-2 cation-exchange resin can be inferred from the data of Soviet investigators[131], who established the inverse dependence of the rate constants on the sorbability of solvents whose electronegative atoms are linked by hydrogen bonds to the sulpho-groups of the catalyst, which entails a decrease of the activity of the latter. At the same time there is a possibility of the solvation of the intermediate cationic complex, which also influences the kinetics of the reaction investigated.

The rates of catalytic reactions in the presence of ion exchangers also depend on the size of the solvent molecules and the reacting substances, which determines in many respects the swellability of the catalyst and the possibility of utilising all the reaction centres in the bulk of its grains[109]. The corresponding relations are manifested most clearly in studies on homologues, for which a decrease in the rate constant with increased size of the reactant molecules in the hydrolysis of esters[36] and the oxidation of aliphatic acids by hydrogen peroxide[14] in the presence of cation exchanger catalysts has been established. It has been shown for the last reaction and esterification in the presence of the KU-2 cation-exchange resins that straight-chain molecules react faster than their isomers, since they penetrate more readily into the catalyst grains. Naturally, apart from steric factors, the reactivity of substances is influenced also by inductive factors[132], the main role being attributed to the latter for straight-chain molecules containing not more than five carbon atoms (on the basis of the satisfactory agreement between the experimental data and the familiar correlation equation). For acids with the iso-structure, the correlation is weakened owing to the increasing importance of the role of the steric factor; the same tendency should be observed with increase of molecular size. For a differential assessment of the above factors, it is desirable not to restrict the treatment to the application of methods of correlation analysis and to supplement them by measurements of the efficiency of ion-exchange resins, using Hammett's procedure[1], and of the partition coefficients of the reactants between the solid phase and the external solution. There is no doubt about the usefulness of this combined approach.

The kinetics of reactions in a stream of reactants flowing through a layer of ion-exchange resin depends on the flow rate as well as the factors enumerated above. The fundamental equations derived for ideal plug flow reactors are usually employed in a kinetic description of such reactions[133]. In the integral form, the kinetic equations are

$$k_{\mathrm{I}}\tau = \ln(1-x), \tag{6}$$

$$k_{\mathrm{II}}\tau = \frac{2.3\gamma}{\rho n_0(\gamma-1)} \lg\frac{1-x}{1-\gamma x}, \tag{7}$$

where $x$ is the fractional conversion, $k_{\mathrm{I}}$ and $k_{\mathrm{II}}$ are the rate constants for first- and second-order reactions respectively, $\tau$ is the contact time, $\gamma$ the molar ratio of the reactants in the second-order reaction, $\rho$ the density of the reaction mass, and $n_0$ the initial number of moles of one reactant in the second-order reaction. Eqn. (6) describes very accurately the kinetics of the inversion of sucrose[112] and Eqn. (7) describes the kinetics of the alkylation of phenol by higher olefins[134] in the presence of sulphonated cation exchangers with a styrene–divinylbenzene matrix.

## IV. A BRIEF DESCRIPTION OF THE APPLICATION OF VARIOUS ION-EXCHANGE RESINS AS CATALYSTS OF REACTIONS OF ORGANIC COMPOUNDS

### 1. Hydrolytic Reactions

The hydrolysis of esters of aliphatic acids and alcohols[36,83,84,92], sucrose[83,112,135,136], acetals[136,137], $\epsilon$-caprolactone[138], and certain purine nucleosides[66] has been achieved in the presence of sulphonic acid and, in a few instances, phosphonic acid cation exchangers. Carboxylic acid cation exchangers have been shown to be highly specific catalysts of the hydrolysis of insulin[139]; a change in the length of the cross-linking agent molecule influenced the specificity of the action of these catalysts. Studies have been made on the kinetics of the hydrolysis of esters of aliphatic acids and aliphatic or aromatic alcohols[36,83,84] and of sucrose[136] in the presence of cation exchangers, the last report quoting the rate constants for inversion and the diffusion coefficients of the substrate in the sulphophenol-formaldehyde membrane used as the catalyst.

Highly basic anion-exchange resins proved to be effective catalysts of the hydrolysis of acrylonitrile[140] and nicotinonitrile[141]. Nicotinamide has been hydrolysed to nicotinic acid[141], which was sorbed by the catalyst, causing its deactivation. $\beta$-Cyanoethoxy-$\beta$-propylamide, formed via ethylene cyanohydrin, has been obtained from acrylonitrile instead of acrylamide, which is a product of the hydrolytic reaction in the presence of cation-exchange resins.

Catalytic hydrolysis of esters in the presence of sulphonic acid cation-exchange resins is of greatest promise for industrial applications; this reaction is virtually unaccompanied by side processes.

### 2. Hydration Reactions

Very few studies have been made on the use of ion exchangers as hydration catalysts. They were devoted to the hydration of 1,2-epoxybutane[142], olefins (propene[143] and isobutene[144]), and isoprene[130] in the presence of sulphonic acid cation-exchange resins and their aim was mainly preparative. In order to improve the conditions of contact of olefins with water and the KU-1 sulphonic acid cation-exchange resin catalysing the hydration reaction, Chaplits[145] and coworkers recommend that the reaction be carried out in the presence of an indifferent solvent. The hydration reactions of unsaturated hydrocarbons are accompanied by their polymerisation, which becomes more pronounced with increased concentration of the monomers in the mixture. In the presence of the carboxylic acid cation-exchange resin Amberlite IRC-84 acrolein and hydracrylaldehyde were hydrated[146]. The hydration of isobutene is used in industry as a method of selective extraction of this olefin[43] from butane–butene cracking fractions.

### 3. Dehydration Reactions

The dehydration of primary[77,93,94,101], secondary[69,70,147,148], tertiary[33,103,121,149], and dihydric alcohols[61] has been successfully achieved on sulphonic acid cation-exchange resins under comparatively mild conditions (as a rule at $t \leqslant 150^\circ$C), which rule out significant losses of capacity as a result of desulphonation. Under these conditions primary alcohols give rise to ethers only, while under more severe conditions olefins can be formed together with the ethers, tertiary alcohols yield only olefins, while secondary alcohols are dehydrated in both ways even at 100°C.[147] It has been shown for isopropyl alcohol that sulphuric acid does not catalyse its dehydration at 100°C. The dehydration of castor oil in the presence of the KU-2 cation-exchange resin has been achieved[150] at 180–230°C. Although the process conditions were much milder compared with earlier studies (see Polyanskii[11], p. 122), nevertheless one should note that a prolonged life of the cation-exchange resin cannot be expected under these conditions either, owing to its desulphonation. The more stable salt-forms with alkali metal counterions do not catalyse dehydration[93], but Amberlite-15 saturated with aluminium ions proved to be catalytically active[148].

In addition to the reactions involving the dehydration of alcohols to ethers and olefins, which frequently takes place simultaneously, there is a possibility of the polymerisation of unsaturated hydrocarbons to oligomers[69,117]. The dehydration itself can play the role of a side reaction in the esterification of dihydric alcohols. A cyclic acetal is formed from propylene glycol[151] and not the isomeric 2,4-dimethyldioxan, as suggested previously.

The dehydration of ethanol, which is of practical importance, can be carried out in the absence of parallel reactions and with a considerable displacement of the equilibrium (investigated by Hsu and Kabel[95]) to the right. The dehydration of dimethylphenylmethanol is believed to be irreversible[117]. The kinetics of these reactions have been described[33,70,93,95,121] and their mechanisms have been examined[69,93,121]. The dehydration of ethanol to diethyl ether and of t-butyl alcohol to isobutene is of interest for use on an industrial scale.

### 4. The Synthesis of Esters

Sulphonic acid cation-exchange resins are the most effective and most frequently used catalysts for the formation of esters from various compounds. The attempt to use phosphonic cation-exchange resins, even macroporous resins, has been unsuccessful[129]. The replacement of soluble acids by sulphonic acid cation exchangers as esterification catalysts sometimes reduces the reaction time[152]

or increases the yield of the desired product[153], apart from the usual advantages.

The main method for the synthesis of esters is esterification in the presence of sulphonic acid cation exchangers, which is achieved by interaction between (1) monohydric alcohols and aliphatic carboxylic[26,52,126,129,153-155], unsaturated[99,109,156], halogenocarboxylic[157], and aromatic acids[80,84,116,124] and (2) between dihydric alcohols and aliphatic monocarboxylic[16,127,158,159] and dicarboxylic acids[160]. In the latter case, the copolycondensation of diethylene glycol with various dibasic acids was carried out and, in order to accelerate the reaction and increase the molecular weight of the polyesters formed, it is recommended that it be performed in the presence of an excess of the alcohol in which the cation exchanger catalyst swells markedly. The favourable influence of the swelling of the cation exchanger in the alcohol on the rate of esterification of acetic acid by 1-butanol was demonstrated in another study[129]. The successful syntheses of esters with t-alkyl radicals and of phosphate esters in non-aqueous media[153,161] as well as the esterification of 20% aqueous solutions of acrylic and methacrylic acids[162] by methanol in the presence of hydroquinone as the polymerisation inhibitor merit particular mention.

In order to accelerate the esterification and displace the reaction equilibrium to the right, the reaction is frequently carried out in the presence of azeotrope-forming solvents, usually aliphatic or aromatic hydrocarbons[110,116]. This is unnecessary in transesterification[102], when anhydrides are made to react with alcohols[160], and when olefins[163] or the corresponding epoxy-derivatives[164] are made to react with acids.

In the presence of cation-exchange resins, there is a possibility of a wide variety of side reactions: dehydration of alcohols, polymerisation of the olefins formed, alkylation of solvents, and dehydration of esters. The kinetics of reactions uncomplicated by side processes have been examined in a number of investigations[89,100,102,124-126] and their mechanisms have been considered in two other studies[52,128].

The reactions between epichlorohydrins and carboxylic acids, leading to formation of monochlorohydrin esters[165] or polyepoxide ester [ether?] resins (see Polyanskii[11], p. 132), proceed via anionic intermediate complexes and are therefore accelerated by anion exchangers.

The synthesis of butyl acetate and other esters in the presence of cation exchangers and the esterification of aqueous solutions of acids are of interest for use on the industrial scale as a method for the utilisation and detoxication of industrial waste.

A continuous method for the manufacture of acrylate and methacrylate esters in the presence of the Dowex-50W cation-exchange resin has been described in a patent[166].

## 5. Alkylation Reactions

Only sulphonic acid cation-exchange resins are used as alkylation catalysts. Compared with aluminosilicates, they ensure an improved yield of the desired products[63]. In contrast to sulphuric acid, they do not cause the formation of sulphoesters and sulphones[167], are less complicated by side reactions involving the polymerisation of olefins and isomerisation[168] as well as transalkylation[167], and ensure the preferential formation of monoalkylphenols (see Polyanskii[2], p. 518). On kinetic grounds, some authors give preference to gel cation exchangers over macroporous cation-exchange resins[56,63,169], but one should bear in mind that pores absorb liquid having the same composition as tha in the external solution, which can increase the yield of dialkylphenols. Other conditions being equal, the nature of the alkylation products depends on the structure of the cation exchanger matrix[56,62,63,170] and reaction temperature[63].

The majority of studies have been devoted to the alkylation of phenols by alcohols[123,170-174], olefins[56,59,60,62,171,175-177], and cyclic dienes[168,175,178,179]. A few studies have been devoted to the alkylation of $\beta$-naphthol by olefins and other hydrocarbons[180], the alkylation of esters by olefins[169,181,182] and alkynes[183], the alkylation of aromatic amines by alcohols[184], and the alkylation of benzene by propene[29].

Apart from the side reactions enumerated above, the alkylation can be accompanied by dealkylation, the isomerisation of alkylphenols and alkyl phenyl ethers[171] as well as alkylating agents[172], and the cyclisation of alkenylphenols to coumarans[176]. In general, the consumption of reactants in side reactions is greater when the reactivity of the substance alkylated in the main reaction is lower. Certain side processes, for example polymerisation, can be reduced to a minimum by promoting the cation exchanger catalyst by sulphur-containing additives[171].

The results of the study of the kinetics of alkylation reactions have been published[29,123,134,185] and a mathematical description of the process has been given[186] whereby one can calculate the degree of conversion of the phenol and the temperature at any point in the reactor. The alkylation mechanism has also been examined[29,63,115,123,170,171].

The studies of Isagulyants and Belov ensured the wide scale industrial application of alkylation reactions in the presence of cation exchangers[167,171]. The alkylation is characterised by high heats of reaction[167,187] and the process is therefore carried out in a cascade of reactors, the heat released being removed in cooling units after each stage. The technological scheme of the alkylation process is described in Kharlambovich and Churkin's monograph[167].

## 6. Polymerisation and Isomerisation Reactions

Sulphonic acid cation exchangers and, in the case of substances with a high reactivity, phosphonic acid cation exchangers are used as catalysts for the polymerisation of aldehydes and unsaturated hydrocarbons to oligomeric products. This concerns the polymerisation of propene[108], $\alpha$-methylstyrene[117], the trimerisation of acetaldehyde[188,189], and formaldehyde[190], and the copolymerisation of $\alpha$-methylstyrene with $\alpha$-olefins[191]. The polymerisation of dimethylcyclosiloxanes has been achieved in the presence of the macroporous KU-23 sulphonated cation-exchange resin[32]. A carboxylic acid cation exchanger, converted into a peracid, has been used as an initiator of the polymerisation of methyl methacrylate and in the copolymerisation of the same ester with styrene[192]. In the presence of highly basic anion-exchange resins in the Cl-form, obtained by the amination of the chloromethylated styrene–divinylbenzene copolymer by various tertiary amines, acrylamide was polymerised and the polymerisation kinetics were investigated[193]. The kinetics of other polymerisation reactions have also been described[189,192].

Sulphonated cation exchangers have been used as catalysts of the isomerisation of hydrocarbons[43,108,194,195] and of the Beckmann rearrangement of cyclohexanone oxime to caprolactam, the desired rearrangement product being obtained in the highest yield in dimethyl sulphoxide[196]. The isomerisation kinetics have been considered in detail[43,108,194].

The polymerisation and isomerisation reactions are sometimes not accompanied by the formation of side products[189], but they frequently accompany one another or other processes. Such complications occasionally give rise to a whole spectrum of products[195], the nature of which depends on the structure of the catalyst employed. A number of workers have examined the mechanisms of the polymerisation reactions[189,193] and of the isomerisation reactions[43,194].

The trimerisation of acetaldehyde has been carried out on an industrial scale; the polymerisation reactions of dimethylcyclosiloxanes and olefins, forming part of industrial cracking fractions, are promising in this respect.

## 7. Condensation Reactions

The majority of studies involving the use of ion exchangers as catalysts of condensation reactions had as their aim the preparative synthesis of particular substances. The condensation of 2-mercaptoethanol with hydrogen sulphide[197], of alcohols with phenols[23,198], mesityl oxide[57,199], trioxan[200], and aldehydes[65], of aldehydes with olefins[53,201-203] (the Prins reaction), dioxan derivatives[204], and α-chloromethylstyrene[205], of phenol with acetone[50,206]†, of polycyclic phenols with boric acid[207], of diols with unsaturated aldehydes[208], of tris(hydroxymethyl)ethane with furfural[209], of higher primary aliphatic amines with sulphur-containing dicarboxylic acids[210], of *o*-phenylenediamine with naphthoic or heterocyclic acids[211], and of *o*-aminophenols with monocarboxylic acids[212] has been achieved in the presence of sulphonated cation exchangers. Anion exchangers have been used as catalysts of the aldol condensation of aldehydes[24,111] and ketones[213] and also for the acceleration of the condensation reactions of ketones with aldehydes[49,214], of aldehydes with nitroalkanes[215] and urea[40,216], and of alcohols with acrylonitrile[217]. In the condensation of aldehydes with urea, a strongly basic anion exchanger is much more effective as a catalyst than a moderately basic resin, but this cannot be regarded as a general rule.

The yield of condensation products is frequently reduced by side reactions[20,24,50,111], which hinders the study of the kinetics of the corresponding reactions and shows that it would be unjustified to overestimate the selectivity of ion-exchange resin catalysts. The results of kinetic studies have been described[24,49,50,57] and the reaction mechanisms have been considered[49,217].

The synthesis of cyclic acetals in the presence of ion-exchange resins and, as far as the authors are aware, a method for the synthesis of bis(hydroxyphenyl)propane have been used on an industrial scale. Various types of the Prins reaction and continuous methods for the synthesis of aminoresins are promising for industrial applications[15].

## 8. Various Reactions

Many reactions, which do not belong to the types considered, are also carried out in the presence of ion-exchange resins. These include various addition reactions, including hydrogenation[49,73,74,218-221], which are carried out in the presence of cation and anion exchangers (containing complex platinum group metal chlorides as the mobile ions), the oxidation of a number of compounds [carboxylic acids[14,222,223], cyclohexanone[224], derivatives of phthalic anhydride[225] (sulphonated cation exchangers are used as oxidation catalysts)], and the decomposition of various aromatic alkyl derivatives of mono- and di-hydroperoxides[13,17,226-228] (also in the presence of sulphonated cation exchangers). It is noteworthy that highly cross-linked gel cation-exchange resins either do not catalyse the disproportionation of hydroperoxides or lose their activity rapidly[17]. The kinetics of these reactions have been investigated[227,228] and two studies have been devoted to the mechanism and kinetics of the oxidation reactions[14,132].

Methods for the decomposition of hydroperoxides and the synthesis of peracids are of interest for incorporation in industrial processes. Recent studies on the thiolysis of 1,3-dioxans are of theoretical interest[229,230].

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The new stage in the development of catalysis by ion-exchange resins considered in this review is characterised by a further improvement of the theoretical level of the relevant research as a result of the wide-scale employment of the kinetic approach. The extensive experimental data obtained reveal in the ion-exchange resin-catalysed reactions features of both homogeneous and heterogeneous catalysis.

Such a general treatment should stimulate the search for a new theoretical model of the catalytic reactions, which takes into account more fully all the aspects of the inter-relations between the ion exchangers and the reacting substances than the Langmuir–Hinshelwood and Wheeler–Thiele models employed at the present time. The necessary preparation for this advance should be ensured by a further development of kinetic studies on a wider basis: this concerns a systematic (and not sporadic, as hitherto) measurement of the partition coefficients and the refinement of their relation to the efficiency of ion-exchange resins using Hammett's method, the study of the influence of the type of solvent on the reaction kinetics, and the regular employment of methods of correlation analysis.

In connection with new theoretical tasks, it is necessary to give more attention to methods for the preparative treatment and investigation of ion-exchange resins as catalysts, in particular it is necessary to justify in greater detail the usefulness of conditioning and to make appropriate recommendations, to elucidate the causes of blocking and to develop regeneration methods, and to synthesise new types of ion exchangers with improved osmotic and thermal stabilities.

While noting the major achievements in catalysis by ion-exchange resins as a method of preparative organic chemistry, one should nevertheless mention the insufficiently wide-scale employment of macroporous, macronetwork, and oleophilic ion-exchange resins. The salt-forms of all resins and the hydroxide-forms of anion-exchange resins have been little used.

Certain advances have been made in the incorporation of ion-exchange resins in industrial processes, but they have still not reached the limit of the existing possibilities.

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While the manuscript was with the Editors, a number of studies devoted to the kinetics of esterification and transesterification[231-234], hydrolysis[235], oxidation[236,237], condensation[238], and alcoholysis[239], catalysed by ion-exchange resins, were published.

† The catalyst is promoted by the addition of 2,2-dimethylthiazolidine.

A series of new studies were devoted to the use of ion exchangers as catalysts of esterification[240-242], hydrolysis[243,244], polymerisation[245,246], condensation[247-251], decomposition[252,253], and alkylation[254-262]. An interesting example of the employment of the catalytic properties of ion-exchange resins for the purification of bisphenols and hydroquinone has been described[263]. A few studies have been devoted to the application in catalysis of cation exchangers[264-266] and anion exchangers[266-269] metallised by Group VIII *d* elements or containing complex transition metal ions as counterions. The use of sulphonated polystyrene on a support consisting of aluminium sheets as a catalyst in a gas–liquid system has been described[270].

The mechanism of the blocking of the catalyst in the hydration of epoxyethane has been considered[271].

Rapid methods for the determination of the properties of ion-exchange resins, which are important for the understanding of their catalytic functions (exchange capacity, total porosity, and ionisation constants), have been described[272-274]. The paper by Polyanskii et al.[275] is devoted to the problem of the inhomogeneity of macroporous ion exchangers and its importance for catalysis, which has not so far been considered in the literature.

A monograph[276] deals with research techniques for ion-exchange resins.

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# Tertiary Amines in Acyl Transfer Reactions

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The mechanism and kinetics of acyl transfer reactions in the presence of tertiary amines are examined and the quantitative relations between the rate of reaction and the structure of the acylating agent, the acylated substrate, the amine, and the solvent, temperature, and the ratio of the efficiencies of intramolecular and intermolecular catalysis are discussed. A number of examples of the application of tertiary amines as accelerators of acyl transfer reactions, which are of practical importance, are presented.
The bibliography includes 282 references.

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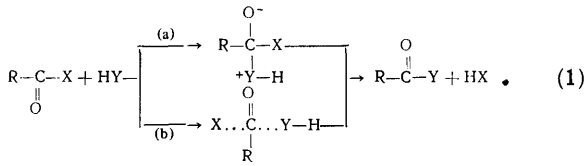
## I. INTRODUCTION

The accelerating influence of tertiary amines (TA) on acyl transfer reactions has been known since the end of the past century, but fundamental studies have been made only in the last decades. In this review, an attempt is made to give a systematic and critical account of these data (using studies published up to 1975) mainly from the standpoint of the reaction mechanism and quantitative allowance for the influence of the structure of the reactants on the reaction rate. The problems of the structure of the products and the synthetic aspects are only briefly discussed, since a relevant review has been published recently [1].

## II. THE REACTION MECHANISM. GENERAL KINETIC RELATIONS

### 1. General Consideration of the Mechanism. Type of Catalysis

Acyl transfer reactions can be described by mechanism (1), which has two main versions—the two-stage reaction (1a) with formation of a tetrahedral intermediate (TI) or the single-stage reaction (1b)†, the transition state of which resembles that of an $S_N2$ reaction:

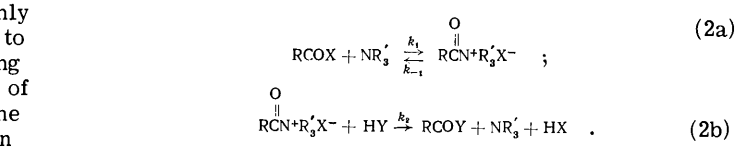


(1)

The compounds RCOX in this reaction are usually acid halides (X = F, Cl, Br, or I), anhydrides (X = OCOR), esters (X = OR′), and more rarely acids (X = OH), amides (X = $NH_2$ or NHR′), etc.; the nucleophiles HY are water, alcohols, phenols, and amines.

†A unimolecular mechanism with formation of the cations $RCO^+$ is fairly rarely encountered and is not considered in this review.

The hypothesis of the nucleophilic catalysis‡ of acyl transfer reactions by tertiary amines [mechanisms (2a) and (2b)] was first put forward at the beginning of the 1950s [2-5]:



(2a)

(2b)

Koshland [2] used it to account for the acceleration of the hydrolysis of acetyl phosphate after the addition of pyridine; he regarded the isolation of solid acetyl-pyridinium chloride as evidence demonstrating the proposed mechanism. However, a direct comparison of the rates of formation and decomposition of the chloride with the overall reaction rate was not made and only the half-reaction times were compared. The same mechanism was proposed [3-5] for the hydrolysis of acetic anhydride (AA) on the basis of the significant influence of steric hindrance in the amine on the reaction rate. This influence was observed also in many other instances (see Section III) and the breakdown of the Brønsted and Hammett–Taft relations was observed when amines with variable steric characteristics were used, which was usually regarded by the authors as evidence for the nucleophilic nature of the catalysis. However, this conclusion cannot be regarded as fully rigorous, since the equilibrium in the formation of a hydrogen bond has been shown recently [6-8] to depend also on the steric structure of the amine, which can therefore influence the rate of reaction also in general base catalysis.

‡We employ the term "catalysis", although in certain cases tertiary amines are removed from the reaction as a result of their interaction with the products HX and this term does not therefore correspond to the strict definition of the concept of the "catalyst". However, the identity of the mechanism and characteristics of these reactions with those of others where tertiary amines are not removed from the reaction sphere justify the use of all cases of the single term "catalysis", the interaction of tertiary amines with HX being regarded as stoichiometric poisoning of the catalyst.

On the other hand, during the last 15 years new facts have been obtained, which can be regarded as evidence in support of nucleophilic catalysis.

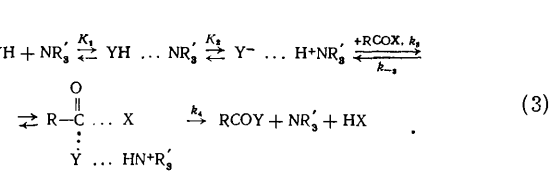
1. The formation in the esterification of racemic alcohols RR'CHOH in the presence of optically active tertiary amines of esters having a single preferred configuration, *S* or *R*, depending on the alcohol and the amine[9]. This is apparently due to the preferential existence of the acylammonium salt (AAS) and the tetrahedral intermediate arising when it interacts with the alcohol in the least hindered conformation. Similar results were obtained for the reaction of phenylmethyl keten with alcohols in the presence of optically active tertiary amines[10].

2. Anomalies in the temperature variation involving either a very slight increase of $k_{cat}$ or even its decrease as the temperature rises, i.e. the apparent activation energy is $E_{act}^{app} \leqslant 0$.[11-13] This is satisfactorily consistent with the hypothesis of the reversible formation of an acylammonium salt, which is highly exothermic in the case of reactive amines. Since $E_{act}^{app} = \Delta H + E_2$ for mechanism (2a, b), where $E_2$ is the activation energy for the second stage (2b), it follows that, when $\Delta H \ll 0$, $E_{act}^{app}$ can also become less than zero. The increase of steric hindrance and decrease of the resonance stabilisation of the acylammonium salt hinder its formation, which leads to a general retardation of the reaction and to an increase of $E_{act}^{app}$. In general base catalysis, the reversible formation of a hydrogen bond is weakly exothermic and $E_{act}^{app} \leqslant 0$ is unlikely.

3. Kinetic relations: the hydrolysis of acetic anhydride is faster by several orders of magnitude in the presence of pyridine than in the presence of $CH_3COO^-$, despite their approximately equal basicities, which indicates different reaction mechanisms[3,4,14].

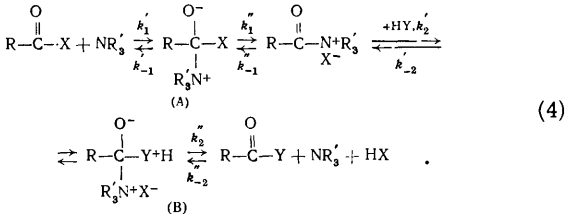
The most detailed and convincing evidence for a nucleophilic mechanism of catalysis by tertiary amines in aqueous solutions was obtained by Fersht and Jencks[14,15], who confirmed experimentally the possibility of the accumulation of analytically measurable concentrations of the acetylpyridinium ion (API), which had been predicted beforehand from an estimate of the free energy of its hydrolysis[16]. In water, which stabilises polar acylammonium salts, it was possible to detect the spectrum of the acetylpyridinium ion ($\lambda_{max}$ = 225 and 272 nm, $\epsilon \simeq$ 7000 and 4400) by the stopped flow method and also by employing the retardation of the hydrolysis of the acetylpyridinium ion by three orders of magnitude compared with its formaton in 9 M $NaClO_4$ solution; the two spectra proved to be identical[14]. It was also found that the rate of hydrolysis of the acetylpyridinium ion synthesised by the method of Sheinkman et al.[17] is equal to the rate measured by the stopped flow method in the direct interaction of acetic anhydride with pyridine in water. This implies that in this reaction (and probably in many analogous reactions) pyridine and other tertiary amines behave as nucleophilic catalysts.

On the other hand, a number of workers noted also the possibility of the operation of general base catalysis via the following mechanism:



(3)

This version will be examined in greater detail in Section III, but, as regards the problem as a whole, one must emphasise that the possibility of nucleophilic catalysi is determined primarily by the comparative basicity (in the general sense—nucleophilicity) of the leaving group and the attacking nucleophile. If the reaction is formulated in the general form (4), taking into account the intermediate tetrahedral intermediates (A) and (B), one may note that the dominant mode of their decomposition involves the elimination of the less basic ("easily removed") group[18]



(4)

Thus, when the leaving group X in RCOX is less basic than the tertiary amine, i.e. $pK_a^{HX} < pK_a^{HN^+R'_3}$, then (A) is converted preferentially into the acylammonium salt. As a result of this, nucleophilic catalysis is of decisive importance in the reactions of acyl derivatives with easily removed groups[19,20] and its efficiency decreases in the sequence of the following groups X: I > Br > Cl > F > RCOO. The specific situation depends on solvent; for example, the hydrolysis of acid fluorides and anhydrides in water is catalysed by tertiary amines[3,5,14,21,22] and the aminolysis of benzoyl fluoride[23] and of the majority of anhydrides in benzene is inhibited by tertiary amines[24,25]. In this medium, $F^-$ and $RCOO^-$ are probably stronger bases than $NR'_3$, which prevents the conversion of (A) into an acylammonium salt. However, for anhydrides of stronger acids, tertiary amines do exhibit catalytic properties[25,26]. Similarly, in the acylation of phenols in $CCl_4$ by acetyltrifluoroacetate in the presence of pyridine and its analogues, the rate of acetylation does not change, while the rate of trifluoroacetylation increases sharply and the latter process becomes of decisive importance[27,28].

On the other hand, the probability of general base catalysis increases in the reactions of substrates with groups which are difficult to remove[15,19,29] and which are more basic than the tertiary amine. For example $k_{cat}/k_0$ for aminolysis in the presence of carboxylic acids[30,31] or 2-hydroxypyridine[32] increases in the following sequence of groups X in ArCOX: Br < Cl < F < OAr.

On the other hand[33], the tetrahedral intermediates (B) will decompose preferentially with formation of the final products if the attacking nucleophile is a weaker acid than the ammonium ion, i.e. $pK_a^{HY} > pK_a^{HN^+R'_3}$. The validity of this condition also depends on the solvent in the general case. For example, in water carboxylic acids do not undergo acylation catalysed by tertiary amines (even in an undissociated form). However, in certain non-aqueous media we may have $pK_a^{RCOOH} > pK_a^{HN^+R'_3}$ and reaction (5),[34] leading to the formation of anhydrides and used for a long time as a method for their synthesis[35], becomes possible:

$$RCOOH + RCO^+NR'_3Cl^- \rightarrow (RCO)_2O + R'_3N \cdot HCl \quad . \qquad (5)$$

Anhydrides do not react further under these conditions. In the acylation of phenols, the situation where $pK_a^{ArOH} < pK_a^{HN^+R'_3}$ is also possible as a function of the solvent; here $k'_{-2} \gg k''_2$ and nucleophilic catalysis does not occur, although general base catalysis via mechanism (3) is possible[27,33,36-39].

When HY = $H_2O$, ROH, or $RNH_2$, the condition $pK_a^{HY} > pK_a^{HN^+R'_3}$ holds always and nucleophilic catalysis of the acylation of these compounds is possible and probably takes place in water and other polar solvents. On the other hand, one should note that, in aprotic solvents with low dielectric constants, the formation of products with a considerable separation of the charges and their intense localisation is energetically unfavourable and such products (to which acylammonium salts and tetrahedral intermediates belong) are characterised by a high energy level. This can lead to their approach to the corresponding transition states and, in the limit, to the occurrence of the reaction via a synchronous mechanism[40].

## 2. The Ratio of the Rates of Individual Stages. Kinetic Relations

In those cases where tertiary amines behave as nucleophilic catalysts of acyl migration, the reaction is usually irreversible under the experimental conditions ($k''_{-2} = 0$) and is described by mechanism (2) if the stage involving the formation of a tetrahedral intermediate is omitted. The problem arises of the ratio of the rates of the stages of this reaction. It has been found[2-5] that the process proceeds via a pseudostationary mechanism (the acylammonium salt does not accumulate)§ and, in the presence of an excess of the nucleophile, the kinetic equation is

$$v = (k_0 + k_{cat}[B]) \cdot [RCOX],$$

where [B] is the concentration of the base form of the amine and $k_0$ and $k_{cat}$ are the rate constants for the spontaneous reaction and the reaction catalysed by the tertiary amine respectively; here $k_0$ is negligibly small compared with $k_{cat}[B]$. The following equation then holds in a medium ensuring the complete dissociation of the acylammonium salt into ions:

$$k_{cat} = \frac{k_1 k_2 [HY]}{k_{-1}[X^-] + k_2 [HY]}$$

{the notation is the same as in mechanism (2), $k'_2 = k_2[H_2O]$ being used for hydrolysis in water}.

The ratio of the rates then depends on the concentrations of HY and the anion X and on their nucleophilic properties characterised by the constants $k_{-1}$ and $k_2$: in water the slowest stage is usually the formation of the acylammonium salt ($v_2 > v_{-1}$, $k_{cat} = k_1$).[2-5] By comparing the influence of pyridine on the hydrolysis of acetic anhydride in water and on the isotope exchange in its reaction with $CH_3^{14}COO^-$ (0.5–1 M), $k_{-1}/k'_2 \simeq 50$ litre mol$^{-1}$ was estimated[21]. A similar value (~80 litre mol$^{-1}$) was found for the hydrolysis of acetyl fluoride in water in the presence of pyridine[22]; here $k_1 = 15$ litre mol$^{-1}$ s$^{-1}$. It follows from these data that the acylammonium salt is in equilibrium with the initial substance[21,42]. The equilibrium is displaced to the left after the addition of dioxan[42,43], probably as a result of the decrease of polarity; when $[H_2O] < 4$ M, pyridine proved to be a weaker nucleophile than the acetate ion[42]. For the acetylpyridinium ion in water¶, $k_1 = 84$ litre mol$^{-1}$ s$^{-1}$, $k_{-1} = 910$ litre mol$^{-1}$ s$^{-1}$, and $k'_2 = 6.9$ s$^{-1}$, so that $k_{-1}/k'_2 = 130$ litre mol$^{-1}$.[14] Thus the reactivity of the acetylpyridinium ion in relation to the acetate ion is almost 4 orders of magnitude greater than in relation to water, assuming that $[H_2O] = 55$ M, $k_2 = k'_2/[H_2O] = 0.125$ litre mol$^{-1}$ s$^{-1}$, and $k_{-1}/k_2 = 7.3 \times 10^3$. Therefore, when the concentration of $CH_3COO^-$ (and in general of the ion $X^-$) is sufficiently high, we have $k_{-1}[X^-] > k_2[HY]$ and

$$k_{cat} = \frac{k_1 k_2}{k_{-1}[X^-]},$$

which has been observed, for example, in acetate buffers[5,42-44]. On the other hand, when the concentration of $X^-$ is extremely low, then, although $k_{-1} > k_2$, $v_{-1} = k_{-1}[X^-][AAS]$ may be smaller than $v_2 = k_2[HY][AAS]$ {in water $k'_2[AAS]$}. Indeed the rate of hydrolysis of acetic anhydride in water in the presence of pyridine is equal to the rate of acylation of anisidine and toluidine under these conditions ($k = 84 \pm 2$ litre mole$^{-1}$ s$^{-1}$) and is independent of the concentration of the acylated amines[14]. Consequently, under the given conditions, the lowest rate is observed for the stage involving the formation of the acetylpyridinium ion, for example we have $v_{-1}/v_2 \simeq 0.1$ and $k_{cat} = k_1$ when $[CH_3COO^-] \leq 10^{-3}$ M.

Since the lyonium ion $H_3O^+$ is the strongest acid in water, other species HY are stronger bases than water and are characterised by higher values of $k_2$. *p*-Toluidine and *p*-anisidine therefore react with the acetylpyridinium ion faster than $CH_3COO^-$ even at a concentration of 0.001 M.

On the other hand, in solvents of low polarity (benzene, dioxan, etc.) the reaction is usually of first order with respect to the acylated nucleophile over a wide range of its concentrations (see Section III, subsections 2 and 3). Within the framework of mechanism (2), this implies that the second stage determines the rate of reaction. This is probably associated with the absence of the dissociation of the AAs ion pair and hence the absence of the free $X^-$ ion in such solvents. The decomposition of the acylammonium salt into the initial components can then be regarded as a unimolecular process[33] and the expression for the rate of reaction becomes

$$v = \frac{k_1 k_2 [RCOX] \cdot [NR'_3] \cdot [HY]}{k_{-1} + k_2 [HY]}.$$

The transition to a unimolecular reaction leads to a considerable gain of activation entropy, as a result of which the process becomes faster and $k_{-1} \gg k_2[HY]$. Then

$$v = \frac{k_1 k_2}{k_{-1}} [RCOX] \cdot [NR'_3] \cdot [HY],$$

which has been observed experimentally. Under these conditions, $k_2$ may be greater than $k_{-1}$ but $v_2 < v_{-1}$ owing to the very low concentration of the acylammonium salt. In the limit, this version of the reaction can be converted into a synchronous process when the involvement of all the reactants in the transition state is responsible for the first order with respect to each.

An intermediate case has been described recently[41,45] involving a decrease of $k_{cat}$ during the acylation of *p*-anisidine and *p*-chloroaniline by sulphonyl bromides in nitrobenzene in the presence of pyridine (or its *N*-oxide), which the authors explained by the occurrence under these conditions of the equilibrium

$$[ArSO_2N^+C_5H_5Br^-] \rightleftarrows ArSO_2NC_5H_5^+ + Br^-.$$

The accumulation of the $Br^-$ ions displaced this equilibrium towards the less reactive ion pair, which decreases $k_{cat}$: the above relation disappears when the experiments

§ This conclusion has been confirmed[41] by the equality of the rates of consumption of the acylating and acylated components: the pre-stationary stage, involving the accumulation of the acylammonium salt, was observed only when the stopped flow method was used[14].

¶ The values for substituted pyridines are listed in Table 2.

are performed in tbe presence of an excess of added bromide[45]. Unfortunately, the authors were unable to calculate the equilibrium constant and the rate constants for the individual forms of the acylammonium salt.

On the other hand, for various stable acylammonium salts, such as acetylimidazolium halides, the relation $k_1 \gg k_2 \gg k_{-1}$ may hold even in non-polar solvents. The second stage is then slowest, but the acylammonium salt accumulates rapidly and irreversibly[46].

### 3. The Structure of the Intermediates

According to the data described above and also results obtained independently by conductimetric[47-49], potentiometric[50], infrared spectroscopic[17,51-66], NMR[57,58], and ultraviolet spectroscopic[14,59,60] measurements (see also Sheinkman et al.[1]), one can assume that acylammonium salts of the type $RCON^+R'_3X^-$ are the main intermediates in many acyl transfer reactions catalysed by tertiary amines†. On the other hand, by analogy with other acyl transfer reactions[65-71], one may assume that the reactions involving the formation and decomposition of acylammonium salts proceed via the tetrahedral intermediates (A) and (B) in Eqn.(4). However, these tetrahedral intermediates are probably fairly unstable, particularly in non-polar solvents, and a shallow minimum corresponds to them on the energy diagram, i.e. the transition states in the stages involving the formation and decomposition of the tetrahedral intermediate are similar to the intermediates themselves as regards energy and structure and in this sense the reaction is close to direct substitution of the $S_N2$ type[15,40]. One must emphasise that, according to some data[67,69-72], proton transfer in (B) is an important stage, since it is the only process which ensures the strengthening of the C–Y bond, i.e. the conversion of the readily removed group (a weak base) HY into a strongly basic group Y. This process is also particularly important in aprotic solvents, where it can occur spontaneously, and requires the cooperation of the base molecule[71]—in this sense one may speak of a combination of base and nucleophilic catalysis.

Table 1. Hydrolysis of the acid chlorides RCOCl in aqueous acetone (10.9 vol.% of water) in the presence of tertiary amines[87].

| R | Temp., °C | $10^4k_0$, $s^{-1}$ | $10^4k_{cat}$, $s^{-1}$ | | | |
|---|---|---|---|---|---|---|
| | | | $(CH_3)_3N$ | $(C_2H_5)_3N$ | pyridine | 2,4,6-trimethylpyridine |
| $CH_3$ | −40 | 0.975 | 35 000 | 7000 | $>10^5$ | 39 |
| $(CH_3)_3C$ | −40 | 0.027 | 770 | 1.2 | 6600 | 5.8 |
| $C_6H_5$ | −40 | 0.0047 | $>10^5$ | 35 000 | $>10^5$ | 30 |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | −40 | 1.22 | 1.2 | 1.2 | 1.79 | 1.1 |
| $2,4,6\text{-}(CH_3)_3\text{-}3,5\text{-}(NO_2)_2C_6$ | +20 | 0.056 | 2.5 | 7 | 93 | 0.17 |

Apart from tetrahedral intermediates, the formation of charge-transfer complexes has been demonstrated in a number of studies[53,73-82] in the first stage of the interaction of acylating agents with tertiary amines. It has come to be assumed that charge-transfer complexes can be converted into acylammonium salts (via a tetrahedral intermediate or via direct $S_N2$ substitution)[75-78], but one-electron transfer with formation of the acyl radical-ions $RCO^\cdot$ and amine radical-ions is more characteristic of these species. As a result of this, acid chloride–tertiary amine and acid anhydride—tertiary amine systems are capable (particularly for aromatic tertiary amines) of initiating effectively radical polymerisation[73,74,80-82].

On the whole, one should note that data for the structures and properties of acylammonium salts are still extremely incomplete, mainly because of their instability. However, stable polymeric acylammonium salts, obtained in the acylation of polyvinylpyridine partly alkylated by bulky groups, have been described recently[83]. The hydrophobic environment of the quaternary nitrogen atom probably prevents further reaction of these acylammonium salts. However, their properties were not investigated in detail.

## III. THE INFLUENCE OF REACTANT STRUCTURE ON THE REACTION RATE

### 1. The Hydrolysis of the Halides and Anhydrides of Carboxylic and Sulphonic Acids

The hydrolysis of acid halides and anhydrides has been one of the first acyl transfer reactions in the presence of tertiary amines which were investigated in detail as regards kinetics, mechanism, and structural relations. A study has been made of the accelerating influence of pyridine on the hydrolysis of acetic anhydride[3,4,84-86] and acetyl phosphate[2]. It has been found that 2-methyl- and 2,6-dimethylpyridines and also quinoline accelerate the process less effectively than 3- and 4-substituted pyridines and isoquinoline, probably owing to steric hindrance. The Bronsted equation holds separately for unhindered and hindered amines with the same proportionality coefficients $\beta$ (0.92) but different constant terms (10.36 and 9.42 respectively). According to Koskikallio[42], triethylamine is only 7 times more reactive in this reaction than pyridine despite a difference in $pK_a$ of almost 6 units (apparently also mainly owing to steric hindrance).

The role of the steric accessibility of the tertiary amine is clearly seen from the data in Table 1, particularly for the chlorides of hindered acids of the type of trimethylacetic acid[87]. Mesitoyl chloride is apparently hydrolysed via an $S_N1$ mechanism and catalysis by tertiary amines is not observed.

If the steric factor in the reaction investigated is constant, it is possible to observe the validity of the Brønsted and Hammett–Taft equations. The influence of the structure of the tertiary amines on the elementary stages of the hydrolysis of acetic anhydride has been examined[14]. It is seen from the results (see Table 2) that both the rate constants ($k_1$) and the equilibrium constants ($K_{eq}$) for the formation of the acetylpyridinium ion vary linearly with the basicity of the tertiary amine and $\beta = 0.87$ and 1.6 respectively. Thus the nucleophilic properties of substituted pyridines in relation to the carbonyl carbon atom vary in parallel with their basicity, the equilibrium nucleophilic properties being much more sensitive to the influence of the substituents than the basicity.

According to Fersht and Jencks[14], this indicates a greater "effective electronegativity" of the acyl group compared with the proton. On the curve relating the

†Other types of reactions of acylammonium salts have also been examined[1,61-64].

reactivity to structure for reactions of nucleophiles with the carbonyl group, pyridines are located close to a break-point[15,88,89]. As a result, while still retaining virtually the maximum dependence of their reactivity on basicity, they form highly reactive and selectively acylating agents (for example $k_{AcO^-}/k_{H_2O} = 7300$ for the acetylpyridinium ion, while the corresponding ratio for the acetylimidazolium ion is 29).[43]

Table 2. The interaction of acetic anhydride with tertiary amines in water (25°C, $I = 1$).[14]

| Amine | $pK_a$ | $k_1$, litre mole$^{-1}$ s$^{-1}$ | $k_{-1}$, litre mole$^{-1}$ s$^{-1}$ | $K_{eq}$ | $k_2$, s$^{-1}$ |
|---|---|---|---|---|---|
| $C_5H_5N$ | 5.51 | 84 | 910 | 0.092 | 6.9 |
| 4-$CH_3C_5H_4N$ | 6.33 | 490 | 262 | 1.86 | 2.3 |
| 3,4-$(CH_3)_2C_5H_3N$ | 6.79 | 1160 | 120 | 9.67 | 1.5 |
| 4-$CH_3OC_5H_4N$ | 6.82 | 935 | 30 | 31.2 | 0.4 |

The rate of reaction of the acetylpyridinium ion with water decreases with increase of the basicity of the initial tertiary amine and $\beta = -0.5$, i.e. water is relatively unselective in relation to these electrophiles. The possibility of direct polar coupling of the substituent with the reaction centre has been demonstrated for the acetyl-4-methoxypyridinium ion[14] and acetyl-4-dialkylamino-pyridinium ions[60]; this has also been confirmed by the correlation of lg $k_2$ and lg $k_1$ with $\sigma^+$. Here $\beta = -0.8$ and the sensitivity of the reaction to the basicity of the leaving group therefore increases with decrease of the reactivity of the electrophile[60]. On the other hand, in the hydrolysis of 3- and 2,3-substituted acetylimidazolium ions, which also exhibit an enhanced resistance to nucleophilic attack (the additional stabilisation corresponds to approximately 2.7 kcal mole$^{-1}$)[14], we have $\beta = 0.55$. Thus the relation between reactivity and sensitivity to the influence of the structure of the reactants on the rates of these reactions is on the whole fairly complex.

The only reaction for which the influence of the simultaneous changes in the structures of the catalyst and the acylating agent on the rate has been investigated is the hydrolysis of arenesulphonyl chlorides in the presence of substituted pyridines (RPy).[90,91] It was found that the correlation with $\sigma^0$ for R (sensitivity coefficient $\rho = -2.68$) and the Brønsted equation ($\beta = 0.45$) hold for the hydrolysis of $C_6H_5SO_2Cl$; the 4-acetyl and 4-cyano-derivatives deviate from this relation, possibly owing to the direct resonance interaction of the substituents with the reaction centre. Analogous correlations have been obtained for different R'$C_6H_4SO_2Cl$ (Table 3), where the coefficients $\beta$ vary linearly with $\sigma$ for R' (the slope is $0.122 \pm 0.002$). The values of $\rho$, characterising the influence of R' (they have been calculated for R' = H, *p*-$CH_3$, or *p*-$CH_3O$; the *para*- and *meta*-nitro-derivatives deviate towards reduced reactivities) increase linearly in their turn with increase of $pK_a$ for the amine (proportionality coefficient $0.114 \pm 0.004$). Thus, contrary to Hammond's postulate, in this series of reactions an increase of the reactivity of the reactants is accompanied by an increase of the coefficients $\beta$ and $\rho$.

Treating these quantities as characteristics of the degree of dissociation and formation of the bond in the transition state‡, the author suggested that, by virtue of its greater polarisability, sulphur forms bonds over greater distances than does carbon and that electron-accepting substituents in the acid chloride and electron-donating substituents in the amine catalyst promote the formation of bonds between them. The transition state thus becomes more "dense", i.e. the sum of the orders of the formed and ruptured bonds increases. On the other hand, electron-donating substituents in the acid chloride facilitate the preferential rupture of the bond, which is faster than the formation of the new bond.

Table 3. The influence of the structure of the sulphonyl chloride R'$C_6H_4SO_2Cl$ and the catalyst RPy on the rate of hydrolysis (water; 0.05 M NaCl solution; 25°C).[91]

| R | $pK_a$ | $\rho$ (with respect to R') | R' | $\sigma$ | $\beta$ (with respect to RPy) |
|---|---|---|---|---|---|
| 3,4-$(CH_3)_2$ | 6.46 | 0.89 | *p*-$NO_2$ | 0.78 | 0.557 |
| 4-$CH_3$ | 6.02 | 0.82 | *m*-$NO_2$ | 0.71 | 0.545 |
| 3-$CH_3$ | 5.68 | 0.78 | H | 0 | 0.457 |
| H | 5.21 | 0.69 | *p*-$CH_3$ | −0.17 | 0.441 |
| 3-$CH_3CO$ | 3.18 | 0.52 | *p*-$CH_3O$ | −0.45 | 0.406 |
| 4-CN | 1.90 | 0.34 | | | |
| 3-CN | 1.39 | 0.30 | | | |

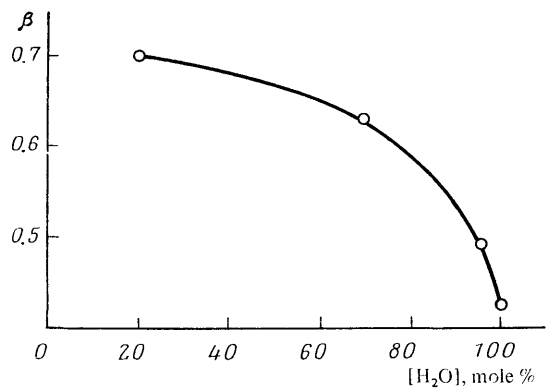



Figure 1. Variation of the Brønsted coefficient $\beta$ with the water content in acetonitrile in the hydrolysis of benzenesulphonyl chloride in the presence of pyridine[92].

However, we believe that the direct correlation of the coefficients $\beta$ with the orders of the formed and ruptured bonds is not always valid. For example, according to data[92] for the hydrolysis of benzenesulphonyl chloride in the presence of pyridine and 4-methylpyridine, $\beta$ increases from 0.43 to 0.70 when the mole fraction of water in the mixture with acetonitrile is reduced from 1 to 0.2, while in 45% aqueous dioxan solution $\beta = 0.79$. Fig. 1 shows that the greatest change in $\beta$ occurs in the presence of small amounts of added organic solvents, where significant changes in the structure of the transition state can hardly be expected.

‡Since the reaction was carried out in water, the acylammonium salt formation stage, regarded here as an elementary process, is probably rate-determining.

The difficulty of taking into account the steric accessibility of the nitrogen atom in the tertiary amine hindered for a long time a quantitative description of the dependence of the catalytic activities of aliphatic tertiary amines on their structure[13,93,94]. Such description has been based on a modified[95] Taft equation [Eqn.(6)], where the steric hindrance in the amines $R_1R_2R_3N$ was chaac: terised, on the basis of the isosteric principle, by the constants $E_N$ which are equal to the Taft steric constants $E_S$ for isosteric hydrocarbon substituents $R_1R_2R_3C$:

$$\lg k = \lg k_0 + \rho^* \sum \sigma^* + \delta E_N \quad . \qquad (6)$$

The applicability of this equation was tested in series where the amines (primary, secondary, and tertiary) behave as nucleophiles[95,96] and then in reactions where tertiary amines function as nucleophilic catalysts[97,98]. An equation relating quantitatively the catalytic activity of aliphatic tertiary amines to their inductive and steric characteristics was obtained for the first time for the hydrolysis of benzoyl chloride in 98% dioxan[97]:

$$\lg k = 2{,}80 - (2{,}0 \pm 0{,}2) \sum \sigma^* + (1{,}39 \pm 0{,}09) E_N .$$

Using this equation and also the analogous expressions for other reactions involving tertiary amines, the values of $E_N$ have been calculated for a fairly large number of tertiary amines[97,98]. These data give rise to the prospect of a quantitative description of many other acyl transfer reactions catalysed by tertiary amines, some of which will be examined in subsequent Sections.

## 2. Alcoholysis of Carboxylic and Sulphonic Acid Halides and Anhydrides

It is surprising that there are almost no literature data on the quantitative characteristics of the influence of tertiary amines on the acylation of phenols and particularly alcohols, which are important processes. For example, the mechanism of the catalysis of the acylation of phenols is still obscure. Thus the greater catalytic effect of tertiary amines in the acylation of phenols compared with alcohols and thiophenol[27,28,37,38] and the increase of this difference between the catalytic effects with increasing basicity of the amine[38] as well as the acidity of the phenol[37] support, according to the authors, a general base catalytic mechanism.

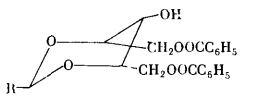
A detailed study of the reaction of $RC_6H_4OH$ with acetic anhydride in carbon tetrachloride in the presence of pyridine bases R'Py showed[99] that there is a satisfactory linear correlation between $\lg k$ and $\sigma^0$ for R with a slope $\rho = +1.52$. On the basis of the observed rate constants and $K_{ass}$ for the reactions of the same phenols with pyridine, the authors calculated the constants $k_B$, which were referred to the interaction of the complex ArOH...PyR' with acetic anhydride, and found that they too obey the Hammett equation with $\rho = +0.99$. The increase of the rate of reaction with enhancement of the electron-accepting properties of R confirms, according to the authors[99], the general base catalytic mechanism (for the non-catalytic reaction, $\rho = -0.82$).[27] $\rho = +0.6$ was also found for the reaction of phenols with benzoyl chloride in dioxan in the presence of triethylamine[39]. Later it was shown[100,101] that the introduction of strong electron-donating substituents R (for example, HO or $CH_3O$) likewise increases the reactivity of phenol, as a result of which the curve relating $\lg k$ to $\sigma$ shows an inflection in the range $\sigma = 0$–$0.1$; a similar inflection has been observed for the relation between $\lg k$ and the $pK_a$ for phenols (in dimethyl sulphoxide).[33] In catalysis by pyridine, the Hammett relation again had a descending branch with $\rho = -0.7$ and an ascending branch with $\rho = +0.4$.[39] According to the authors[33,39,100], these phenomena indicate a change in the mechanism of the catalytic reaction from nucleophilic for basic phenols ($\beta > 0$, $\rho < 0$) to the general base catalytic mechanism for acid phenols ($\beta < 0$, $\rho > 0$). The lower (by two orders of magnitude) catalytic activity of pyridine compared with that of triethylamine is also regarded as an argument in support of the above hypothesis[102]. However, one should note that the inflection in the Hammett or Brønsted plot can also be accounted for by the increased contribution of the direct polar coupling of electron-donating substituents of the type RO to the reaction centre[101]. We believe that one cannot fully rule out also the possibility of nucleophilic catalysis in the acylation of phenols—the inflection in the $\lg k$–$\sigma$ or $\lg k$–$pK_a$ curve can then be explained by a change in the relative rates of the stages [for example $k_2'$ and $k_2''$ in mechanism (4)]. The ready acylation of phenols by an equimolar amount of RCOOH in the presence of pyridine and chlorocyclophosphazene $(PNCl_2)_3$ has been explained[103] from the standpoint of nucleophilic catalysis. The reaction probably proceeds via the formation of a cyclophosphazenylpyridinium salt followed by interaction with RCOOH and the formation of an acylammonium salt.

The available information about the influence of the structure of the acylating agent in catalytic alcoholyses is limited to the above comparison of acetic anhydride, trifluoroacetic anhydride, and acetyl trifluoroacetate and also data[99] showing a decrease of the rate of acylation of *m*-nitrophenol in the presence of 3- and 4-quinolines by the anhydrides $(RCO)_2O$ in the sequence $CH_3 > C_2H_5 >$ iso-$C_3H_7 >$ t-$C_4H_9$. The proportionality between $\lg k$ in this series and the values of $E_S$ (or $E_S^0$) supports a steric type of effect although one cannot claim this with complete confidence in view of the relation between the values of $\sigma^*$ and $E_S$ for certain substituents R.[104]

Even less is known about the kinetics and structural characteristics of the acylation of alcohols. Since alcohols are weak acids and fairly strong nucleophiles, one may expect that tertiary amines will behave as nucleophilic catalysts in their acylation. This is confirmed by Bird's data[9], already mentioned, for the acylation of racemic alcohols RR'CHOH in the presence of optically active tertiary amines. It has been shown[105] that the methanolysis of a number of aliphatic acid halides in the presence of triethylamine proceeds via two competing mechanisms: via the formation of an acylammonium salt and via dehydrohalogenation with formation of a keten, which reacts further with methanol. Nucleophilic catalysis apparently also operates in the methanolysis of tetrachlorophthalic anhydride in the presence of pyridine[106]; by virtue of steric hindrance, dimethylaniline does not catalyse the process and actually gives rise to an inactive complex; because of this, the reaction is described by a kinetic equation of the Michaelis–Menten type.

The influence of the structure of tertiary amines and acylating agents has been investigated by Rogne[107] in the methanolysis of aromatic sulphonyl chlorides in the presence of pyridine and its methyl derivatives. As in hydrolysis (see Section III, subsection 1), electron-donating substituents in the tertiary amine and electron-accepting substituents in $RC_6H_4SO_2Cl$ increase the rate of reaction, the influence of R being more effectively described by the Hammett equation when $\sigma^+$ constants are used ($\rho^+ = 0.63$).

Similarly the rate of acylation of 5-hydroxy-1,3-dioxan derivatives of the type



where R = H or $C_6H_5$, by the chlorides of *para*-substituted benzoic acids and benzenesulphonic acid in pyridine is similarly correlated with the values of $\sigma^+$ ($\rho^+ = 0.83-0.95$ and 0.85 respectively)[108]. This indicates an appreciable contribution of the conjugation of the substituent with the reaction centre in the transition state. It was shown in the same study[108] that, in contrast to the majority of cyclic compounds where the equatorial hydroxy-group is more reactive than the axial group[108,109], in this case the axial epimers are more reactive; the authors explained this by the influence of the electronegative oxygen atoms in the ring.

Until very recently, there were no literature data for the influence of the structure of aliphatic alcohols on the rate of their catalytic acylation. We were able to show only recently[110,111] that this influence can be described by the extended Taft equation. The equation for the alcoholysis of benzoyl chloride in tetrachloroethylene is§

$$\lg (k/k_0) = (2.1 \pm 0.3)\,\sigma^* + (1.4 \pm 0.3)\,E_{S\,(RCH_2)}\ , \qquad (7)$$

the coefficients of sensitivity to inductive ($\rho^*$) and steric ($\delta$) influences being independent of the structure of the amine catalyst[111]. This shows that the electron density at the oxygen atom of the nucleophile increases during activation. Consequently the rate-determining stage of the process under the given conditions is attack by the alcohol on the carbonyl carbon accompanied by the transfer of a proton, the degree of dissociation of the O–H bond predominating over the degree of formation of the C–O bond[110]. The importance of the proton transfer xtage, which has been demonstrated theoretically[71] (see Section II, subsection 3), was also confirmed by studies of the isotope effect. In contrast to reactions in water, where the first stage is rate-determining and $k_H/k_D = 1.1 \pm 0.1$,[90,112] an isotope effect is observed in alcoholysis in a non-aqueous medium, indicating the involvement of proton transfer in the rate-determining stage[113]. One should note that similar considerations are applicable also to the acylation of phenols and the observed sign of $\rho^*$ in relation to the nucleophile cannot thus be regarded as a criterion of the type of catalysis.

The influence of the structure of tertiary amines on their catalytic effectiveness in the acylation of alcohols and phenols obeys the same relations as in the hydrolytic reactions. Thus the Brønsted equation holds for 3- and 4-substituted pyridines, high values of $\beta$ (between 0.85 and 0.93) being characteristic of the acylation of phenols, with the exception of the alcoholysis of trifluoroacetaldehyde ($\beta$ was not calculated[36] but an estimate based on the authors' data leads to $\beta \simeq 0.3$), probably owing to its higher reactivity.

The influence of pyridines in the methanolysis of sulphonyl chlorides can be described by the Brønsted ($\beta = 0.55$) and Hammett ($\rho = -3.0$) equations. The high negative value of $\rho$ shows, according to the author[107], that the first stage is rate-determining because of the high concentration of the nucleophile and the fairly high polarity of the medium. At the same time the lower solvating capacity of methanol compared with water leads to a more negative entropy of solvation (by approximately 15 e.u.) and decreases the overall rate of the process by two orders of magnitude.

As in other cases, sterically hindered 2- and 2,6-substituted pyridines (including 2-dimethylaminopyridine) exhibit a weak catalytic activity. The steric factor is particularly important when aliphatic tertiary amines are used. Thus a correlation between the rate of reaction and $\Sigma E_S$ for a number of tertiary amines of approximately equal basicity, $\delta = 0.84$ and 0.72 respectively, has been found in the benzoylation of phenol and *p*-nitrophenol in dioxan[102]. However, the approach based on the summation of the steric constants of substituents attached to nitrogen is inaccurate, since, in contrast to the polar characteristics, the steric characteristics are non-additive[114]. The application of equations of the type of Eqn.(6), using the steric characteristics of amines as a whole, is apparently more promising. Indeed, we were able to show[111] that the catalytic activity of tertiary amines in the benzoylation of alcohols in tetrachloroethylene is described by Eqn.(8) and that its parameters $\rho^*$ and $\delta$ are independent of the structure of the acylated alcohol:

$$\lg (k/k_0) = (-2.1 \pm 0.2) \sum \sigma^* + (0.91 \pm 0.09)\,E_N. \qquad (8)$$

Thus the influence of the structure of the alcohol and the amine on the rate of reaction is additive and the overall Eqn.(9) does not contain cross terms. This indicates a constant composition of the transition state for all the systems investigated in the coordinate space of the reaction, which is probably evidence for the occurrence of the reaction under these conditions by a nearly synchronous mechanism, owing to the weak solvating capacity of the solvent[40,110]. An increase of the latter increases the possibility of a shift of the transition state in the coordinate space, which leads to a relation between the rate of reaction and its sensitivity to changes in structure. This is manifested by the appearance of cross terms—in acylation in dioxan, for example, the correlation equation has the following form:

$$\lg k = 1.35 + 1.97\sigma^*_{(R)} + 1.34E_{S\,(RCH_2)} - 2.1 \sum \sigma^*_{(N)} + 0.92E_N\ , \qquad (9)$$

$$\lg k = 1.32 + 1.49E_{S\,(RCH_2)} - 1.71 \sum \sigma^*_{(N)} + 0.89E_N - 0.37\sigma^*_{(R)} \cdot E_N + \\ + 0.81 \sum \sigma^*_{(N)} \cdot E_{S\,(RCH_2)}. \qquad (10)$$

### 3. The Acylation of Amines by Carboxylic and Sulphonic Acid Halides and Anhydrides

The aminolysis of acid halides and anhydrides in the presence of tertiary amines is one of the most thoroughly investigated reactions owing to systematic studies by the Donets School of Chemistry¶. It has been shown for the reaction of benzoyl chloride with substituted anilines in benzene[24,117–119] that tertiary amines can be divided into

§ The steric effect of the group RO in Eqn.(7) is described by the constants $E_S$ for the $RCH_2$ groups, which are approximately isosteric with the RO groups.

¶ These investigations were continued by studies on the catalytic activities of amides, *N*-oxides, and other *O*-nucleophilic catalysts[115,116], the consideration of which is outside the scope of the present review.

several groups in terms of their catalytic activity, within which the Brønsted and Hammett–Taft equations hold†. On the other hand, it has been found that the catalytic activity of tertiary amines (with comparable basicities) falls on passing from unhindered heterocyclic amines to 2-substituted pyridines, quinoline, and dialkylanilines. Aliphatic cyclic tertiary amines are much weaker catalysts than would be expected from their basicity, because they are subject to an appreciable steric hindrance. For this reason, the linear Brønsted plot (Fig. 2) corresponding to these substances lies below the corresponding plot for the pyridines, although the slopes of the straight lines are virtually the same (0.81 ± 0.05 and 0.86 ± 0.01) [119]; the points corresponding to amines such as triethylamine lie lower still. Similar relations have been observed for the aminolysis of toluene-*p*-sulphonyl bromide in a 1 : 1 nitrobenzene–cyclohexane mixture [120,121].

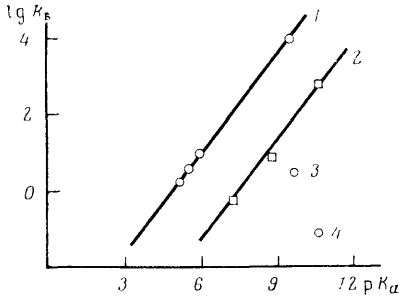



Figure 2. The Brønsted correlation for the reaction of benzoyl chloride with *m*-chloroaniline catalysed by tertiary amines [199]: 1) pyridine bases; 2) cyclic amines; 3) trimethylamine; 4) triethylamine.

The combination of a high capacity for resonance stabilisation, basicity, and steric accessibility is probably responsible for the extremely high catalytic efficiency of *N*-aryl- and *N*-alkyl-imidazoles [47,122–124]; the acylammonium salt is then unusually stable and can be fairly readily isolated and characterised [14,47]. Imidazole itself is relatively inactive as a catalyst, but its hydrochloride, which in some respects resembles acylammonium salts, is capable of transferring the acyl group to *m*-chloroaniline [125].

Further studies demonstrated the dependence of the efficiency of the catalyst on the properties of the acylating agent and the acylated substrate. Thus the catalytic activity diminishes in the aminolysis of ArCOHal with increase of the strength of the C–Hal bond, i.e. on passing from the bromide to the chloride, while the aminolysis of benzoyl fluoride is actually inhibited by pyridine [23,32]. Triethylamine catalyses the acylation of butylamine by benzoyl cyanide [126], while the aminolysis of the majority of carboxylic acid anhydrides is inhibited by pyridine [24,25,127].

† The catalytic activity of tertiary amine hydrochlorides has been noted in the aminolysis reaction [11,24,47,117–119], which is probably associated with the effect of the ion pair $C_5H_5N^+ \cdots Cl^-$ as a bifunctional catalyst.

However, catalysts may be observed on passing to the anhydrides of stronger acids: trichloroacetic [25], *p*-phenylthiobenzoic [128], and sulphonic acids [26]. On the other hand, the catalytic effect is observed following the enhancement of the nucleophilic properties of the tertiary amine, for example, in the case of 4-*NN*-dimethylaminopyridine [25], or when bifunctional catalysts of the type of 2-hydroxypyridine are used [32]. In the latter case, the change in the mechanism of catalysis is revealed by the change in its relative efficiency for different acylating agents: the $k_{cat}/k_0$ ratio for $C_6H_5COX$ diminishes in the following sequence of X: F ≫ Cl > Br.

The efficiency of the catalysis increases also on enhancement of the electron-accepting properties of the substituents in the acid halide, although the effect is not very great (see Table 4, Nos. 3–6). The polarisability of the reaction centre has a much greater influence on the catalytic activity of tertiary amines; Table 4 (Nos. 8 and 9) shows that, in the aminolysis of *p*-nitrobenzenesulphonyl bromide [129], pyridine is 30–40 times more effective than in the aminolysis of benzoyl chloride. An even greater catalytic effect has been observed in the reactions of sulphonic acid anhydrides [26], despite the opposite influence of the solvent, an increase of the polarity of which has been shown [46,130] to decrease $k_{cat}/k_0$.

Table 4. Efficiency of the catalytic effect of tertiary amines in the acylation of anilines $RC_6H_4NH_2$ (benzene, 25 °C).

| No. | Acylating agent | R | Catalyst | $k_0$, litre mole$^{-1}$ s$^{-1}$ | $k_{cat}$, litre$^2$ mole$^{-2}$ s$^{-1}$ | $k_{cat}/k_0$, litre mole$^{-1}$ | Reference |
|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5COCl$ | H | Pyridine | $6.99 \cdot 10^{-2}$ | 8.8 | 136 | 118, 119 |
| 2 | $C_6H_5COCl$ | *p*-$NO_2$ | Pyridine | $4.2 \cdot 10^{-5}$ | 0.152 | 3600 | 118, 119 |
| 3 | $C_6H_5COCl$ | *m*-Cl | Pyridine | $3 \cdot 10^{-3}$ | 2.0 | 660 | 127 |
| | | | | $3.4 \cdot 10^{-3}$ | 1.9 | 450 | 118, 119 |
| 4 | *p*-$(CH_3)_2NC_6H_4COCl$ | *m*-Cl | Pyridine | $1.74 \cdot 10^{-4}$ | $7.16 \cdot 10^{-2}$ | 410 | 127 |
| 5 | *p*-$NO_2C_6H_4COCl$ | *m*-Cl | Pyridine | $1.71 \cdot 10^{-2}$ | 15.2 | 890 | 127 |
| 6 | *p*-$C_6H_5C_6H_4COCl$ | *m*-Cl | Pyridine | $2.72 \cdot 10^{-3}$ | 2.0 | 730 | 23 |
| 7 | *p*-$C_6H_5C_6H_4COBr$ | *m*-Cl | Pyridine | 0.249 | 239 | 936 | 23 |
| 8 | *p*-$NO_2C_6H_4SO_2Br$ | H | Pyridine | $3.46 \cdot 10^{-6}$ | $2 \cdot 10^{-2}$ | 6420 | 129 |
| 9 | *p*-$NO_2C_6H_4SO_2Br$ | *m*-Cl | Pyridine | $9.12 \cdot 10^{-8}$ | $2.3 \cdot 10^{-3}$ | 25 100 | 129 |
| 10 | $(CCl_3CO)_2O$ | *p*-$NO_2$ | *p*-Dimethylaminopyridine | 2.86 | 94.7 | 36 | 25 |
| 11 | $(CH_3CO)_2O$ | H | *p*-Dimethylaminopyridine | $2.15 \cdot 10^{-3}$ | 1.02 | 475 | 25 |
| 12 | $(p\text{-}NO_2C_6H_4CO)_2O$ | H | *p*-Dimethylaminopyridine | $1.4 \cdot 10^{-2}$ | 22.8 | 1580 | 127 |
| 13 | $(p\text{-}ClC_6H_4SO_2)O$ * | *m*-$NO_2$ | *p*-$CH_3C_6H_4N(CH_3)_2$ | $1.27 \cdot 10^{-3}$ | 156 | 12 000 | 26 |

*In nitrobenzene.

Analysis of the results based on Kirkwood's equation led the authors [46,130] to the conclusion that the polarity of the activated complexes in catalytic and non-catalytic reactions is approximately the same ($\mu_{\neq}$ = 19.8 and 19.6 D respectively), but in the catalytic process the activated complex is larger owing to the involvement of three molecules in its formation.

The efficiency of the tertiary amine depends significantly also on the properties of the acylated amine; thus it has been shown [118,120,129] that $k_{cat}/k_0$ increases with decrease of the basicity of the arylamine and the catalytic effect is shown most clearly for weakly basic amines. As a result of this, the values of $\rho$, characterising the sensitivity of the reaction to the influence of substituents in $ArNH_2$, decrease on passing from the non-catalytic to the

catalytic process, from −2.67 to −1.35 for the reaction with $C_6H_5COCl$ [118] and from −3.98 to −2.8 for the reaction with $p$-$NO_2C_6H_4SO_4Br$.[120,129] Finally, the influence of temperature on the above processes is expressed, in conformity with the relations discussed in Section II, by a decrease of the efficiency of the catalysis with increase of temperature.

### 4. Reactions of Esters

The influence of tertiary amines on the reactions of esters has been investigated for a long time and in great detail partly in connection with their similarity to many enzymatic processes. Greatest attention has been devoted in this connection to imidazole, which enters into the active centres of many hydrolases and is also probably an acyl transferring agent in the biosynthesis of acetylcholine[131,132]. Imidazole is involved in nucleophilic reactions via its tertiary nitrogen atom; on the other hand, the presence of the secondary nitrogen atom makes possible the elimination of the proton from the acylammonium salt, which leads to fairly stable acylimidazoles[133].

In conformity with what has been said in Section II, imidazole and other tertiary amines may catalyse via the nucleophilic mechanism only the hydrolysis of activated esters (phenol, thiol, etc. esters)[29,134-144] if $\Delta pK_a \leq 3$ for ArOH and the imidazolium ion. When $\Delta pK_a > 3$, the cooperation of general base catalysis with nucleophilic catalysis is necessary[137] and, for $\Delta pK_a \gg 3$, only general base catalysis is observed[137,140,145] or there is no catalysis at all[136,137]. The lactonisation of the amide and ester of $o$-hydroxymethylbenzoic acid is catalysed by imidazole and other bases[146,147], probably via the general base mechanism, as shown by the ratio $k_{H_2O}/k_{D_2O} = 3.46$ and the Brønsted coefficient (0.87).[147] The ability of imidazole to catalyse the hydrolysis of *NO*-diacetylserine amide has also been noted[148].

The solvent has a significant influence on the ratio of the basicities of the leaving group and the amine and hence on the type of catalysis. Thus the aminolysis of 2,4-dinitrophenyl acetate in benzene and chlorobenzene[149,150] is catalysed by pyridine, in contrast to aqueous solutions, probably via the general base mechanism. The fundamental argument used by the authors has been the observation of a correlation between $\lg k_{cat}$ for catalysts of different chemical types and their proton-accepting capacity, characterised by the constants for association with phenol[149] or $p$-fluorophenol[150], and also the fairly high values of $E_{cat}^{app}$ (7–10 kcal mole$^{-1}$).[151] On the other hand, the absence of correlation between the basicity of tertiary amines and their catalytic activity in the aminolysis of 2,4-dinitrophenyl acetate and other similar esters has been interpreted[152] as evidence for nucleophilic catalysis. Thus the problem cannot be regarded as solved.

Without going into the details of the mechanism of the reactions of esters, which have been considered in a number of monographs[18,29,89,153-155], we shall merely emphasise that the transition state in the rate-determining stage in such reactions is apparently extremely polar and close to a tetrahedral complex with separated charges[18,29,89]. This explains the decrease of the rate of reaction following the addition of alcohol to water[156]‡.

As in other instances, in the reactions of esters the catalytic activity of amines of the same type is described satisfactorily by the Hammett or Brønsted equation, but different correlation lines correspond to different classes. The Brønsted coefficient is usually approximately 0.7 to 0.8 [134,135] (the value of 1.62 obtained in one investigation[136] is probably erroneous due to the small number of compounds investigated). Substituted imidazoles are again the most active (for comparable basicities) and are followed in this respect by pyridines and the relatively less active aliphatic tertiary amines[135,136] as well as 2- and 2,6-substituted pyridines[159-162]. On the other hand, it has been found for the reaction of the esters $2,4\text{-}(NO_2)_2C_6H_3OOCR$ with aniline[152] and the hydrazides $p$-$R'C_6H_4CONHNH_2$ [163] that the catalytic activity of pyridine increases in the following sequence of R: $CH_3 < C_6H_5 < p\text{-}NO_2C_6H_4$ and in the following sequence of R′: $H < CH_3O < Br$. Thus the observed relations are typical for nucleophilic reactions, so that the authors' hypothesis of general base catalysis appears doubtful.

It has been shown for triazoles[164] as well as pyridine and phthalazine[165] that the catalytic activity of tertiary amines increases following the appearance of several neighbouring atoms in the heterocycle, which is associated, according to the authors, with the repulsion of the neighbouring lone electron pairs, resulting in an enhancement of the nucleophilic properties of the compound[165].

The efficiency of catalysis increases significantly when bifunctional derivatives are used in which the nucleophilic attack on the nitrogen is accompanied by proton transfer, the importance of which has already been mentioned. Thus, in the hydrolysis of $p$-nitrophenyl acetate (NPA), 2-hydroxy-, 2-hydroxyethyl-, and 4-($\gamma$-hydroxypropyl)-pyridines are much more active than the corresponding picolines[166]; serine and histidine are more active still. The mercaptoalkyl derivatives of imidazole and benzimidazole[167,168] and also 2-($o$-hydroxyphenyl)imidazole [169] are extremely efficient as catalysts. On the other hand, 4-($\beta$-diethylaminoethyl)- and 4-(diethylaminomethyl-imidazoles are less effective than imidazole itself[170]. It has been found[171] that the aminoalcohols $RR'NCH_2CH_2OH$ catalyse the decomposition of many phenyl esters, behaving at the same time as acyl transferring agents. According to the authors, *N*-nucleophilic catalysis does not occur in this case, the aminoalcohols undergoing *O*-acylation with subsequent rapid hydrolysis of the resulting esters.

Another interesting group of facts includes the effects observed in many instances in studies of the hydrolysis of esters, analogous to those noted in enzymatic catalysis. Thus the attainment of the maximum reaction velocity at a certain substrate concentration (Michaelis–Menten kinetics) and inhibition of the reaction by its products[172], which is characteristic of many enzymatic systems, have been observed in the hydrolysis of $p\text{-}NO_2C_6H_4OC(O)OCH_2CH_2\dot{N}^+.(CH_3)_2C_{12}H_{25}$ in the presence of *N*-stearoylhistidine; the rate of this reaction is 2000 times higher than in catalysis by *N*-acetylhistidine[173]. Similar phenomena have been observed in the hydrolysis of 4-carboxyphenyl acetate in

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‡The decrease of the rate of acylation of neutral nucleophiles by nitrophenyl esters on passing to a micellar medium, characterised by a lower value of $\epsilon$ than water, has also been explained by the unfavourable influence of the non-polar environment[156-158].

the presence of 1-aminomethyl-4-(4'-imidazolyl)naphthalene[174]. Some of these effects (for example, kinetics simulating saturation) may be associated with the aggregation of the esters of higher aliphatic acids in water[175], but the fundamental cause is apparently the hydrophobic interaction of the catalyst with the substrate, which decreases the activation entropy. This probably accounts for the sharp increase of the rate of hydrolysis of the esters $p$-$NO_2C_6H_4OOCC_nH_{2n+1}$ in the presence of alkylimidazoles with increase of the number of carbon atoms in the substrate and the catalyst§ (see Table 5)[176-178].

Table 5. The influence of hydrophobic properties on the hydrolysis of the esters $C_nH_{2n+1}COOC_6H_4NO_2$ in the presence of the alkylimidazoles $C_mH_{2m+1}N{=}$ in water at 25°C.[177]

| $n$ (in ester) | $k_{OH}$, litre mole$^{-1}$ s$^{-1}$ | $k_{cat}$, litre mole$^{-1}$ s$^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| | | $m=2$ | $m=4$ | $m=6$ | $m=8$ | $m=10$ |
| 1 | 12.1 | 0.40 | 0.40 | 0.43 | 0.45 | 0.61 |
| 3 | 6.75 | 0.35 | 0.36 | 0.36 | 0.39 | 0.45 |
| 5 | 6.34 | 0.32 | 0.39 | 0.40 | 0.49 | 2.39 |
| 7 | 3.24 | 0.045 | 0.20 | 0.48 | 0.76 | 5.54 |
| 9 | 0.48 | 0.014 | 0.019 | 0.15 | 0.93 | 11.7 |

Polymeric catalysts of the hydrolysis of esters are of interest. In this respect, detailed studies have been made on partially alkylated polyvinylpyridines[65,180-184], polyaziridines[185], polyvinylimidazoles and the copolymers of vinylimidazole with other monomers[186-191,193], and the polyoxyethylene ester of $N$-benzoylhistidine[192]. In many instances these catalysts exhibited an efficiency several orders of magnitude higher than the corresponding monomers, the effect being particularly pronounced in the hydrolysis of esters with long hydrocarbon chains[185,190]. It is suggested that the active centres in these polymers are tertiary amino-groups, which behave as nucleophilic[65,181-183,186] or general base[185] catalysts (possibly in cooperation with other groups[186]); on the other hand, the efficiency of the catalysis is associated mainly with the concentration of the reactants in the active cavities formed by the hydrophobic parts of the polymer chain and the ammonium groups. However, one should bear in mind the fact that the effect of the concentration of the reactant may be extinguished owing to the decrease of the true reaction rate caused by the weak solvating capacity of the medium[156-158], which may be the reason for the insignificance of the effects in many instances[186,190].

(4-Imidazolyl)methoxy- or β-(4-imidazolyl)ethylaminocyclodextrins, in which the imidazole moiety and the OH group of the cyclodextrin act synchronously, combining with the acyl which is subsequently hydrolysed, constitute an unusual type of polymeric catalysts[194]. This mechanism, resembling the action of serine hydrolases, ensures the acceleration of the hydrolysis of NPA by a factor of 50 to 200.

§A similar phenomenon has been observed in the reaction of the same esters with the amines $C_nH_{2n+1}NH_2$ under the conditions of catalysis by a second amine molecule[179].

## 5. The Reactions of Isocyanates

It has been known for a long time that tertiary amines accelerate the reactions of nucleophiles with isocyanates[195-197]. The similarity of this process to the reactions of acid halides is clear from a review[93] and from the literature[98,198-206], namely the dependence of the catalytic activity of tertiary amines on their basicity and steric accessibility and the absence of correlation between $\lg k_{cat}$ and $pK_a$. On the other hand, there is satisfactory correlation based on Eqn.(6) and, as can be seen from Table 6, the reactions of isocyanates with alcohols are less sensitive to the structure of the tertiary amine than the analogous reactions of acid chlorides. When nucleophiles of the same type are varied (ROH, Table 6, Nos. 1 to 3), the values of $\rho$ and $\delta$ remain virtually constant, while, on passing to butanethiol (Table 6, No.4), the sensitivity of the reaction to both effects increases[98], probably by virtue of the greater bulk and greater polarisability of the sulphur atom compared with the oxygen atom. Bridged cyclic amines of the type of diazabicyclo-octane (DABCO) and quinuclidine are very effective catalysts in all cases, mainly because the degree of the steric hindrance is low (DABCO is close to trimethylamine as regards the value of $E_N$), while the basicity is high.

Table 6. The correlation parameters of the catalytic activity of tertiary amines in the reactions of phenyl isocyanate with nucleophiles in accordance with Eqn.(6).

| No. | Nucleophile | Conditions | $\lg k_0$ | $\rho$ | $\delta$ | Refs. |
|---|---|---|---|---|---|---|
| 1 | $C_4H_9OH$ | Toluene; 49.69° | 0.9 | −0.94 ± 0.03 | 0.94 ± 0.04 | 97,205 |
| 2 | $C_4H_9OH$ | Cyclohexane–dioxan (2:1); 31° | 0.7 | −0.78 ± 0.22 | 0.57 ± 0.08 | 98,199 |
| 3 | $(C_4H_9)_2CHCH_2OH$ | Benzene; 24° | 0.6 | −0.79 ± 0.45 | 0.37 ± 0.15 | 98,200 |
| 4 | $C_4H_9SH$ | Toluene; 25° | 1.6 | −1.00 ± 0.23 | 0.67 ± 0.09 | 98,198 |

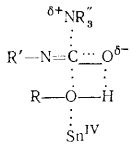
The importance of the steric factor suggests a nucleophilic mechanism of the catalytic reaction with formation as an intermediate of the dipolar ion

$$R{-}N{=}\overset{O}{\overset{|}{C}}{-}{}^{+}NR'_3 \leftrightarrow R{-}\overset{-}{N}{-}\overset{O}{\overset{\|}{C}}{-}{}^{+}NR'_3,$$

the stability of which increases owing to the resonance delocalisation of the negative charge. This leads to the possibility of observing this product by infrared spectroscopy[207] and also to the possibility of the separate determination of $k_1$ and $k_2/k_{-1}$; such data have been obtained for the reaction of phenyl isocyanate with alcohols in the presence of triethylamine and pyridine[93,196].

The efficiency of catalysis decreases in the following series of substances: butanol > water > diphenylurea[208] and increases with increase of solvent polarity[196,209] (non-specific solvation probably plays the main role[209]) and also after the addition of organotin compounds[209]. The latter themselves catalyse the reactions of isocyanates and their

role probably consists in activating the alcohol. Here the transition state is probably



### 6. Various Reactions

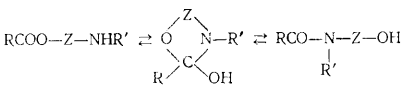
Among other reactions involving acyl transfer, the catalytic effect of tertiary amines has been observed in the aminolysis of carbamates[210] and the hydrolysis of a number of amides[211-215]. In most cases, the authors postulated the general base or general acid mechanism of catalysis[213,214] although Stauffer[212] adduced evidence supporting nucleophilic catalysis of the hydrolysis of trifluoroacetanilide by imidazole buffers.

In certain new studies, examples of unusually effective catalysis have been described. Thus the rate of hydrolysis of tetraethyl pyrophosphate catalysed by substituted benzimidazoles in the excited state has been found to be similar to the diffusional rate ($k \approx 10^{10}$–$10^{11}$ litre mole$^{-1}$ s$^{-1}$), which has been explained by the increase of the basicity of the catalyst on excitation to the singlet state and by the decrease of the energy barrier to the formation of the acylammonium salt[216].

A study of the hydrloysis of 2-hydroxy-4-nitrophenyl sulphate[217] showed that polyaziridine, partly alkylated by dodecyl- and methylene-imidazole residues, accelerates the reaction by a factor of $10^{12}$, while imidazole itself exhibits only a weak catalytic activity. According to the authors, this effect is caused by the hydrophobic interaction of the substrate with the dodecyl groups and the subsequent nucleophilic catalysis by imidazole.

## IV. INTRAMOLECULAR CATALYSIS

The acyl transfer reactions with the intramolecular involvement of a tertiary amino-group are in many respects analogous to the N → O acyl migration with participation of a primary or secondary amino-group, which takes place, according to modern ideas[218-223], via the following mechanism (without taking into account the possible proton transfers):

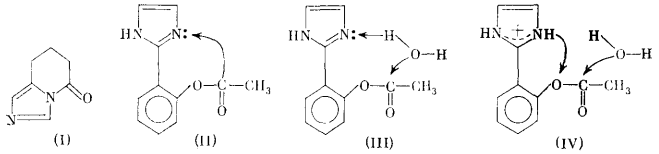


However, since the acylammonium salts are unstable, they behave merely as reactive intermediates and the tertiary amino-group may be regarded as a nucleophilic catalyst. Among reactions of this type, studies have been made mainly on the reactions of amino-esters and to a less extent on the acylation of aminoalcohols.

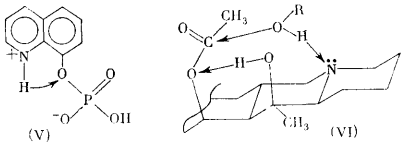
### 1. Hydrolysis and Other Reactions of Aminoesters

Intramolecular catalysis in the reactions of aminoesters is determined, like intermolecular catalysis, by the properties of the alkoxy-residue eliminated. If the amino-group in the anion $R'_2N-Z-O^-$ is more basic than $O^-$, the acyl residue in the ester $RCOO-Z-NR'_2$ may be transferred to the nitrogen atom with formation of the acylammonium salt $RCO(R')^+_2N-Z-O^-$, which undergoes further nucleophilic attack (nucleophilic catalysis)[29]. This mechanism is characteristic of activated esters, such as aryl (4-imidazolyl)butyrates[224,225]; in this case, the intermediate is the lactam (I). The amide and the methyl ester of the same acid are hydrolysed without the participation of neutral imidazole, although in the case of the amide the influence of the protonated form of imidazole was noted. Nucleophilic catalysis has been proposed also for the hydrolysis of *o*-(4-imidazolyl)phenyl esters[226,227], but, subsequently it was concluded on the basis of the ratio $k_{H_2O}/k_{D_2O} = 3.23$ and the activation parameters that general base catalysis operates in the reactions of these esters[228].

It has been shown[144] that the mechanism of the catalysis of the hydrolysis of substituted 2-imidazolylphenyl acetates depends on pH: in the alkaline region, nucleophilic catalysis (II) operates, in a neutral medium there is general base-catalysed cooperation with attack by imidazole on water (III), while in a weakly acidic medium general acid catalysis by the protonated form of imidazole (IV) operates:



The same possibilities occur also in other instances. Thus, according to some workers[228-232], general acid catalysis obtains in the hydrolysis of the zwitter-ion of 8-quinolinyl phosphate (V)[229] and substituted 4-benzimidazolylpeptides[230], while general base catalysis, confirmed by the ratio $k_{H_2O}/k_{D_2O} = 2.35$, operates in the hydrolysis and hydrazinolysis of 8-acetoxyquinoline[228,231] and also in the solvolysis of cevadine and other Ceveratrum alkaloids [for example, compound (VI)]; in the latter case, general acid catalysis by the OH group operates simultaneously[232]:



On the other hand, in the hydrolysis of 8-hydroxyquinoline monoesters with succinic or glutaric acid, a nucleophilic mechanism of catalysis, confirmed by the ratio $k_{H_2O}/k_{D_2O} = 1.05$, has been demonstrated[233].

In a few studies, where the efficiencies of the intermolecular and intramolecular catalysis were compared, the predominance of the latter has been demonstrated. Thus, it has been found[234] that the ratio of the rate constants for the hydrolysis of the esters $(CH_3)_2N(CH_2)_3.COOC_6H_4R$ ($k_I$) and the bimolecular hydrolysis of aryl acetates in the presence of trimethylamine ($k_{II}$) varies from 1260 (for R = H) to 5370 mole litre$^{-1}$ (for R = *p*-$NO_2$); here the entire gain is apparently achieved as a result of the effect associated with the mutual approach of the functional groups, resulting in a gain of translational entropy. The effect for δ-dimethylaminovalerate esters is smaller by a factor of 1.6–2.7 because the five-membered ring in the transition state is more favourable than

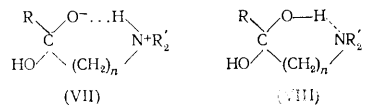
the six-membered ring. The values of $k_I/k_{II}$ for γ-(4-imidazolyl)butyrate esters are lower by two orders of magnitude—ranging from 94 (for R = *p*-$NO_2$) to 24 mole litre$^{-1}$ (for R = H).

In the hydrolysis of non-activated aminoesters, a significant catalytic effect by the tertiary amino-group has been found only in the case of 4-(β-acetoxyethyl)imidazole[224,227] and 5-acetoxymethyl-1-methylimidazole[235], which has been explained by the favourable nature of the cyclic transition state arising in this case in the O → N acyl transfer. In the remaining instances investigated, the introduction of a tertiary amino-group into the ester molecule accelerates its hydrolysis by not more than a factor of two (see Table 7) owing to the inductive effect of the amino-group[236-239]. The hydrolysis of esters of this kind is described by the general correlation equations for esters with a variable alcoholic component[238,240] and an appreciable catalytic effect (of the kind postulated, for example, by Schätzle et al.[241]) is therefore not observed.

Table 7. The influence of the amino-group on the alkaline hydrolysis of the aminoesters $RCOOCH_2CH_2X$.

| R | Conditions | $k$, litre mole$^{-1}$ s$^{-1}$ | | | | $\frac{k_{N(CH_3)_2}}{k_H}$ | $\frac{k_{+NH(CH_3)_2}}{k_{+N(CH_3)_3}}$ | References |
|---|---|---|---|---|---|---|---|---|
| | | X = H | X = $N(CH_3)_2$ | X = $+N(CH_3)_3$ | X = $+NH(CH_3)_2$ | | | |
| $CH_3$ | Water, 25° 0.07 M $KClO_4$ $I$ = 0.1 | 0.045 | 0.1 | 1.48 | 42.6 | 2.2 | 28.8 | 245 |
| | | — | — | 2.0 | 39.1 | — | 19.6 | 246 |
| $CH_2=C(CH_3)$ | Water, 25° $I$ = 0.5 | 0.035 | 0.042 | 0.60 | 16.5 | 1.2 | 27.5 | 238 |
| $C_6H_5$ | Water, 25° $I$ = 1 | 0.03 | 0.058 | 0.56 | 16 | 1.9 | 28.5 | 249 |
| $C_6H_5$ | 30 wt.% alcohol, 60° $I$ = 0.1 | 0.058 | 0.011 | 3.7 | 150 | 1.9 | 40.5 | 237 250 252 |

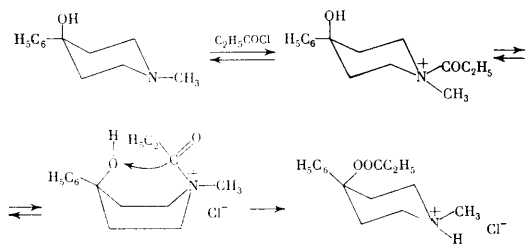
Table 7 shows that esters containing a charged ammonium group are hydrolysed much faster than their neutral analogues. For quaternary ammonium derivatives, this effect[242,243] is associated with the electrostatic interaction between the positively charged nitrogen atom and the negative charge arising in the transition state in alkaline hydrolysis and in this instance it is hardly useful to speak of catalysis, as was done by Smith and Williams[244]. On the other hand, the acceleration of the reaction by a factor of 20–40 for protonated aminoesters (see Table 7) is in all probability associated with the general acid catalysis by the N–H$^+$ group. This is confirmed by the decrease or disappearance of the above difference in compounds whose rigid structure prevents the approach of N$^+$–H to the ester group[252-256]. At the same time no evidence has been obtained for the N$^+$–H...O–C hydrogen bond in aminoesters by infrared spectroscopy[239,246-248] and PMR.[251] This suggests that the main effect in these instances is the stabilisation of a transition state close to the tetrahedral adduct (VII) as a result of proton transfer and the formation of the neutral compound (VIII) and not an increase of the charge δ$^+$ on the carbonyl carbon atom owing to the formation of a hydrogen bond, as suggested in a number of investigations[241,245,247,248]. The decrease of the degree of charge separation should lead to the "unfreezing" of the solvent and the corresponding gain of entropy of solvation. Indeed, it has been found[250] that the acceleration of the hydrolysis of the protonated forms of aminoesters is associated exclusively with the increase of the pre-exponential term (lg $A$). A similar conclusion was reached in a study of the hydrolysis of aminoacid esters[257]:



(VII) (VIII)

## 2. Acylation of Aminoalcohols

The hypothesis that nucleophilic catalysis by a tertiary amino-group is possible in the esterification reaction has been used for a long time to account for the large differences between the reactivities of the stereoisomers of heterocyclic aminoalcohols[258-263]. Thus it has been suggested[258] that 1-methyl-4-phenyl-4-piperidinols and *trans*-decahydro-4-quinolinols, having an axial OH group, react with propionyl chloride via the formation of an intermediate acylammonium salt and its intramolecular rearrangement via the mechanism



In epimers with an equatorial OH group, such rearrangement is difficult and acylation did not take place under the experimental conditions. It has been found[262,263] that only the 3-azabicyclo[3,3,1]nonan-9-ol isomer containing the OH and $CH_3N$ groups in the *syn*-positions is acylated.

This mechanism was confirmed quantitatively for the first time in a study[264] where it was shown that, on passing from cyclohexanol to 1,3-dimethyl-4-piperidinol, the rate of benzoylation in tetrachloroethylene (at 25°C) increases by more than four orders of magnitude. This demonstrated the occurrence of intramolecular catalysis, the efficiency of which was appreciably higher for compounds with an axial OH group, which agrees well with qualitative data[258]. Comparison of the rate constants for the bimolecular process and the trimolecular benzoylation of cyclohexanol in the presence of *N*-methylpiperidine led to the conclusion that the intramolecular catalysis in these systems is approximately 100 times more effective than the intermolecular catalysis.

Data concerning the involvement of a tertiary amino-group in the acylation of acyclic aminoalcohols have been fairly contradictory until recently. Thus the acceleration of the esterification of the alcohols $(C_6H_5)_2C(OH)(CH_2)_nNR_2$ relative to non-nitrogen-containing analogues was not observed[265]. Possibly this was due to steric factors hindering the intramolecular catalysis, since a high reactivity of the aminoalcohols has been demonstrated qualitatively in a number of other investigations[266-268]. This was confirmed quantitatively for the first time in a study[269] of the reaction of benzoyl chloride with the alcohols $Ar(R)C(OH)(CH_2)_nNR'_2$ in dioxan. It was shown

that the introduction of the $R'_2N$ group increases the reactivity of the alcohol by 6–8 orders of magnitude. The reaction was of first order with respect to the aminoalcohol in all cases, which demonstrates the occurrence of intramolecular catalysis, the efficiency of which decreases appreciably when $R' = CH_3$ is replaced by $R' = C_2H_5$ because of the steric hindrance to the formation of the aminoacyl salt. The ease of the subsequent $N \rightarrow O$ acyl migration was found to depend on the steric environment of the hydroxyl (Ar and R) and on the size of the ring formed.

The above correlation equations (9) and (10) for the benzoylation of alcohols in tetrachloroethylene and dioxan subjected to intermolecular catalysis by tertiary amines enabled us to calculate the rate of the hypothetical acylation of aminoalcohols under the conditions of catalysis by a second aminoalcohol molecule ($k_{III}$) and the ratio $k_{II}/k_{III}$, characterising the "effective" concentration of the catalyst. Table 8 shows that intramolecular catalysis is least effective in the esterification (in tetrachloroethylene) of diethylaminoethanol, which is most hindered among the alcohols investigated. The decrease of steric hindrance as a result of the increase in chain length of the replacement of the $(C_2H_5)_2N$ group by $(CH_3)_2N$ increases sharply the ratio $k_{II}/k_{III}$. An even more marked effect is attained when tetrachloroethylene is replaced by dioxan, which probably promotes proton transfer in the intermediate adduct.

Table 8. Acylation of aminoalcohols by benzoyl chloride at 25 °C.

| Aminoalcohol | Tetrachloroethylene | | | Dioxan | | |
|---|---|---|---|---|---|---|
| | $10^2 k_{III}$, litre$^2$ mole$^{-2}$ s$^{-1}$ [calc. from Eqn.(9)] | $10^2 k_{II}$, litre mole$^{-1}$ s$^{-1}$ (expt.) | $k_{II}/k_{III}$, mole litre$^{-1}$ | $10^2 k_{III}$, litre$^2$ mole$^{-2}$ s$^{-1}$ [calc. from Eqn.(10)] | $10^2 k_{II}$, litre mole$^{-1}$ s$^{-1}$ (expt.) | $k_{II}/k_{III}$, mole litre$^{-1}$ |
| $(C_2H_5)_2NCH_2CH_2OH$ | 0.24 | 0.092 | 0.4 | 0.23 | 4.7 | 20 |
| $(C_2H_5)_2NCH_2CH_2CH_2OH$ | 0.23 | 2.2 | 9.6 | 0.20 | 21 | 108 |
| $(CH_3)_2NCH_2CH_2CH_2OH$ | 5.0 | 35 | 7.0 | 4.5 | 1230 | 270 |
| $(CH_3)_2NCH_2CH_2OH$ | 3.4 | 34.6 | 10.1 | 2.7 | 6400 | 2370 |

The steric factor probably also plays an important role in the reactivity of the stereoisomeric 2-dimethylamino-1-phenyl-1-propanols, among which the *erythro*-isomer is esterified much faster by benzoyl chloride in methylene chloride[270] than the *threo*-isomer ($k = 1.0$ and 0.0039 litre mole$^{-1}$ s$^{-1}$ respectively). According to the authors, this is also associated with the stronger hydrogen bond in the latter isomer, which decreases the accessibility of the nitrogen atom to nucleophilic attack.

## V. EXAMPLES OF THE PRACTICAL APPLICATIONS OF TERTIARY AMINES AS ACCELERATORS OF ACYLATION REACTIONS

Since these problems have been described in detail[1,93], we shall consider only a few of comparatively new data. A series of studies by Korshak and coworkers on the polycondensation of aromatic acid dichlorides with bisphenols demonstrated the high catalytic efficiency of tertiary amines[7,271-272], the yield and the molecular weight of the polyarylate depending on the structure of the tertiary amine[7,99]. The polymers obtained are characterised by fairly narrow molecular weight distribution[271] and in many instances by a significant predominance of certain "frozen" rotational forms[272], which gives rise to the prospect of the synthesis of stereoregular polycondensation polymers. Thus it has been shown[273] that triethylamine gives rise to more complete interaction of diamines with tetracarboxylic acid dianhydrides accompanied by the formation of polyamides in the form of elastic films. Furthermore, tertiary amines are also effective catalysts of the synthesis of carborane-containing polyaminoamides; depending on the solvent and the structure of the tertiary amine employed, it is possible to obtain in this case soluble linear, soluble branched, or insoluble cross-linked polymers[274]. The use of tertiary amines as polycondensation catalysts leads in many instances to an improvement of the stability and mechanical and thermal properties of polyurethanes[275,276] and polyesters[277-279].

Examples of specific structural and stereospecific acylation in the presence of tertiary amines concern a different aspect of their application in acylation reactions. Thus, using triethylamine as the catalyst, Kurita achieved for the first time the direct selective *O*-tosylation of *o*-aminophenol[280]; it is of interest that, in the presence of pyridine, only *N*-acylation takes place. In the esterification of glycosides, it was also found that products involving the acylation of different hydroxyls are obtained on treatment with acetic anhydride and acetyl chloride in pyridine[281]. When sterically hindered alcohols, such as 1-methyl and 1-ethynylcyclohexanols, 2,4,6-trimethylphenol, etc., have to be acylated, 4-dialkylaminopyridine are effective catalysts[282]. The same substances have proved useful in the esterification of tertiary alcohols which are unstable in the presence of acids, namely linalool, 1,1-dimethoxy-4-methylpent-2-yn-4-ol, as well as methyl cholate and other steroid derivatives.

Generalisation and analysis of the accumulated data permit the conclusion that the possibilities of tertiary amines as acyl transfer catalysts have been by no means exhausted and further studies will undoubtedly expand the use of these compounds in industrial and laboratory practice.

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# Latest Research on the Hydrosilylation Reaction

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The latest (1964-1974) literature data on the hydrosilylation reaction are surveyed and the results of studies on hydrosilylation, the possibility of using new catalysts, new applications, and the commonest side reactions are considered. The bibliography includes 428 references.

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## I. INTRODUCTION

During recent years, the hydrosilylation reaction has become the most popular method for obtaining a wide variety of carbofunctional organosilicon monomers. Thus, whereas during the first decade after its discovery (in 1947) approximately 150 publications with 500 examples of the reaction were devoted to hydrosilylation, during the last decade after the publication of the first monograph on hydrosilylation[1] (1964) the number of relevant publications already exceeded 1500. They describe approximately 10 000 instances of the application of the hydrosilylation reaction not only in the synthesis of monomers, but also in the formation of a new type of organosilicon polymers (the polyaddition reaction).

Attempts at a systematic arrangement of the enormous amount of experimental data on the hydrosilylation of unsaturated compounds (up to 1967) and on the employment of the hydrosilylation reaction for the synthesis of carbofunctional organosilanes (up to 1971) were undertaken in two major reviews[2,3]. Individual problems of hydrosilylation have been considered also in a number of other reviews[4-21].

This review surveys the results of research on hydrosilylation, gives a systematic account of data on the utilisation of new catalysts, and examines new possibilities for the application of the hydrosilylation reaction on the basis of data published up to 1975.

## II. NEW CATALYSTS

Chloroplatinic acid is the catalyst most frequently used for the hydrosilylation of the C=C double bond and the C≡C triple bond. It is usually employed in the form of a solution in isopropyl alcohol. However, in many instances, in order to avoid side reactions[22-32], shorten the induction period[33], and increase the yield of the isomer with a terminal silyl group[13,34], a solution of $H_2PtCl_6.6H_2O$ in tetrahydrofuran has been used. In some cases the catalyst was prepared in methanol[35], ethanol[36-39], butanol[40-46], 2-methyl-2-propanol[47,48], octanol[49-60], a 2-propanol–benzene mixture[61], cyclohexanone[62], dimethyl ether of ethylene glycol[63-67] or diethylene glycol[68-69], ethyl acetate[70], methyl benzoate[71,72], and dimethyl phthalate[73-77]. An active catalyst was obtained by treating $H_2PtCl_6.6H_2O$ with dichloromethylsilane at 20°C for 12 h.[78,79]. Chloroplatinic acid has also been used together with a buffer solution of a strong acid in water[80,81].

Since chloroplatinic acid may form a complex with the initial ethylenic or acetylenic compound, complexes of platinum derivatives with various unsaturated compounds, namely ethylene[82-91], cyclohexene[82,85,92-97], styrene and its derivatives[98-103], vinylsiloxanes[88,104-114], vinylpyridine[115,116], ethylene and pyridine[117-119], ethylene and phosphines[120,121], and alkylethylenes[21,122,123], as well as complexes with cyclopropane[124-128], ketones[62,129-131], nitriles[132-134], phosphines[132,135-142], phosphines on polymeric carriers[143,144], dialkyl sulphides[145-148], and sulphoxides[149] have been proposed as hydrosilylation catalysts.

The use of bivalent and quadrivalent platinum complexes of pyridine has also been described[132,150,151]. Sometimes amines (butylamine[152], tributylamine[153], and triethylenediamine[154,155]) were added to chloroplatinic acid in order to increase the yield of the reaction product, but in other instances the addition of amines inhibited hydrosilylation[21,22,33,156,157]. The addition of a small amount of amines can alter appreciably the mode of hydrosilylation (towards the formation of the β-isomer in the case of styrene[132]). Two-centre $Me_3PtI$ complexes[158] with pyridine[159,160] and hexamethyldiplatinum have also been used[158].

Platinum complexes on inorganic[144] and organic[143,161-164] polymeric carriers have begun to be employed on a wide scale recently. Polymeric platinum chelates with di-(8-hydroxy-5-quinolinyl)methane have also been proposed as hydrosilylation catalysts[165]. A solution of chloro-osmic acid in ethanol catalyses the addition of dichloromethylsilane to vinylsilanes, like chloroplatinic acid[166,167]. Palladium complexes, for example $(Ph_3P)_4Pd$,[140,168-176] $(Ph_3P)_2PdCl_2$,[144,168,177] $(PhCN)_2PdCl_2$,[177-180] $(Ph_3P)_2.(p\text{-quinone})Pd$,[140] $(Ph_3P)_2.$ .maleic anhydride.Pd,[140,181] and palladium complexes of diorganophosphinoalkylpolysiloxanes[144,182] proved to be effective catalysts of the hydrosilylation of alkenes and polyenes. The palladium(II) complexes of menthyldiphenylphosphine and neomenthyldiphenylphosphine have been used for the asymmetric hydrosilylation of styrene and cyclic conjugated dienes[178].

A wide variety of rhodium(I) complexes proved in many instances to be not inferior to platinum compounds as regards catalytic activity. Complexes of triphenylphosphine $[(Ph_3P)_3RhCl]$ [31,144,183-196] and diphenylphosphine $[(Ph_2PH)_3RhCl]$, [197] the triorganophosphinerhodium carbonyls $(Ph_3P)_2(CO)RhCl$, [187,188] $(Ph_3P)_3(CO)RhH$, [185,196] and $(Et_3P)_2(CO)RhCl$, [187] the rhodium carbonyl $[RhCl(CO)_2]_2$, [185,187] the olefin complex $[(C_2H_4)_2RhCl]_2$, [86,198] the bisdimethylglyoximato-complex $[(Ph_3P)(C_4H_7N_2O_2)Rh]_2$, [199-203] and certain others[204-206] have been proposed. The activity of the rhodium catalysts in the reaction of trichlorosilanes with hexene diminishes in the sequence[187]

$$[RhCl(CO)_2]_2 > (Ph_3P)_2(CO)RhCl > (Ph_3P)_3RhCl > (Et_3P)_2(CO)RhCl .$$

$(Ph_3P)_3RhCl$ in methylene chloride is less active in the reaction of dimethylphenylsilane with ethylene than $H_2PtCl_6.6H_2O$ in tetrahydrofuran[31]. The latter is also less sensitive to the effect of substituents in the benzene rings of aryldimethylsilanes. It has been shown that $[(C_2H_4)_2.RhCl]_2$ is a more active catalyst than $(Ph_3P)_3RhCl$. [198] Its use for the hydrosilylation of *cis*- and *trans*-hept-2-enes with trichlorosilane leads to trichloro-n-heptylsilane (as for $H_2PtCl_6$). [198]

The rhodium complexes of phosphines have been used successfully also for the hydrosilylation of C=O [195,207-219] and C=N [220-222] bonds. The asymmetric hydrosilylation of carbonyl compounds has been carried out in the presence of complexes with chiral ligands[142,208-210,213,215,218,219,223].

Rhodium complexes on polymeric carriers have been prepared recently[143,144,224-228] and it has been observed that these complexes catalyse effectively the addition of trialkyl- and trialkoxy-silanes to alkenes and of trialkoxysilanes to vinyl ethers and only slightly the addition of trichlorosilane to alkenes. On the other hand, the analogous platinum complexes catalyse the reactions with trichlorosilane more effectively than those with triethylsilane[143]. Ruthenium complexes have also been used for hydrosilylation[196,229,230], but iridium complexes of the type $(Ph_3P)_2(CO)IrCl$ have proved to be inactive[188].

New possibilities in the hydrosilylation reaction arose following the application of nickel complexes[132,169,170,231-243]. Thus, whereas the reaction of trichlorosilane with styrene in the presence of $H_2PtCl_6$ leads to the formation of a mixture of $\alpha$- and $\beta$-adducts with the $\beta$-isomer predominating (35 : 65), when $(Ph_3P)_2NiCl_2$ is used as the catalyst the main product is the $\alpha$-isomer (80 : 20), [231] while the use of $\pi$-$C_5H_5(CO)Ni$ [240] and $Ni(CO)_4 + Ph_3P$ (1 : 2) [132] yields exclusively the $\alpha$-isomer. The yield of hydrosilylation products, which usually does not exceed 20% in the presence of the phosphonickel catalyst, can be raised to 75% by employing CuCl as the cocatalyst. The mixture then contains up to 95% of the $\alpha$-isomer[213].

Acrylonitrile, methyl acrylate, vinyl acetate, cyclohexa-1,4-diene, and isoprene give rise to normal addition products only, even in the presence of dichloro[1,1-bis-(dimethylphosphino)ferrocene]nickel(II), which caused a marked disproportionation of the silane (83% of chloromethyloctylsilane) in the addition of dichloromethylsilane to oct-1-ene[234]. The $NiCl_2$ complex with 1,2-bis(dimethylphosphino)-*o*-carborane [(Dmpc).$NiCl_2$], containing an electron-accepting ligand, promotes the formation of $\alpha$- and $\beta$-isomers even in reactions with alk-1-enes[237]. For example, when propene interacted with trichlorosilane at 120°C for 20 h in the presence of (Dmpc).$NiCl_2$ ($10^{-3}$ mole per mole of the olefin), the addition product consisting of dichloroisopropylmethylsilane and dichloromethyl-n-propylsilane in proportions of 41 : 59 was formed in 40% yield[237]:

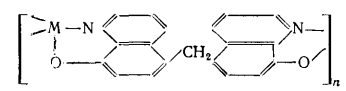
$$CH_3CH{=}CH_2 + MeSiHCl_2 \rightarrow \underset{\displaystyle CH_3}{CH_3CHSiCl_2Me} + CH_3CH_2CH_2SiCl_2Me .$$

The reactions involving pent-2-ene and hex-2-ene result in the formation, together with n-alkyl derivatives (20–50%), also of the products of the addition of the hydrosilane to the double bonds of the non-isomerised alk-2-enes[237].

Using *trans*-$[(+)$-$(R)$-$(PhCH_2)MePhP]_2NiCl_2$, it was possible to achieve the asymmetric hydrosilylation of $\alpha$-methylstyrene with dichloromethylsilane, which gave 31% of the $\beta$-adduct with a 17.6% enantiomeric excess of the *R*-isomer[238].

Ziegler systems of the type $M(acac)_n$–$AlEt_3$ (M = Ni, Co, or Fe) catalyse the addition of trialkyl- and trialkoxysilanes to 1,3-dienes, promoting the formation of 1,4-adducts. The nickel catalysts are the most active among them[239,244].

The catalytic activity of the polymeric chelates of Group VIII metals with di-(8-hydroxy-5-quinolinyl)methane



is determined by the nature of the metal M. For example, the platinum chelate is active in the reaction of trichlorosilane with hex-1-ene (2 h, 100°C, yield 70%). When M = Ni, the yield of trichlorohexylsilane was only 5%, while the rhodium and palladium chelates do not catalyse the reaction. In the reaction with triethoxysilane, the rhodium chelate (92%) proved to be more active than the platinum chelate (85%), while the palladium and nickel chelates showed virtually no catalytic activity[165]. The nature of the metal determines also the ratio of the $\alpha$- and $\beta$-isomers in the reaction of trichlorosilane with styrene: 95% $\beta$ for M = Rh, 92% $\beta$ for M = Pt, and 19% $\alpha$ for M = Pd. [165] The reaction of trichlorosilane with buta-1,3-diene in the presence of the palladium chelate results in the formation of 86% of *cis*-1-trichlorosilylbut-2-ene, while in the presence of the platinum chelate a mixture of four products is formed: *cis*-1-trichlorosilylbut-2-ene (16%), *trans*-1-trichlorosilylbut-2-ene (37%), 1-trichlorosilylbut-3-ene (14%), and 1,4-bis(trichlorosilyl)butane (4%). [165]

$Co_2(CO)_8$, [31,185,193,245-247] $HCo(CO)_4$, [248-250] $(Ph_3P)_3CoH_3$, [251] and other cobalt complexes [245,251,252] have been used for the hydrosilylation of alkenes. Dicobalt octacarbonyl also catalysed the $\alpha$-addition of chlorodimethylsilane to acrylonitrile[185].

The hydrosilylation of $\alpha$-alkenes[253-256] and acetylenes[256] is also catalysed by $Fe(CO)_5$. Here the initial alkene reacts in four ways: it interacts with the hydrosilane to form both the addition product and the dehydrocondensation product, isomerises, and is hydrogenated[254]:

$$PrCH{=}CH_2 + MeEt_2SiH \xrightarrow{Fe(CO)_5} MeEt_2SiCH_2CH_2Pr + MeEt_2SiCH{=}CHPr + C_5H_{12} + \text{isomeric pentenes.}$$

Dimanganese decacarbonyl[245] and cyclopentadienylmanganese tricarbonyl[257,258] have also been used as hydrosilylation catalysts.

Copper compounds [$Cu_2O$, $Cu_2Cl_2$, and $Cu(acac)_2$] in mixtures with organic cyanides are effective catalysts of

the hydrosilylation of acrylonitrile, promoting the formation of the $\beta$-adduct in the reaction with both trichlorosilane (70–78%) and dichloromethylsilane (80%).[259]

The addition of hydrosilanes of different olefins in high yields is initiated by $\gamma$-radiation[260-267] in view of the absence of side reactions, which are unavoidable in thermal addition[1,268].

Peroxides have been rarely used in recent years for the initiation of the hydrosilylation of the C=C bond[269-272], although a new catalyst has in fact been proposed, namely dicyclohexyl peroxycarbonate[273]. At the same time, the hydrosilylation of the N=N bond was actually achieved for the first time in the presence of a peroxide[274].

It has also been shown that the use of peroxy-catalysts in conjunction with ultraviolet irradiation permits the hydrosilylation of $\alpha$-alkenes[275-278] and cyclohexene[275] with trichlorosilane at a low temperature (0–20°C). The yields of the addition products reach 80–95%. Dichloromethylsilane also reacts fairly satisfactorily with alk-1-enes, while triethylsilane, triphenylsilane, triethoxysilane, and 3*H*-heptamethyltrisiloxane do not react under these conditions (30–40°C, 38 h).[277] The use of bis-(trimethylsilyl)mercury as the sensitiser accelerates the addition of trichlorosilane to oct-1-ene under the influence of ultraviolet irradiation by a factor greater than two relative to the reaction initiated by t-butyl peroxide[275]. The photochemical hydrosilylation of 1,3-dienes by trialkylsilanes takes place in the 1,4-positions and is catalysed by chromium hexacarbonyl[279].

## III. THE PROPERTIES OF HYDROSILYLATION

### 1. The Reactivity of Hydrosilanes

Kinetic studies on the hydrosilylation of hept-1-ene in the presence of $H_2PtCl_6.6H_2O$ showed that the rate of reaction decreases with increase of electron density at the hydrogen atom[31]:

$$\begin{array}{cccc} HSiCl_3 > EtSiHCl_2 > Et_2SiHCl > Et_3SiH \\ 3.00 \quad 2.64 \quad 1.94 \quad 1 \end{array} .$$

However, the changes are not additive and are not correlated with the inductive Taft constants $\sigma^*$, so that the differences between the reactivities in this series of hydrosilanes cannot be accounted for solely by the inductive effects of the substituents.

The rate of hydrosilylation of hex-1-ene increases on passing from tripropylsilane to diethoxypropylsilane[31]:

$$\begin{array}{ccc} Pr(EtO)_2SiH > Pr_2EtOSiH > Pr_3SiH \\ 15.26 \quad 4.33 \quad 1 \end{array} .$$

When the reaction is carried out in the presence of $H_2PtCl_6.6H_2O$, triethoxysilane proves to be less reactive than diethoxypropylsilane[31]; on the other hand, in the presence of $(Ph_3P)_3RhCl$ or $Co_2(CO)_8$ triethoxysilane proves to be more reactive[193]:

| | $(EtO)_3SiH$ | $>$ | $Pr(EtO)_2SiH$ | $>$ | $Pr_2EtOSiH$ | $>$ | $Pr_3SiH$ |
|---|---|---|---|---|---|---|---|
| $(Ph_3P)_3RhCl$ | 42.8 | | 28.4 | | 5.4 | | 1 |
| $Co_2(CO)_8$ | 119.0 | | 59.5 | | 27.5 | | 1 |

When rhodium complexes with phosphine ligands on a modified silica gel are used in the reactions with hexene, heptene, and ethyl vinyl ether, triethoxysilane also exhibits an enhanced reactivity:

$$(EtO)_3SiH > Et_3SiH > HSiCl_3 .$$

Trichlorosilane proved to be most reactive in the reaction of decene in the presence of the analogous platinum catalyst[144]:

$$HSiCl_3 > (EtO)_3SiH > Et_3SiH .$$

The increase of the rate of reaction with decrease of electron density in the Si–H bond has also been observed in the addition of aryldimethylsilanes $p$-$XC_6H_4(CH_3)_2SiH$ to ethylene. The rate of reaction in the presence of $(Ph_3P)_3RhCl$ increases on passing from dimethyl-$p$-methoxy-, to dimethyl-$p$-chloro-phenylsilane[31]:

$$\begin{array}{ccc} Cl > H > MeO \\ 1.35 \quad 1 \quad 0.78 \end{array} .$$

It is noteworthy that, in hydrosilylation in the presence of platinum, rhodium, and ruthenium complexes, the rate of reaction depends also on the stability of the complex of the catalyst and the hydrosilane[280], which can lead to reactivity series inconsistent with the corresponding series based on the variation of reactivity established in the reactions involving $H_2PtCl_6$. For example, the yield of the product of the hydrosilylation of hexene in the presence of $(Ph_3P)_3RhCl$ decreases on passing from $Ph_3SiH$ (100%) to $Et_3SiH$ (60%) and $HSiCl_3$ (8%),[188]. The decrease of the yield of the hydrosilylation product with increase of the number of chlorine atoms has also been observed for chloroethylhydrosilanes[198], which is consistent with the series based on the increase of the stability of the complexes $(Ph_3P)_2RhH(SiCl_nR_{3-n})X$.[188] However, when a competition addition reaction was carried out, hydrosilanes with a greater number of chlorine atoms proved to be more reactive both in the presence of $(Ph_3P)_3RhCl$ [193] and $[(C_2H_4)_2RhCl]_2$.[198]

Hydrosilylation under the influence of dinuclear platinum complexes of styrene proceeds as a two-stage process owing to the conversion of the initial compounds into complexes with a much lower catalytic activity. The rates of cleavage of the olefinic complexes and of addition in the second stage of the reaction increase with decrease of the strength of the Si–H bond[98]:

$$MeSiHCl_2 > Me_2SiHCl > Me_3SiH .$$

Other reactivity series have also been obtained for hydrosilanes, namely for the hydrosilylation of $\alpha$-alkenes in the presence of $H_2PtCl_6$:[281]

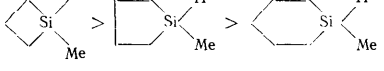
$$\begin{array}{ccc} PrSiHCl_2 > EtSiHCl_2 > MeSiHCl_2 \\ 2.75 \quad 1.80 \quad 1 \end{array} .$$

and for the hydrosilylation of vinylsilanes in the presence of $H_2PtCl_6$:[282]

$$\begin{array}{ccccc} HSiCl_3 > MeSiHCl_2 > Me_2SiHCl > Et_3SiH \\ 6.75 \quad 2.88 \quad 1.62 \quad 1 \end{array} .$$

Analogous series were obtained for the hydrosilylation of octene in the presence of phosphinonickel complexes[234] and of allylmalonic acid esters in the presence of $H_2PtCl_6$.[283]

The reactivity of hydrosilacycloalkanes in the reaction with ethylene in the presence of 5% Pt/C decreases in the sequence[284]




Under these conditions, all the hydrosilacycloalkanes are much more reactive than their acyclic analogues[284]. In the competition reaction, the addition of the latter is inhibited until most of the hydrosilacycloalkane has reacted.

Furyl-[285], thienyl-[286], and ferrocenyl-hydrosilanes[287-290] are also very reactive.

In the reaction with $\alpha$-methylstyrene in the presence of $H_2PtCl_6$, cyclic hydrosilanes can be arranged in the following sequence in terms of decreasing reactivity:

$$(MeSiHO)_4 > (EtSiHO)_4 > (MeSiHNH)_4 > (EtSiHNH)_4 > (EtSiHS)_3 .$$

The series is consistent with the sequence based on the decrease of the electronegativity of the heteroatom[291,292].

Hydrosilazanes $(Me_2SiH)_2NR$ are also less reactive than the corresponding hydrosiloxanes[33,293]. The rate of their addition to allyldiethylamine decreases in the following sequence as a function of the group linked to the nitrogen atom[33,294]:

$$Ph > iso\text{-}Bu > H > Me, PhCH_2 .$$

The trisilylamines $(Me_3Si)_2NSiHMe_2$ and $(Me_2SiH)_3N$ react with olefins with difficulty in the presence of $H_2PtCl_6$.[269,295,296] This cannot be accounted for solely by the influence of steric factors, because under these conditions tris(dimethylsilyl)methane adds to octene with a satisfactory yield[269]. The increase of electron density at the silicon atom owing to the $p_\pi - d_\pi$ interaction in the N–Si bond plays a definite role in the decrease of the reactivity of compounds with an N–Si–H group. The sequence based on the decrease of reactivity

$$(Me_2SiH)_2NH > (Me_2SiH)_3N > Me_2SiHNR_2$$

shows that the reactivities of these compounds in the hydrosilylation reactions are determined by a set of different factors (conjugation, capacity for complex formation with the catalyst, and steric hindrance).

In contrast to trichlorosilane, in the reaction with alk-2-enes and alk-3-enes dichlorosilane forms in the presence of $H_2PtCl_6$ the corresponding 2- and 3-substituted derivatives instead of the n-alkyl derivatives[297].

Kinetic studies on the hydrosilylation of hexene, styrene, and its derivatives by organosilanes $RSiH_3$ in the presence of $H_2PtCl_6$ have led to the conclusion that hydrosilanes with aromatic groups are more reactive than alkylsilanes[24] and attack on the reaction centre by the olefin proceeds more readily the more marked are the electron-accepting properties of the substituent at the silicon atom[24,25,298]:

$$ClC_6H_4 > C_6H_5 > cyclo\text{-}C_6H_{11} > C_4H_9 > iso\text{-}C_5H_{11} .$$

The steric effects at the first stage of the reaction do not play a significant role. As the number of substituents on the hydrosilane increases, its reactivity falls[28]:

$$RSiH_3 > R_2SiH_2 > R_3SiH .$$

The hydrosilylation of *N*-propargylpiperidine, *N*-propargylperhydroazepine, and *N*-propargylmorpholine with triethylsilane in the presence of $H_2PtCl_6$ results in the formation of $\gamma$-adducts (relative to nitrogen) having the *trans*-configuration. On passing from triethylsilane to dibutylmethylsilane, 3*H*-heptamethyldisiloxane, and triethoxysilane, there is a gradual increase of the content of the $\beta$-adduct in the reaction products and for the last compound the yields of the $\gamma$- and $\beta$-adducts are almost equal[299].

The mode of hydrosilylation of styrene by halogenohydrosilanes in the presence of $H_2PtCl_6$ and the yield of products depend also on the nature of the halogen. The addition of alkylfluorosilanes leads to a mixture of $\alpha$- and $\beta$-isomers[300-302]. Under these conditions, the formation of the $\alpha$-isomer predominates in the presence of dialkylfluorosilanes[300]. Hydrofluorophenyl-, hydrofluorodiphenyl-, and hydrofluoro-$\alpha$-naphthyl-silanes are more reactive in competition addition reactions than the corresponding chlorohydrosilanes[303]. At the same time arylfluorohydrosilanes form a mixture of isomers with the $\alpha$-isomer predominating, while the arylchlorosilyl group adds only to the terminal carbon atom of the double bond[303,304].

The ratio of $\alpha$- and $\beta$-isomers formed in the hydrosilylation of acrylonitrile in the presence of the ternary catalyst $Bu_3N-(Me_2NCH_2)_2-CuCl$ decreases after the introduction of alkyl groups into the hydrosilane molecule[305]:

$$HSiCl_3 > PhSiHCl_2 > MeSiHCl_2 > Ph_2SiHCl > PhMeSiHCl > Me_2SiHCl .$$

The relative rate constants for the interaction of hexene with hydrosilanes under the influence of $\gamma$-radiation decrease in the following sequence[263]:

$$\begin{array}{ccccc} HSiCl_3 & > & Ph_3SiH & > & Et_3SiH \\ 100 & & 10 & & 1 \\ Ph_3SiH & > & Ph_2SiHCl & > & PhSiHCl_2 \\ 13.6 & & 2.4 & & 1 \end{array}$$

The first sequence can be accounted for by the activating influence of electronegative substituents on the reactivity of the intermediate radicals $X_3SiCh_3\dot{C}HR$, and the second by the possibility of the stabilisation of the chlorosilane radicals due to $p_\pi - d_\pi$ interaction.

## 2. The Influence of the Structure of the Unsaturated Compound on the Rate and Mode of Hydrosilylation

Certain regularities have also been established in the study of the influence of the structure of the unsaturated compound on the rate and mode of hydrosilylation. In the hydrosilylation of the C=C double bond in the presence of $H_2PtCl_6$, the reactivity of olefins is proportional to the electron density in the double bond[306]. Steric hindrance decreases the rate of reaction. The following reactivity series have been established for the addition of trichlorosilane to olefins at 120°C in the presence of $H_2PtCl_6$:[306]

$$\begin{array}{ccccccc} BuCH_2CH{=}CH_2 & > & Bu(CH_2)_4CH{=}CH_2 & > & cis\text{-}BuCH{=}CHMe & > & trans\text{-}BuCH{=}CHMe \\ 1.5 & & 1 & & 0.73 & & 0.5 \\ & & & > & cis\text{-}(trans\text{-})PrCH{=}CHEt & & \\ & & & & 0.35 & & \\ Me_3CCH_2CH{=}CH_2 & > & Me_3CCH{=}CH_2 & > & trans\text{-}Me_2CHCH{=}CHMe & & \\ 1.5 & & 1.06 & & 0.68 & & \\ & & PhCH_2CH{=}CH_2 & > & PhCH{=}CH_2 & & \\ & & 0.71 & & 0.54 & & \end{array} .$$

Another series was obtained in the hydrosilylation by alkyldichlorosilanes in the presence of $H_2PtCl_6$:[281]

$$\begin{array}{ccccc} PrCH{=}CH_2 & > & BuCH{=}CH_2 & > & AmCH{=}CH_2 \\ 1.39 & & 1.16 & & 1 \end{array} .$$

In the presence of $H_2PtCl_6$ [297] and $[(C_2H_4)_2RhCl]_2$, [198] alk-2-enes and alk-3-enes react with greater difficulty than alk-1-enes. Thus, whereas the yield of trichloro-n-heptylsilane in the reaction of trichlorosilane with hept-1-ene in the presence of $[(C_2H_4)_2RhCl]_2$ is 54% (85°C, 2 h), its yield in the reaction with *cis*-hept-2-ene does not exceed 10%, while in the reaction with *trans*-hept-2-ene it is only 1%.[198] On the other hand, in the presence of $(Ph_3P)_4Pt$ [137] and peroxides [271], the alkenes could not be hydrosilylated at all.

The hydrosilylation of compounds whose molecules contain several double bonds permits the comparative estimation of their reactivities. Thus the addition of dichloromethylsilane to hexa-1,5-diene (equivalent double

bonds) in the presence of $H_2PtCl_6$ involves both bonds[70,307], while in the addition to the natural terpene myrcene

$$(CH_3)_2\overset{(c)}{C}=CHCH_2CH_2C(\overset{(b)}{CH_2})-\overset{(a)}{CH}=CH_2,$$

which has three types of double bonds, the reactivity of the latter in the reaction with trichlorosilane in the presence of $H_2PtCl_6$ decreases in the sequence (a) > (b) > (c).[308,309]

The study of the hydrosilylation of unsaturated silanes containing two different unsaturated groups at the silicon atom by chlorodimethylsilane in the presence of $H_2PtCl_6$ made it possible to establish the following reactivity series[282]:

$$HC\equiv C>CH_2=CH>CH_2=CHCH_2>CH_2=C(CH_3)CH_2>CH_2=CH>CH_2=CHC_6H_4.$$

In the reaction with phenylsilane, the reactivity of unsaturated compounds decreases in the sequence[25,298,310]:

$$p\text{-}CH_3C_6H_4CH=CH_2>PhCH=CH_2>p\text{-}ClC_6H_4CH=CH_2.$$

A similar behaviour, involving an increase of the conversion and of the rate of reaction with increase of electron density in the double bond, was observed also in the hydrosilylation of substituted styrenes by dichloromethylsilane in the presence of the platinum–styrene complexes[98].

Certain other reactivity series of unsaturated compounds have also been obtained[291,311]; in reactions with hydrocyclosiloxanes:

$$PhCH=CH_2>PhCH(CH_3)=CH_2>CH_2=C(CH_3)COOMe>CH_2=CHCH_2CN;$$

in reactions with hydrocyclosilazanes:

$$PhCH=CH_2>CH_2=C(CH_3)COOMe>CH_2=CHCH_2CN>CH_2=CHCN;$$

in reactions with hydrocyclosilthianes:

$$PhCH(CH_3)=CH_2>CH_2=CHCH_2CN>CH_2=CHCN.$$

In the hydrosilylation of monosubstituted acetylenes $RC\equiv CH$ by triethylsilane in the presence of $H_2PtCl_6$, the amount of $\beta$-isomers increases with enhancement of the electron-donating properties of R.[21,312] The use of tetrahydrofuran as the reaction medium decreases the amount of the $\alpha$-isomer[21,313,314].

## IV. NEW APPLICATIONS OF HYDROSILYLATION

During recent years, it has been possible to achieve for the first time the hydrosilylation of the C=N, N=N, and N=O bonds.

Triethylsilane adds to *N*-substituted aldimines in the presence of $ZnCl_2$ at 150°C:[315]

$$PhCH=NR + HSiEt_3 \rightarrow PhCH_2N(R)SiEt_3.$$

Nickel and platinum halides behave similarly[316]. Rhodium complexes are much more active catalysts of the hydrosilylation of ketimines by trialkylsilanes and diorganosilanes, which makes it possible to carry out the addition at a lower temperature (30–50°C).[220,222] Their reactivity decreases in the sequence[221]

$$(Ph_3P)_3RhCl \gg (Ph_3P)_2Rh(CO)Cl > [(\text{hexa-1,5-diene})RhCl]_2 > [(\text{cyclo-octa-1,5-diene})RhCl]_2 > PdCl_2 > (Ph_3P)_2PdCl_2.$$

Palladium catalysts are less active but they can be used also for the addition of trialkylsilanes to the isocyanate group[317].

Trimethylsilane reacts with pyridine in the presence of palladium on charcoal (30°C, 25 h) with formation of *N*-trimethylsilyl-1,2-dihydropyridine (25%), *N*-trimethylsilyl-1,4-dihydropyridine (35%), *NN'*-bis(trimethylsilyl)-1,1'-dihydro-4,4'bipyridyl (25%), *N*-trimethylsilyl-1,2,3,6-tetrahydropyridine (12%), and many other trimethylsilylhydropyridines[318–321]. The Pd/C catalyst is more active than Rh/C, $PdCl_2$, Pt/C, and Ru/C. However, Rh/C acts more selectively, directing the process mainly towards the formation of *N*-trimethylsilyl-1,4-dihydropyridine[320,321]. In the reaction involving 3-methylpyridine in the presence of Pd/C, there is quantitative addition to the 1,4-positions. 4-Methylpyridine reacts four times as slowly as pyridine and the addition of trimethylsilane to 2-methylpyridine could not be achieved at all[321].

Triphenylsilane adds to the N=N bond of diethylazodicarboxylate in the presence of t-butyl peroxide in boiling benzene. The reaction proceeds slowly: the attainment of a 70% yield of the product requires eleven days. The addition was much faster under ultraviolet irradiation in the presence of t-butyl peroxide (3.5 h, yield 77%):[274,322]

$$EtOOCN=NCOOEt + HSiPh_3 \rightarrow EtOOCN(SiPh_3)-NHCOOEt.$$

At a higher temperature (140°C), triphenylsilane adds to azobenzene (yield 30%):[322]

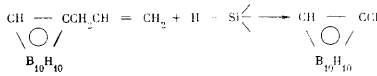
$$PhN=NPh + HSiPh_3 \rightarrow PhNHNPhSiPh_3.$$

Trimethylsilane adds to the N=O bond in trifluoronitrosomethane both under the influence of ultraviolet light and in the presence of $H_2PtCl_6$:[323]

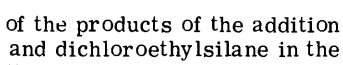
$$CF_3N=O + HSiMe_3 \rightarrow CF_3NHOSiMe_3 + (CF_3)_2NOSiMe_3.$$

Together with the normal addition products (43 and 74% respectively), the *O*-trimethylsilyl derivative of bis(trifluoromethyl)hydroxylamine is also formed (28 and 16%).[323] Under the influence of ultraviolet light, trichlorosilane adds slowly to trifluoronitrosomethane (15 h, yield 17%). Trifluorosilane is much more reactive under these conditions (yield 80%).[324]

The addition of chlorohydrosilanes[325–330], alkoxyhydrosilanes[331–333], and hydrosiloxanes[326,334–338] to alkenylcarboranes in the presence of Pt/C, $H_2PtCl_6$, $FeCl_3$, or in the absence of catalysts (>200°C) leads to the corresponding alkylcarboranylsilanes and carboranylsiloxanes:



Trichlorosilane adds to 2-vinylfuran in the presence of $H_2PtCl_6$ on heating a tetrahydrofuran solution in a closed vessel to 80–85°C. After heating for 18 h, the yield of the hydrosilylation product is 60%:[339]



The yield of the products of the addition of dichloromethylsilane and dichloroethylsilane in the presence of $H_2PtCl_6$ is 70%, while the yield of the addition reactions involving ethoxy- and acetoxy-silanes is lower (approximately 50%) and that of the reactions with trialkylsilanes is lower still (approximately 30%).[339,340]

Unsaturated derivatives and other oxygen-containing heterocycles, namely oxetan[341–343] and tetrahydropyran[344–348], have been hydrosilylated.

It has been shown that alkenyl sulphides[349-353] combine with various hydrosilanes in the presence of platinum catalysts, like unsaturated ethers[1,3]:

$$RSCH_2CH{=}CH_2 + H{-}Si\langle \rightarrow RSCH_2CH_2CH_2Si\langle \ .$$

The hydrosilylation of unsaturated sulphones proceeds in the same way[354].

In the presence of several double bonds in the molecule whose positions relative to the sulphur atom are different, the bond most remote from the sulphur atom is the first to be hydrosilylated[355]:

$$CH_2{=}CH(CH_2)_nSCH{=}CH_2 + H{-}Si\langle \rightarrow \rangle SiCH_2CH_2(CH_2)_nSCH{=}CH_2 \ .$$

When the reaction was initiated by ultraviolet light, it was possible to achieve the quantitative addition of trichlorosilane, dichloromethylsilane, and trimethylsilane to bis(trifluoromethyl)aminoethylene[356,357]:

$$(CF_3)_2NCH{=}CH_2 + HSiCl_3 \rightarrow (CF_3)_2NCH_2CH_2SiCl_3 \ .$$

Azines derived from unsaturated ketones[358,359], 1-vinylsilatrane[369], and ketenes[361,362] have been hydrosilylated in the presence of $H_2PtCl_6$:

$$[CH_2{=}CHCH_2CH_2C(CH_3){=}N{-}]_2 + H{-}Si\langle \rightarrow \left[\rangle Si(CH_2)_4C(CH_3){=}N{-}\right]_2 \ ;$$

$$N(CH_2CH_2O)_3SiCH{=}CH_2 + H{-}Si\langle \rightarrow N(CH_2CH_2O)_3SiCH_2CH_2Si\langle \ ;$$

$$R_2C{=}C{=}O + H{-}Si\langle \rightarrow R_2C{=}CHOSi\langle \ .$$

It has been shown for the reaction with optically active hydrosilanes that the hydrosilylation of alkenes in the presence of $H_2PtCl_6$ and $[(C_2H_4).PtCl_2]_2$ proceeds with retention of configuration[90,363,364], which confirms to a certain extent the coordination reaction mechanism put forward[2,12,16,25,28,31,77,86,90,291,298,306,364-367].

## V. ANOMALOUS AND SIDE REACTIONS

In many cases the hydrosilylation of alkenes is accompanied by other processes associated with the reactions of the initial olefin, hydrosilane, or reaction intermediates. The commonest reactions of this kind are isomerisation[86,143,185,188,197,198,254,256,296,368,369] and hydrogenation[25,254,310] of the initial alkene and in some cases telomerisation[187,270].

The reaction of trichlorosilanes with 1-propylcyclohexene in the presence of $H_2PtCl_6$ proceeds with migration of the double bond and involves the formation of trichloro-3-cyclohexylpropylsilane, while the unreacted olefin consists of 1-propylcyclohexene (33%), 3-propylcyclohexene (3%), 4-propylcyclohexene (3%), and 1-propenylcyclohexane (2%):[85]

$$\bigcirc{-}C_3H_7 + HSiCl_3 \rightarrow \bigcirc{-}(CH_2)_3SiCl_3 \ .$$

Isomerisation is observed also in the hydrosilylation of $\beta$-pinene[370,371], and bicyclo[2,2,1]hepta-2,5-diene[372].

The hydrosilylation of arylalkenes $Ph(CH_2)_nCH{=}CH_2$ ($n$ = 1 or 2) and $PhCH{=}CH(CH_2)_mH$ ($m$ = 0-4) in the presence of $H_2PtCl_6$ is accompanied by isomerisation and leads to the formation of two products: with a terminal silyl group and with a silyl group located at the carbon atom adjoining the phenyl group[303]. For example:

$$PhCH_2CH{=}CH_2 + HSiCl_3 \rightarrow Ph(CH_2)_3SiCl_3 + PhCH(SiCl_3)CH_2CH_3 \ ;$$
$$PhCH{=}CHCH_3 + Me_2SiHCl \rightarrow Ph(CH_2)_3SiClMe_2 + PhCH(SiClMe_2)CH_2CH_3 \ .$$

With increase of $n$, the amount of the isomer with a terminal silyl group increases, falling as $m$ increases. The yield of this isomer rises in the following sequence of hydrosilanes[303]:

$$Me_2SiHCl > MeSiHCl_2 > HSiCl_3 \ .$$

The hydrosilylation of monosubstituted acetylenes in the presence of a mixture of nickel acetylacetonate and triethylaluminium is accompanied by dimerisation[239]:

$$2\,RC{\equiv}CH + HSiX_3 \rightarrow CH_2{=}CRCR{=}CHSiX_3 + RCH{=}CHCR{=}CHSiX_3 \ .$$

Dimerisation also occurs in the hydrosilylation of buta-1,3-diene in the presence of palladium catalysts[140,169,170]:

$$CH_2{=}CHCH{=}CH_2 + R_3SiH \rightarrow CH_3CH{=}CHCH_2CH_2CH{=}CHCH_2SiR_3 \ .$$

Various side reactions can occur in the hydrosilylation of unsaturated compounds containing functional groups capable of reacting with hydrosilanes. Thus, whereas trialkylsilanes add to perfluorocyclobutene on heating to 250°C, the reaction with 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene under analogous conditions involves condensation and reduction instead of addition[373]:

$$\begin{matrix} CF_2{-}CCl \\ | \quad \| \\ CF_2{-}CCl \end{matrix} \xrightarrow{R_3SiH} \begin{matrix} CF_2{-}CCl \\ | \quad \| \\ CF_2{-}CSiR_3 \end{matrix} + \begin{matrix} CF_2{-}CH \\ | \quad \| \\ CF_2{-}CCl \end{matrix} + R_3SiCl + HCl \ .$$

The hydrosilylation of allyl chloride[374,375] and methylallyl chloride[376] in the presence of $H_2PtCl_6$ is also accompanied by reduction. The ratio of the addition and reduction products depends on the structure of the hydrosilane, decreasing as chlorine atoms are replaced by methyl, phenyl, and ethoxy-groups[374,375]:

$$\underset{5.7}{HSiCl_3} > \underset{2.7}{MeSiHCl_2} > \underset{1.82}{PhSiHCl_2} > \underset{1.45}{Me_2SiHCl} > \underset{1.2}{MePhSiHCl} > \underset{0.38}{Ph_2SiHCl} > \underset{0.11}{MePh_2SiH}$$
$$EtSiH_2Cl > EtSiHCl_2 > Et_2SiHCl > (EtO)_3SiH > Et_3SiH$$

In the presence of $H_2PtCl_6$, triphenylsilane and methyldiphenylsilane reduce the nitro-group of $m$-nitrostyrene, while alkylchlorohydrosilanes add to the C=C double bond without affecting the nitro-group[377].

In the hydrosilylation of unsaturated esters by chlorohydrosilanes and alkoxyhydrosilanes, the cleavage of the C-O bond is also frequently observed[378-382]. For example, the hydrosilylation of allyl trifluoroacetate by dichloromethylsilane in the presence of $H_2PtCl_6$ involves the formation, together with dichloro-[3-(trifluoroacetoxy)-propyl]methylsilane (52%), of a number of other cleavage, reduction, and further reaction products[384]:

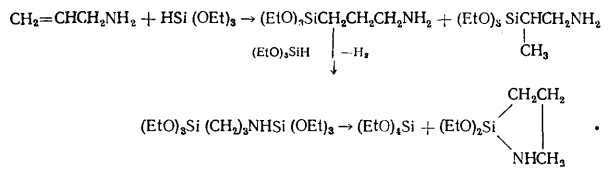
$$CF_3COOCH_2CH{=}CH_2 + MeSiHCl_2 \rightarrow \begin{cases} CF_3COO(CH_2)_3SiCl_2Me & (52.2\%) \\ CF_3COOCH_2CH_2CH_3 & (3.3\%) \\ CH_3SiHCl(OCOCF_3) & (\sim 13\%) \\ + \ MeSiCl_3 & (9.4\%) \\ + \ PrSiCl_2Me & (12.2\%) \\ + \ CF_3COO(CH_3)_3Si(OCOCF_3)ClMe & (7,3\%) \end{cases} .$$

The addition of trichlorosilane to vinyl acetate under the influence of $\gamma$-radiation is accompanied by the reduction of the carbonyl group to the methylene group[265]:

$$CH_3COOCH{=}CH_2 + HSiCl_3 \rightarrow CH_3CH_2OCH_2CH_2SiCl_3 \ .$$

Belyakova et al.[385] was the first to show convincingly that the hydrosilylation of unsaturated compounds containing other functional groups[1,3] in the presence of $H_2PtCl_6$

may involve the silylation not only of the hydroxy- or carboxy-group, but also of the primary amino-group:



In hydrosilylation in the presence of platinum catalysts, the disproportionation of the initial hydrosilane is sometimes observed[296, 369, 375, 384, 386-390], for example:

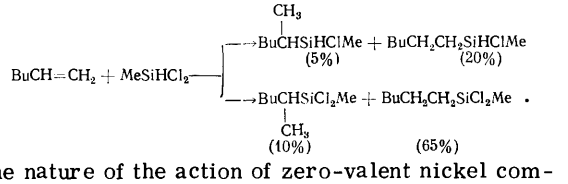
$$2\,PhSiHCl_2 \rightarrow Ph_2SiHCl + HSiCl_3\ ;$$

$$2\,Et_2SiHF \rightarrow Et_2SiH_2 + Et_2SiF_2\ .$$

In the presence of nickel catalysts this takes place to a more marked extent. The disproportionation of the hydrosilane in the hydrosilylation of alkenes, styrene, cyclohexene, and cyclo-octadiene in the presence of phosphinonickel complexes involves the formation of two different adducts[233, 234]:

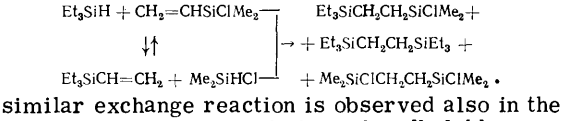
$$RCH{=}CH_2 + MeSiHCl_2 \rightarrow RCH_2CH_2SiCl_2Me + RCH_2CH_2SiHClMe + MeSiCl_3\ .$$

When the reaction of dichloromethylsilane with hex-1-ene is carried out in the presence of $[Me_3SiCH_2PBu_2]_2NiBr_2$ (120°C, 6 h), as many as four adducts are formed[232]:



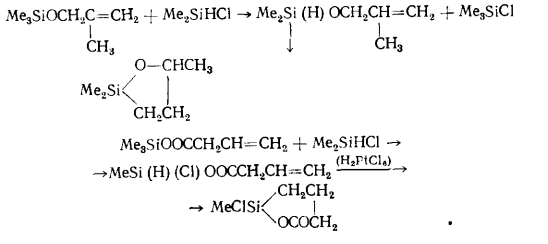
The nature of the action of zero-valent nickel complexes, for example $(Ph_2PCH_2)_2(C_2H_4)Ni$, is comparable to that of the action of the corresponding nickel(II) complexes, but in the presence of the latter the induction period is longer[233]. The yield of the reaction product and the ratio of the anomalous and normal adducts increase with increase of the electron-donating capacity of the ligands and substituents in the olefin[234].

The reaction of triorganosilanes with chlorovinylsilanes is accompanied by the exchange of the hydrogen atom and the vinyl group of the initial silanes[391]:

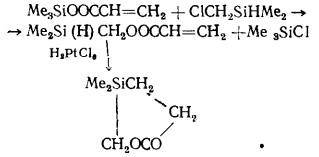


A similar exchange reaction is observed also in the hydrosilylation of alkoxyvinylsilanes by alkylchlorohydrosilanes[392] and of pentamethylvinyldisilane by dichloromethylsilane[393].

The hydrosilylation of trimethylsilyl ethers of unsaturated alcohols[389, 394-396] and esters of unsaturated acids[397-399] by chlorodimethylsilane in the presence of $H_2PtCl_6$ is accompanied by the transilylation of the initial unsaturated silane with subsequent cyclisation owing to the intramolecular hydrosilylation of the intermediate allyloxy- and acyloxy-hydrosilanes, for example:



The interaction of acryloyloxytrimethylsilane with (chloromethyl)dimethylsilane proceeds with dissociation of the C–Cl bond and the formation of a six-membered lactone[400]:



During the recent 1½ years (from January 1975 to July 1976), 200 new studies on the hydrosilylation reaction were published, which indicates the growing popularity of this method of synthesis of organosilicon monomers and polymers.

A detailed study was made of the catalytic activity of nickel catalysts in reactions with carbonyl compounds[401-404] and of rhodium catalysts in reactions with olefins[405]. It has been shown[406] that $(Ph_3P)_3RhCl$ is an effective catalyst of the hydrosilylation of acrylonitrile not only by chlorohydrosilanes but also by trialkylsilanes (the $\alpha$-isomers are formed). The hydrosilylation of buta-1,3-diene has been investigated in detail in the presence of rhodium[407], palladium[408, 409], and nickel[410, 411] catalysts. New catalytic systems have been proposed for this reaction: nickel[412] or cobalt[413] salts mixed with sodium hydrodi-(2-methoxyethoxy)aluminate.

The study of hydrosilylation established that the reactivities of hydrosiloxanes[414] and vinylsiloxanes[415] $Me_{3-n}RSi(OSiMe_3)_n$ (R = H or vinyl) in this reaction decrease with increase of $n$. In the hydrosilylation of acetylenic compounds[416-420], the reaction rate increases with electron density in the triple bond and is to a large extent determined by the steric properties of the groups attached to the silicon atom.

It has been found that the hydrosilylation of divinyl sulphide by diethylsilane is accompanied by cyclisation with formation of a derivative of a new heterocyclic system—3,3-diethyl-2,4-dimethyl-1-thia-3-silacyclobutane[421].

Studies on the asymmetric hydrosilylation[422-428] of the C=C, C=N, and C=O bonds are developing to an increasing extent, which is of interest both for the synthesis of chiral amines and alcohols with a high optical purity and for the determination of the mechanism of the hydrosilylation reaction.

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# The Synthesis of Polycyanates by the Polycyclotrimerisation of Aromatic and Organoelement Cyanate Esters

V.A.Pankratov, S.V.Vinogradova, and V.V.Korshak

Studies on the synthesis and properties of a new class of heat-resistant and thermostable polymers, obtained by the polycyclotrimerisation of aromatic and organoelement cyanate esters, are examined. Attention has been concentrated on studies devoted to the given reaction, the influence of the structure of polycyanates on their properties, and the specific features of these polymers due to the regularity of their structure. A number of general characteristics of polycyclotrimerisation, i.e. its usefulness as a method of synthesis of cross-linked thermostable polymers, are discussed. The bibliography includes 160 references.

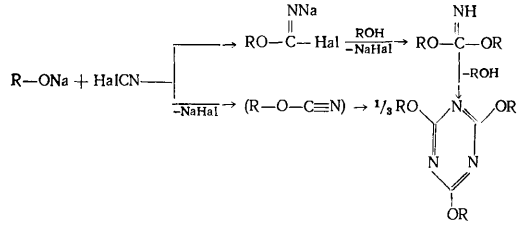
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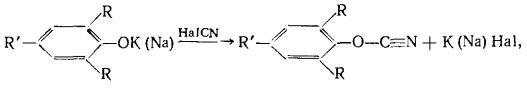
## I. INTRODUCTION

Cyanic acid HO–C≡N is involved in 1,3-prototropic tautomerism with isocyanic acid O=C=NH as a result of which esters of both cyanic acid (R–O–C≡N, cyanates) and the isomeric esters of isocyanic acid (R–N=C=O, isocyanates) are known. However, whereas isocyanates were discovered by Wurtz in the initial period of the development of organic chemistry in 1849,[1] the first examples of cyanates were synthesised by Stroh and Gerber as late as 1960.[2] Isocyanates assumed practical importance only 100 years after their discovery. Judging from the vigorous development of research on the chemistry of cyanates, one may predict with confidence that the corresponding period for these substances will be much shorter.

The attempts to synthesise cyanate esters were begun in 1857[3-13]. In the main, investigators tried to solve this problem by the reaction of phenoxides (or alkoxides) with halogenocyanogens[3-11], but cyanate esters were not isolated and the main reaction products were cyanuric acid esters. It was shown that an imino-ester of carbonic acid is formed as an intermediate under these conditions[9,13] and that the reaction mechanism can be represented as follows:

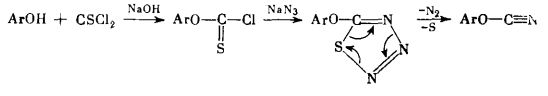


Nevertheless Stroh and Gerber[2] and later other investigators[14,15] succeeded in synthesising cyanate esters in this way from sterically hindered phenols:

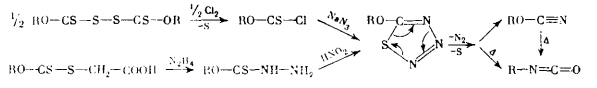


where R = t-$C_4H_9$ and R′ = $C_6H_5$.

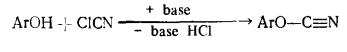
It was not until 1964 that several new methods of synthesis of compounds of this class were proposed[16-22]. Martin and coworkers[16-19] obtained aromatic and then aliphatic cyanates by the thermolysis of 1,2,3,4-thiatriazoles via the following mechanism:



Jensen and Holm[20,21] achieved the synthesis of aliphatic cyanates using a somewhat different scheme:



A method of synthesis of cyanate esters from phenols and acid alcohols involving their interaction with a halogenocyanogen in the presence of a hydrogen halide acceptor, which is promising from the standpoint of its application in industry, has been proposed by Grigat and Pütter[22]:



The reaction takes place at temperatures between −20° and +20° C in an organic solvent (for example acetone) and the yields of cyanates are nearly quantitative.

A number of other methods of synthesis of cyanates have been described in the literature[23-28], but they suffer from disadvantages such as a large number of stages and low yields, as a result of which they are less promising for practical purposes.

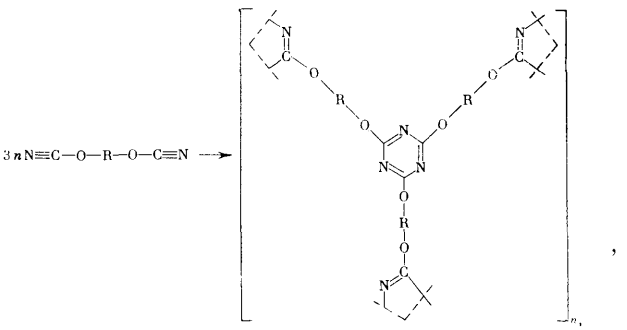
Bearing in mind that a number of reviews on the synthesis and properties of cyanate esters have already been published[29-34], we shall not concern ourselves in the present review with this field and attention will be concentrated on polymers based on cyanates and the processes leading to their formation.

The studies in the field of polymers based on cyanate esters developed only in the last decade. However, a sufficient number of data on these polymers, which are of interest from both theoretical and practical points of view, are already available and need to be surveyed. This applies particularly to research on the polycyclotrimerisation of cyanates, which has led to the discovery of many interesting general features of this new and promising method of synthesis of cross-linked thermostable polymers.

Studies on the polycyclotrimerisation of cyanate esters have been mainly designed to investigate the features of this reaction and the synthesis of new structures as well as various properties of polycyanates. The literature data have been reviewed in the same order in the present article. In addition, we shall consider also the few studies described in the literature on the synthesis of other less thoroughly investigated cyclopolymers based on cyanate esters.

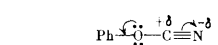
## II. THE CHARACTERISTICS OF THE POLYCYCLOTRIMERISATION REACTION OF CYANATE ESTERS

The polycyclotrimerisation reaction of dicyanate esters with formation of cross-linked polymers (polycyanates) proceeds via the mechanism:



where R are different aromatic and organoelement groups.

Aryl cyanates are more reactive than nitriles because of the more electrophilic properties of the carbon in the N≡C group owing to the electron-accepting effect of the aryloxy-group[35,36]. Martin and Brause[36] established that the oxygen atom in the compounds HR–O–C≡N has an electron-donating effect on the aromatic group and at the same time enters into mesomeric interaction with the carbon of the nitrile group. However, the involvement of the unpaired electrons of oxygen in the mesomerism of the ring is greater than in the mesomerism of the nitrile group of aryl cyanates:



which promotes the enhancement of the electrophilic properties of the carbon of the N≡C group.

At the same time, like nitriles, aryl cyanates exhibit nucleophilic properties due to the presence in the N≡C group of the lone electron pair of the nitrogen atom and of electron-donating π-bonds. The cyclotrimerisation of cyanates is therefore accelerated by catalysts of both anionic and cationic type, depending on whether the nucleophilic nitrogen atom or the electrophilic carbon atom is attacked.

In recent years, Korshak and coworkers[37,38] put forward the concept of the heterogeneity of polymer linkages owing to the occurrence of a number of side reactions, apart from the main reaction involving the formation of the polymer system. Such "defectiveness" of the structure of a particular polymer leads in most cases to an impairment of properties such as heat resistance and thermal stability, physicomechanical parameters, etc.

It has been shown in many studies on the polymerisation of isocyanates, ethynyl derivatives, nitriles, and other compounds that the polycyclotrimerisation of these compounds involves, apart from the main process, numerous side reactions (chain polymerisation, dimerisation, etc.). Methods of synthesis excluding these side reactions have not so far been found[39-52] and the synthesis of polymers with a virtually defect-free structure is an urgent problem whose solution will permit a considerable improvement of many of their parameters and may lead to the formation of materials with qualitatively new properties.

A high selectivity in the cyclotrimerisation of the N≡C–O groups is characteristic of the polycyclotrimerisation of dicyanates with formation of cross-linked polymers. This is one of the fundamental features of the polycyclotrimerisation of these groups, which distinguishes them from other functional groups, such as the nitrile, isocyanate, ethynyl, etc. groups.

Furthermore, an exceptionally important feature is that, when the process is carried out under certain conditions, the cyclotrimerisation of the N≡C–O groups of tricyanates proceeds with virtually quantitative conversion. All these factors promote the achievement of "pure" polycyclotrimerisation with few defects and the formation of highly cross-linked polymers with a regular chemical structure[53-65].

Indeed the cyclotrimerisation of monofunctional cyanate esters led to the isolation of cyanurates in quantitative yields and no side products (dimers, linear polymers, etc.) could be detected chromatographically or by other methods[29,30,55,57,58]. Comparison of the spectroscopic and other characteristics of the polymers, obtained by polycyclotrimerisation and by specific synthesis from cyanuryl chloride and bisphenols, demonstrated their complete identity[54,55]. The absence of the signal characteristic of polyconjugated systems from the ESR spectra of polycyanates fails to confirm the possibility of the linear polymerisation of the N≡C groups of cyanates[55]. Furthermore, in the study of the polymerisation of dicyanates by infrared spectroscopy, it was not possible to detect either the dimerisation or isomerisation of the N≡C–O group; the infrared spectra did not contain absorption bands characteristic of linear acomethine structures either. In the discussion of the properties of polycyanates below, we shall consider also other direct and indirect evidence indicating the high selectivity of the cyclotrimerisation of NCO groups in the synthesis of these polymers.

One must nevertheless stipulate that the possibility of side reactions cannot of course be fully ruled out in the polycyclotrimerisation of aromatic cyanate esters. However, bearing in mind the entire set of the available literature data on this process, these reactions presumably take place to only a slight extent.

The comparative catalytic activities of various protic and aprotic acids and bases as well as their mixtures were investigated, using as an example 2,2-di-(4-cyanatophenyl)-propane, in the bulk polycyclotrimerisation of aryl dicyanates[56]. It was found that in the initial stages the polycyclotrimerisation of the N≡C–O groups of aryl dicyanates obeys the relations of the quasi-unimolecular reaction. The rate constants and activation energies for this process, carried out in the presence of various types of catalysts, were calculated and it was shown that the catalytic activities of tertiary amines and phenols are proportional to their $pK_a$ values and increase with the basicity of amines and the acidity of phenols. The corresponding correlations have been deduced.

The influence of the chemical structure of initial dicyanates of the type

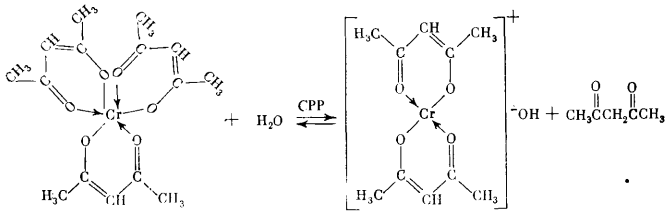
$$NCOC_6H_4—A—C_6H_4OCN,$$

where A = $CH_2$, $C(CH_3)_2$, $C(CF_3)_2$, $CHC_6H_5$, or $C(CH_3)(C_6H_5)$, on their reactivity in polycyclotrimerisation in the presence of zinc chloride has been investigated and it has been shown that the rate of the process in the first stage is determined by the inductive effect of the substituents at the central carbon atom of the initial dicyanate, increasing as they become more electronegative. At more advanced stages of the reaction of the N≡C–O groups of the dicyanate, the rate depends also on the steric factors of the substituents at the central carbon atom of the dicyanate[56].

A series of studies by Bonetskaya and coworkers[57,59-62] were devoted to a detailed investigation of the kinetics and heats of the cyclotrimerisation and polycyclotrimerisation of aryl cyanates. Thus the kinetics of the cyclotrimerisation of phenyl isocyanate to triphenyl cyanurate have been investigated in solution in ditolylmethane in the presence of chromium(III) acetylacetonate with the aid of a double calorimeter[57] and it was shown that the reaction is autocatalytic. Its maximum rate is proportional to the catalyst concentration and the square of the monomer concentration. The heat of cyclotrimerisation of phenyl cyanate was determined as $\Delta H = -28.1 \pm 1.0$ kcal mole$^{-1}$. The stabilisation energy of the *s*-triazine ring has also been estimated and it has been noted that the ring is stabilised both as a result of the delocalisation of electrons with formation of a system resembling the π-electron system of the benzene ring and by the partial polarisation of the ring nitrogen–carbon bond. In order to estimate the stabilisation energy of the *s*-triazine ring, the experimental heat of the cyclotrimerisation of phenyl cyanate (PC) to triphenyl cyanurate (TPC) was compared with the heat of this reaction in the gaseous state ($\Delta H = -58.2$ kcal mole$^{-1}$). The latter quantity was calculated from the heats of formation of phenyl cyanate and triphenyl cyanurate evaluated additively from the increments for the corresponding groups[66] ($\Delta H_f = 29.7$ and 30.9 kcal mole$^{-1}$). The authors regard the difference $\Delta H = 26$ kcal mole$^{-1}$ between the experimental and theoretical heats as the stabilisation energy of the *s*-triazine ring (the stabilisation energy of the benzene molecule is approximately 36 kcal mole$^{-1}$).[57]

The kinetics of the polycyclotrimerisation of 2,2-di-(4-cyanatophenyl)propane (CPP) have been investigated and its heat measured by direct calorimetric determinations under conditions analogous to those of a model reaction[59-61]; it was established that the polycyclotrimerisation of CPP involves mainly the same kinetic features as the cyclotrimerisation of phenyl cyanate. The average heat of polycyclotrimerisation of CPP is[59,60] $\Delta H = -56.8$ kcal mole$^{-1}$, i.e. 28.4 kcal mole$^{-1}$ per N≡C–O group. The close agreement of this value with the heat of cyclotrimerisation of phenyl isocyanate ($\Delta H = -28.1$ kcal mole$^{-1}$) confirms, according to the author, the high selectivity of the polycyclotrimerisation of aryl dicyanates.

The cyclotrimerisation of aryl cyanates in the presence of chromium(III) acetylacetonate is autocatalytic (the variation of the rate with time passes through a maximum), although the reaction products [triphenyl cyanurate when phenyl cyanate is the starting material and oligomers in the polycyclotrimerisation of 3,2-di-(4-cyanatophenyl)propane] do not catalyse the process[57,59-62]. One of the causes of autocatalysis is probably the fact that chromium(III) acetylacetonate is catalytically inactive in the initial state. It was established[59] that the presence of traces of water in the reaction system has an appreciable influence on the rate of polycyclotrimerisation of CPP and traces of acetylacetone in the reaction mass after the latter had been thermostatted at 140°C were detected by gas–liquid chromatography. It was found that the addition of water to the reaction system increases and that of acetylacetone decreases the rate of reaction[62]. The results suggested that the active form of the catalyst is formed with participation of water and is in equilibrium with the normal form of the catalyst:




The autocatalytic nature of the cyclotrimerisation of aryl cyanates in the presence of chromium(III) acetylacetonate is associated with the accumulation of the active form of the catalyst as the reaction proceeds.

The enthalpy, entropy, and Gibbs free energy of the polycyclotrimerisation of crystalline and liquid CPP to a regularly cross-linked amorphous polymer have been calculated[63] (Table 1). The enthalpy of polymerisation found at 420 K (147°C), i.e. $-\Delta H_{pol} = 53.2$ kcal mole$^{-1}$, agrees within the limits of experimental error with the enthalpy of polymerisation determined by direct calorimetric measurements ($-\Delta H_{pol} = 56.8$ kcal mole$^{-1}$),[60] which confirms yet again that the polycyclotrimerisation of aryl dicyanates always proceeds in the same way. The decrease of entropy on polymerisation with formation of cross-linked systems, determined for the first time by Lebedev et al.,[63] proved to be −36 e.u., which is approximately 30% larger than for linear polymerisation.

Table 1. Thermodynamic parameters of the polycyclotrimerisation of 2,2-di-(4-cyanatophenyl)propane*.

| *T*, K | $-\Delta H^\circ_{pol}$, kcal mole$^{-1}$ | $-\Delta S^\circ_{pol}$, kcal mole$^{-1}$ K$^{-1}$ | $-\Delta G^\circ_{pol}$, kcal mole$^{-1}$ |
|---|---|---|---|
| | Monomer(c) ⇌ polymer(g) | | |
| 100.00 | 44.5 | 7.88 | 43.7 |
| 200.00 | 45.2 | 12.7 | 42.7 |
| 298.15 | 45.9 | 15.5 | 41.3 |
| 355.83 | 46.2 | 16.4 | 40.3 |
| | Monomer(l) ⇌ polymer(g) | | |
| 355.83 | 52.5 | 34.1 | 40.3 |
| 400.00 | 52.9 | 35.9 | 38.8 |
| 420.00 | 53.2 | 35.9 | 38.1 |

*The physical state of the monomer and polymer is indicated in brackets: c—crystalline; g–glass; l–liquid.

Table 1 shows that, in the temperature range 100–420 K, $\Delta H^\circ_{pol} < 0$ and $\Delta S^\circ_{pol} < 0$, which implies that CPP is a monomer with an upper limiting polymerisation temperature of 1480 K, i.e. much higher than the temperature of the onset of the thermal decomposition of the monomer and polymer. (Below 1480 K, there are no thermodynamic obstacles to the conversion of the monomer into a polymer, while above this temperature the polymer cannot be obtained.)

The absolute value of $\Delta G^{\circ}_{pol}$ shows that the equilibrium in the polymerisation reaction is almost completely displaced towards the formation of the polymer[63].

## III. INDIVIDUAL EXAMPLES OF POLYCYANATES

### 1. Homopolymers of Aromatic and Organoelement Dicyanate Esters

Table 2 presents the structures and melting points of di- and tri-functional aromatic and organoelement cyanate esters described in the literature as well as certain thermal characteristics of the polymers based on them. In most cases the monomers are crystalline substances with melting points much lower than those of the hydroxy-compounds from which they were obtained. Certain organoelement dicyanates (see Nos. 33 and 34, Table 2) are liquids at these temperatures. The temperatures of the onset of deformation (from thermomechanical curves) and the temperatures of the onset of decrease in weight (from thermogravimetric data obtained in air) are quoted in Table 2 as the thermal characteristics whereby a comparative assessment of the polymers is possible. Unfortunately there are no data on the behaviour of a number of polycyanates, which have been described largely in patents, at elevated temperatures.

Table 2. Di- and tri-functional aromatic and organoelement cyanates and the thermal characteristics of the polymers based on them.

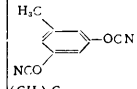
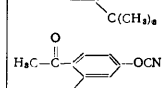
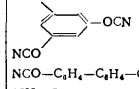
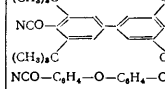
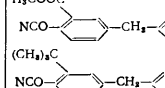
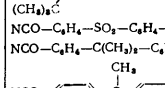
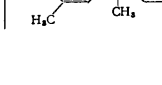
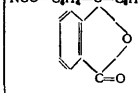
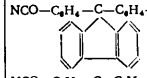
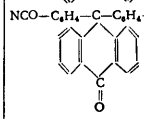
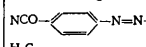
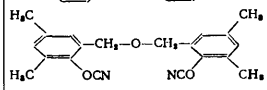
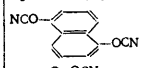
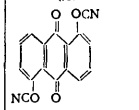
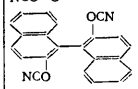
| No. | Initial cyanate | M.p., °C | $T_{o.d.}$, °C* | $T_{w.l.}$, °C** | References |
|---|---|---|---|---|---|
| 1 | m-NCO–$C_6H_4$–OCN | 78–79,5 | 360 | 390 | 22,30,53,67–69 |
| 2 | p-NCO–$C_6H_4$–OCN | 115–116 | 395 | 390 | 22,30,53,67–69 |
| 3 |  | 72–74 | — | — | 30 |
| 4 |  | 130 | — | — | 70,71 |
| 5 |  | 78–80 | — | — | 72 |
| 6 |  | 102 | — | — | 22,30 |
| 7 | NCO–$C_6H_4$–$C_6H_4$–OCN | 133–133,5 | 380 | 390 | 30,54 |
| 8 |  | 263 | — | — | 30 |
| 9 | NCO–$C_6H_4$–O–$C_6H_4$–OCN | 88–89 | 400 | 380 | 54 |
| 10 | NCO–$C_6H_4$–$CH_2$–$C_6H_4$–OCN | 107.5–108 | 370 | 400 | 53,69 |
| 11 |  | 100–101 | — | — | 30 |
| 12 |  | 206 | — | — | 2,30 |
| 13 | NCO–$C_6H_4$–$SO_2$–$C_6H_4$–OCN | 182–183 | 360 | 360 | 30,54 |
| 14 | NCO–$C_6H_4$–$C(CH_3)_2$–$C_6H_4$–OCN | 81.5–82 | 385 | 385 | 30,53,54,69 |
| 15 |  | 77–78 | 280 | 330 | 54 |

Table 2 (Cont'd).

| No. | Initial cyanate | M.p., °C | $T_{o.d.}$, °C* | $T_{w.l.}$, °C** | References |
|---|---|---|---|---|---|
| 16 | NCO–$C_6H_4$–$C(CF_3)_2$–$C_6H_4$–OCN | 87.5–88 | 360 | 395 | 53,54,69 |
| 17 | NCO–$C_6H_4$–C(H)($C_6H_5$)–$C_6H_4$–OCN | 72.5–73 | 410 | 410 | 53,54,69 |
| 18 | NCO–$C_6H_4$–$C(CH_3)$($C_6H_5$)–$C_6H_4$–OCN | 87–88 | 370 | 395 | 53,54,69 |
| 19 | NCO–$C_6H_4$–$C(C_6H_5)_2$–$C_6H_4$–OCN | 190.5–191.5 | 360 | 400 | 53,54,69 |
| 20 |  | 134–135 | 385 | 405 | 53,54,69 |
| 21 |  | 162.5–163 | 375 | 400 | 53,54,69 |
| 22 |  | 169–170 | 395 | 400 | 53,54,69 |
| 23 |  | 163 | — | — | 71 |
| 24 |  | 107–108 | — | — | 30 |
| 25 |  | infus. | — | — | 30 |
| 26 |  | infus. | — | — | 30 |
| 27 |  | 149 | — | — | 30 |
| 28 | NCO–$C_6H_4$–C(–$B_{10}H_{10}$)–C–$C_6H_4$–OCN | 158–159,5 | 370 | 370 | 73 |
| 29 | NCO–$C_6H_4$–$CH_2$–C(–$B_{10}H_{10}$)–C–$CH_2$–$C_6H_4$–OCN | 152–153 | 370 | 370 | 74,75 |
| 30 | NCO–$CH_2$–C(–$B_{10}H_{10}$)–C–$C_6H_4$–C(–$B_{10}H_{10}$)–C–$CH_2$–OCN | 135–136 | 300 | 380 | 76,77 |
| 31 | NCO–$CH_2$–C(–$B_{10}H_{10}$)–C–$CH_2$–OCN | 127.5–128 | 280 | 360 | 78,79 |
| 32 | m-NCO–$CH_2$–$CB_{10}H_{10}C$–$CH_2$–OCN | 63–64 | 290 | 370 | 78,79 |
| 33 | NCO–$CH_2$–$(CF_2)_3$–$CH_2$–OCN | — | 350 | 360 | 80,81 |
| 34 | NCO–$CH_2$–$(CF_2)_4$–$CH_2$–OCN | — | 340 | 350 | 80,81 |

* Here and henceforth the temperature of the onset of deformation ($T_{o.d.}$) was determined from the thermomechanical curve for a load 0.8 kgf $cm^{-2}$ and a heating rate of 80 k $h^{-1}$.

** The temperature of the onset of weight loss ($T_{w.l.}$), obtained from thermogravimetric analysis (heating rate 4.5 K $min^{-1}$), was assumed to be the temperature corresponding to the point of intersection of the tangents to the curve in the region where weight loss begins.

The polycyanates listed in Table 2 are highly cross-linked heterochain polymers the nodes of the networks of which consist of *s*-triazine rings, while the internodal fragments comprise the residues of aromatic bisphenols, polyphenols, and organoelement glycols and phenols. The data in Table 2 show that the presence of these thermally stable groups in the polycyanate structure promotes a high thermal stability of the latter. Furthermore, the results obtained in thermomechanical studies on polycyanates have demonstrated (see Table 2) that the temperatures of the onset of deformation are in most cases in the region close to the temperatures of the onset of weight loss, i.e. the

heat resistance of these highly structured rigid systems is limited by their thermal stability. The thermal, physicomechanical, and other properties of the most interesting polycyanates will be discussed below.

There are no literature data on polycyanates with unsubstituted aliphatic internodal fragments. Presumably the presence of flexible polymethylene chains in place of rigid aromatic rings in the polycyanate structure should have promoted an increase of the elasticity of these materials but, naturally, it would have been accompanied by some decrease of the thermal stability of the polymers. It is noteworthy that the initial monomers for such polymers, aliphatic cyanate esters, cannot be obtained from glycols and halogenocyanogens; on heating, they also readily isomerise to isocyanates[29].

It has been found that the hypothetical structures of polycyanates with aliphatic internodal fragments can be achieved by the introduction of perfluoro-groups in the $\alpha$-position relative to the cyanate group. Such fluorine-containing mono- and di-cyanates were obtained for the first time[81] by the reaction of the corresponding alcohols with chlorocyanogen in the presence of triethylamine. These cyanates are resistant to isomerisation and polymerise readily with formation of polymers whose thermal stability is not inferior to that of aromatic polycyanates[80]. Depending on the proportions of the mono- and di-cyanates taken for copolymerisation, polymers with glass points between $-40°$ and 350°C were obtained. They can be used as thermostable films, adhesives, and elastomers with improved fire resistance[80].

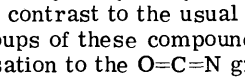
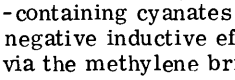
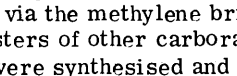
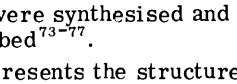
One of the most interesting examples of organoelement polycyanates comprises polymers containing carborane groups in the internodal fragments. A report on the synthesis of carborane-containing aliphatic cyanates based on 1,2- and 1,7-dihydroxymethylcarboranes was published in 1971.[78] In contrast to the usual aliphatic cyanates, the N≡C–O groups of these compounds proved to be resistant to isomerisation to the O=C=N groups. The resistance to isomerisation in such cases, as well as that of fluorine- and chlorine-containing cyanates[30,81], can be accounted for by the large negative inductive effect of the carborane ring, transmitted via the methylene bridges[78]. Subsequently dicyanate esters of other carborane-containing glycols and bisphenols were synthesised and polymers based on them were described[73-77].

Table 3 presents the structures of carborane-containing dicyanates and certain properties of their polymers. A characteristic feature of polymers based on dicyanatomethylcarboranes is lower heat resistance compared with aromatic polycyanates, but, as regards the temperature of the onset of weight loss, they are similar to their carbocyclic analogues[79]. The most interesting property of these polymers is the large amount of carbon-containing residue at elevated temperatures (between 500° and 1000°C), frequently with retention of a definite strength.

Like aromatic analogues, carborane-containing polymers are characterised by high physicomechanical parameters (specific impact strength up to 30 kgf cm $cm^{-2}$, bending strength up to 1700 kgf $cm^{-2}$, Brinell hardness up to 1500 kgf $cm^{-2}$, etc.); they can be readily converted into manufactured articles by the usual methods for working with thermoreactive polymers without the evolution of volatile materials[73-79]. Their conversion into manufactured articles is facilitated also by the fact that the initial monomers have relatively low melting points, ranging from 63°C (*m*-dicyanatomethylcarborane) to 158°C (1,2-dicyanatodiphenylcarborane).[73-79]

Owing to the strong adhesion of carborane-containing cyanates to various materials and other properties of practical value, which are indicated above, these polymers are used as heat resistant and thermostable films, coatings, binders for glass-fibre-reinforced plastics, adhesives, etc., particularly when a high resistance to ablation is necessary[73-79]. Large carbon-containing residues have been observed up to 1000°C for carborane-containing polycyanates not only when the latter were thermostatted in air but also in an inert atmosphere. Thus the polycyanate based on 1,2-di-(4-cyanatophenyl)carborane loses 2% of its weight in air at 900°C and 16% at the same temperature in an atmosphere of helium. In view of the low availability at the present time of carborane-containing monomers, it is of considerable interest that small amounts of added carborane-containing cyanates appreciably increase the thermal stability of polycyanates when they are copolymerised with the usual aromatic dicyanates[82]. Thus, whereas the polymer based on 2,2-di-(4-cyanatophenyl)propane without a carborane-containing additive loses 58% of its weight on heating in air for 1 h at 350°C, the weight loss by the polycyanates to which 0.25 mole % of 1,2-dicyanatodiphenylcarborane has been added amounts to 27%.[82]

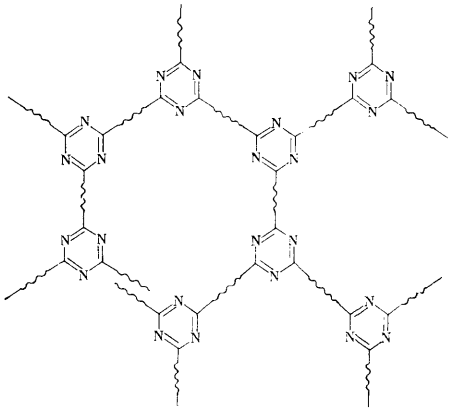
Table 3. Properties of carborane-containing polycyanates.

| No. | Initial dicyanate | Properties of polycyanates: boron content, % | $T_{o.d.}$, °C | $T_{w.l.}$ in air, °C | coke residue at 900°C, % | References |
|---|---|---|---|---|---|---|
| 1 |  | 42.53 | 280 | 360 | 105 | 78,79 |
| 2 | m-$NCOCH_2$–$CB_{10}H_{10}C$–$CH_2OCN$ | 42.53 | 290 | 370 | 110 | 78,79 |
| 3 | p-$NCOCH_2$–$CB_{10}H_{10}C$–$CH_2OCN$ | 42.53 | 310 | 350 | 102 | 79 |
| 4 |  | 28.58 | 370 | 370 | 98 | 73 |
| 5 |  | 45,71 | 370 | 370 | 92 | 76,77 |
| 6 |  | 26.67 | 370 | 380 | 92 | 74,75 |

## 2. Polycyanates Based on Oligomers with Terminal Cyanate Groups

Apart from polymers based on low-molecular-weight monomeric dicyanates, polymers obtained by the polycyclotrimerisation of oligomeric dicyanate esters are of considerable interest because it is possible to regulate easily in this way both the length and the chemical structure of the internodal fragment, achieving thereby the specific synthesis of polymers with a particular set of properties.

As for the polycyanates discussed above, the structure of the polymers obtained from oligomeric dicyanate esters consists of a trifunctional network with *s*-triazine rings at its nodes; the internodal distance is determined by the length of the initial oligodicyanate:



There are interesting data for polycyanates based on mono- and di-cyanates containing oligomeric fluoroalkylene and fluoroalkylene oxide linkages having the general formula[83]

$$F_3C(CFX)_aA(CFX)_bCH_2OCN \text{ and } NCOCH_2(CFX)_aB(CFX)_bCH_2OCN,$$

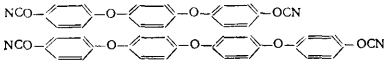
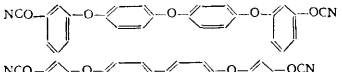
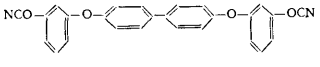
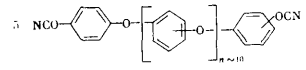
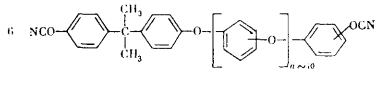
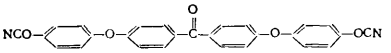
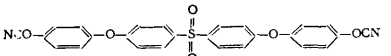
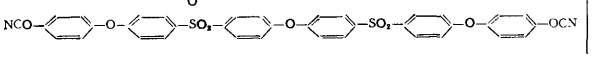
where X = fluorine or perfluoroalkyl while A and B are a C–C bond or an $O(CFXCF_2O)_c$ group. These polymers are distinguished by resistance to the action of solvents and are used for impregnation and as adhesives, films, and binders for rocket fuel.

A number of polymers based on oligoarylene oxides with terminal cyanatophenyl groups have also been described in patents[84,85] (Table 4). The initial bisphenols were obtained by the Ullmann stepwise condensation of the corresponding aromatic dihalogeno-compounds with potassium methoxyphenoxide and subsequent hydrolysis of the methoxy-groups. The authors achieved the homopolymerisation of the dicyanates of oligoarylene oxides as well as their copolymerisation with aliphatic perfluorocyanates by heating the reactants at 50–200°C[84,85]. It was noted that the polymerisation temperature may be reduced to 25–100°C in the presence of catalysts, which were $AlCl_3$, $BF_3$, $FeCl_3$, $TiCl_4$, $ZnCl_2$, protic acids such as HCl, the salts of weak acids (NaOAc, NaCN, KSCN, and $NaHCO_3$), as well as basic compounds, for example NaOMe, KOH, pyridine, and triethylamine. The polymers obtained have a high thermal stability and rigidity and can be used as adhesives, coatings, and binders. The ultimate shear strength of the aluminium–aluminium adhesive seam, formed using the dicyanates[84] hardened for 1 h at 177°C and a pressure of 2 atm, are presented in Table 5.

Table 5. The ultimate strengths of the Al–Al adhesive seam formed using oligoarylene oxide dicyanates as the adhesives[84].

| No. of initial dicyanate in Table 4 | Ultimate strength, kgf cm$^{-2}$ | | | | | |
|---|---|---|---|---|---|---|
| | –55° | 24° | 82° | 121° | 149° | 177° |
| 1 | 308 | 308 | 273 | 210 | — | 95 |
| 2 | 280 | 280 | 245 | 245 | 140 | 70 |
| 3 | 385 | 266 | 245 | 203 | 140 | 84 |
| 8 | 112 | 126 | 98 | 126 | — | 91 |

Table 4. The structures and melting points of oligoarylene oxide dicyanates.

| No. | Dicyanate | M.p., °C |
|---|---|---|
| 1 |  | 133–135 |
| 2 |  | 110–115 |
| 3 |  | 98–100 |
| 4 |  | 120 |
| 5 |  | 100 |
| 6 |  | 100 |
| 7 |  | 139–140 |
| 8 |  | 70 |
| 9 |  | 120 |

The synthesis of the dicyanates of oligoaryleneoligosulphones[86] and the oligoarylates[87] and polycyanates based on them[88] has been achieved recently. In contrast to earlier patents[84,85], in this case the initial oligoaryleneoligosulphones with terminal hydroxy-groups were obtained by the condensation of the dihalogeno-derivatives of diphenyl sulphone with alkoxides derived from 2,2-di-(4-hydroxyphenyl)propane in dimethyl sulphoxide[86]:

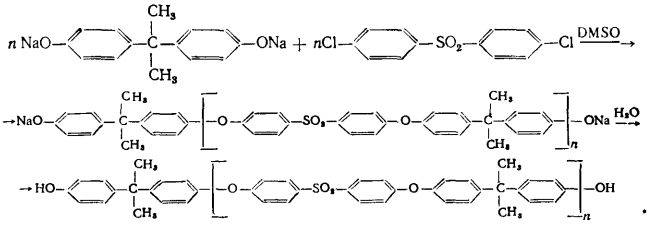
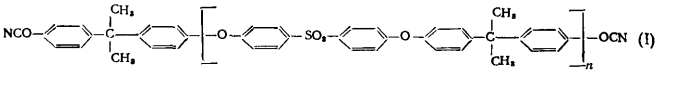
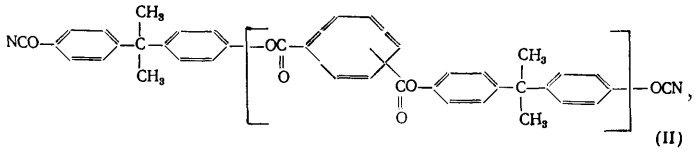


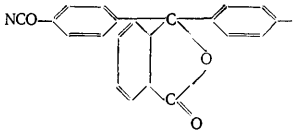
Table 6 presents certain thermal characteristics of a number of polycyanates based on the dicyanate esters of oligoaryleneoligosulphones:

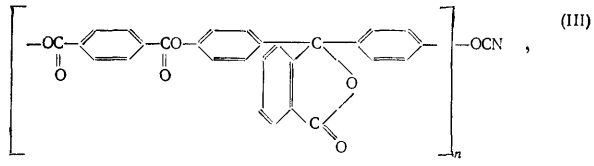


and oligoarylates:

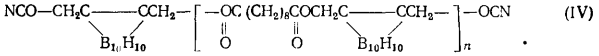


(II)





(III)



(IV)

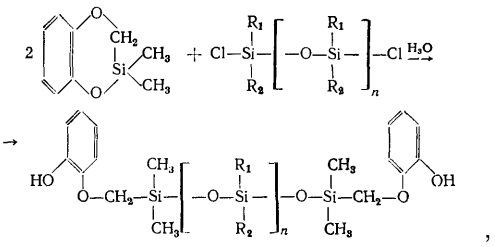
Table 6. Thermal characteristics of network polymers based on the oligomeric dicyanates (I), (II), (III), and (IV).

| $n$ | $T_{w.l.}$, °C | | $T$ (5%), °C* | | $T$ (10%), °C* | | $T_{o.d.}$, °C |
|---|---|---|---|---|---|---|---|
| | in air | in argon | in air | in argon | in air | in argon | |
| | | | Polymers based on oligodicyanates (I) | | | | |
| 1 | 360 | 370 | 400 | 380 | 415 | 400 | 240 |
| 3 | 380 | — | 420 | — | 435 | — | 220 |
| 5 | 400 | 390 | 440 | 410 | 450 | 420 | 190 |
| 10 | 405 | — | 435 | — | 460 | — | 190 |
| | | | Polymers based on oligodicyanates (II) | | | | |
| 1 | 345 | 350 | 390 | 365 | 410 | 380 | 220 |
| 3 | 330 | — | 380 | — | 400 | — | 210 |
| 5 | 340 | 350 | 390 | 375 | 425 | 390 | 190 |
| | | | Polymers based on oligodicyanate (III) | | | | |
| 5 | 350 | — | 390 | — | 400 | — | 290 |
| | | | Polymers based on oligodicyanate (IV) | | | | |
| 7 | 300 | — | 345 | — | 380 | — | 10 |

*Temperatures at which the polymer loses 5 and 10% of its weight respectively.

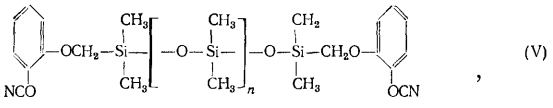
The study of the influence of the degree of cross-linking on the heat resistance of these polymers showed that, with increase of the degree of cross-linking, the glass temperatures of the polymers increase relative to linear high-molecular-weight polymers with a similar structure. Furthermore, in contrast to high-molecular-weight linear analogues, the thermomechanical curves for polycyanates show a viscoelastic plateau, the upper temperature limit of which is between 300° and 350°C, depending on the structure of the initial oligomer[88]. The region of the viscoelastic state of a carborane-containing oligoester was found to lie in the temperature range from 10° to 350°C, i.e. the polymer is an elastomer at room temperature.

Oligomeric dicyanates and oligodimethyl- and methylphenyl-siloxanes have also been used as the starting compounds for the synthesis of polycyanates[88-95]. The initial bisphenols for the synthesis of these dicyanates were obtained[88,89,93,94] by the cohydrolysis of $\alpha\omega$-dichlorosiloxanes with 2,2-dimethylbenzo-2-sila-1,4-dioxan via the following mechanism:

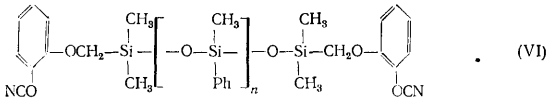


where $n$ = 1 - 150 for $R_1 = R_2 = CH_3$, $n$ = 1-20 for $R_1$ = $CH_2$ and $R_2 = C_6H_5$, and $n$ = 1-10 for $R_1 = R_2 = C_6H_5$.

Dicyanate esters based on these bisphenols were synthesised by acylating them with halogenocyanogens in the presence of tertiary amines[88,90]. Two types of oligomeric organosilicon dicyanates were obtained:



(V)



(VI)

Certain properties of the polymers based on these compounds are listed in Table 7.

Table 7. Properties of organosilicon polycyanates[88,89] based on the oligomeric dicyanates (V) and (VI).

| $n$ | Glass point, °C | $T_{w.l.}$, °C | |
|---|---|---|---|
| | | in air | in argon |
| | Polymers based on oligodicyanates (V) | | |
| 0 | 180 | 250 | 260 |
| 1 | 14 | 260 | — |
| 5 | −70 | 290 | 300 |
| 10 | −75 | 300 | — |
| 25 | −80 | 345 | 325 |
| 50 | −100 | 330 | — |
| 70 | −100 | 340 | — |
| 100 | −120 | 360 | 300 |
| | Polymers based on oligodicyanates (VI) | | |
| 3 | −10 | 285 | — |
| 5 | −20 | 300 | — |
| 10 | −25 | 300 | — |

Depending on the length of the siloxane chain between the nodes of the network, these polymers have glass points between −120° and 180°C. It has been shown that organosilicon polycyanates have a high thermal stability and the region of their viscoelastic state lies within a wide temperature range: from −120° to 340°C, i.e. up to the temperatures of the onset of their degradation[88,91,95].

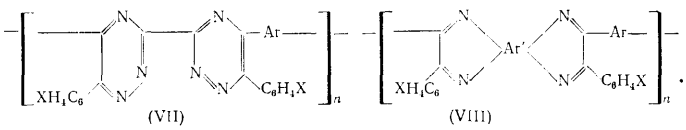
There are also patent data for cross-linked plastics obtained by the polycyclotrimerisation of the terminal N≡C−O groups of a prepolymer synthesised from the product of the reaction of $\epsilon$-caprolactone with various bisphenols[96]. These polymers have a high strength and hardness, exhibit strong adhesion, and can be used as coatings, binders, insulators, etc. The formation of

phenol-formaldehyde resins containing cyanate groups, by treating a novolak resin with chlorocyanogen in the presence of tertiary amines, has been described[97,98]. The polymers, hardened at elevated temperatures, are recommended as plastics, adhesives, and coatings.

### 3. Polymers with Cyanate Side Groups

Studies devoted to the modification of known polymers by the introduction into their structure of reactive cyanate groups have been published[99-102]. Subsequent cyclotrimerisation of these groups or their interaction with various compounds yields cross-linked systems, which makes it possible to impart many new valuable properties to the initial polymers.

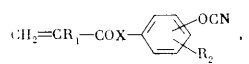
Thus Hergenrother[99] obtained high-molecular-weight polyphenylene-*asym*-triazines having the general formula (VII), where Ar = *m*- or *p*-$C_6H_4$ or *p*-$C_6H_4OC_6H_4$ and X = H, $C_2H_5$, $OCH_3$, $OC_6H_5$, $C_6H_5$, OH, Br, CN, OCN, $OC_6H_4CN$, and polyphenylenequinoxalines having the general formula (XIII), where Ar and X are the same as above (X can be in addition $CH_3$) and Ar′ = $C_6H_3C_6H_3$ or $C_6H_3COC_6H_3$.



(VII) (VIII)

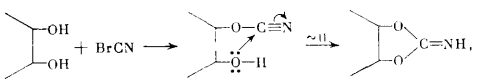
It has been shown that heat treatment of polymers with cyanate groups entails their cross-linking as a result of the cyclotrimerisation of the groups, which leads to a raising of the glass points of the resulting polymers compared with the initial polymers.

A method for the synthesis of cyanates from polymers containing vinyl groups and having the general formula



where $R_1$ = H, $CH_3$, or Cl, $R_2$ = H, Alk($C_{1-4}$), or Cl and X = O or H, has been described[100]. The above cyanates have been homopolymerised or copolymerised via the vinyl group with butadiene, isoprene, various acrylates, styrene, α-methylstyrene, and other compounds. Linear polymers were obtained with different contents of cyanate side groups. These polymers, which were subsequently heat-treated at 70–200°C, were converted into cross-linked systems as a result of the cyclotrimerisation of N≡C–O groups[100].

A method has been patented for the synthesis of polymers with cyanate groups, which were subsequently used to bind organic compounds containing a primary or secondary amino-group or an OH group[101]. For this purpose, a polymer containing primary or secondary OH groups (for example cellulose, agar, etc.) is treated with cyanate esters having the general formula $R(OCN)_X$ (R = halogenoalkyl and substituted or unsubstituted aromatic or heterocyclic groups and *x* = 1 or 2). Such a cyanate-activated polymer is capable of binding aminoacids and other compounds. The mechanism of the interaction of mercerised cellulose with bromocyanogen has been investigated[102] and it has been established that this results in the formation of cellulose iminocarbonate via the mechanism



the product being capable of interacting with protein. Such cellulose treated with BrCN has been used successfully as a matrix for the binding of biologically active proteins and their insolubilisation.

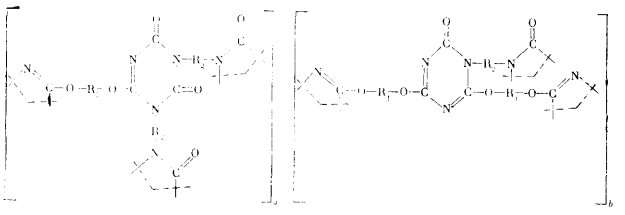
### 4. Copolymers of Cyanate Esters

The modification of the properties of polycyanates in the desired manner can be achieved by the copolymerisation of dicyanates with one another, with monocyanates, and with various compounds to form network structures and also non-cross-linked soluble polymers.

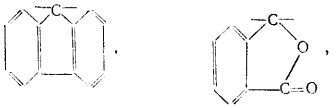
An advantage of the copolymerisation of dicyanates with one another is that the mixtures of monomers are converted into a melt at lower temperatures than the initial dicyanates during their homopolymerisation and do not crystallise from the melt on cooling, which greatly simplifies the technology of the processing of such polymers[103]. Furthermore, by varying the structure and proportions of the initial dicyanates, it is possible to alter specifically properties of the polycyanates such as heat resistance, thermal stability, and physicomechanical parameters[82,103,104].

The copolymerisation of aryl dicyanates with monocyanate can yield, depending on the ratio of the initial monomers, polycyanates with different degrees of cross-linking as well as fusible and soluble polymers[82,104]. However, the physicomechanical properties of such copolymers are greatly inferior to those of the homopolymers of dicyanates and are sharply impaired with decrease of the degree of cross-linking. This is probably associated with the breakdown of the regularity of the cross-linking occurring in the homopolymerisation of dicyanates, so that cross-linked copolymers of aryl dicyanates with monocyanate become analogous to randomly cross-linked rigid-chain polymers (epoxide and phenol-formaldehyde polymers, polymers of the polyphenylene type, etc.) as regards physicomechanical properties[103]. Furthermore, the breakdown of the regularity of the cross-linking by the introduction of monocyanate into the polymers leads to a decrease of their heat resistance and thermal stability compared with homopolymers[103].

The synthesis of copolymers of isocyanates with cyanates having the general formula



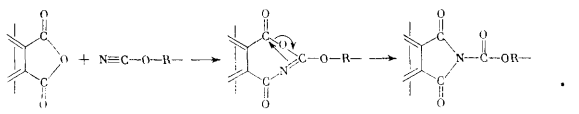
has also been described[105]. Here $R_1$ and $R_2$ are aromatic mono-, bi-, or poly-cyclic groups containing the H, N≡C–O, $CH_3$, F, Cl, Br, N=C=O, $NH_2$, or OH ring substituents. Bicyclic groups can be separated by $-CH_2-$, $-C(CH_3)_2-$, $-C(CF_3)_2-$, $-O-$, $-SO_2-$,



bridges, siloxane fragments, and aliphatic, cyclic aliphatic, arylalkyl, and fluorine- or boron-containing groups.

The resulting copolymers of isocyanates with cyanates have effective temperature characteristics and satisfactory physicomechanical parameters. They can be used as thermostable compositions, coatings, varnishes, binders for glass-fibre-reinforced plastics, etc.[105] Thus the copolymer of 9,9-di-(4-cyanatophenyl)fluorene and 9,9-di-(4-isocyanatophenyl)fluorene begins to decompose in air (according to thermogravimetric data) at 440°C and the temperature of the onset of deformation is 480°C.

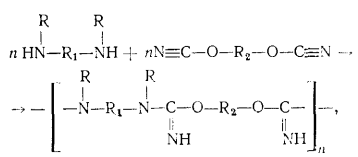
The interaction of acid anhydrides with cyanate esters, leading to the formation of imidocarbonates, was described in 1970:[106]



This interesting reaction of cyanate esters was used to synthesise a new type of polymer—polyimidocarbonates[107-109]. These polymers were obtained by the migration copolymerisation of various dianhydrides of tetracarboxylic acids and aryl dicyanates in the melts or in solution in a high-boiling organic solvent. Depending on the structure of the initial compounds, the polymers had a softening temperature in the range 230–260°C, the temperature of the onset of their decomposition in air was in the range 300–350°C, and $\mu_{int}$ in DMF was up to 0.5 dl $g^{-1}$. In order to determine the structures of the polymers obtained, the authors[108,109] synthesised compounds simulating the main chain of polyimidocarbamates, namely *N*-(phenoxycarbonyl)phthalimide, di-*NN'*-(phenoxycarbonyl)pyromellitimide, and 4,4'-di-(*N*-phthalimidacarbamatophenyl)-2,2-propane.

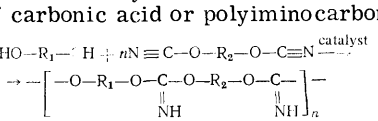
Certain characteristics of the formation of polyimidocarbamates were investigated in relation to the interaction of 2,2-di-(4-cyanatophenyl)propane and the dianhydride of pyromellitic acid[109]. It was found that, for an equimolar reactant ratio, the product is a linear, fusible, and soluble polyimidocarbamate. With increase of the content of cyanate groups in the initial mixture and also when polyfunctional esters or acid anhydrides with a functionality > 2 are used, the products are cross-linked, infusible, and insoluble polymers[107]. The synthesis of a number of linear polymers based on bifunctional cyanates has been described[72,110,111].

It is also known that cyanate esters readily interact with primary and secondary amines, forming isourea ethers[25,29,30]. The migration copolymerisation of primary and secondary diamines with dicyanates yielded polymeric isourea ethers or polyisoureas[110,111] via the mechanism:



where $R_1$ is an aliphatic, alicyclic, arylalkyl, aryl, or heterocyclic group, R = H, alkyl, or aryl, and $R_2$ = aryl, alkyl, or a heterocycle. When cyanates or amines with a functionality > 2 are used, the products are cross-linked polymers[110,111].

The copolymerisation of cyanates with glycols and bisphenols proceeds similarly with formation of polymeric iminoesters of carbonic acid or polyiminocarbonates[72]:



However, in contrast to the synthesis of polyisoureas, the formation of polyiminocarbonates proceeds in the presence of bases such as alkali metal alkoxides, hydroxides, carbonates, metal hydrides, tertiary amines, etc.[72]

Departure from equimolar ratios in the case of bifunctional starting materials leads to the formation of polymers with terminal cyanato- or hydroxy-groups[72].

## IV. THE SPECIFIC FEATURES OF THE PROPERTIES AND STRUCTURES OF POLYCYANATES

Polycyanates are a new class of polymers with a regular network structure. Aromatic polymers having this type of structure with a high degree of cross linking were previously unknown. The change from the previously known randomly cross-linked structures to structures with a regularly constructed network, as in polycyanates, should have led to a quantitative change in many properties of the polymers. Indeed a number of unusual properties drew attention already in the first studies on polycyanates. Subsequently these polymers were investigated in greater detail and new properties, unusual for cross-linked polymeric systems, were found.

The results of studies devoted to a detailed investigation of thermal, physicomechanical, and other properties of polycyanates as well as the structural parameters of these polymers are discussed below. Particular attention has been devoted to the specific features of polycyanates due to their regularly cross-linked structure.

The majority of polytriazines, to the class of which polycyanates belong, are known to exhibit an enhanced thermal stability[45,47,55,112-115] due to the aromatic nature of the triazine ring whose thermal stability is close to that of the benzene ring[55,115-118]. A number of studies on the influence of the chemical structure of the initial monomers on the thermal stability of the polycyanates have been described in the literature[55,115,118,120]. Furthermore, in the majority of papers on the synthesis and properties of these polymers, certain characteristics of their thermal stability are also quoted. Investigations of the thermal stability of polymers having this type of structure but obtained by the polycondensation or polymerisation of monomers containing an existing *s*-triazine ring are also of definite interest[47,121,122].

Table 8. Results of the thermogravimetric analysis of polycyanates on heating in air (at a rate of 4.5 K $min^{-1}$).

| Polycyanate | Initial aryl dicyanate | Decrease in weight of polymers, % | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 300° | 350° | 400° | 450° | 500° | 550° | 600° |
| PTs-19 | NCO—$C_6H_4$—$CH_2$—$C_6H_4$—OCN | — | 1 | 3 | 19 | 27 | 56 | 73 |
| PTs-1 | NCO—$C_6H_4$—$C(CH_3)_2$—$C_6H_4$—OCN | — | 2 | 9 | 42 | 51 | 65 | 93 |
| PTs-15 | NCO$C_6H_4$—$C(CF_3)_2$—$C_6H_4$OCN | 1 | 2 | 5 | 17 | 27 | 58 | 82 |
| PTs-17 | NCO$C_6H_4$—C(H)($C_6H_5$)—$C_6H_4$OCN | — | — | 2 | 20 | 31 | 46 | 78 |
| PTs-34 | NCO$C_6H_4$—$C(CH_3)$($C_6H_5$)—$C_6H_4$OCN | 1 | 4 | 16 | 41 | 52 | 75 | 95 |
| PTs-23 | NCO$C_6H_4$—$C(C_6H_5)_2$—$C_6H_4$OCN | — | — | 6 | 26 | 32 | 45 | 70 |
| PTs-2 | 3,3-di-(4-cyanatophenyl)phthalide | — | 1—2 | 2 | 20 | 33 | 50 | 80 |
| PTs-9 | 9,9-di-(4-cyanatophenyl)fluorene | — | — | — | 17 | 22 | 38 | 72 |
| PTs-10 | 9,9-di-(4-cyanatophenyl)-10-anthrone | — | 2 | 6 | 19 | 28 | 50 | 79 |
| PTs-1V | 1,2-di-(4-cyanatophenyl)carborane | — | — | — | 10 | 4 | 0 | 4.5** |
| PTs-R | *m*-NCO—$C_6H_4$—OCN | — | 1 | 11 | 23 | 31 | 46 | 71 |
| PTs-G | *p*-NCO—$C_6H_4$—OCN | — | 5 | 17 | 36 | 45 | 58 | 92 |
| PTs-4 | *p,p'*-NCO—$C_6H_4$—$C_6H_4$—OCN | — | 5 | 18 | 27 | 37 | 67 | 96 |

*The designations of the polycyanates here and in Tables 9 and 10 are the same as in the original papers[54,64,115,119,120].

**In contrast to other polymers, the carborane-containing polycyanate shows a 4.5% increase in weight at 600°C in air.

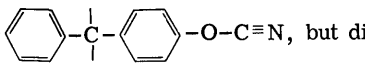
A comparative study has been made of the thermal and thermo-oxidative degradation under dynamic and isothermal conditions of polycyanates obtained by the polycyclotrimerisation of aryl dicyanates having the general structure  , but differing in the substituents at the central carbon atom [119]. The data obtained by the authors are presented in Tables 8–10.

Table 9. Results of the thermogravimetric analysis of polycyanates on heating in helium.

| Polycyanate | Decrease in weight of polymers, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 350° | 400° | 450° | 500° | 550° | 600° | 700° | 900° |
| PTs-19 | 2 | 7 | 25 | 31 | 38 | 46 | 40 | 55 |
| PTs-1 | 4 | 9 | 25 | 37 | 53 | 57 | 60 | 65 |
| PTs-15 | 3 | 8 | 25 | 31 | 54 | 61 | 65 | 68 |
| PTs-17 | 4 | 12 | 17 | 29 | 40 | 50 | 54 | 57 |
| PTs-34 | — | 1 | 12 | 21 | 31 | 37 | 40 | 43 |
| PTs-23 | — | 1 | 7 | 13 | 20 | 28 | 32 | 33 |
| PTs-2 | 1 | 3 | 12 | 22 | 33 | 39 | 43 | 46 |
| PTs-9 | — | 1 | 6 | 13 | 17 | 24 | 28 | 31 |
| PTs-10 | 1 | 5 | 17 | 23 | 31 | 35 | 39 | 42 |
| PTs-1V | 2 | 7 | 12 | 14 | 14 | 14 | 15 | 16 |
| PTs-R | 4 | 10 | 28 | 34 | 38 | 42 | 48 | 57 |
| PTs-G | 1 | 5 | 22 | 36 | 41 | 45 | 51 | 59 |
| PTs-4 | 3 | 9 | 22 | 27 | 31 | 34 | 40 | 47 |

Table 10. Results of the thermogravimetric analysis of polycyanates under isothermal conditions.

| Polycyanate | Decrease in weight of polymers, %* | | | | | |
|---|---|---|---|---|---|---|
| | 5 min | 10 min | 20 min | 30 min | 40 min | 60 min |
| PTs-19 | 1/5 | 2/8 | 3/12 | 4/15 | 4/17 | 4/20 |
| PTs-1 | 2/23 | 4/31 | 7/42 | 8/49 | 9/54 | 10/58 |
| PTs-15 | 4/7 | 4/ 8 | 5/12 | 5/13 | 5/13 | 5/14 |
| PTs-17 | 11/63 | 15/69 | 18/73 | 19/75 | 20/75 | 20/77 |
| PTs-34 | 2/3 | 2/6 | 2/10 | 2/12 | 2/15 | 2/18 |
| PTs-23 | 3/7 | 4/9 | 4/10 | 5/11 | 5/12 | 5/14 |
| PTs-2 | 2/4 | 2/6 | 2/8 | 2/8 | 2/8 | 2/9 |
| PTs-9 | 2/3 | 2/4 | 2/5 | 2/6 | 2/6 | 2/6 |
| PTs-10 | 2/3 | 3/4 | 3/5 | 3/5 | 3/5 | 3/6 |
| PTs-1V | 0/0 | 0/0 | 0/1 | 0/1 | 0/1 | 0/1 |
| PTs-R | 3/7 | 5/10 | 7/13 | 9/16 | 8/17 | 8/18 |
| PTs-G | 2/— | 4/— | 5/— | 5/— | 5/— | 5/— |
| PTs-4 | 1/3 | 2/6 | 3/8 | 4/9 | 4/10 | 4/10 |

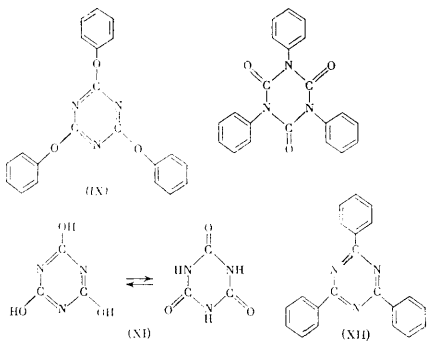
*Number on the left—at 300°C, number on the right—at 350°C.

It was found that the decomposition reaction of polycyanates with different structures in air is of the same type; it proceeds in several stages and is accompanied by the evolution of heat. This is indicated by the exothermic effects observed in the temperature ranges 380–420° and 490–580°C. In the first decomposition stage, the decrease in weight is 20–40% and in the second stage up to 90%. An exception is the thermo-oxidative degradation of the polycyanate based on dicyanatodiphenylcarborane. The beginning of the decrease in the weight of this polymer is observed at 390°C and at 450°C the weight loss is 10%. On further increase of temperature, the weight of the polymer rises and at 650°C is 107% of the initial value. The weight then again gradually decreases, amounting to approximately 96% of the initial value at 850°C (Table 8). Other carborane-containing polycyanates behave similarly [72,75,77,79].

In an inert atmosphere, the decomposition of polycyanates also proceeds in two stages. Under these conditions the temperatures of the onset of decrease in weight and the temperature ranges corresponding to the vigorous decomposition of polycyanates are somewhat displaced towards higher temperatures compared with degradation in air [55,119]. Large residues of carbon are characteristic of the degradation of polycyanates in an inert atmosphere up to 900°C [55, 119].

In the series of polycyanates based on aryl dicyanates with different substituents at the central carbon atom, polymers with polycyclic groups (phthalide, fluorene, or anthrone types) at the central carbon atom in the initial dicyanate have a high thermal stability [55,119].

In order to investigate further the processes occurring following the exposure of polycyanates to elevated temperatures, a study was made of the kinetics of the decomposition of polycyanates based on 2,2-di-(4-cyanatophenyl)-propane (PTs-1), 4,4′-dicyanatobiphenyl (PTs-4), and 9,9-di-(4-cyanatophenyl)fluorene (PTs-9), as well as the degradation of the model compounds diphenyl cyanurate (IX), triphenyl isocyanurate (X), cyanuric acid (XI), and triphenyl-*s*-triazine (XII) [115,120]:



(IX) (XI) (XII)

A study of the degradation process in air and *in vacuo* showed that the decomposition of polycyanates proceeds as a first-order reaction and obeys the Arrhenius equation. A comparative study of the kinetics of the decomposition of the polymers PTs-1, PTs-4, and PTs-9 *in vacuo* and in air showed that the polycyanate based on 9,9-di-(4-cyanatophenyl)fluorene, containing bulky subgroups, is more resistant to the action of high temperatures than the other two polymers. It was established that the presence of moisture in the polymers has a significant influence on the nature and degree of their decomposition.

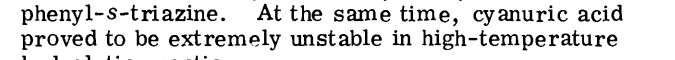
The study of the degradation products of polycyanates showed that they consist mainly of $CO_2$, CO, $H_2$, compounds containing the triazine ring (cyanuric acid and its phenyl esters), phenol, and bisphenols. Furthermore, benzene, biphenyl (in the degradation of the polycyanate PTs-4) and fluorene (in the degradation of the polycyanate PTs-9) were detected in the degradation products.

Since the polycyanates investigated are highly structured complex systems, a detailed investigation of the degradation of which presents certain difficulties, a study was made of the degradation of triphenyl cyanurate, a compound which simulates the principal bonds in the three-dimensional structure of the polymer, to elucidate the mechanism of the decomposition process [55,115]. The results of the study of the degradation of this compound by chromatographic and mass-spectrometric methods showed that, as in the degradation of the polymers PTs-1, PTs-4, and PTs-9, the principal decomposition products are carbon oxide, phenol, and cyanuric acid. Comparison of the

thermal stabilities of the above model compounds derived from triazine permitted the conclusion that triphenyl-*s*-triazine exhibits the highest thermal stability (CO, $CO_2$, and $H_2$ were not detected in the volatile degradation products up to 500°C)[115]. The presence of water at high temperatures has virtually no influence on the temperature limits of the stability of triphenyl isocyanurate and triphenyl-*s*-triazine. At the same time, cyanuric acid proved to be extremely unstable in high-temperature hydrolytic reactions.

The study of the decomposition products of polycyanates and their model compounds led to a degradation mechanism involving heterolytic and homolytic decomposition reactions[115]. It has been suggested that the degradation of polycyanates begins with the hydrolytic cleavage of the ester linkage and is accompanied by the subsequent decomposition of the triazine ring via both heterolytic and homolytic mechanisms. It has been noted that the effect of the hydrolysis of the ester linkage in the early stages may be somewhat suppressed by the introduction of bulky side groups into the polycyanate chain[115].

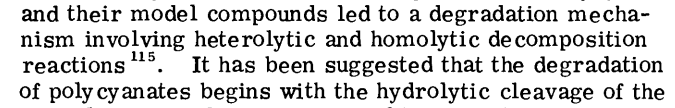
The influence of molecular weight ($M_C$) and of the chemical nature of the internodal fragments of polycyanates on their thermal and thermo-oxidative degradation has also been investigated[88]. In the polymers chosen for investigation, the internodal fragments were oligoarylene-oligosulphones:



$$-OC_6H_4C(CH_3)_2C_6H_4-[-OC_6H_4SO_2C_6H_4OC_6H_4C(CH_3)_2C_6H_4-]_n-O-,$$

$n = 1, 3, 5, 10$ ,

oligoarylates:

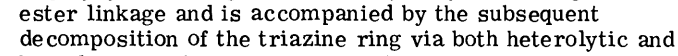


$-OC_6H_4C(CH_3)_2C_6H_4-[-OCOC_6H_4COOC_6H_4(CH_3)_2C_6H_4-]_n-O-$, $n=1,3,5$ and



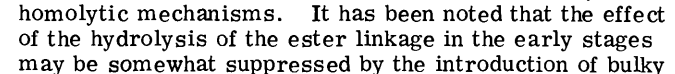
$-OC_6H_4-$ (C(O)O ring) $-C_6H_4-[-OCOC_6H_4COOC_6H_4-$ (C(O)O ring) $-C_6H_4-]_n-O-$, $n=5$,

a carborane-containing oligoester:



$$-OCH_2-C(B_{10}H_{10})-C-CH_2-[-OCO(CH_2)_8COOCH_2-C(B_{10}H_{10})-C-CH_2-]_n-O-,\ n=7,$$

and oligosiloxanes:



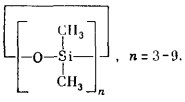
where $n$ = 3, 5, or 10 for $R_1 = CH_3$ and $R_2 = C_6H_5$ and $n$ = 0, 1, 5, 10, 25, 50, 70, or 100 for $R_1 = R_2 = CH_3$.

It was found that polycyanates based on oligoarylene-oligosulphones exhibit the highest thermal and thermo-oxidative stability (Table 6). An increase of $M_C$ of these polymers entails some increase in thermal stability. When oligoarylates are used as the internodal fragments, $M_C$ has hardly any influence on the temperature of the onset of decrease in their weight in air and in an inert atmosphere[88]. $CH_4$, $H_2$, and $CO_2$ were detected in the gaseous decomposition products of polycyanates with oligoarylene-oligosulphone internodal fragments, while in those with oligoarylate fragments CO was also detected.

The carborane-containing polymer has a lower temperature of the onset of decomposition in air compared with polycyanates containing oligoarylene-oligosulphone and oligoarylate internodal fragments, but, as for other carborane-containing polycyanates[73,75,77,79], it is characterised by a higher coke content at 900°C, while aromatic polymers are combusted almost entirely in air at 900°C.

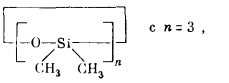
A study of the degradation of polycyanates containing oligosiloxane fragments of different lengths between the network nodes showed that an increase of $M_C$ entails an increase of the thermal and thermo-oxidative stabilities of the polymers, but, starting with a specific value of $M_C$, the thermal stability remains constant or actually diminishes somewhat.

The nature of the degradation of silicon-containing polycyanates, particularly at elevated temperatures, is the opposite of that of aromatic polycyanates, which are combusted almost in their entirety in air but leave appreciable carbon residues in an inert atmosphere at temperatures in the range 700–900°C. Appreciable coke residues, increasing with increase of $M_C$, are observed in the thermo-oxidative degradation of organosilicon polymers at high (up to 900°C) temperatures. On the other hand, siloxane-containing polycyanates decompose almost entirely on degradation in argon and for high values of $M_C$ the coke residues are insignificant. These findings have been explained[88] by the fact that, in the presence of oxygen, the siloxane chains form a structure via the organic groups attached to silicon, while in an inert atmosphere they are depolymerised with liberation of low-molecular-weight products having the structure



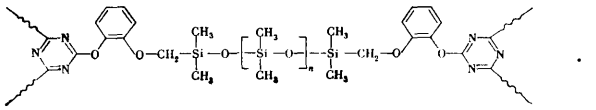
$n = 3$–$9$.

$H_2$, $CH_4$, and $CO_2$ were detected in the gaseous degradation products of silicon-containing polycyanates, while 2,2-dimethylbenzo-2-sila-1,4-dioxan (DMBD), catechol, the cyclic siloxane

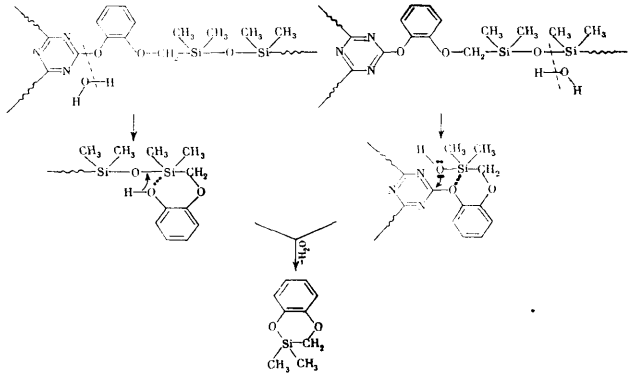


с $n = 3$ ,

with $n$ = 3 ($D_3$) and $n$ = 4 ($D_4$), and other compounds were found among the low-molecular-weight substances[88]. Table 11 presents data obtained by pyrolytic gas chromatography for the composition of the low-molecular-weight products of the degradation of organosilicon polycyanates with the following structure of the internodal fragment:



A possible mechanism for the degradation of organosilicon polycyanates has been suggested on the basis of data obtained in the study of this process[88]. Thus the formation of 2,2-dimethylbenzo-2-sila-1,4-dioxan (Table 11), detected in considerable amounts in the degradation products, can proceed via the mechanism:



Interesting data have been obtained in a study[123] of the influence of the structure of the initial dicyanate esters, in particular the nature of the substituents at the central carbon atom of aryl dicyanates, on the physical characteristics of the polymers based on them. The results obtained in this and a number of other investigations[54,55,73-77,80,124-126] are presented in Table 12.

Table 11. The compositions of the degradation* products of polycyanates with oligodimethylsiloxane internodal fragments.

| n** | Degradation temp., °C | Amount of evolved products, mole/mole of structural unit | | | | | |
|---|---|---|---|---|---|---|---|
| | | DMBD | catechol | $D_3$ | $D_4$ | $D_5$ | $D_{7-9}$ |
| 0 | 300 | 1.680 | 0.430 | 0.220 | 0.070 | 0.020 | 0.005 |
| 0 | 350 | 2.035 | 0.520 | 0.220 | 0.110 | 0.015 | 0.010 |
| 0 | 450 | 0.895 | 0.128 | 0.270 | 0.130 | 0.020 | 0.015 |
| 0 | 550 | 0.437 | 0.028 | 0.320 | 0.130 | 0.015 | 0.020 |
| 5 | 300 | 2.450 | 0.270 | 0.240 | 0.090 | 0.030 | 0.010 |
| 5 | 350 | 1.930 | 0.215 | 0.270 | 0.140 | 0.030 | 0.015 |
| 5 | 450 | 0.650 | — | 0.770 | 0.290 | 0.050 | 0.040 |
| 5 | 550 | 0.535 | — | 1.550 | 0.710 | 0.130 | 0.110 |
| 100 | 300 | — | — | 16.200 | 12.400 | 1.290 | 0.290 |
| 100 | 450 | — | — | 26.500 | 20.000 | 2.670 | 0.540 |
| 100 | 550 | — | — | 20.000 | 35.500 | 6.420 | 0.960 |

*The specimens were maintained at a specified temperature for 15 min.

**$n$ is the number of repeating groups $-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-$ in the internodal fragment.

Table 12. Physical properties of polycyanates.

| No. | Impact strength, kgf cm cm$^{-2}$ | Ultimate bending strength × $10^{-3}$, kgf cm$^{-2}$ | Brinel hardness × $10^{-3}$, kgf cm$^{-2}$ | Density at 20°C, g cm$^{-3}$ | Packing coefficient | Result of X-ray diffraction analysis ** | References |
|---|---|---|---|---|---|---|---|
| 1 | 18 | 1.92 | 1.40 | 1.414 | 0,688 | a.(cr.) | 54,55,123 |
| 2 | 12 | 1.73 | 1.50 | 1.431 | 0.697 | cr.(1.ord.) | 54,55,123 |
| 7 | 6 | 1.47 | 1.60 | 1.319 | 0.689 | cr.(m.ord.) | 54,123 |
| 9 | 20 | 1.60 | 1.35 | — | — | a. | 54 |
| 10 | 23 | 1.22 | 1.10 | 1.307 | 0.688 | cr.(m.ord.) | 54,55,123 |
| 13 | 18 | 1.80 | 1.25 | — | — | a. | 54 |
| 14 | 30 | 1.40 | 1.20 | 1.235 | 0.686 | a.(cr.) | 54,55,123 |
| 16 | 24 | 1.46 | 1.25 | 1.528 | 0.682 | a. | 54,55,123 |
| 17 | 10 | 1.59 | 1.35 | 1.255 | 0.689 | » | 54,55,123 |
| 18 | 17 | 1.85 | 1.46 | 1.229 | 0.684 | » | 54,55,123 |
| 19 | 5 | 1.62 | 1.63 | 1.220 | 0.681 | » | 54,55,123 |
| 20 | 6 | 2.02 | 1.65 | 1.322 | 0.673 | » | 54,55,123 |
| 21 | 5 | 1.54 | 1.70 | 1.269 | 0.688 | » | 54,55,123 |
| 22 | 6 | 1.69 | 1.60 | 1.288 | 0.685 | cr.(1.ord.) | 54,55,123 |
| 28 | 8 | 1.85 | 1.70 | — | — | a. | 73 |
| 29 | 30 | 1.30 | 1.60 | — | — | » | 74,75 |
| 30 | 17 | 1.50 | 1.40 | — | — | » | 77 |
| 31 | 15 | 1.40 | 1.30 | — | — | » | 79 |
| 32 | 14 | 1.20 | 1.40 | — | — | » | 79 |
| 33 | 20 | — | — | — | — | » | 80 |
| 34 | 30 | — | — | — | — | » | 80 |

*The numbers of the polymers correspond to those in Table 2.

**a. amorphous, a.(cr.) amorphous with signs of crystallinity, cr.(1.ord.) crystalline with a low degree of order, and cr.(m.ord.) crystalline with a moderate degree of order.

The most striking feature of the study of a systematic series of polycyanates[54,55,123] based on bicyclic aromatic dicyanates (see Nos. 7–29, Table 12), differing in the nature of the bridge group between the phenyl groups, is that the polymers obtained from dicyanates having a flexible bridge group and small substituents at the central carbon atom (polymers Nos. 9–16, Table 12) have anomalously high specific impact strengths (up to 30 kgf cm cm$^{-2}$ in contrast to all known cross-linked aromatic polymers[127] On the other hand, the presence at the central carbon atom of identical and aromatic substituents (polymers Nos. 17–19) and also of polycyclic groups (polymers Nos. 20–28) leads to an appreciable decrease of this parameter in cast polycyanate specimens. However, in the latter instances the bending strength of the polycyanate is somewhat enhanced[54,55,103,123]. This type of influence of the structure of the substituents at the central carbon atom in bifunctional derivatives was also observed previously for a series of heterochain linear polymers[128-131].

The decrease of the distance between the network nodes to a single phenylene group (polycyanates derived from 1,3- and 1,4-dicyanatobenzenes) leads to an appreciable increase of the specific impact and bending strengths of the cast polymer specimens[123]. Furthermore, block specimens of aromatic and a number of organoelement polycyanates have high bending strengths, a Brinell hardness of approximately 1000–1700 kgf cm$^{-2}$, a tensile strength in excess of 1000 kgf cm$^{-2}$, a modulus of elasticity of approximately 30 000–50 000 kgf cm$^{-2}$, and a relative elongation on extension of 3–6%.[54,55,73-77,80,123,126] These polymers retain effective physicochemical properties also at elevated temperatures, as can be seen from Table 13 for the polycyanate based on 2,2-di-(4-cyanatophenyl)propane.

Table 13. Physicomechanical properties of the polycyanate based on 2,2-di-(4-cyanatophenyl)propane at different temperatures.

| Temp., °C | Tensile strength, kgf cm$^{-2}$ | Relative elongation, % | Modulus of elasticity, kgf cm$^{-2}$ |
|---|---|---|---|
| 20 | 1100 | 4.5 | 32 000 |
| 200 | 650 | 5.6 | 22 000 |
| 250 | 500 | 6.1 | 17 000 |

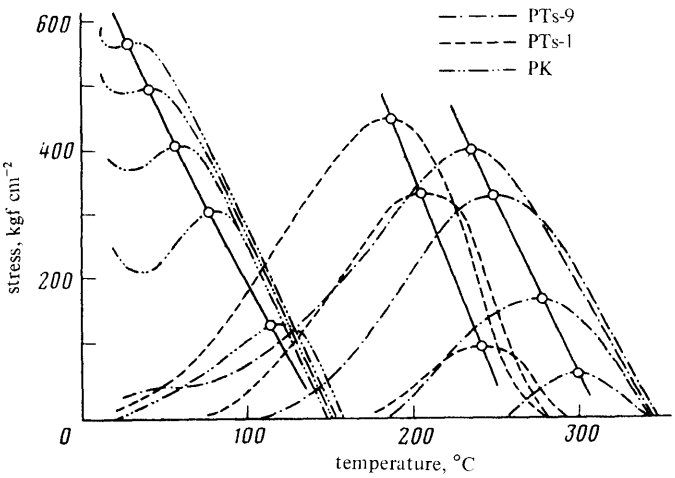
In order to elucidate the causes of the unusual mechanical properties of polycyanates, a study was made of the formation of the supermolecular structures of these polymers at different stages of their synthesis, starting from the initial monomer [2,2-di-(4-cyanatophenyl)propane] and continuing as far as the regular network system, with virtually quantitative conversion of the functional groups[64]. It was found that material with a globular structure is formed initially in polycycloprimerisation against the background of the characteristic cryptocrystalline structure of the monomer[64]. The size of the globules does not remain constant during polymerisation but gradually diminishes from approximately 500 to 100–200 Å. Subsequently the globules were found to aggregate in the final stage of polymerisation (for the conversion of the N≡C–O groups of approximately 98%) into fibrille-like formations.

Simultaneously with the study of the supermolecular structure of the polycyanates, the relaxation properties of the solid networks at different stages of the conversion of the N≡C–O groups of the initial monomer were also investigated[64]. With an increase of the degree of conversion, the relaxation curves are initially displaced towards highe

stresses and, after the attainment of approximately 90% conversion of the monomer, begin to shift to the region of lower stresses. The parameters of the Kohlrausch equation were calculated for various stages of the process. The results show that, as the polycyclotrimerisation of aryl dicyanates proceeds and with the consequent increase of the regularity of the network formed, the nature of the supermolecular structure of the polymer alters, which leads in its turn to a steady change of the mechanical properties of the network system–to an increase of elasticity[64].

It may be that, in the usual thermoreactive systems, the formation of a regular defect-free network can also lead to polymeric materials with an enhanced resistance to impact stresses and with an improved elasticity.

The study of the thermomechanical properties[53] of polycyanates showed that the temperatures of the onset of their deformation lie in a comparatively narrow range (360–410°C). However, the nature of the thermomechanical curves for polycyanates suggests that the deformation temperature is related to the degradative processes occurring in the polymers. This is confirmed by the fact that the temperatures of the onset of decomposition of polycyanates in air (from thermogravimetric data) lie in this region.




The regions corresponding to the effectiveness of the polycarbonate based on 2,2-di-(4-hydroxyphenyl)propane (PC) and the polycyanates based on 2,2-di-(4-cyanatophenyl)-propane (PTs-1) and 9,9-di-(4-cyanatophenyl)fluorene (PTs-9).

For a more detailed comparison of the heat resistances of highly cross-linked polycyanates synthesised from the dicyanate esters of bisphenols of different structures, the regions where the polymers can be used effectively were determined over a wide range of temperatures and mechanical stresses (see Figure).[123] The similarity of the non-isothermal stress relaxation curves and the curves bounding the region where the polymer is efficient, obtained for highly cross-linked systems (polycyanates) and for the linear heterochain polymers investigated in detail in previous studies[128–132], is striking; the Figure presents the polycarbonate curve as an example. The replacement of the isopropylene group by the fluorene group leads to an increase of the heat resistance of polycyanates over the entire range of temperatures and stresses investigated.

A study was also made of the influence of a number of other features of the structure of the initial dicyanate esters on the parameters of the region of the effective use of the polycyanates based on them[123]. It has been shown for polycyanates based on the oligomeric dimethylsiloxane dicyanates (V) that $M_C$ has a significant influence on many physicomechanical parameters of these polymers[88,91,95]. With decrease of $M_C$, an increase of tensile strength ($\sigma_t$) and the modulus of elasticity ($E_t$) as well as a decrease of the relative elongation on extension ($\epsilon_t$) are observed (Table 14).

Table 14. The influence of $M_C$ on the physicomechanical properties of organosilicon polycyanates based on the oligodicyanates (V).

| Number of dimethylsiloxane groups in internodal fragment | $\sigma_t$, kgf cm$^{-2}$ | $\epsilon_t$, % | $E_t$, kgf cm$^{-2}$ |
|---|---|---|---|
| 1 | 25 | 12 | 208 |
| 5 | 4 | 40 | 10 |
| 25 | 2 | 50 | 3 |
| 50 | 1 | 90 | 1 |
| 70 | 1 | 120 | 1 |

The packing coefficients for monolithic specimens of many amorphous and weakly crystalline linear polymers, having a large variety of structures and obtained by both polymerisation and polycondensation, vary within extremely narrow limits[133] and their packing densities are approximately the same ($k_{av}$ = 0.681). The packing coefficients have also been recently calculated for sterically structured systems[123]; these parameters for a number of polycyanates are listed in Table 12.

It has been found that the packing coefficients for closely cross-linked polymers with a wide variety of structures lie within a narrow range (0.673–0.697), the average value of the parameter for the polycyanates (0.686) being close to the average value for linear polymers (0.681). The virtual identity of the packing coefficients for linear and cross-linked polymers shows that the amorphous and weakly crystalline sterically structured, infusible, and insoluble polymers are just as closely packed as the linear, fusible, and soluble polymers.

The data for the packing of aromatic polycyanates led to the hypothesis that the mobility of the $C_{sp^3} - C_{sp^2}$ bond between the central carbon atom and the phenyl groups of the internodal fragments of the network exerts the main influence on the physical properties of many of these polymers, differing in the nature of the substituents at the central carbon atom[123].

The packing coefficients have also been calculated[88] for cross-linked polymers based on the dicyanates of oligoarylates, oligosulphones, and oligomeric methylphenyl- and dimethyl-siloxanes with different values of $M_C$ (see Tables 6 and 7). For the majority of polymers investigated as well as for polycyanates based on aryl dicyanates, the packing coefficients are found to be close to $k_{av}$ = 0.681. An exception are polymers containing dimethylsiloxane fragments of different lengths between the network

nodes. These polymers are characterised by anomalously low packing coefficients, decreasing with increase of $M_c$ from 0.651 (for $n = 0$) to 0.587 (for $n = 100$). The fact that the porosity of these systems is zero[88] makes it possible to attribute these anomalously low values to the loose packing of the macromolecules of the organosilicon polycyanates.

The principal parameters of the network structure of polycyanates have been investigated using as an example the polycyanates based on the oligomeric dicyanates (II) and (V) by the method derived from the statistical theory of viscoelasticity[88]. The investigation was performed by measuring the stress relaxation for a constant deformation and biaxial extension of film polycyanate specimens with oligosiloxane ($n = 5$, 25, 50, 70) and oligoarylate ($n = 1$ or 3) internodal fragments. The experimental and calculated parameters of the structures of these polymers are listed in Table 15. Evidently the experimental values of the average (numerical) molecular weight ($M_{ce}$) and the concentrations of the active chains $(V_c/V)_e$ per unit volume of the cross-linked polymers are close to the theoretical values $M_{ct}$ and $(V_c/V)_t$, which demonstrates the regularity of the networks of the polymers.

**Table 15.** Parameters of the network structures of polymers based on the oligomeric dicyanates (V) and (II).

| $n$ | $M_{ce}$, g mole$^{-1}$ | $M_{ct}$, g mole$^{-1}$ | $10^4(V_c/V)_e$, mole cm$^{-3}$ | $10^4(V_c/V)_t$, mole cm$^{-3}$ | $\frac{(V_c/V)_e}{(V_c/V)_t}$ |
|---|---|---|---|---|---|
| Polymers based on oligodicyanates (V) | | | | | |
| 5 | 500 | 800 | 21.00 | 13.86 | 1.50 |
| 25 | 3300 | 2280 | 3.00 | 4.39 | 0.70 |
| 50 | 4400 | 4133 | 2.24 | 2.36 | 0.98 |
| 70 | 7300 | 5614 | 1.30 | 1.23 | 0.74 |
| Polymers based on oligodicyanates (II) | | | | | |
| 1 | 700 | 686 | 16.34 | 17.35 | 0.94 |
| 3 | 1100 | 1352 | 11.09 | 8.87 | 1.25 |

A very interesting feature of many polycyanates is their capacity for crystallisation. Crystalline cross-linked polymers are known, but their internodal segments were flexible aliphatic and siloxane fragments with $M_c$ of at least 2100 and the crystalline structures of the cross-linked polymers were fully analogous to those of the initial crystalline oligomers and were in essence determined by them[134-139].

Korshak, Pankratov, and coworkers[140] were the first to obtain, using polycyanates, cross-linked, rigid-chain, fine-mesh network polymers with a completely different crystalline structure than that of the initial crystalline monomer: the formation of the crystalline structure of the network polymer takes place during its synthesis. In an X-ray diffraction study of the polycyanate based on 1,4-dicyanatobenzene, the authors[140] showed that, by altering the conditions of synthesis, it is possible to obtain polymers having the same chemical constitution but a different structure. Thus, whereas the specimen obtained in a solvent had a fully amorphous structure, the diffractometer trace for the specimen synthesised in bulk showed additional distinct reflections indicating the formation of a crystalline structure; $M_c = 108$ for this polymer. The authors suggested that, during polycyclotrimerisation in bulk, the polycyanate macromolecules are stacked in the form of parallel corrugated layers. However the tendency towards crystallisation[53-55,123] has also been observed for polycyanates based on a number of other dicyanates (Table 12)†. It appears that, when the initial monomer and the polycyclisation conditions are suitably chosen, structures of this kind can be obtained in a highly crystalline state.

The capacity of polycyanates for crystallisation as well as many other unusual properties of these polymers are a consequence of the regularity of their structure, produced as a result of the highly selective cyclotrimerisation of the N≡C–O groups of the initial monomers and the virtually quantitative completion of the polycyclotrimerisation reaction.

In conclusion, we may note the following fundamental advantages of both polycyclotrimerisation, as a new method for the synthesis of polymers, and of the polycyanates obtained by this method from aromatic and organoelement cyanate esters.

The initial monomers (cyanates) are obtained by a technologically simple procedure from a raw material which is produced industrially. In most cases, these monomers are relatively infusible substances, stable on storage even when catalysts are deposited on them.

Cyanates are polycyclotrimerised both in the presence and absence of catalysts and the process can be interrupted at the stage of oligomers having a consistency ranging from a viscous liquid to solid products readily soluble in many organic solvents (acetone, toluene, alcohol, chloroform, etc.). The manufacture of articles from cyanates in the form of monomers or oligomers is carried out by the traditional methods for the working of thermoreactive polymers without the evolution of volatile materials.

The high selectivity of the reaction and the occurrence of the latter with virtually quantitative conversion of the functional groups are characteristic of the polycyclotrimerisation of cyanates, which makes it possible to obtain regularly cross-linked polymers with strictly specified internodal distances made up of *s*-triazine rings. Polycyanates are therefore the first examples of a series of polymers obtained by polycyclotrimerisation for which it is possible to achieve in practice the hypothetical possibilities of this promising synthesis of polymers, particularly for the preparation of heat-resistant and thermostable materials.

It has been shown for aromatic polycyanates that, in contrast to the randomly cross-linked systems, these polymers possess, by virtue of the regularity of their chemical structure, anomalously high physicomechanical parameters for fine-mesh network rigid-chain polymers of this kind and in many cases are capable of crystallisation.

All these useful qualities of polycyanates as well as their effective adhesion to various materials permit their employment in many fields in modern engineering. Polycyanates are used as plastics[52-55,64,73-77,80,88,97,98,105,145], adhesives[73-77,80,84,85,88,96-99,105,146,147], and binders for glass-fibre-reinforced plastics[55,73-77,80,96,148-151], solid rocket fuel[152], and other materials[153,154] possessing in most cases enhanced heat resistance and thermal stability.

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†It is noteworthy here that this interesting phenomenon has also been observed for rigid highly cross-linked polymers obtained by the polycyclotrimerisation of arylbis(cyanamides)[141-144].

During the preparation of the manuscript for the press, a number of studies devoted to the synthesis [155-158] and properties of polycyanates [159] and the investigation of the kinetics and heats of the polycyclotrimerisation of aryl cyanates were published [160].

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# The Influence of the Magnetic Field on Processes Involving Radicals and Triplet Molecules in Solutions

R.Z.Sagdeev, K.M.Salikhov, and Yu.M.Molin

The results of studies of the influence of a constant magnetic field on reactions involving free radicals and triplet molecules in solutions are examined and the theoretical principles of the influence of the magnetic field on the recombination processes of free radicals (taking into account the spin effect) and the quenching of triplets are described. The theoretical models are compared with experimental data.
The bibliography includes 95 references

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## I. INTRODUCTION

The research on the effects of the magnetic field in the kinetics of chemical reactions has been prosecuted since the end of the last century. Nevertheless, the range of systems in which reliable effects have been observed has been very limited until recently.

The influence of the magnetic field on the fluorescence of iodine vapour was observed in 1913.[1] This effect was interpreted by Franck and Grotrian[2] as a result of the changed rate in the magnetic field of a competing non-radiative process—magnetic predissociation. Since then, the magnetic predissociation of molecules has continued to attract the attention of investigators (see, for example,

Refs. 3–8). However, iodine molecules are apparently still the only example for which magnetic predissociation has been investigated experimentally.

The direct influence of magnetic predissociation on the rates of chemical reactions has been observed by Falconer and Wasserman[9], who noted that the photoisomerisation of but-2-ene catalysed by $I_2$ vapour is accelerated following the application of an 85 kG magnetic field.

The magnetic effect in heterogeneous catalytic reactions has attracted the attention of investigators, However, these studies did not lead to reproducible results (see, for example, Figueras Roca[10]), with the exception of the *ortho–para* conversion of hydrogen[11,12].

Yet another interesting example of the influence of the magnetic field on physicochemical processes is the acceleration of the destruction of positronium[13]. The Zeeman interaction of positronium with the magnetic field mixed the *ortho*- and *para*-levels and thereby reduces the lifetime of the long-lived triplet state.

Research into the influence of the magnetic field on reactions in solution has so far yielded negative results as a rule and the reported observation of the effect has frequently not been confirmed by subsequent experiments. In his review[14] of studies up to 1945, Selwood noted only one investigation[15] where the effect of the magnetic field on the rate of homogeneous reactions had been observed. Effects amounting to several per cent have been found in reactions during which the overall magnetic susceptibility of the system changed. This study was subsequently quoted in many communications, but even these results have been questioned. On repeating the experiments for two reactions which have been stated[15] to be most sensitive to the magnetic field, Kazakov[16] failed to confirm the effect. Selwood also reported[14] that he had attempted to reproduce certain results in the patent literature concerning the control of chemical reactions by the magnetic field. Negative results were obtained in all cases.

Reports concerning the observation of effects due to the magnetic field, which were not confirmed by other workers, were also published subsequently. Thus, Schmid et al.[17] reported the retardation by a factor of 8 of the polymerisation of styrene in a 16 000 G field at 80°C, but Collins and Bryce[18] were unable to reproduce this effect. Nor did the magnetic field affect the rate of decomposition of benzoyl peroxide[19]—the inhibitor of the polymerisation of styrene.

This situation led to scepticism concerning the problem as a whole. This was also promoted by the prolonged absence of any ideas concerning the possible physical mechanisms for an appreciable influence of the magnetic field on chemical reactions in solution. The possibility of the displacement of the chemical equilibrium owing to a change in magnetic susceptibility during the reaction has been considered theoretically[20]. Even under the most favourable conditions, the relative change in the equilibrium constant did not exceed $10^{-4}$ at room temperature according to these estimates.

The idea of the orienting effect of the magnetic field on the electron spins of free radicals or other paramagnetic species has been frequently discussed. However, under the usual experimental conditions (room temperature, magnetic field up to 10 000 G), the Boltzmann difference between the probabilities of different spin orientations is too small to result in appreciable effects.

The possibility of the orientation of molecules as a whole in the magnetic field, which might have influenced in some way their chemical reactivity, was considered finally. This effect has been shown[21] to be significant only for very large molecules (or conglomerates of molecules) with an anisotropic magnetic susceptibility (for example, the DNA molecules and for reactions in liquid crystals). The influence of the magnetic field on reactions in liquid crystals has been observed experimentally[22], but in the general case this effect cannot play an appreciable role.

In view of all the above considerations, ten years ago the majority of investigators believed that the magnetic field cannot have an appreciable influence on reactions in solutions, with the possible exception of biological systems. However, recently the attitude to this problem has changed radically. This was promoted by the observation of two phenomena. Firstly, magnetic effects were noted in processes involving triplet excitons in solids[23–25] (these problems are discussed in detail in the review by Sokolik and Frankevich[26]). The above studies stimulated research on analogous effects in solutions. Secondly, the phenomenon of chemically induced nuclear polarisation was discovered[27,29] and explained[29,30], which permitted the formulation of a clear-cut physical mechanism of the possible influence of the magnetic field on chemical radical reactions in solutions.

A number of experimental studies have been made in recent years on the influence of the magnetic field on the chemical reactions of free radicals and on processes involving triplet excited molecules in solutions. A fairly detailed theory of the effect of the magnetic field on the rates of these processes has been developed, an important feature of which involves allowance for cage effects characteristic of reactions in solutions. The results of these studies are summarised in the present review.

## II. THE MECHANISMS BY WHICH MAGNETIC FIELDS INFLUENCE CHEMICAL REACTIONS WITHIN THE FRAMEWORK OF THE MODEL OF THE "CAGE" RECOMBINATION OF RADICAL PAIRS

We shall consider initially radical reactions—the largest class of chemical reactions in which an effect of the magnetic field may be expected. It is now known that this influence can arise in the stage involving the recombination† of two radicals in a single "cage" and forming a radical pair (RP). The "cage" is understood in a fairly wide sense of the word—it is a region of effective recombination of the radicals of the given pair with one another[31]. As long as there are two radicals in this region, the probability of their reaction with other molecules is negligibly small compared with the probability of their recombination with one another. During their lifetime in the "cage", the radicals can undergo numerous repeated collisions. In the theory of radical reactions in solutions, two cases of cage recombination are distinguished. The first involves the recombination of correlated radical pairs, i.e. radical pairs in a definite spin state—singlet or triplet. Such radical pairs arise, for example, as a result of unimolecular decomposition under the influence of heat, light, or ionising radiation. The second case includes the reactions of non-correlated radical pairs (the so called F-pairs) where two randomly colliding radicals recombine. In such pairs, the statistical weight of the singlet state is 1/4 and that of the triplet state 3/4. The recombination reaction of radical pairs is selective with respect to the spin and as a rule takes place in the singlet

†The term "recombination" is used here in a wide sense and includes also disproportionation reactions.

state. The reaction probability therefore changes if the multiplicity of the radical pair is altered during its lifetime in the cage (see Fig. 1).

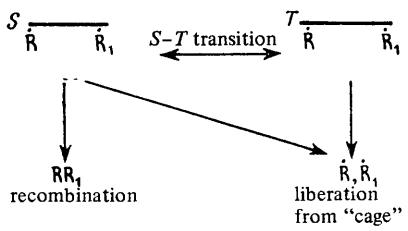



**Figure 1.** Schematic illustration of the processes occurring on recombination of radical pairs in the "cage". The efficiency of the recombination of a singlet radical pair decreases owing to the $S-T$ transition. A triplet radical pair can recombine solely after a $T \rightarrow S$ transition.

We shall consider in greater detail the mechanisms of singlet–triplet ($S-T$) transitions in radical pairs, since, according to the results of a theoretical study, the rates of these transitions can in fact be sensitive to the external magnetic field. Brocklehurst [32] put forward in 1969 the first idea, with a physical basis, concerning the possible mechanism of the influence of the magnetic field on singlet–triplet transitions in radical pairs. He examined the elementary process, typical for radiation chemistry, involving the recombination of an electron (or radical-anion) with its parent radical-cation. According to Brocklehurst [32], these two species form a singlet radical pair, since the initial ionisable molecule was in the singlet state. The transition of the pair to the triplet state can occur by the relaxation of electron spins. Since the electron paramagnetic relaxation times of radicals may depend on the magnetic field strength, the magnetic field may affect the ratio of the yields of the singlet and triplet excited molecules formed as a result of the recombinaton of these radical-ions. Although it is now clear that mechanisms leading to singlet–triplet transitions are more effective for free radicals or radical-ions, Brocklehurst's idea has not lost its importance for the prediction of field effects in systems with short paramagnetic relaxation times. It has been used in the development of a theory of the influence of the magnetic field on the quenching of excited triplet states in solutions [33].

A decisive step in the formulation of the most important mechanisms of $S-T$ transitions in radical pairs was made by Lawler and Evans in 1971, already on the basis of the advances in the field of chemically induced nuclear polarisation [34]. These investigators were the first to formulate the idea that the singlet–triplet transitions in radical pairs, invoked to account for chemically induced nuclear polarisation, must affect also the probability of the recombination of the radicals in the pair. They examined two mechanisms of the singlet–triplet transition in the pair: owing to the difference between the Zeeman frequencies of the radicals (the $\Delta g$ mechanism) and owing to the hyperfine interaction (the HFI mechanism) and showed that the efficiencies of the two mechanisms depend on the magnetic field strength. Subsequently these mechanisms were examined in detail in a number of studies. The manifestations of the $\Delta g$ mechanism [35–40] and the HFI mechanism [38,41–48] have been analysed.

Within the framework of the $\Delta g$ mechanism, the singlet state of the radical pair becomes mixed with only one of the triplet states $T_0$, having a zero projection of the overall spin of the unpaired electrons in the radical pair on the direction of the external magnetic field, i.e. only $S-T_0$ transitions are induced. This mechanism does not involve the two triplet states $T_{+1}$ and $T_{+1}$. The essential features of the $\Delta g$ mechanism for the evolution of the radical pair are illustrated in Fig. 2. The singlet spin state of the radical pair can be represented schematically by two magnetic moments processing about the direction of the field $H_0$ in such a way that their sum remains zero (Fig. 2*a*).

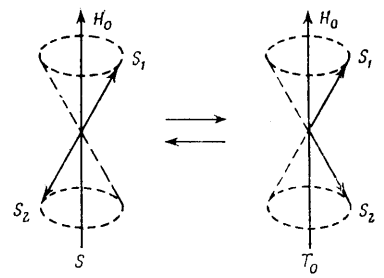



**Figure 2.** Schematic illustration of the $S-T_0$ transition via the $\Delta g$ mechanism. The difference between the Larmor precession frequencies of the $S_1$ and $S_2$ spins leads to transitions between the $S$ and $T_0$ states of the radical pair.

In the triplet state, the overall spin of the radical pair is unity and the $T_0$ state can therefore be represented in terms of the model illustrated in Fig. 2*b*). If the Larmor frequencies of the precession of the spin moments of the radical pair are different, then transitions between two reciprocal configurations of the vectors, shown in Fig. 2, will occur periodically during the precession, i.e. the difference between the Larmor frequencies of the radical pair spins leads to $S-T_0$ transitions. Their frequency is proportional to the difference between the Larmor frequencies of the radicals in the pair and increases linearly with the strength of the constant external magnetic field.

The manifestation of the HFI mechanism of the transitions of radical pairs in strong magnetic fields ($\gtrsim$1000 G) is similar to that of the $\Delta g$ mechanism: the local field induced by the HFI is combined with the external field and gives rise to a difference between the precession frequencies of the spin moments of the unpaired electrons of the radical pair, which leads to $S-T_0$ transitions. However, in weak external magnetic fields, comparable to the local field, a fundamental difference between the two mechanisms is observed: HFI begins to induce transitions from the singlet state to all three triplet states. The qualitative difference of the HFI mechanism is due to the fact that the magnetic spin moments of the unpaired electrons of the radical pair precess about the overall external and local (HFI) fields. In strong external fields, the direction of the overall field virtually coincides with that of the external magnetic field and the projection of the electron spin moments on to $H_0$ therefore remains the same. On the

other hand, in weak fields the overall field may not have the same direction as the external field, which results in the possibility of transitions not only to the $T_0$ state but also to the $T_{\pm 1}$ states.

Thus two fundamental mechanisms of the influence of the external magnetic field on the kinetics of chemical radical reactions have now been recognised: the $\Delta g$ and the HFI mechanisms. In the former case, the interaction, responsible for the singlet–triplet transitions in the radical pair in the cage, is itself intensified with increase of the magnetic field strength. In the second case, the field effect is associated with the dependence of the number of effectively operating channels for the singlet–triplet transitions in the radical pair in the "cage" on the magnetic field strength.

## III. DYNAMICS OF THE RADICAL PAIR SPINS

We shall now consider the singlet–triplet evolution of radical pairs. The following probability of the $S-T_0$ transition has been obtained for the $\Delta g$ mechanism [34-40]:

$$p_{ST_0} = \sin^2\left(\frac{1}{2}\Delta g \beta \hbar^{-1} H_0 t\right), \quad (1)$$

where $\Delta g$ is the difference between the $g$-factors of the radicals in the pair and $\beta$ is the Bohr magneton. Hence it is seen that the radical pair oscillates between the $S$ and $T_0$ states at a frequency

$$\omega_{ST_0} = |\Delta g| \beta \hbar^{-1} H_0. \quad (2)$$

For short times, when $\omega_{ST_0} t < 1$, the probability of the $S-T_0$ transition varies with the square of the magnetic field strength $H_0$:

$$p_{ST_0} \simeq \frac{1}{4}(g_1 - g_2)^2 \beta^2 \hbar^{-2} H_0^2 t^2. \quad (3)$$

Over a long time interval, where $\omega_{ST_0} t > 1$, there are on average equal contributions of the $S$ and $T_0$ states of the radical pair.

The singlet–triplet evolution of the radical pair in the case of the HFI mechanism is more complex, since under these conditions there is a possibility of transitions to all the triplet states and the transitions via different channels interfere with one another. Comparatively simple results are obtained only for short times, when $|A| t < 1$ ($A$ is the isotropic HFI constant) and the transitions via different channels are combined additively. In this case, the interaction of unpaired electrons with all the magnetic nuclei may be characterised by a single mean-square HFI constant [45]:

$$A_{\text{eff}} = \left\{\sum_k A_{1k}^2 + \sum_n A_{2n}^2\right\}^{1/2}, \quad (4)$$

where $A_{1k}$ and $A_{2k}$ are the HFI constants of the radicals in the pair. In a zero external magnetic field, the probability of the transition of the radical pair from the singlet to the triplet state is

$$p_{ST}^0 \simeq \frac{3}{16} A_{\text{eff}}^2 t^2. \quad (5)$$

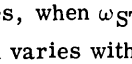
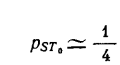
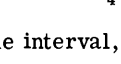
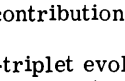
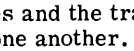
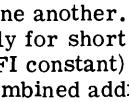
Correspondingly, the following expression has been obtained for strong fields when $g\beta\hbar^{-1}H_0 > A_{\text{eff}}$:

$$p_{ST_0}^{\infty} \simeq \frac{1}{16} A_{\text{eff}}^2 t^2. \quad (6)$$

Thus, for radical pairs with sufficiently short lifetimes, i.e. when the condition $A_{\text{eff}} t < 1$ holds, the ratio of the probabilities of the $S-T$ transitions in a zero field and in a strong field is 3, which corresponds exactly to the number of transition channels operating effectively in weak and strong fields.

For arbitrary lifetimes, the calculations of the probabilities of the $S-T$ transitions in radical pairs become more complex even in the two limiting cases of zero and strong fields. Calculations have therefore been made only for the simplest model radical pairs [41-47]. Table 1 presents the probabilities of the $S-T$ transitions for certain systems. As was to be expected, the calculations for short times yield $p_{ST}^0 = 3p_{ST_0}^{\infty}$. However, for comparatively long-lived radical pairs, a very remarkable feature of the HFI mechanism is observed: the probability of the $S-T$ transitions in weak fields, where three competing $S-T_0$, $T_{+1}$, $T_{-1}$ transition channels operate, is sometimes smaller than in strong fields where only one $S-T_0$ channel operates. Such anomalous properties are shown by radical pairs numbered V and VI in Table 1. This feature of the HFI mechanism is discussed in detail by Sarvarov and Salikhov [46].

Table 1. The probabilities of the $S-T$ transitions induced by the hyperfine interaction (nuclear spin $I = 1/2$).

| No. of pair | RP | $p_{ST}^0$ | $p_{ST}^{\infty}$ |
|---|---|---|---|
| I |  | $\frac{3}{16}\sin^2(At) + \frac{3}{4}\sin^2\left(\frac{A}{2}t\right)$ | $\frac{1}{2}\sin^2\left(\frac{1}{2}At\right)$ |
| II |  | $\frac{2}{3}\sin^2\left(\frac{3}{4}At\right)$ | $\frac{1}{2}\sin^2\left(\frac{1}{2}At\right)$ |
| III |  | $\frac{2}{3}\sin^2\left(\frac{\sqrt{3}}{4}At\right) + \frac{1}{3}\sin^2\left(\frac{\sqrt{3}}{2}At\right)$ | $\frac{1}{2}\sin^2\left(\frac{1}{2}At\right)$ |
| IV |  | $\frac{20}{27}\sin^2\left(\frac{3}{4}At\right) + \frac{4}{27}\sin^2\left(\frac{3}{2}At\right)$ | $\frac{1}{2}\sin^2\left(\frac{A}{2}t\right) + \frac{1}{8}\sin^2(At)$ |
| V |  | $\frac{3}{4}\sin^2\left(\frac{A}{2}t\right)$ | $\sin^2\left(\frac{A}{4}t\right)$ |
| VI |  | $\frac{15}{32}\sin^2(At) + \frac{3}{8}\sin^2\left(\frac{A}{2}t\right)$ | $\frac{1}{4}\sin^2\left(\frac{3}{4}At\right) + \frac{3}{4}\sin^2\left(\frac{A}{4}t\right)$ |

The above results were obtained on the hypothesis that the exchange interaction of the unpaired electrons of the radical pair is insignificant. This corresponds to the initial model where the $S-T$ transitions occur in the interval between two repeated collisions of the pair radicals, when the distances between the unpaired electrons are fairly large and the exchange integral $J$ is small, and not at the instant of direct contact between the radicals. However, in some cases the exchange interaction is presumably significant and this alters the process dynamics. In particular, such a situation can occur in biradical systems [49].

The nature of the influence of the exchange interaction on the $S-T$ transitions can be predicted fairly readily for the $\Delta g$ mechanism. Indeed, when no account is taken of the exchange interaction, the energy levels of the $S$ and $T_0$

states coincide, so that the transitions take place between two resonance levels. The exchange interaction splits the $S$ and $T_0$ levels, stops their resonance, and reduces the probability of the $S$ and $T$ transition [37].

In the HFI mechanism, the influence of the exchange interaction on the dependence of the $S-T$ mixing on the field is qualitatively different: the efficiency of the $S-T$ transitions passes through a maximum in the region of magnetic fields where the Zeeman splitting of the triplet levels is comparable to the singlet–triplet splitting and the singlet is in resonance with one of the triplet states, $T_{+1}$ or $T_{-1}$.

However, the exchange interaction ceases to play a role in singlet–triplet transitions if the lifetimes of the radical pairs in the "cage" are fairly short. Indeed, it can be shown that, for short-lived radical pairs, where $(\omega^2_{ST_0} + 4J^2)^{1/2}t < 1$, the probability of transition via the $\Delta g$ mechanism is independent of $J$ and coincides with the result defined by Eqn.(3) for $J = 0$. Similarly, in the case of the HFI mechanism of the singlet–triplet transition for short-lived radical pairs, where $(A^2_{\text{eff}} + J^2)^{1/2}t < 1$, the results defined by Eqns.(5) and (6) remain valid regardless of the exchange interactions.

Thus the dynamics of the radical pair spins are fully described in the case of the $\Delta g$ transition mechanism. For the HFI mechanism, calculations have been made of the dependence of the transitions of the radical pair on the magnetic field strength in the simplest systems, which made it possible to discover certain general characteristics over the singlet–triplet evolution of radical pairs. However, in the general case, a quantitative discussion of the effects due to the HFI mechanism, apparently requires calculations for each specific pair of radicals, since the transition probability depends significantly on the number of magnetic nuclei and the magnitude and signs of the HFI constants.

## IV. PHENOMENOLOGICAL MODELS OF THE RECOMBINATION OF RADICALS IN THE "CAGE"

Two models are considered for a phenomenological description of the recombination of radicals in the "cage": the diffusion [31] and exponential [25,29] models. According to the diffusion model, the "cage" for a radical pair consists of a region with a radius of approximately $10^{-7}$ cm and the lifetime of the radicals in the "cage" is determined by the time which they take to traverse this region. For solutions where the diffusion coefficient of radicals is $10^{-5}$ cm$^2$ s$^{-1}$, their lifetime in the "cage" is $10^{-9}-10^{-10}$ s.[31] This time can increase significantly, for example for highly viscous solutions. The recombination of radical pairs is treated phenomenologically. It is assumed that there is a reaction region, included between two concentric spheres with radii $r_0 - a$ and $r_0$, and that the recombination of singlet radical pairs in this region is characterised by a unimolecular constant $k(s^{-1})$.

Highly reactive radicals recombine on first contact with one another if the radical pair is in the singlet state. However, if the reactivity is not quite so high, repeated collisions of the radicals in the pair contribute to the overall recombination probability in addition to the first contact. Within the framework of the diffusion model, singlet–triplet transitions occur in the periods between collisions.

The statistics of repeated collisions in the "cage" have been examined in detail by Noyes [31]. On the basis of numerical calculations for repeated molecular collisions within the framework of "jumps" (the so-called random flight model), Noyes proposed the following approximation to the statistical weight $f(t)$ of the radicals in the "cage" involved in repeated encounters after a time $t$ when the initial distance between the pair radicals exceeds their collision radius by the distance of a single elementary jump [50]:

$$f(t)dt = \frac{0.24}{\tau}\frac{dt}{(t/\tau + 0.44)^{3/2}}, \quad (7)$$

with $\tau$ as the average time of a single elementary jump, a typical value of which is $\tau \simeq 10^{-11}$ s.

The exponential model of recombination differs significantly in its physical postulates from the diffusion model. In this model, repeated collisions of the radicals are not taken into account and it is assumed that a singlet–triplet transition occurs directly in the reaction zone. The liberation of radicals from the "cage" is described as unimolecular decomposition of the pair with a Poisson distribution of the radical pair lifetimes:

$$f(t)dt = \frac{dt}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right), \quad (8)$$

where $\tau_C$ is the average lifetime of the radical pair in the "cage". The recombination of the radical pair in the singlet state competes with the process involving the liberation of the radicals from the "cage". The model described has been used in the theory of chemically induced nuclear polarisation [29] and in the theory of the triplet–triplet annihilation of electronically excited states in crystals [26].

The exponential model can describe adequately the kinetics of the recombination of radical pairs in the "cage" in a number of situations. When the solution contains a large number of radical traps, the probability of repeated contact between two given radicals becomes negligible and the "cage" recombination will correspond to the exponential model. The latter may be useful also when the radicals are held in the "cage" as a result of the formation of complexes or Coulombic attraction (in the recombination of radical-ions).

## V. APPROXIMATE CALCULATIONS OF THE EFFECT OF THE MAGNETIC FIELD IN RADICAL REACTIONS

For approximate estimates of the nature and scale of the field dependence of the probability of the recombination of radicals in the "cage" within the framework of the diffusion model, it is sufficient to restrict the treatment to a single repeated collision. It is then possible to calculate the probability of the $S-T$ transition averaged over the radical pair *ensemble*, using, for example, the distribution defined by Eqn.(7) with respect to the repeated collision times. Within the framework of the exponential model, one must find for such an estimate the probability of the $S-T$ transitions during the residence time of the radicals in the "cage", without taking into account recombination, averaged with the aid of the distribution defined by Eqn.(8). Presumably the efficiency of the recombination of the radical pair is proportional to the average population of the singlet state of the radical pair. The results of exact calculations confirm that this hypothesis is reasonable.

We shall now consider the results of estimates for an initial singlet pair. The following equations have been obtained for the probability of $S-T_0$ transitions induced by the $\Delta g$ mechanism: (a) within the framework of the exponential model [34]

$$\bar{p}_{ST_0}=\frac{1}{2}\frac{\omega^2_{ST_0}\tau_c^2}{1+\omega^2_{ST_0}\tau_c^2} \tag{9}$$

and (b) within the framework of the diffusion model[80]:

$$\bar{p}_{ST_0}=0.30\sqrt{\omega_{ST_0}\tau}. \tag{10}$$

We may note that the last result was obtained subject to the additional assumption that the quantity under the square root sign is small, which is true in most cases.

The typical differences between the $g$-factors of free radicals are $\Delta g \simeq 10^{-4}$–$10^{-3}$. Assuming that the lifetime of the radical pair in the "cage" is in the range $\tau_c \simeq 10^{-10}$–$10^{-9}$ s and that $\tau \simeq 10^{-11}$ s, we find that the $\Delta g$ mechanism should have a relatively weak influence on the probability of radical recombination in laboratory fields $H_0 \simeq 10^{-4}$ G. However, with increase of the viscosity by 1–2 orders of magnitude or for systems with a larger difference between the $g$-factors, the effects of the magnetic field may be considerable.

Table 2. The average probabilities of the $S-T$ transition in the radical pair for the diffusion model taking into account only one collision ($A\tau < 1$).

| No. of pair | $\overline{p^0_{ST}}$ | $\overline{p^\infty_{ST}}$ | No. of pair | $\overline{p^0_{ST}}$ | $\overline{p^\infty_{ST}}$ |
|---|---|---|---|---|---|
| I | $0.30\sqrt{A\tau}$ | $0.15\sqrt{A\tau}$ | IV | $0.34\sqrt{A\tau}$ | $0.20\sqrt{A\tau}$ |
| II | $0.24\sqrt{A\tau}$ | $0.15\sqrt{A\tau}$ | V | $0.22\sqrt{A\tau}$ | $0.21\sqrt{A\tau}$ |
| III | $0.30\sqrt{A\tau}$ | $0.15\sqrt{A\tau}$ | VI | $0.31\sqrt{A\tau}$ | $0.24\sqrt{A\tau}$ |

Note. The relation $\overline{p^0_{ST}} > \overline{p^\infty_{ST}}$ holds for all the radical pairs.

The results of calculations of the average probability of the $S-T$ transitions are summarised in Tables 2 and 3 for the HFI mechanism in the same systems for which Table 1 lists the solutions of the dynamic problems of the singlet–triplet evolution of the radical pair. The estimates which are based on the formulae quoted in Tables 2 and 3 for typical HFI parameters $A \simeq 10^8$–$10^9$ $s^{-1}$ and the parameters of the diffusion of radicals in solution $\tau_c \simeq 10^{-9}$ s and $\tau \simeq 10^{-11}$ s show that the probability of the $S-T$ transition changes by approximately 0.1 with increase of the magnetic field strength from zero to $H_0 \gg A$. There is a corresponding change in the probability of the recombination of radicals in the "cage". It follows from the data in Table 2 that the field effect depends on the specific structure of the radicals. The effect is small for radical pairs in which an anomalous time variation of the $S-T$ transitions is observed (for example, the radical pairs V and VI in Table 1). In this case, the contribution of the short- and long-lived radical pairs frequently cancel out on being averaged and the effect diminishes (Table 3).

For nuclei with a spin $I > \frac{1}{2}$, the probability of $S-T$ transitions has been calculated only in the case of radical pairs with a single magnetic nucleus [43,45]. Within the framework of the exponential model, the following results have been obtained for the initial singlet radical pair:

$$\bar{p}^0_{ST}=\frac{1}{2}\frac{I(I+1)A^2\tau_c^2}{1+\left(I+\frac{1}{2}\right)^2A^2\tau_c^2}, \tag{11}$$

$$\bar{p}^\infty_{ST_0}=\frac{1}{2(2I+1)}\sum_{m=-I}^{I}\frac{A^2m^2\tau_c^2}{1+A^2m^2\tau_c^2}.$$

Eqns. (11) make it possible to treat the changes in the radical recombination probability following isotopic substitution.

Table 3. The average probabilities of the $S-T$ transition in the radical pair for the exponential model.

| No. of pair | $\overline{p^0_{ST}}$ | $\overline{p^\infty_{ST}}$ |
|---|---|---|
| I | $\frac{3}{8}\left\{\frac{A^2\tau_c^2}{1+4A^2\tau_c^2}+\frac{A^2\tau_c^2}{1+A^2\tau_c^2}\right\}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ |
| II | $\frac{3}{4}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ |
| III | $\frac{1}{4}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}+\frac{1}{2}\frac{A^2\tau_c^2}{1+3A^2\tau_c^2}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ |
| IV | $\frac{5}{6}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}+\frac{2}{3}\frac{A^2\tau_c^2}{1+9A^2\tau_c^2}$ | $\frac{1}{4}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}+\frac{1}{4}\frac{A^2\tau_c^2}{1+4A^2\tau_c^2}$ |
| V* | $\frac{3}{8}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ | $\frac{1}{8}\frac{A^2\tau_c^2}{1+{}^1/_4A^2\tau_c^2}$ |
| VI* | $\frac{15}{16}\frac{A^2\tau_c^2}{1+4A^2\tau_c^2}+\frac{3}{16}\frac{A^2\tau_c^2}{1+A^2\tau_c^2}$ | $\frac{9}{32}\frac{A^2\tau_c^2}{1+{}^9/_4A^2\tau_c^2}+\frac{3}{32}\frac{A^2\tau_c^2}{1+A^2\tau_c^2/4}$ |

Note. The relation between $\overline{p^0_{ST}}$ and $\overline{p^\infty_{ST}}$ for radical pairs Nos. V and VI depends on $A\tau_c$: $\overline{p^0_{ST}} > \overline{p^\infty_{ST}}$ when $A\tau_c \leqslant 1$ and $\overline{p^0_{ST}} < \overline{p^\infty_{ST}}$ when $A\tau_c > 1$; for the remaining pairs, $\overline{p^0_{ST}} > \overline{p^\infty_{ST}}$.

## VI. GENERALISATION OF THE THEORY OF THE DIFFUSION RECOMBINATION OF RADICAL PAIRS AND RADICALS IN HOMOGENEOUS SOLUTIONS

A more detailed description of the influence of the magnetic field on radical reactions and also a description of the effect of the polarisation of nuclear and electron spins during chemical reactions required a revision of the traditional theory of the recombination of radicals in solution taking into account singlet–triplet transitions. Such generalisation of the theory for the recombination of correlated radical pairs has been achieved [37,45,47,51,52]. The theory of the recombination of radicals in random encounters in space, which takes into account logically the spin selection rules in the reaction and the role of interactions removing the spin prohibition, has been formulated [38,45]. In the generalised theory, it is necessary to

take into account simultaneously the changes in the spin and spatial coordinates of the radicals. This can be done using the formalism of the density matrix[53]. It has been shown [37,45,47] that the density matrix $\rho(\boldsymbol{r},t)$ of the *sub-ensemble* of radical pairs where the radius-vector between the radicals assumes a value $r$ at time $t$ satisfies the equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=\hat{Q}_0\rho(\mathbf{r},t)-\frac{i}{\hbar}[\hat{V}(\mathbf{r}),\rho(\mathbf{r},t)]+D\Delta\rho(\mathbf{r},t), \tag{12}$$

where the first term on the right-hand side specifies the change in the pair spin density matrix without taking into account the interaction between the radicals, $\hat{V}$ represents the Hamiltonian for the interactoin between the unpaired electrons of the radical pair, and the last term describes the kinematic change in the pair density matrix owing to the mutual diffusion of the radicals.

In some studies[51,52], an additional term which takes into account the destruction of the radical pair as the result of recombination, was introduced into the right-hand side of Eqn.(12). Other workers [37,45,47] take into account the recombination reaction by introducing the appropriate conditions at the boundary of the reaction zone. The probability of the recombination of the radical pair is

$$p_{\text{rec}}=4\pi r_0^2 D\cdot Tr\int_0^\infty \mathrm{d}t\nabla\rho(\mathbf{r},t)|_{r=r_0}, \tag{13}$$

where $Tr$ indicates convolution with respect to the spin variables of the radical pair.

Specific calculations for radical pairs have been achieved hitherto only in terms of the $S-T_0$ approximation. If the initial distance between the radicals is $R_0$ for all radical pairs, then the field dependence of the recombination probability for the $\Delta g$ mechanism of the $S-T_0$ transition is described by the following relations[37]: (a) for a singlet precursor of the radical pair

$${}^{S}p_{\text{rec}}=\frac{r_0}{R_0}\frac{1}{1+q}\left[1+x+\cos\left(\frac{R_0-r_0}{r_0}x\right)\exp\left(-\frac{R_0-r_0}{r_0}x\right)\right]\Big/\left(2+\frac{1+2q}{1+q}x\right) \tag{14}$$

and (b) for a triplet precursor of the radical pair:

$${}^{T}p_{\text{rec}}=\frac{1}{3}\frac{r_0}{R_0}\frac{1}{1+q}\left[1+x-\cos\left(\frac{R_0-r_0}{r_0}x\right)\exp\left(-\frac{R_0-r_0}{r_0}x\right)\right]\Big/\left(2+\frac{1+2q}{1+q}x\right). \tag{15}$$

The following notation has been introduced in the above expressions:

$$q=D/kar_0,\quad x=(\omega_{ST_0}\tau_D)^{1/2},\quad \tau_D=r_0^2/2D. \tag{16}$$

The parameter $q$ defines the nature of the recombination: the rate of recombination is limited by the mutual diffusion of radicals for $q<1$ and by the reaction of radicals in the reaction zone (primary "cage") for $q>1$; $k$ is the rate constant for the recombination in a singlet pair ($s^{-1}$).

If the $S-T_0$ transitions are fairly rapid and there is sufficient time for their repeated occurrence during the lifetime of the radical pair in the "cage", then it follows from Eqns.(14) and (15) that the rate of recombination of the radical pair in the reaction zone is described by an average effective rate constant equal to $k/2$. The dependence of the recombination probability on field strength in moderate fields is described by equations which are qualitatively the same, as regards the nature of the dependence on $H_0$, as the approximate formulae obtained above taking into account only a single repeated encounter of the radicals. As an illustration, Fig. 3 presents the variation of the recombination probability of radical pairs with the magnetic field calculated from the formulae obtained by Salikhov et al.[37] The curves in Fig. 3 correspond to radical pairs which are initially located at the boundary of the reaction zone and correspond to different values of the parameter $\lambda$:

$$\lambda=\frac{k}{k+D/ar_0}. \tag{17}$$

Fig. 3 shows that the probability of the recombination of the initial singlet radical pair should fall with increase of the magnetic field and that of the triplet pair should increase.

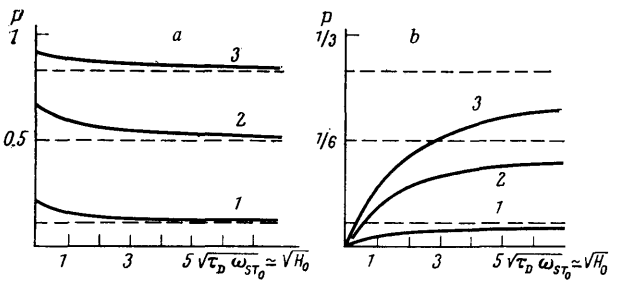



Figure 3. Variation with the magnetic field of the probability of the recombination of singlet (*a*) and triplet (*b*) radical pairs for the $\Delta g$ mechanisms of the $S-T$ transition corresponding to different values of $\lambda$: 1) 0.2; 2) 0.66; 3) 0.91.

The conditions for the observation of the field effect in the case of a triplet radical pair are particularly favourable, since in zero fields, where the $\Delta g$ mechanism is ineffective, the recombination product should be altogether absent.

In contrast to the recombination of correlated radical pairs, in the recombination of radicals in space one must consider the reaction of an *ensemble* of radicals randomly distributed in the system. The kinetic equations for the change in the spin density matrix for radicals A and B owing to their recombination reaction have been obtained[38,45] and are of the following form:

$$\left(\frac{\partial\rho^{\text{A}}}{\partial t}\right)_{\text{rec}}=-c_{\text{B}}(0)D\cdot Tr_{\text{B}}\int_{s(R)}\mathrm{d}s\Delta\rho^{\text{AB}}(r,t),$$
$$\left(\frac{\partial\rho^{\text{B}}}{\partial t}\right)_{\text{rec}}=-c_{\text{A}}(0)D\cdot Tr_{\text{A}}\int_{s(R)}\mathrm{d}s\Delta\rho^{\text{AB}}(r,t), \tag{18}$$

where $c_{\text{A}}(0)$ and $c_{\text{B}}(0)$ are the initial radical concentrations in solution. The right-hand sides of these equations describe the kinematic flux of the pair density matrix $\rho^{\text{AB}}$ from the "cage". Hence the solution of Eqns.(12) must be substituted as $\rho^{\text{AB}}$. However, in contrast to the recombination of radical pairs, for the reaction in a homogeneous solution with fairly long distances between the radicals, the following boundary condition must be adopted in conformity with the hypothesis that the correlation is weakened[54].

$$\rho^{\text{AB}}(r,t)\xrightarrow[r\to\infty]{}\rho^{\text{A}}(t)\times\rho^{\text{B}}(t). \tag{19}$$

Kinetic equations for the concentrations of radicals can be obtained from Eqn. (18) and (19) using the relations

$$c_{\text{A}}(t)=c_{\text{A}}(0)\cdot Tr\rho^{\text{A}}(t),\quad c_{\text{B}}(t)=c_{\text{B}}(0)\cdot Tr\rho^{\text{B}}(t). \tag{20}$$

The dependence of the recombination rate constant on the magnetic field has been analysed [38] with the aid of these equations in two cases: when the radicals have different $g$-factors and when one of the partners has a single magnetic nucleus with a spin of 1/2. For the $\Delta g$ mechanism, the recombination rate constant is

$$k_0 = 4\pi r_0 DF, \quad F = \frac{1}{2}\,\frac{1+x}{2(1+q)+(1+2q)x}. \tag{21}$$

Hence it follows that $k_0$ increases with the strength of the external magnetic field. This implies that the triplet radical pairs make the dominant contribution to the effect in random encounters. The influence of the magnetic field is particularly marked in diffusion-controlled reactions where $q < 1$. Fig. 4*a* presents the results of the calculation of the field dependence of the recombination efficiency in the encounter of two radicals for two values of $\lambda$.

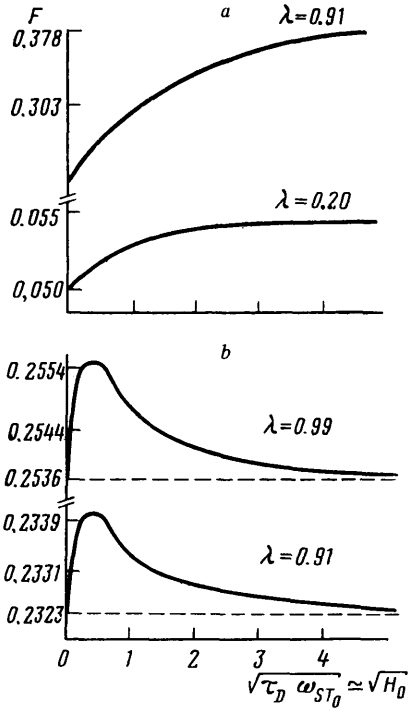



Figure 4. The efficiency of the recombination of radicals involved in random encounters in solution for the $\Delta g$ (*a*) and HFI ($A\tau = 0.01$) (*b*) mechanisms of the transitions in the radical pair in the "cage".

An interesting feature of the diffusion recombination of radicals in homogeneous solutions is that it reaches a steady state only for times of the order of the lifetime of the radical pair in the "cage" [55]. It has been shown [38] that singlet–triplet transitions increase the time taken by the reaction to attain kinetic conditions. For the $\Delta g$ mechanism, the rate of recombination tends to a steady-state value defined by Eqn. (21) in accordance with the law

$$k_0(t) = k_0\left(1 + \frac{r_0}{(\pi Dt)^{1/2}}\,2F\right). \tag{22}$$

Hence it follows that magnetic effects may be manifested also in the region where the recombination kinetics attain a steady state.

In $S$–$T$ transitions with a main HFI mechanism, exact relations for the field dependence of the rate constant have been so far obtained only when one of the radicals of the pair has a single magnetic nucleus with a spin of 1/2. [38] The results are illustrated in Fig. 4*b*, which demonstrates one of the unexpected but possible characteristics of the HFI mechanism: in fields $H_0$ comparable to the local field due to HFI there is a possibility of a maximum in the reaction efficiency. We may note that the changes in $F$ in regions of the maximum greatly exceed the difference between the values of $F$ in zero and strong magnetic fields. Presumably the appearance of the maximum is not obligatory for all radicals and should depend on their specific structure.

## VII. EQUATIONS DESCRIBING THE RECOMBINATION OF RADICALS WITHIN THE FRAMEWORK OF THE EXPONENTIAL MODEL

Bearing in mind that the exponential model of the recombination of radicals in solutions is widely used in the consideration of spin effects, we shall quote the corresponding kinetic equations. In the recombination of radical pairs, the pair density matrix satisfies the equation

$$\frac{\partial \rho^{AB}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{AB}, \rho^{AB}] - \frac{k}{2}(\hat{P}\rho^{AB} + \rho^{AB}\hat{P}) - \frac{1}{\tau_c}\rho^{AB}. \tag{23}$$

where the last term describes the liberation of the radicals from the "cage" and the penultimate term describes the destruction of the radical pair as a result of recombination; $\hat{P}$ is the projection operator onto the singlet state of the radical pair.

The kinetic equations describing the recombination of radicals in homogeneous solutions assume the following form [25,40,45]:

$$\left(\frac{\partial \rho^A}{\partial t}\right)_{rec} = -4\pi r_0 D \cdot c_B(0) \cdot T r_B(\rho^A \times \rho^B - \rho^{AB}),$$
$$\left(\frac{\partial \rho^B}{\partial t}\right)_{rec} = -4\pi r_0 D \cdot c_A(0)\, T r_A(\rho^A \times \rho^B - \rho^{AB}), \tag{24}$$

in which the pair matrix is found from the solution of the equation

$$\frac{\partial \rho^{AB}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{AB}, \rho^{AB}] - \frac{k}{2}(\hat{P}\rho^{AB} + \rho^{AB}\hat{P}) - \frac{1}{\tau_c}(\rho^{AB} - \rho^A \times \rho^B), \tag{25}$$

where, in contrast to Eqn. (23), account was taken also of the formation of the radical pair as a result of the random entry of two radicals into the "cage".

We may note that Eqns. (24) and (25) agree with the initial equations of the theory of the triplet–triplet annihilation of excitons in crystals [25] and of the quenching of excited triplet molecules in solutions [33]. We shall therefore return to these equations in the discussion of the quenching of the luminescence in solutions in the text below.

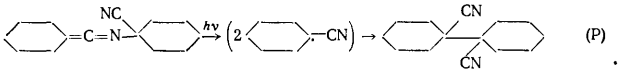
The solution of these equations show [40] that the exponential model yields qualitatively the same field dependence of the reaction efficiency as the diffusion model. Furthermore, exact calculations within the framework of the exponential model confirm the validity of the conclusions reached on the basis of approximate calculations.

## VIII. SPIN EFFECTS IN RADICAL REACTIONS

The models enumerated above for the description of the influence of the magnetic field on radical reactions are based on the hypothesis that spin effects play an important role in such reactions. We shall consider the experimental evidence for the manifestation of spin prohibitions in the recombination reactions of free radicals.

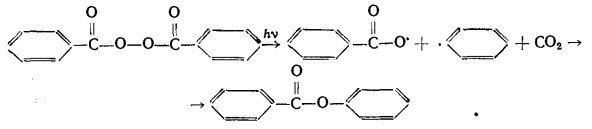
We shall consider in the first place the recombination of correlated radical pairs in the "cage", where the recombination efficiency may be expected to depend on the spin multiplicity of the radical pair (in the absence of mechanisms of rapid transitions between different spin states).

The influence of the spin multiplicity of radical pairs has been taken into account in a number of studies where direct and sensitised photolytic reactions were compared. Thus Fox and Hammond[56] observed an appreciable difference between the yields of the products of the recombination of two cyanocyclohexyl radicals in the photolysis of *N*-(1-cyanocyclohexyl)pentamethylene ketenimine:



(P)

In direct photolysis (via an excited singlet state) in carbon tetrachloride, approximately 24% of succinonitrile (P) is formed. The triplet-sensitised decomposition under the same conditions gives only 8% of compound (P). Thus the probability of the recombination of singlet radical pairs is in this case three times greater than that of the triplet pairs. Similar effects have been observed in the direct and sensitised photolysis of benzoyl peroxide[57]:




The yield of phenyl benzoate was approximately 3% for the triplet radical pairs and approximately 8% for the singlet pairs.

The effects of the spin multiplicity of the sensitiser on the formation of phenyl benzoate have been investigated recently for the same system[58]. Benzoyl peroxide solutions in toluene or benzene were irradiated by light from a high-pressure mercury lamp in the presence of aromatic hydrocarbons (naphthalene, fluorene, phenanthrene, etc.), which are singlet sensitisers, and also of aromatic ketones—acetophenone, benzophenone, and 2-methylbenzophenone. The latter are typical triplet sensitisers. It has been shown that the yield of phenyl benzoate is $\leqslant 3.0\%$ in the presence of triplet sensitisers and $\geqslant 10\%$ in the presence of singlet sensitisers.

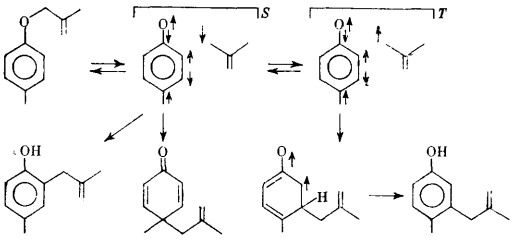
Another class of reactions in which spin prohibition may be manifested includes the recombination of radicals in space. When two radicals react in each collision, the rate of their recombination will be determined solely by the rate of diffusion. The rate constant for such a diffusion-controlled reaction is defined by the expression

$$k_D = \left(\frac{4\pi N}{1000}\right)(\sigma_A + \sigma_B)(D_A + D_B), \qquad (26)$$

where $N$ is the Avogadro number, $D_A$ and $D_B$ are the diffusion coefficients of the radicals A and B in the reaction medium, and $\sigma_A$ and $\sigma_B$ are their reaction radii.

However, one should bear in mind that two radicals recombine in the collision only when the radical pair formed as a result of their encounter is in the singlet state. Since the probability of singlet encounters is 1/4, presumably the measured values of $k_D$ should be smaller by a factor of 4 than those predicted by Eqn.(26). Analysis of the experimental results for the kinetics of the recombination of organic radicals does indeed show this relation. The values of $k_D$ calculated by Eqn.(26) for the most typical experimental conditions are approximately $8 \times 10^9$ litre mole$^{-1}$ s$^{-1}$.[59] On the other hand, the measured constants for bimolecular radical reactions do not as a rule exceed $2 \times 10^9$ litre mole$^{-1}$ s$^{-1}$.[59]

The above behaviour does not apparently obtain in reactions involving hydrogen atoms, H, OH and $HO_2$ radicals, and solvated electrons [60]. They are of interest for the process under consideration, because they are not sterically hindered and have zero activation energy. However, it has been found that the experimental values of $k_D$ for these reactions are close to those calculated by Eqn.(26). The causes of the apparent absence of spin prohibition in reactions of this class have been examined[60]. The very interesting possibility of the influence of the electron spin on the orientation effect in radical reactions is discussed in another investigation[61]. In the Claisen photochemical rearrangement (the photolysis of allyl *p*-methylphenyl ether), the authors observed the formation of the product of the substitution of the allyl group not only in the *ortho*- and *para*-positions but also in the *meta*-position in the aromatic ring. In the analogous thermal rearrangement, *meta*-products are not formed. The possibility of the formation of *meta*-products in the photochemical rearrangement can be understood by examining the following mechanism proposed on the basis of the analysis of the effects of chemically induced nuclear polarisation in this reaction:




The radical pairs formed in the singlet state yield mainly *ortho*- and *para*-substitution products. For triplet pairs, *ortho*- and *para*-substitution is spin-prohibited. However, the spin density is negative in the *meta*-position, so that addition of the allyl radical in this position can occur in the triplet radical. According to the authors, this in fact explains the formation of the *meta*-product.

The above examples show that the electron spin effects have in many instances a very marked influence on the kinetics of the recombination of free radicals. Consequently, when the rates of radical reactions are considered, account must be taken of electron spin prohibitions.

We shall now consider the effects of nuclear spin in radical recombination reactions. It follows from the above theoretical analysis that the hyperfine interaction of nuclei with electrons in the radical pair can lead to a singlet–triplet transition, i.e. to a change of the multiplicity of the radical pair. Since the HFI energies are different for different nuclear isotopes, one may expect differences between the recombination efficiencies of the radical pairs containing these isotopes. We shall call this phenomenon the magnetic isotope effect, in contrast to the usual kinetic isotope effect [34,37].

Experimental studies on isotope effects in radical reactions have been comparatively few and are practically all concerned with the rate of decomposition of organic peroxides and azo-compounds (see, for example, Seltzer and Hamilton [62] and Rummel et al. [63]). In many cases, anomalously large secondary isotope effects were observed in the thermal analysis of hydrogen- and deuterium-containing compounds ($k_H/k_D \simeq 1.3-1.4$) [63] which it would be tempting to interpret in terms of the difference between the magnetic properties of hydrogen and deuterium. The HFI constants for H and D are indeed known to differ by a factor of approximately 7. Consequently there is a greater probability of a change in the spin state (from $S$ to $T$) in hydrogen-containing radical pairs and thus one may expect that the efficiency of the reverse recombination of the primary pair, with reformation of the initial compound, will be smaller than for the deuterium analogue.

Unfortunately, in all these cases one cannot rule out the possibility that the isotope effect arises in the primary decomposition of the molecule and not in the reactions of the radical pair. There is then a possibility of an alternative explanation of the nature of the observed isotope effects, associated with the differences between the zero-point vibrational energies [64]. We shall only mention that a quantitative interpretation of the secondary isotope effects within the framework of these ideas involves considerable difficulties. We are familiar with only one study where a direct isotope effect on the rate of recombination of the radical pair was observed [65]. We shall consider it in greater detail. A study was made of the thermal decomposition of azobisisobutyronitrile (AIBN) and [12-D]AIBN in chlorobenzene at 65 °C. The decomposition mechanism can be represented in the following form:

$$R{-}N_2{-}R \xrightarrow{k_I} (2R^{\cdot}) + N_2 \quad ,$$

$$(2R^{\cdot}) \xrightarrow{k_{II}} \text{recombination},$$

$$(2R^{\cdot}) \xrightarrow{k_{III}} 2R^{\cdot}\ \text{(diffusion)},$$

$$\dot{R}{=}N{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^{\cdot}}}}} \quad ,$$

where round brackets represent the cage. The cage effect in this system has been studied in a large number of investigations and is well known. The authors were able to measure the quantity $a = k_{III}/(k_{II} + k_{III})$ which is inversely proportional to the efficiency of the recombination within the cage. It was found that $a_H = 0.56 \pm 0.015$ and $a_D = 0.51 \pm 0.015$. Since the radical recombination reaction ($k_{II}$) has virtually zero activation energy, the usual kinetic isotope effect is impossible. The observed difference between $a_H$ and $a_D$ has been attributed [65] to the influence of the mass of the radicals on their diffusion from the "cage". According to the authors, the probability of the diffusion of heavy radicals (with D) is lower, so that $a_D < a_H$. However, this explanation conflicts with the accepted theory of radical recombination in the "cage" [66]. According to Koenig and Fischer [66], the opposite effect should be observed—heavier radicals should give rise to a smaller yield of the recombination product (i.e. $a_D > a_H$).

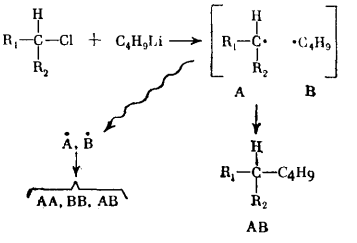
The observed effect can be simply explained on the basis of the different magnetic properties of the isotopes. In this case, it is possible to estimate quantitatively the expected magnitude of the isotope effect.

According to Eqn. (4), the effective HFI constants for radical pairs are $4 \times 10^8$ and $10^9$ rad $s^{-1}$ for [12-D]AIBN and [12-H]AIBN respectively. On substituting these values in the theoretical expression for the radical pair recombination probability (see Table 2, RP I), we find that the calculated isotope effect on the radical recombination efficiency (approximately 10%) agrees well with the observed value.

The above discussion shows that the possibility of the manifestation of "magnetic" effects must be borne in mind in the analysis of the nature of the experimental kinetic isotope effects in radical recombination reactions.

## IX. EXPERIMENTAL DATA FOR THE INFLUENCE OF THE MAGNETIC FIELD ON RADICAL REACTIONS

A number of studies, where the influence of the magnetic field on the rate of radical reactions was considered, have now been made. Some [41,42,47,48,67-69] were devoted to the reactions of alkyl-lithium with arylchloromethanes in solutions. The observation and analysis of the effects of the chemically induced polarisation of $^1H$, $^{19}F$, and $^{13}C$ nuclei showed that these reactions proceed via the following radical mechanism:




Thus the initial pair of two alkyl radicals in the singlet state is the direct precursor of the final product.

It has been observed [42] that, following an increase of the magnetic field from the terrestrial field (approximately 0.5 G) to $H = 20\,000$ G, the ratio of the main products AB and AA changes appreciably in the reaction of pentafluorobenzyl chloride ($R_1 = C_6F_5$ and $R_2 = H$) with butyl-lithium in boiling hexane. In a high magnetic field, [AB]/[AA] increases by 30%. It is readily seen that the observed effect is in good qualitative agreement with the HFI mechanism of the influence of the magnetic field discussed above. Indeed, in a strong field the probability of the $S-T$ transition in the pair of pentafluorobenzyl and butyl radicals diminishes, which entails an increase in the probability of the radical recombination within the cage. The latter leads in its turn to an increase of [AB]/[AA] with increasing magnetic field strength.

The study of the overall variation of [AB]/[AA] with field strength for this reaction [48] confirmed that the observed effect is due to the HFI mechanism. Fig. 5 illustrates the experimental variation of the ratio of the products AB and AA with the magnetic field strength for the reaction of pentafluorobenzyl chloride with butyl-lithium. The curve is S-shaped with a transitional region corresponding to $H \simeq 50-200$ G. Approximate calculations for the HFI model predict precisely this type of dependence of the population of the singlet state $p_S$ and the corresponding probability of the recombination of the singlet radical pairs on the magnetic field [48]. Fig. 6 illustrates the variation of $p_S$ with the magnetic field strength for several values of the HFI constant for a model radical pair with a single proton, calculated within the framework of the exponential model. Fig. 6 (curve *1*) shows that $p_S$ for radical pairs with $At < 1$ increases with increasing magnetic field and that the transitional region corresponds to

$H \simeq A/\gamma$. In the system investigated, the radical pair contains several magnetic nuclei and an appreciable change in $p_S$ should be observed in fields $H \simeq A_{eff}/\gamma = \frac{1}{\gamma}(\sum_i A_i^2)^{1/2} \simeq$ 60 G. Thus theoretical estimates within the framework of the HFI model agree satisfactorily with experiment.

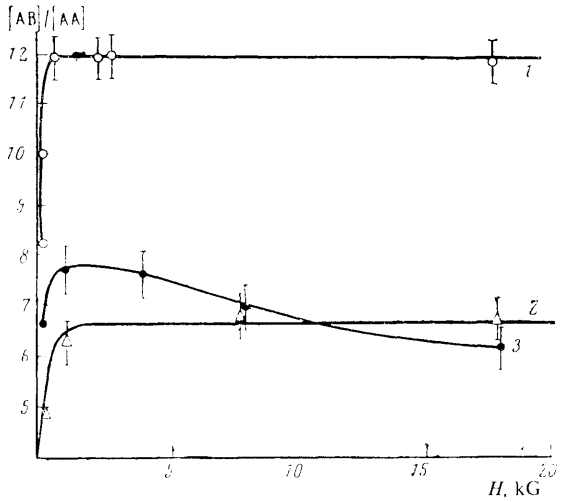



Figure 5. Experimental variation of the ratio of the reaction products AB and AA with the magnetic field strength in the reaction of $C_4H_9Li$ with pentafluorobenzyl chloride (curve *1*), *p*-fluorobenzyl chloride (curve *2*), and chlorodi-(pentafluorophenyl)methane (curve *3*).

It has been shown [69] that the influence of the magnetic field can also be observed in reactions of butyl-lithium with a series of other arylchloromethanes $\begin{matrix} R_1 \\ \\ R_2 \end{matrix}\!\!\diagdown\!\!\diagup\!\!\text{CHCl}$, where $R_1 = C_6H_5$ and $R_2 = H$ (1), $R_1 = C_6H_4F$ and $R_2 = H$ (2), and $R_1 = R_2 = C_6F_5$ (3). The field dependence of [AB]/[AA] for compound (2) is of the same form as for the reaction of pentafluorobenzyl chloride with butyl-lithium (Fig. 5). Consequently, the magnetic field effects in this system are described by the HFI mechanism. On the other hand, in the reaction of chlorodi(pentafluorophenyl)methane in strong fields, an appreciable decrease of [AB]/[AA] is observed instead of a plateau (Fig. 5). The increase of [AB]/[AA] in fields ranging from 0.5 to 1000 G for chlorodi(pentafluorophenyl)methane is described satisfactorily by the HFI mechanism. The decrease of this ratio on further increase of $H$ has been explained [68,69] by the difference between the Zeeman energies of the electrons in the radical pair ($g_1\beta H - g_2\beta H$), which provides an additional mechanism of the singlet–triplet transition (the $\Delta g$ mechanism) and leads to a decrease in the probability of the radical recombination within the cage. A study of the effects of the chemically induced polarisation of the $^1H$ and $^{19}F$ nuclei did indeed demonstrate an appreciable difference between the *g*-factors of the di(pentafluorophenyl)methyl and butyl radicals [70]. The field dependence of the population of the singlet states of the radical pair has been calculated [68] within the framework of the exponential model with a simultaneous examination of the HFI and $\Delta g$ mechanisms of the $S$–$T$ transition in a radical pair with the same magnetic nucleus With a suitable choice of parameters, the calculated curve agrees satisfactorily with experimental curve (cf. Figs. 5 and 6).

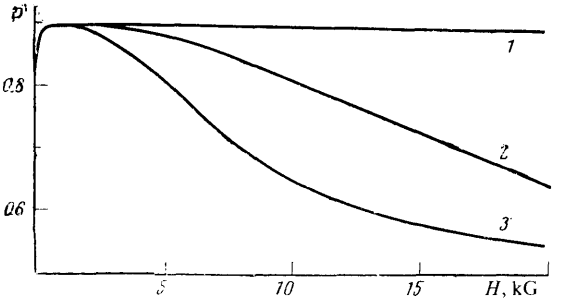



Figure 6. Calculated variation of the population of the singlet state of the radical pair having a single magnetic nucleus with the external magnetic field: *S* precursor; $\tau_c = 10^{-9}$ s; $A = 10^9$ rad $s^{-1}$; $\Delta g$: 1) 0; 2) 0.005; 3) 0.01.

The parameters specified in theoretical models to which the observed influence of the magnetic field corresponds have been discussed [48]. Using the experimental values $\{[AB]/[AA]\}_\infty = 12.2$ and $\{[AB]/[AA]\}_0 = 8.5$ for the reaction of pentafluorobenzyl chloride with $C_4H_9Li$ within the framework of the diffusion model of the radical pair for $A_{eff} = 10^9$ rad $s^{-1}$, $\tau = 6 \times 10^{-10}$ s was obtained as the time of the diffusion jump. This value exceeds appreciably the typical diffusion jump times ($10^{-11}$ s) for solvents with the usual viscosities. In order to account for this discrepancy, the authors [48] used the hypothesis [71] according to which the radicals in the system investigated are not involved in the reactions in a free state but in the form of a complex with an associated species of the organolithium compound. It is reasonable to expect that the characteristic diffusion time of such a conglomerate will be much longer than for a typical radical pair (approximately $10^{-11}$ s).

Thus one may conclude that, in order to obtain appreciable effects of the magnetic field on radical reactions (tens per cent), it is necessary to investigate reactions where the intermediate free radicals exhibit an anomalously low mobility ($10^{-9}$–$10^{-10}$ s). One of the ways of reducing diffusional mobility is to carry out the reactions in viscous solvents. It has been shown [42] for the above reaction of pentafluorobenzyl chloride with $C_4H_9Li$ that an increase of the viscosity of the solvent on passing from hexane to cyclohexane does indeed increase the magnetic effect. In the usual instances of radical reactions in solvents with normal viscosities ($\tau \simeq 10^{-11}$ s), insignificant magnetic effects are to be expected ($\lesssim 10\%$), these may not be susceptible to detection by the existing analytical methods. Analysis of the literature shows that all the published examples where the absence of an effect of the magnetic field on radical reactions in solvents has been demonstrated [18,19,72] can be included in precisely this class.

An interesting observation of the effects of the magnetic field has been made in a study [73] of the recombination of a pair of negative and positive radical ions. The idea of

the experiment was as follows. The solvent (squalane) molecule was ionised by pulse irradiation with fast electrons. Fluorene molecules, present in solution at a low concentration, capture both the electron and the parent positive ion. This results in the formation of a singlet pair of radical-ions linked by Coulombic forces and inevitably recombining. Before recombination, the radical pair may undergo the $S-T$ transition. The formation and recombination of the radical-ions can be represented schematically as follows:

$$S \rightsquigarrow S^+ + e^- , \quad (27)$$

$$S^+ + M \longrightarrow S + M^+ , \quad (28)$$

$$e^- + M \longrightarrow M^- , \quad (29)$$

$$M^+ + M^- \longrightarrow M^* + M . \quad (30)$$

Here S is the solvent (squalane), M the fluorene molecule, and M* the excited singlet and triplet states of fluorene. Presumably, as in the recombination of neutral free radicals, the magnetic field can influence the rate of the $S-T$ transition and hence the ratio of the excited singlet and triplet molecules.

An important experimental advantage in the study of this process has been the fact that the product of the recombination of the radical-ions is a molecule in an electronically excited state. The existing optical methods make it possible to determine with a high accuracy the concentrations of both singlet (from the fluorescence) and triplet (from the absorption) states. It is noteworthy that, in contrast to the radical reactions discussed above, the radical-ions formed in the pair cannot emerge from the "cage" and recombine with a probability of unity, since the initial distance between the charges (50–150 Å) is smaller than the Onsager radius for the solvent investigated (300 Å).

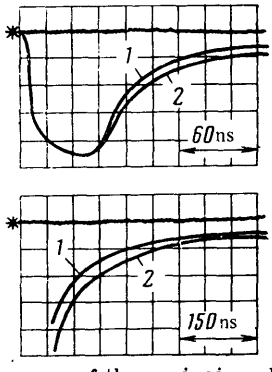



Figure 7. Oscillogram of the emission observed in the pulse radiolysis of a 0.01 M solution of fluorene in squalane in a 3 M eV electron accelerator[73]: 1) without a magnetic field; 2) in a 1000 G magnetic field.

Fig. 7 presents the oscillogram of the emission spectrum observed in the pulse radiolysis of a 0.01 M solution of fluorene in squalane using an electron accelerator with an energy of 3 M eV. Evidently, in a magnetic field ($H$ = 1000 G) the emission intensity after the pulse (approximately 50 ns) is appreciably higher. The observed effect implies that the population of the precursor singlet radical-ion pairs increases in the magnetic field, which can be explained qualitatively within the framework of the HFI model. A study[73] of the field dependence of the fluorescence intensity confirmed this conclusion. Fig. 8 shows that the overall form of the experimental curve is analogous to that calculated for the HFI mechanism (cf. Fig. 6). Since the yield of the singlet states increases in the magnetic field, one may expect a simultaneous decrease in the yield of the excited triplet states. Although in the latter case the situation is greatly complicated owing to the longer lifetime of the triplet states, the authors[73] nevertheless succeeded in observing experimentally a slight decrease of the concentration of triplets in the magnetic field (Fig. 8). It is noteworthy that, in control experiments with an anion, where the mechanisms of the magnetic effects discussed above do not operate, the magnetic field has almost no influence on the yield.

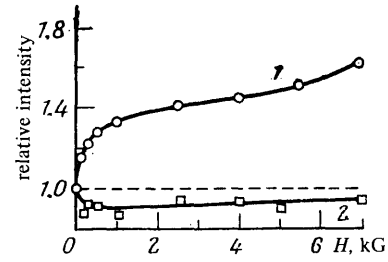



Figure 8. The influence of the constant magnetic field on the intensity of fluorescence (curve *1*) and absorption (curve *2*) in the pulse radiolysis of fluorene solutions in squalane[73]. The fluorescence and absorption were observed at 100 ns intervals after the pulse.

Analogous experiments designed to investigate the magnetic effects on the recombination of fluorene radical-ions in solutions have been carried out using a source of $\gamma$-radiation. The results of the measurements of the fluorescence intensity on radiolysis in different magnetic fields are illustrated in Fig. 9. It is noteworthy that, in contrast to the earlier investigation[73], here a study was made of the recombination of radical-ions in solvents of different viscosities. For the most viscous solvent (squalane), the effect of the magnetic field on the fluorescence yield and hence on the population of the singlet radical pairs is a maximum. In benzene, which had the lowest viscosity, the field effect could not be observed at all, while an intermediate situation was noted for cyclohexane. These results as well as those discussed above[42] confirm the theoretical conclusion that an increase of solvent viscosity can increase significantly the effect of the magnetic field in the recombination of the radical pair.

In conclusion, we shall consider the possibility of an effect by the magnetic field on radical reactions in solids. In this case, the decrease of diffusional mobility should in general favour the magnetic effects within the framework

of the mechanisms considered, with participation of radical pairs. So far there have been no reports in the literature of experimental observations of such effects.

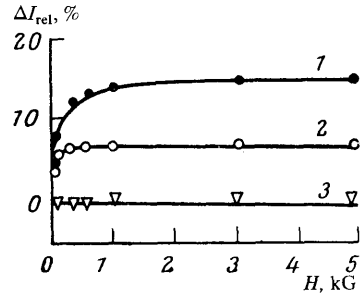



Figure 9. The influence of the magnetic field on the fluorescence intensity ($\Delta I_{rel}$ is the increase of the intensity) in the $\gamma$-radiolysis of fluorene solutions in different solvents: 1) squalane; 2) cyclohexane; 3) benzene[74].

The influence of the magnetic field on the concentration of free radicals in the low-temperature photolysis of formaldehyde has been investigated[75] by ESR. The system is of interest because the pair formed as a result of the photolysis

$$H_2CO \xrightarrow{h\nu} H\dot{C}O + \dot{H}$$

contain radicals with very high HFI constants: atomic hydrogen with $A$ = 500 g and the formyl radical with $A$ = 132 G. Only the formyl radical is detected in the ESR spectrum at 77 K, while the H atom is insufficiently stable under these conditions. The kinetics of the accumulation of HĊO radicals were studied in magnetic fields of 75 and 6200 G directly in the cavity of the ESR spectrometer (the residual magnetic field was 75 G). The experiments showed that the steady-state concentration of formyl radicals is higher in the photolysis in a high field (Fig. 10). The most important mechanisms of the destruction of HĊO radicals, leading to the establishment of a steady-state concentration, are associated with the following reactions:

$$H\dot{C}O \rightarrow \dot{H} + CO, \quad (31)$$

$$\dot{H} + H\dot{C}O \rightarrow H_2CO, \quad (32)$$

$$\dot{H} + H\dot{C}O \rightarrow H_2 + CO. \quad (33)$$

It has been suggested[75] that the magnetic field influences the recombination of a formyl radical and a hydrogen atom in a random encounter within the matrix [reactions (32) and (33)]. Indeed the sign of the effect corresponds qualitatively to the HFI mechanism of the influence of the magnetic field on $F$ pairs.

Analogous experiments, carried out with deuteroformaldehyde[75], failed to show an appreciable effect of the magnetic field on the steady-state light-induced concentration of DĊO radicals. According to the authors, this may be associated both with the lower HFI constants for the D atoms and DĊO radicals compared with Ḣ and HĊO and with the reduced mobility of atomic deuterium.

The effects of the magnetic field on the radiation-induced polymerisation of methyl methacrylate and acetaldehyde have been investigated at low temperatures[76,77] and it was found that the magnetic field influences both the rate of polymerisation and the molecular weight of the polymers formed. Since these processes can proceed via a free-radical mechanism, presumably the mechanisms of the influence of the magnetic field on the radical pair reactions examined above operate in these cases too. Both chain initiation and quadratic chain termination are magnetically sensitive stages of radical polymerisation.

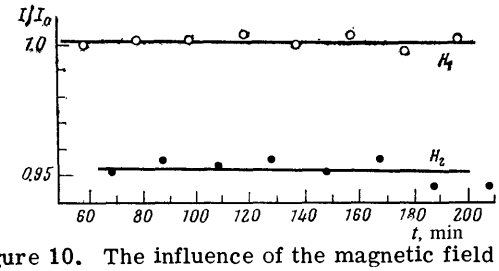



Figure 10. The influence of the magnetic field on the steady-state photochemically induced concentration of formyl radicals in the low-temperature photolysis of formaldehyde at 77 K ($H_1 > H_2$).[75]

In conclusion of this section, we may quote that the influence of the magnetic field on radical reactions is now fairly well understood. At the same time, it is clear that the regions where the expected effects should be maximum are so far not susceptible to experiment. This involves in the first place carrying out the reactions under conditions where the diffusional mobility of the radicals is lower by 1–2 orders of magnitude than the usual mobility and, in the second place, the study of the products of the triplet radical pairs within the "cage", where the effect of the relative change in the rate of reactions should be particularly pronounced.

## X. PROCESSES INVOLVING TRIPLET MOLECULES

Like free radical reactions, processes involving triplet molecules can be selective with respect to spin and can depend for this reason on the external magnetic field. As already mentioned in the introduction, such dependence was observed for the first time in solid organic crystals[23–26]. These studies stimulated analogous research on liquids. Spin-selective processes, which have been investigated experimentally in liquids and for which an effect of the magnetic field has been observed, are listed below.

1. The quenching of the excited triplet state by a free radical[78,79]. This process has a doublet final state and the quenching step can therefore occur only in collisions where the triplet molecule and the radical are in a collective doublet state.

2. Triplet–triplet annihilation[80]. In a random encounter in solution, a pair of triplet molecules can form singlet, triplet, and quintet states with respect to the total spin. Quenching takes place in the singlet state, since it leads to the formation of molecules in ground and excited singlet states.

3. The quenching of excited triplet states by oxygen [81]. Since oxygen has a triplet ground state, this process is analogous to the triplet–triplet annihilation and is also spin-selective.

4. The photochemical oxidation of aromatic hydrocarbons [82]. The primary stage in this reaction is the formation of an excited singlet oxygen molecule as a result of the collision of an excited triplet hydrocarbon molecule with oxygen in the ground state. The influence of the magnetic field on this process has so far been established only for the reaction in the solid phase.

The influence of the magnetic field on the above processes is interpreted in terms of a mechanism formally identical with that examined for the recombination reactions of free radicals. According to the dominant view, the magnetic field influences the dynamics of the spins of two paramagnetic species, i.e. the rate of change of the multiplicity of the pair of paramagnetic species which have collided in solution. The change in multiplicity can occur both on direct contact of the species and during their lifetime in the "cage", during the intervals between repeated collisions of a given pair of paramagnetic species.

As in the recombination of radicals, the change in spin multiplicity can again be induced by the $\Delta g$ and HFI mechanism. However, the transitions due to the dipole–dipole interaction of the unpaired electrons of each of the triplet molecules are more effective for the latter. In solutions, the thermal motion of triplet molecules modulates this dipole–dipole interaction in a random fashion, which leads to an effective paramagnetic relaxation of the triplet molecules. These relaxation transitions mix the states of two paramagnetic species with different multiplicities. Thus the influence of the magnetic field on elementary processes involving triplet molecules in solutions is interpreted as the result of the field dependence of the relaxation transitions caused by the fluctuating dipole–dipole interaction in the triplet molecules. We point out yet again that this interpretation is quite equivalent to the mechanism proposed by Brocklehurst [32] to account for the effect of the magnetic field in radiation-chemical reactions.

The influence of the magnetic field on processes involving triplet molecules in solutions has been examined theoretically by Atkins and Evans [33], who investigated comparatively non-viscous solutions where the molecular rotation is fairly rapid so that stochastic perturbation theory and the Redfield equation can be used to calculate the kinetic coefficients describing the relaxation transitions [33]. A theory of the processes under consideration may be developed on the basis of the fundamental equations which were quoted above in the discussion of the radical recombination reaction [Eqns. (12)–(25)]. The specific features of a real system are reflected in the formulation of the equations for the pair density matrix $\rho AB$.

Atkins and Evans calculated the probability of the triplet–triplet annihilation in arbitrary magnetic fields. The following expression has been obtained for the ratio of the intensities of the fluorescence accompanying this annihilation in strong (approximately 10 000 G) and zero magnetic fields:

$$I_H/I_0 = 1 - 0.61\Phi_{TT}(k(0)\tau_a)^{1/2}, \quad (34)$$

where $\tau_a$ is the duration of the elementary step in translational diffusion, $\Phi_{TT}$ is related to the probability $\lambda_T$, that the triplets which have collided will be annihilated subject to the condition that the pair was in the singlet state during the encounter, by the expression

$$\Phi_{TT} = \lambda_T/(1-\lambda_T); \quad (35)$$

and $k(0)$ is the spectral density of the dipole–dipole interaction at zero frequency:

$$k(0) = (D^2 + 3E^2)\tau_r. \quad (36)$$

Here $D$ and $E$ are the principal values of the dipole–dipole interaction tensor and $\tau_r$ is the characteristic rotational relaxation time.

Analogous reasoning for the quenching of triplet molecules by radicals leads to the following results [33]:

$$I_H/I_0 = 1 + 0.95\Phi_{DT}(k(0)\tau_a)^{1/2}, \quad (37)$$

where $\Phi_{DT}$ is related to the probability of the quenching of the triplet $\lambda_D$ in such a collision, where the pair was in the doublet state, by the expression

$$\Phi_{DT} = \lambda_D^2/\left(1 - \frac{4}{3}\lambda_D + \lambda_D^2\right). \quad (38)$$

Theoretical analysis shows that the probabilities of the triplet–triplet annihilation and of the quenching of the triplet biradicals in solutions should decrease with increasing magnetic field strength. The opposite variation with the field should be observed for the fluorescence intensity in such a case. The theory predicts in addition that the transitional region is located in fields corresponding to the equality of the Zeeman and rotational frequencies.

The theoretical results [33] are in good qualitative and quantitative agreement with numerous experiments [80–90]. Tables 4–6 list systems in which the magnetic field has an effect on the elementary processes involving triplet molecules.

Table 4. Experimental results for the influence of the magnetic field on the rate of triplet–triplet annihilation in solutions (for delayed fluorescence).

| Reaction | Change in luminescence intensity, % (for H = 8 kG)** | References |
|---|---|---|
| $T + T \rightarrow S + S_0$ | | |
| $(\text{Anthracene})^T + (\text{Anthracene})^T$ | | |
| in dimethylformamide | 4–5 | 80 |
| in acetonitrile | 2 | 81 |
| $(\text{Pyrene})^T + (\text{Pyrene})^T$ | | |
| in dimethylformamide | 2–3 | 81 |
| in acetonitrile | 1–2 | 81 |
| in cyclohexane | 6–7 | 84 |
| $(\text{1,2-Benzanthracene})^T + (\text{1,2-Benzanthracene})^T$ | | |
| in cyclohexane | 4 | 84 |
| $(\text{Anthracene})^T + (\text{Anthracene})^T$ in $CH_2Cl_2$ | 5 | 85 |
| $T + T \rightarrow E^* + S_0$ | | |
| $(\text{Pyrene})^T + (\text{Pyrene})^T$ | | |
| in cyclohexane | 6–7 | 84 |
| $(\text{1,2-Benzanthracene})^T + (\text{1,2-Benzanthracene})^T$ | | |
| in cyclohexane | 3 | 84 |

*E = excimer.

**In the magnetic field, the luminescence intensity diminishes, indicating a decrease in reaction rate.

The first successful observation of the influence of the magnetic field was made in 1969 by Faulkner and Bard in a study of the delayed fluorescence of anthracene in solution on photoexcitation [80]. Delayed fluorescence (DF) is known to arise as a result of the formation of an excited singlet state on annihilation of two triplet states: $T + T \rightarrow$

$S + S_0$ ($T$ and $S$ are the excited triplet and singlet states and $S_0$ is the ground state of the molecule). The DF intensity is then defined by the expression

$$I_{DF} = \frac{1}{2}\Phi_f k_a (I_a \Phi_T \tau)^2, \quad (39)$$

where $\Phi_f$ is the probability of fluorescence, $k_a$ the rate constant for the triplet–triplet annihilation, $I_a$ the rate of absorption of light, $\Phi_T$ the probability of the formation of the triplet state, and $\tau$ the lifetime of the triplet state.

It has been observed[80] that the DF intensity decreases with increase of the magnetic field strength (see Fig. 11 and Table 4). In principle, both $\Phi_T$ and $k_a$ are magnetically sensitive quantities. Experiments on sensitised photolysis permitted a more unambiguous solution of this problem. Whereas in direct photolysis the triplet states of anthracene arise as a result of an intercombination transition from excited singlet states, on sensitisation they are populated in a triplet–triplet energy transfer process. Consequently, in such cases the efficiency of the formation of triplet states $\Phi_T$ is determined by different processes. It has been shown[80] that the variation of the DF intensity with the magnetic field is the same for both direct and sensitised photolysis. This enabled the authors[80] to conclude that the observed variation of the DF intensity in the magnetic field is due to the influence of the latter on the triplet–triplet annihilation rate constant. The decrease of the rate of the triplet–triplet annihilation in the magnetic field (to 7%), manifested in the DF spectra, was subsequently observed also for a number of other systems (see Table 4). It is noteworthy that the effect of the magnetic field depends strongly on the solvent, which apparently indicates a significant role of the medium in the annihilation processes. In a study of DF in pyrene and 1,2-benzanthracene solutions[84], it was possible to observe the influence of the magnetic field not only on the fluorescence of the monomeric molecules but also on that of dimers (exciplexes).

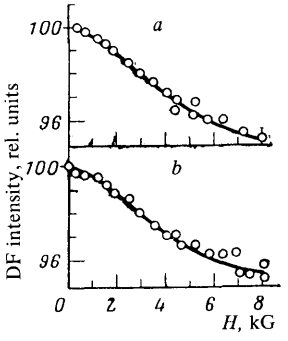



Figure 11. The effect of the magnetic field on the intensity of delayed fluorescence observed in the photolysis of anthracene in solution in chloroform (*a*) and dimethoxyethane (*b*) [80].

Numerous experimental studies have been devoted to the quenching of triplet states by free radicals (Table 5). In the presence of radicals, the DF lifetime is appreciably shortened and the effect of the magnetic field on the fluorescence intensity is of the opposite sign (the intensity increases with increase of the field strength). The usual mechanism for the process is

$$T + T \xrightarrow{k_a} S + S_0, \quad (40)$$

$$T + R \xrightarrow{k_R} S_0 + R, \quad (41)$$

$$T \xrightarrow{k_0} S, \quad (42)$$

where R is a quenching agent in a doublet state (free radical).

Table 5. Experimental results for the influence of the magnetic field on the quenching of triplet states by radical-ions.

| Reaction $R + T \rightarrow R + S_0$ | Concentration of radicals (molecules), M | Change in luminescence intensity, % (H = 8 kG)* | Method of recording | Refs. |
|---|---|---|---|---|
| Radical-cation of Würster's Blue + (Anthracene)$^T$ in $CH_2Cl_2$ | $1.8 \times 10^{-7}$ ($8.0 \times 10^{-5}$) | 2 | DF | 79 |
| | $2.1 \times 10^{-7}$ ($1.1 \times 10^{-3}$) | 6 | DF | 85 |
| | $3.6 \times 10^{-7}$ ($1.0 \times 10^{-7}$) | 9 | DF | 85 |
| *p*-Benzoquinone radical-anion + (Anthracene)$^T$ in $CH_2Cl_2$ | $1.6 \times 10^{-7}$ ($1.0 \times 10^{-3}$) | 3 | DF | 85 |
| Radical-cation of Würster's Blue + (Pyrene)$^T$ in dimethylformamide | $1.0 \times 10^{-3}$*** ($5.0 \times 10^{-3}$) | 8 | ECLF | 84 |
| | $1.0 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 20 | ECL | 84 |
| Radical-cation of Würster's Blue +(Rubrene)$^T$ in dimethylformamide | $1.5 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 30 | ECL | 86 |
| *p*-Benzoquinone radical-anion + (Rubrene)$^T$ in dimethylformamide | $2.4 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 15 | ECL | 86 |
| Rubrene radical-ion + + (Rubrene)$^T$ in dimethylformamide | $1.0 \times 10^{-3}$ | 12 | ECL | 86 |
| Radical-cation of Würster's Blue + (1,3,6,8-Tetraphenylpyrene)$^T$ in dimethylformamide | $0.23 \times 10^{-3}$ ($0.15 \times 10^{-3}$) | 26** | ECL | 86 |
| 10-Methylphenothiazine radical-cation + (Fluoranthene)$^T$ in dimethylformamide | $2.4 \times 10^{-3}$ ($3.0 \times 10^{-3}$) | 14 | ECL | 86 |
| Radical-cation of Würster's Blue +(Anthracene)$^T$ in dimethylformamide | $14.4 \times 10^{-3}$ ($10.3 \times 10^{-3}$) | 18 | ECL | 87 |
| Radical-cation of Würster's Blue + (9,10-Diphenylanthracene)$^T$ in dimethylformamide | $14.6 \times 10^{-3}$ ($10.5 \times 10^{-3}$) | 5 | ECL | 87 |
| Tri-*p*-tolylamine radical-cation + (9,10-Diphenylanthracene)$^T$ in tetrahydrofuran | $1.0 \times 10^{-3}$ ($1.0 \times 10^{-3}$) | 15 | ECL | 88 |

*The DF and ECL intensity increases in the magnetic field, indicating a decrease of the rate of reaction.
**H = 6 kG.
***For the ECL experiments, the "radical concentration" column lists the concentrations of the initial compounds from which the radical-ions are formed.

The magnetic field affects reactions (40) and (41) in the same way, decreasing the constants $k_a$ and $k_R$. However, it is readily seen that, when reaction (41) predominates over reaction (40), the DF intensity, determined by the overall concentration of triplets, will decrease in the magnetic field. The change in the nature of the influence of the magnetic field on DF can be readily traced when the relative concentration of radicals is varied (see Table 5): the effect increases with increasing concentration of the radical-ions.

Together with the DF method, electrogenerated chemiluminescence (ECL) has been widely used to investigate the effect of the magnetic field on elementary processes involving triplet states. The idea of such experiments is as follows. In an electrochemical cell containing an electrolyte (as a rule tetrabutylammonium perchlorate) and the test compound (for example, anthracene), the radical-ions $R^+$ and $R^-$ are produced. The subsequent processes are listed below:

$$R^+ + R^- \rightarrow R + T \quad \text{(electron transfer)},$$
$$R^+ + T \rightarrow R^+ + S_0 \quad \text{(quenching of triplets by radical-ions)},$$
$$T + T \rightarrow S + S_0 \quad \text{(triplet-triplet annihilation)},$$
$$R^+ + S \rightarrow R^+ + S_0 \quad \text{(quenching of singlet by radical-ions)},$$
$$T \rightarrow S \quad \text{(non-radiative processes), etc.}$$

The luminescence intensity due to the excited singlet states is recorded in the experiments.

Virtually all the systems in which the influence of the magnetic field on ECL was observed belong to the class of reactions with an "energy deficit", since the energy evolved on electron transfer is insufficient for the direct formation of the excited singlet state. It has been shown in a number of studies that in such systems the luminescence intensity increases with increasing magnetic field strength (up to 30%). This effect is usually explained by the fact that radical-ions play an important role in the reactions as triplet quenching agents. Since the excited states generated in ECL processes are formed together with radical-ions, the rate of quenching by the latter species undoubtedly constitutes the main factor influencing the luminescence intensity. The excited singlet states are quenched less effectively owing to their short lifetime. Table 5 presents the effects of the magnetic field for a single field strength $H \simeq 8$ kG in the systems investigated. Fig. 12 illustrates as an example the typical variation of the ECL intensity with the magnetic field. We may note that this type of variation is in full agreement with the theory of Atkins and Evans [33].

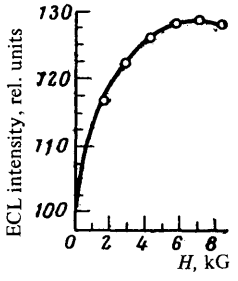



Figure 12. The influence of the magnetic field on the intensity of the electrogenerated chemiluminescence in a system containing rubrene and the radical-cation of Würster's Blue. [86]

The influence of the magnetic field on the quenching of the delayed fluorescence of anthracene and pyrene by molecular oxygen has been observed [81] (see Table 6). As for quenching by radicals, the magnetic field increased the DF intensity. The observed effect has been explained [81] by the following mechanism:

$$T + T \rightarrow S + S_0, \quad (43)$$

$$T + {}^3O_2 \rightarrow S + {}^1O_2. \quad (44)$$

Table 6. Experimental results for the influence of the magnetic field on the quenching of triplet states by oxygen [81].

| Reaction | Oxygen pressure, atm | Change in DF intensity, % ($H$ = 8 kG) |
|---|---|---|
| (Anthracene)$^T$ + (Anthracene)$^T$ in dimethylformamide* | 0 | -3 |
| | $3.0 \times 10^{-3}$ | +3 |
| | $6.0 \times 10^{-3}$ | +5 |
| (Pyrene)$^T$ + (Pyrene)$^T$ in dimethylformamide** | 0 | -2 |
| | $6.0 \times 10^{-3}$ | +1 |

*Anthracene concentration $2.1 \times 10^{-4}$ M.
**Pyrene concentration $2.6 \times 10^{-4}$ M.

At high oxygen concentrations, reaction (44) predominates and the DF intensity should therefore increase. The formation of singlet oxygen as a result of the reaction with an excited triplet hydrocarbon molecule [a reaction of type (44)] is probably the primary stage of the photochemical oxidation reaction. Since this reaction depends on the magnetic field, presumably the rate of photochemical oxidation of aromatic hydrocarbons is also sensitive to the magnitude of the magnetic field. The effect of the magnetic field in the photochemical oxidation reaction has so far been observed only in the solid phase [82]. The influence of the magnetic field on the surface conductivity of solid tetracene has been noted in the presence of oxygen [82]. The observed effect has been explained by the influence of the field on the photochemical oxidation reaction, leading to an increase of photoconductivity.

## XI. OTHER SYSTEMS

The two classes of processes examined do not exhaust all the systems in which effects of the magnetic field have been observed. The mechanisms of these effects in such instances can be regarded as fairly well understood, but, together with these, there have been reports of magnetic effects whose mechanism remains obscure.

There have been fairly numerous studies on the influence of the magnetic field on biochemical processes, including the effects of preliminary magnetisation. Polish workers [91-93] have published several reports about the influence of the magnetic field on reactions involving hydrogen peroxide. The effect of the preliminary magnetisation has also been observed in a number of instances. On the other hand, we may note that magnetic effects in the decomposition of hydrogen peroxide itself have not been observed [18]. Interesting data have been obtained by Hammond [94] in a study of the photochemical *cis–trans* isomerisation of stilbene and piperylene. The magnetic field (up to 9 kG) affects both the rate of reaction and the

steady-state photochemically generated isomer ratio when the reaction is sensitised by aromatic ketones. The magnitude of the effect is approximately 10%. On the other hand, the magnetic field has no influence when the process is carried out without a sensitiser.

The only available explanation of this effect, described in the literature, is similar to that of the explanation of the $\Delta g$ effect in radical pairs [95].

## XII. CONCLUSION

The influence of a constant magnetic field on processes involving free radicals and excited triplet states in solutions (radical recombination, triplet–triplet annihilation, quenching of triplet states by free radicals, the interaction of triplets with molecular oxygen, etc.), has now been reliably established and physically justified models of these phenomena have been proposed. The theoretical models are based on the postulate that the magnetic field alters the probability of the intercombination transition in pairs of reacting species. It is remarkable that even energetically weak influences (smaller than $kT$), such as hyperfine interactions and the difference between the Zeeman frequencies, can lead to appreciable effects of the magnetic field. The role of these interactions does not consist in overcoming energy barriers, but depends on the fact that they constitute a kind of "key", which may alter the multiplicity of the pair of reactants and result in their conversion from a multiplet, where the reaction is spin-forbidden, into a reactive state and conversely. Thus the effects of the magnetic field under consideration involve the manifestation of the spin prohibition rules in reactions of free radicals and triplet molecules. The magnetic isotope effect may be regarded as yet another important manifestation of spin prohibitions in radical recombination reactions. It is due to the fact that different nuclear isotopes differ in the magnitude of the hyperfine interaction responsible for the singlet–triplet transitions in the radical pairs.

Summarising the development of this research, one should note that the existing theoretical models describe satisfactorily the available experimental literature data not only qualitatively but also quantitatively. The range of processes in which magnetic effects may be observed, the scale of these effects, and the conditions most favourable for their observation have been clearly outlined.

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# Weak Hydrogen Bonds

V.K.Pogorelyi

The literature data on the properties of hydrogen bonds involving the elements in the Third, Fourth, and Fifth Periods are surveyed and an attempt is made to determine the factors which have a decisive effect on the proton- and electron-donating capacities in series of compounds of the same type formed by elements in different Periods and Groups.
The bibliography includes 222 references.

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## I. INTRODUCTION

Hydrogen bonds play an important role in various chemical, physical, and biological reactions[1], which is the reason for the increasing interest in the study of various systems with hydrogen bonds. However, the majority of investigations have been concerned with hydrogen bonds in compounds formed by the elements in the Second Period, such as nitrogen, oxygen, fluorine, and (to a lesser extent) carbon. Extensive experimental[1-7] and theoretical[8-11] data have accumulated in this field and have been to a large extent reviewed. Hydrogen bonds involving elements in the Third and subsequent Periods have been investigated much less. The available information about this problem is sporadic and frequently contradictory. Until recently, it used to be assumed[1] that these elements either do not tend to form hydrogen bonds or give rise to relatively weak bonds.

In recent years, there has been a significant growth of interest in the so called weak† hydrogen bonds for two reasons. Firstly, the course of chemical processes is determined not only by strong interactions associated with large changes in the energy of the reactants but also by weak interactions, which influence the process probability but hardly alter the energy spectrum of the reaction. Such interactions play an especially important role not only in chemical but also in biological systems. Secondly, studies of this kind extend significantly our ideas about the nature of the hydrogen bond.

This review deals with studies on weak hydrogen bonds involving the atoms of Group V–VII elements. A separate section is devoted to the properties of hydrogen bonds involving sulphur compounds, since after the publication of the review of Zuika and Bankovskii[12], the literature was supplemented by numerous quantitative data. This section includes also studies which showed that the properties of hydrogen bonds between interacting molecules determine not only the kinetics but also the mechanism of the fast proton exchange reaction. Particular attention has been devoted to the identification of the factors which determine the nature of the changes in the proton- and electron-donating capacities in the hydrogen bond as a function of the electronic structure of the relevant atoms, i.e. as a function of their position in the Periodic System.

In this paper, an attempt is made to survey and analyse the available literature data (up to 1974 inclusive) for the properties of weak hydrogen bonds and about the influence of these bonds on protolytic reactions, such as tautomerism and rapid proton exchange.

## II. THE HYDROGEN BOND INVOLVING SULPHUR COMPOUNDS

### 1. MERCAPTANS AND THIOPHENOLS

#### (a) Self Association

There is no doubt about the self association which occurs in liquid mercaptans RSH and their solutions in inert solvents as a result of the SH...S hydrogen bonds. The spectroscopic and physicochemical studies on this problem have been considered in detail in a review[12]. However, the vast majority of the relevant data are qualitative. Quantitative results on the self association of mercaptans have been obtained by Miller and coworkers[13-16] using NMR. Hu and Miller[16] studied the self association of mercaptans in terms of the variation of the chemical shift of the SH protons ($\tau_{SH}$) with concentration in carbon tetrachloride or cyclohexane solution. The measured dimerisation constants $K$ showed that the tendency towards self association increases in the sequence $C_6H_5SH \ll C_2H_5SH < n\text{-}C_3H_7SH < i\text{-}C_3H_7SH < n\text{-}C_4H_9SH$.

The hydrogen bond strengths $\Delta H$ in the self-associated species of mercaptans, aminomercaptans, and mercaptoethers have been obtained[16-24]. According to Yablonskii et al.,[21] $-\Delta H = 0.1-0.4$ kcal mole$^{-1}$ for the SH...S hydrogen bonds and $-\Delta H = 0.5-0.8$ kcal mole$^{-1}$ for the SH...O bonds in mercaptoethers. Hu and Miller[16] determined the SH...S bond strength in the self-associated mercaptan species from the temperature variation of $\tau_{SH}$. As in the study of Marcus and Miller[15], relatively low values of $K$ were obtained. It was found that the bond strength ($-\Delta H \simeq 1$ kcal mole$^{-1}$) is likewise low and depends little on the nature of the substituents. A low SH...S bond strength is indicated by the results of quantum-chemical calculations

†We employ the term weak for hydrogen bonds whose formation involves the elements in the Third, Fourth, and subsequent Periods.

for the hydrogen bond in $H_2S$ solutions[25-27] ($-\Delta H \simeq 1.7$ kcal mole$^{-1}$). The infrared spectroscopic studies on certain mercaptans at reduced temperatures by Alencastro and Sandorfy[28] agree with these data. The tendency towards self association increases on passing to aminomercaptans.

Table 1 shows that mercaptans form weak hydrogen bonds, whose strength is much lower than that of the analogous alcohol complexes. This can be explained by the fact that, on passing from oxygen to sulphur, there is an appreciable decrease of the proton- and electron-donating capacities of the hydrogen bond (see below).

When the mercaptan molecule contains electronegative atoms such as oxygen and nitrogen (mercaptoethers and aminomercaptans), the tendency towards self association should increase, since there is an increase in the proton-donating capacity of the SH group and the possibility of the formation of the SH...O and SH...N hydrogen bonds with stronger electron donors appears.

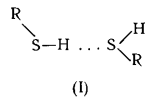
**Table 1.** The thermodynamic characteristics of the hydrogen bond in the dimers of certain mercaptans.

| RSH | $k^{30°}$, litre mole$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. | References |
|---|---|---|---|---|
| n-$C_3H_7SH$ | 0.0051 | 0.9 | 13 | 16 |
| iso-$C_3H_7SH$ | 0.0050 | 0.8 | 13 | 16 |
| n-$C_4H_9SH$ | 0.0035 | 0.8 | 14 | 16 |
| t-$C_4H_9SH$ | 0.0014 | 1.1 | 16 | 16 |
| $C_6H_{11}SH$ | 0.0001 | 0.7 | 15 | 16 |
| HSH | — | 1.7** | 18 | 20 |
| $C_6H_5SH$ | — | 1.2 | — | 17 |
| $R_{3-n}(CH_2CH_2SH)_n^*$ | — | 1.9—2.5** | — | 19 |

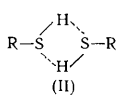
*The SH...N bond, in the remaining cases the SH...S bond.
**The infrared spectroscopic method, in the remaining cases the NMR method.

A study has been made[29] of the self association of *p*-substituted thiophenols and the interaction of the SH groups with the heteroatoms of the substituents has been observed. *p*-Amino- and *p*-fluoro-thiophenols are self-associated to a greater extent than thiophenol itself owing to the formation of the SH...N and SH...F bonds.

The structure of the self-associated thiol species constitutes at the present time the most controversial problem. With the exception of rigid systems, such as those in crystals, or systems with fixed configurations, such as those in biopolymers, it is difficult to characterise the geometry of the hydrogen bond. Since a linear hydrogen bond is usually stronger, presumably open-chain dimers (I) should be formed preferentially in solution. Indeed quantum-chemical calculations for $NH_3$, $H_2O$, $H_2S$, and HF have shown that type (I) dimers are energetically preferable[30-34]. However, the relatively low entropies of the hydrogen bond (Table 1) can be explained by the formation of cyclic dimers (II)[16]:



(I)



(II)

Structures (I) and (II) probably exist in solution. According to data[16,28] for aromatic thiols, apart from dimers (I) and (II) there is a possibility of complexes with the hydrogen bonds SH...$\pi$, the formation of which should lead to an additional increase in the complexity of the structure of the solution. However, the conclusion[15] that the thiophenol self-associated species have a tetrameric structure in carbon tetrachloride solution at a normal temperature is doubtful, since the infrared spectra show bands corresponding to self-associated species of a higher order than dimers only at low temperatures[28].

On the basis of the available data[16,17,35,36], one can formulate a series in terms of the decrease of the hydrogen bond strength ($-\Delta H$, kcal mole$^{-1}$) in the self-associated species of the alkyl compounds or hydrides of various elements:

$$ROH(\sim 4) > RNH_2(\sim 3.5) > RSH(\sim 1) \gg R_3CH$$

or

$$HF > H_2O > H_3N > H_2S \gg H_4C.$$

Evidently this series agrees with the electronegativity series for the corresponding elements.

(b) Association

The results of the study of physicochemical properties and spectroscopic investigations have shown that mercaptans and thiophenols form associated species in proton-donating solvents via the SH...O, SH...N, SH...Cl, etc. hydrogen bonds. However, there are relatively few quantitative data for the properties of these bonds and a systematic treatment of the latter is not available. The first quantitative characteristics of association involving thiophenol as the proton donor were obtained by NMR[37-39]. A detailed study of the hydrogen bonds in the 1 : 1 associated species of certain mercaptans with various electron donors has been made by Hu et al.,[40] who investigated hydrogen bonds of the type SH...S, SH...O, SH...O=C, SH...O=S, SH...O=P, and SH...N. It was found that the strengths of these bonds are low (Table 2) and change little when the electron donor is altered. For the same electron donor, the strengths of hydrogen bonds with various alkanethiols are virtually constant.

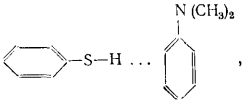
**Table 2.** The thermodynamic characteristics of the hydrogen bonds between certain mercaptans and different electron donors[40].

| Donor | $t$, °C | $\Delta\tau_C$, p.p.m. | $10^2K$, litre mole$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|---|
| | | iso-$C_3H_7SH$ | | | |
| $(CH_2)_4S$ | 32.6 | 1.65 | 3.1 | 0.8 | 9.0 |
| $(CH_3)_2S$ | 32.2 | 0.92 | 3.7 | 0.5 | 8.0 |
| $(CH_3)_2CO$ | 32.2 | 1.24 | 4.7 | 0.9 | 9.0 |
| $(CH_2)_4O$ | 30.2 | 0.81 | 6.1 | 1.0 | 9.0 |
| $(CH_3O)_2SO$ | 30.4 | 0.51 | 12.0 | 0.9 | 7.0 |
| $(C_2H_5O)_3PO$ | 31.5 | 2.41 | 6.5 | 1.0 | 9.0 |
| $[(CH_3)_2N]_3PO$ | 44.2 | 15.28 | 2.0 | 1.1 | 11.0 |
| $CH_3CN$ | 31.2 | 0.45 | 13.0 | 0.6 | 6.0 |
| $[(CH_3)_2N]_2CO$ | 34.9 | 2.22 | 5.9 | 1.1 | 9.0 |
| | | n-$C_4H_9SH$ | | | |
| $(CH_3)_2SO$ | 34.2 | 0.95 | 17.0 | 0.9 | 6.0 |
| $(C_2H_5O)_3PO$ | 34.2 | 1.47 | 12.0 | 1.0 | 8.0 |
| | | t-$C_4H_9PH$ | | | |
| $(CH_2)_4S$ | 36.0 | 0.38 | 14.0 | 0.7 | 6.0 |
| $(CH_3)_2S_2$ | 36.0 | 1.23 | 3.1 | 0.6 | 9.0 |
| $(CH_3)_2CO$ | 35.2 | 0.97 | 6.4 | 0.9 | 8.0 |
| $O(CH_2—CH_2)_2O$ | 31.9 | 1.06 | 5.5 | 0.6 | 8.0 |
| $HCON(CH_3)_2$ | 36.0 | 1.41 | 8.4 | 0.9 | 8.0 |
| $(CH_3)_2SO$ | 31.9 | 0.60 | 30.0 | 0.9 | 5.0 |
| $(C_2H_5O)_3PO$ | 32.7 | 2.43 | 6.9 | 1.0 | 8.0 |

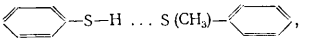
Table 2 and literature data[37,38] show that there is no correlation for the association of thiols with various electron donors between the chemical shift on complex formation $\Delta\tau_C$ and the bond strength‡. The equilibrium constant $K$ is likewise unrelated to the bond strength[40]. Its changes for different electron donors are determined mainly by the change in entropy.

Hydrogen bonds involving thiophenol have been investigated to a somewhat greater extent. The thermodynamic characteristics of the hydrogen bonds between thiophenol and electron donors of different types have been obtained[43,44]. The association of thiophenol, thiocresol, and *p*-bromothiophenol with ethylene trithiocarbonate has been studied by ultraviolet spectroscopy[45]. The dimerisation constants obtained ($K_2$, litre mole$^{-1}$) were used to establish a series based on the variation of the proton-donating capacity of the thiophenols investigated: *p*-bromothiophenol (0.87) > *p*-thiocresol (0.75) > thiophenol (0.64). This series is inconsistent with the expected acidities of the thiophenols[46,47] (which was also noted by Mukherjee et al.[45]) and with the conclusions reached by the present author and Gragerov[39]. Possibly the discrepancies are due to the inaccuracies in the determination of $K_2$.

The present author and Kukhtenko[48] studied by NMR the association of thiophenol and its derivatives with electron donors of the *n*- and $\pi$-types: anisole, dimethyl-aniline, and thioanisole. The concentration and temperature variation of $\tau_{SH}$ showed that thiophenol forms mainly complexes of the $\pi$-type with dimethylaniline:




while n-complexes are mainly formed with thioanisole:




for which $-\Delta H = 1.6$ kcal mole$^{-1}$ and $-\Delta S = 9.0$ e.u. were obtained. It was found that the probabilities of the formation of *n*- and $\pi$-complexes with anisole are almost identical. The hydrogen bond formed by thiophenol with butyl methyl ether is characterised by the following parameters: $-\Delta H = 2.7$ kcal mole$^{-1}$ and $-\Delta S = 9.6$ e.u. Comparison of the heats of association of thiophenol with this ether and acetone showed that the ketone forms a stronger bond ($-\Delta H = 3.2$ kcal mole$^{-1}$).[39] This result conflicts with the view[49] that ethers should form stronger hydrogen bonds than ketones, since the lone electron pair of the oxygen atom in ketones has a greater amount of *s* character ($sp^2$ hybridisation). This treatment is based solely on the donor–acceptor model of the hydrogen bond and does not take into account the contribution of the electrostatic interaction, which is probably significant for ketones owing to the strong polarisation of the bond in the carbonyl group.

The data obtained[37,48] make it possible to arrange the bases investigated in a series in terms of decreasing $\pi$-electron-donating capacity in relation to the formation of hydrogen bonds with thiophenol: *NN*-dimethylaniline > anisole > benzene > thioanisole. Thioanisole is a less effective $\pi$-electron donor, since the $\pi$-electron density in its ring may be reduced owing to $\pi$–$d$ conjugation. Furthermore, the $p$–$\pi$ conjugation in thioanisole is less effective than, for example, in anisole itself, since the difference between the energy levels of the $p$ and $\pi$ electrons ($\Delta n = 1$) hinders the interaction of these orbitals[50]. The above hypotheses agree with the type of change in the Hammett $\sigma$ constants on passing from alkoxy- to alkylthio-substituents[51].

The influence of the electronic nature of the substituents in both proton donor and electron donor molecules on the spectroscopic and thermodynamic characteristics of the SH...O=C hydrogen bond in the thiophenols–acetophenones system has been investigated[52] by NMR. As was to be expected, the stability of the associated species increases with increase of the electron-accepting capacity of the substituents in the thiophenol ring. The dependence of $\Delta H$ on the Hammett $\sigma$ constants is described by the equation

$$\Delta H_A = 2.2 + 1.9\sigma. \quad (1)$$

The energy of the hydrogen bond increases with increasing electron-donating capacity of the substituent in the acetophenone molecule:

$$-\Delta H_B = 2.4 - 1.2\sigma. \quad (2)$$

Comparison of the reaction constants for the two series investigated ($\rho_A/\rho_B = -1.6$) shows that the changes in the properties of the proton donor and electron donor under the influence of substituents affect to an equal extent the strengths of the hydrogen bonds between thiophenols and acetophenones. The change in $\Delta H$ for the S–H...O=C hydrogen bond in this system is more sensitive to the change in the properties of the proton donor than in those of the electron donor.

In a study of the OH...O hydrogen bonds between *p*-substituted 2,6-di-t-butylphenols and anisoles or acetophenones[53], the opposite relation was obtained—the change in the OH...O bond strength was found to be more sensitive to changes in the properties of the electron donor. Comparison of the properties of the SH...O=C and OH...O=C hydrogen bonds reveals not only quantitative differences (the SH...O=C bond is weaker) but also qualitative differences—the changes in the properties of the proton acceptor and proton donor respectively play the main role in the variation of the OH...O=C and SH...O=C hydrogen bond strengths.

The hydrogen bond between thiophenol and acetic acid has been investigated[54] and the quantities $K^{45°} = 0.38$ (mole fraction)$^{-1}$, $-\Delta H = 1.2$ kcal mole$^{-1}$, and $-\Delta S = 5.9$ e.u. have been determined. Despite the much lower acidity of thiophenol than that of acetic acid ($pK_a = 6.52$ and 4.76 respectively[47]), thiophenol in fact functions as the proton donor and the acid as the electron donor. The reason for this is probably that OH...S hydrogen bonds, which the acid might form as the proton donor, cannot compete in strength with the OH...O=C bonds in the acid dimers, since electron-donating functions are appreciably weakened on passing from oxygen to sulphur[55-58].

The thermodynamics of the hydrogen bond being substituted thiophenols and thiobenzoic acids has been studied[59]. The latter differ sharply from acetic acid in the proton- and electron-donating properties. In this system too, it was also found that thiophenol behaves as the proton donor on formation of hydrogen bonds, while the thiolo-form of thiobenzoic acid is the electron donor despite the fact that thiophenol is the weaker acid. Of the two possible dimer structures




‡ The weak temperature variation of $\Delta\tau_C$ may be neglected[41,42].

structure (III) is apparently preferable, since hydrogen bonds of the type SH...S cannot compete with bonds of the type SH...O as regards strength. We may note that the effects of substituents (Table 3) are consistent with the proposed structure of the associated species.

Thus the available data[54,59] show that, when thiophenol is involved in association with acetic and thiobenzoic acids, and probably with other carboxylic acids, there is preferential formation of dimers in which thiophenol plays the role of the proton donor and the carbonyl group of the acid is the electron donor (SH...O=C). These bonds are probably stronger than the OH...S and even more so the SH...S hydrogen bonds, which might be formed if the acid and thiophenol changed roles, since the increase of electron-donating capacity when S is replaced by O has a greater effect on the energy of the hydrogen bond than the weakening of the proton-donating capacity on passing from OH to SH.[55]

Table 3. The spectroscopic and thermodynamic characteristics of the hydrogen bond in the association complexes of thiophenols with thiobenzoic acids.

| R | $\Delta\tau_C$, p.p.m. | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|
| | $R_A-C_6H_4SH+C_6H_5COSH$ | | |
| 2,5-$(CH_3)_2$ | 1.85 | 1.9 | 8.1 |
| 4-$OCH_3$ | 1.58 | 2.0 | 8.1 |
| 4-$CH_3$ | 2.08 | 2.1 | 9.6 |
| H | 1.52 | 2.1 | 8.3 |
| 4-Cl | 1.70 | 2.2 | 9.3 |
| 2,5-$Cl_2$ | 1.75 | 2.5 | 11.4 |
| | $C_6H_5SH+R_n-C_6H_4COSH+CCl_4$ | | |
| 4-$OCH_3$ | 1.58 | 2.0 | 6.6 |
| H | 1.52 | 1.7 | 6.2 |
| 4-Cl | 1.41 | 1.6 | 6.9 |

Thus the structure of the complexes and the properties of the hydrogen bonds are determined by the proton- and electron-donating capacities of the interacting components and not by their acidity or basicity, and in many cases the acidity and proton-donating capacity vary in opposition (for example, on passing from thiophenol to phenol the acidity decreases, while the proton-donating capacity increases sharply[60-62]).

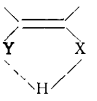
(c) The Intramolecular Hydrogen Bond

The presence of the intramolecular SH...B (B = O, N, or Cl) intramolecular hydrogen bonds in *o*-substituted thiophenols has been noted in a number of studies[63-69]. The NMR and infrared spectra as well as measurements of the dipole moments of a series of substituted thiophenols confirmed[70] the presence of an intramolecular hydrogen bond in *o*-halogeno-, *o*-methoxy-, *o*-nitro-, and *o*-methoxycarbonyl derivatives. The SH...B intramolecular hydrogen bond causes an appreciable increase in the intensity of the absorption band due to the vibrations of the SH group without a significant shift of the wavenumber. A much stronger hydrogen bond has been observed in *o*-methoxycarbonylthiophenol, in the molecule of which a six-membered chelate ring may be formed as a result of the intramolecular hydrogen bond.

It has been shown[71] that the SH group does not form an intramolecular hydrogen bond in $\alpha$-mercaptocarboxylic acid esters, while a bond of this kind persists in thiosalicylic acid and its esters even in solution in acetonitrile. According to Ginzburg and Loginova[66], $-\Delta H = 0.9$ kcal mole$^{-1}$ for the S–H...O=C hydrogen bond in thiosalicylic acid.

In contrast to $\omega$-*NN*-dialkylaminomercaptans[72], in aminothiophenols chelation is found to occur owing to the SH...N or NH...S hydrogen bonds[73]. It follows from the infrared spectra that such bonds are not formed in *o*-aminophenols or are significantly weaker. Consequently the proton- and electron-donating functions of sulphur are more effective than those of oxygen in the formation of intramolecular hydrogen bonds, while in association processes the opposite behaviour is observed. These findings are consistent with the calculations on intermolecular and intramolecular hydrogen bonds involving sulphur and oxygen atoms[74,75].

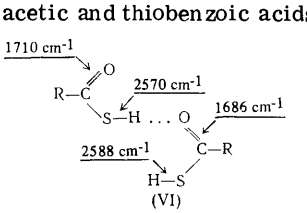
In rigid systems, such as five-membered chelates with intramolecular hydrogen bonds, the large size of the sulphur atom and diffuseness of its 3*p* orbitals ensure more satisfactory conditions than in oxygen for the overlapping of the interacting orbitals on formation of the bonds. Consequently the properties of the intramolecular hydrogen bonds



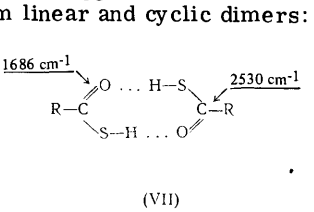

are determined by the nature of the proton donor and acceptor, the linearity of the XH...Y bond, and the distance between the donor and acceptor atoms[76].

2. THIOCARBOXYLIC AND PHOSPHOROTHIOIC ACIDS

Thiocarboxylic acids RC(O)SH should form more stable self-associated species than thiophenols and mercaptans via the SH...O=C hydrogen bonds. However, the literature data on this problem are contradictory. Thus it has been suggested[77] that the degree of self-association of thioacetic acid is low in view of the observed decrease of the wavenumber and increase of the intensity of the $\nu$(SH) infrared band on passing from the gas to the liquid. In the gas phase[78] and in carbon tetrachloride solutions[79], no signs of the self-association of thioacetic acid were observed, which conflicts with the results of another study[80], where the intensities of the $\nu$(C=O) and $\nu$(SH) bands of thioacetic and thiobenzoic acid were found to vary with concentration, indicating unambiguously the formation of SH...O=C hydrogen bonds. The chemical shift of the SH protons was also found to depend on the concentration of thiobenzoic acid in benzene[81] and of thioacetic acid in carbon tetrachloride[82]. It has been suggested[83] that thioacetic and thiobenzoic acids form linear and cyclic dimers:




(VI)




(VII)

With decrease of temperature, the probability of the formation of the cyclic structure (VII) increases.

All the foregoing considerations suggest that the occurrence of the self-association of thiocarboxylic acids has been established. The present author[84,85] obtained by NMR data for the structures and thermodynamic characteristics of the hydrogen bonds in the self-associated species of *p*-substituted thiobenzoic acids. It was found that $-\Delta H = 6.2$ kcal mole$^{-1}$ and $-\Delta S = 21$ e.u. for the unsubstituted acid. Comparison with data for benzoic acid[86] ($-\Delta H = 10.6$ kcal mole$^{-1}$ and $-\Delta S = 18.8$ e.u.) showed that the S–H...O=C bonds are much weaker than the O–H...O=C bonds. On the other hand, thiobenzoic acids are much more self-associated than thiophenols and mercaptans. It has been shown[84] that the values of $\Delta H$ and $\Delta S$ for thiobenzoic acid represent the overall effect of the formation of two hydrogen bonds. Consequently the acid dimers have the cyclic structure (VII). These results apply solely to the thiolo-form of the acid (VIII), since in inert solvents the presence of the thiono-form (IX) was not observed[87,88].

In electron-donating solvents, the complex-formation process is accompanied by the formation of a new molecular structure with mobile protons, which are involved in rapid exchange with the protons of the OH groups of the solvent (methanol, acetic acid). This is probably associated with the formation of appreciable amounts of the thiono-tautomer owing to the displacement to the right of the equilibrium

$$\underset{\text{(VIII)}}{C_6H_5C(O)SH} \rightleftarrows \underset{\text{(IX)}}{C_6H_5C(S)OH}$$

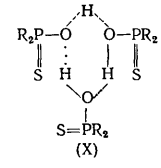
compared with the solution in carbon tetrachloride. The present author believes that this influence of electron-donating solvents on the state of the thiol–thione equilibrium should be sought by comparing the properties of the self-associated species and complexes formed with the solvent by the tautomeric species (VIII) and (IX).

As a result of complex formation with the electron donor (B), the self-associated species of the acid (VII) decompose. The associated species of the thiono-form $C_6H_5C(S)O–H..B$ produced under these conditions are more stable than those of the thiolo-form $C_6H_5C(O)S–H...B$, since the hydroxy-group is a more effective proton donor in the hydrogen bond than the mercapto-group. This in fact leads to the appearance in solution of an appreciable amount of the thione tautomer (IX).

The present author also investigated[85] the influence of substituents on the self-association of thiobenzoic acids (Table 4). The relation obtained between $\Delta H$ and the Hammett $\sigma$ constants suggests that the change in the proton-donating capacity of the mercapto-group plays a decisive role in the alteration of the stability of the self-associated species of thiobenzoic acids. The change in the electron-donating capacity of carbonyl oxygen is of secondary importance and can affect only the magnitude but not the sign of the reaction constant $\rho$ in the Hammett equation. For thiobenzoic acids, this quantity ($\rho = 1.8$) is significantly smaller than the value found[39] for the association of thiophenols with acetone ($\rho = 2.4$).

On passing from mono- to di-thiobenzoic acid, the tendency towards self-association decreases sharply. According to infrared spectroscopic data, all the signs of the self-association of dithiobenzoic acid vanish already in a 20% solution in carbon tetrachloride[89]. This can be explained by the fact that the SH...S=C hydrogen bond formed in dithiobenzoic acid dimers is much weaker than the S–H...O=C bond in monothiobenzoic acid dimers.

In contrast to thiocarboxylic acids, the monothio-derivatives of phosphorus-containing acids exist in inert solvents in the form of the thione tautomers[90]. The self-association of diethylphosphinothioic, *o*-ethyl methylphosphonothioate, and diethyl phosphorothioate has been investigated by NMR[91] in carbon tetrachloride solution on the basis of the temperature and concentration variation of the chemical shift of the hydroxyl protons. Analysis of these data by Lippert's method[92] showed that the main type of equilibrium in solutions of the above acids is monomer ⇌ trimer. It was established that the values $-\Delta H \simeq 18$ established for the monothio-derivatives of phosphorus-containing acids correspond to the overall effect of the formation of three hydrogen bonds of the type OH...O and that the trimers have the cyclic structure



(X)

Consequently the thiophosphoryl sulphur cannot compete with the hydroxyl oxygen as the electron donor in the hydrogen bond.

Table 4. The spectroscopic and thermodynamic characteristics of the self-association of the acids *p*-$RC_6H_4C(O)SH$ in $CCl_4$ solution ($\Delta S = -21$ e.u.).

| R | $\Delta\tau_c$, p.p.m. | $K^{27°}$, (mole fraction)$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $\sigma$ |
|---|---|---|---|---|
| $OCH_3$ | 1.33 | 0.40 | 5.7 | —0.268 |
| H | 1.33 | 0.95 | 6.2 | 0.000 |
| F | 1.34 | 0.95 | 6.2 | 0.062 |
| Cl | 1.32 | 1.83 | 6.6 | 0.227 |

Table 5. The spectroscopic and thermodynamic characteristics of the hydrogen bond in the self-associated species of organophosphorus monothio-acids $R_1R_2P(S)OH$.

| $R_1$ | $R_2$ | $\tau_0$, p.p.m. | $\Delta\tau_c$, p.p.m. | $10^{-3}K^{40°}$, (mole fraction)$^{-2}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|---|---|
| $C_2H_5$ | $C_2H_5$ | 3.80 | 1.47 | 4.0 | 18.0 | 41.8 |
| $C_2H_5O$ | $CH_3$ | 4.39 | 2.00 | 5.7 | 17.8 | 40.5 |
| $C_2H_5O$ | $C_2H_5O$ | 4.47 | 2.19 | 10.0 | 18.0 | 39.4 |

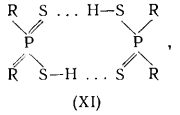
The data in Tables 4 and 5 show that, on passing from thiobenzoic acids to thio-derivatives of phosphorus-containing acids, there is a sharp increase of the ability to form self-associated species. This is due to the increase of the strength of the hydrogen bond when the mercapto-group is replaced by the hydroxyl as the proton donor, although this involves a significant gain in entropy, caused by the increased complexity of the structure of the self-associated species.

Thus the structures and properties of the self-associated species of monothio-acids depend on the position of the thiol–thione equilibrium. As stated above, in thiobenzoic acids the equilibrium is displaced towards the thiolo-tautomer, which results in the formation of the cyclic dimers (VII) with oxygen as the electron donor, similar to the carboxylic acid dimers[93]. For thio-derivatives of phosphorus-containing acids, the equilibrium is displaced towards the thiono-form, dimers of type (VII) becoming less stable owing to the reduced electron-donating capacity of sulphur and cyclic trimers (X), with oxygen as the donor, whose structure resembles that of the self-associated species of alcohols, are formed[94].

The self-association of dithio-derivatives of phosphorus-containing acids has been investigated in greater detail. Thus the infrared spectra of solutions of diethyl and dimethyl phosphorodithioates[95] and of phenyl phenylphosphonodithioate and ethyl ethylphosphonodithioate[89] in carbon tetrachloride showed a splitting of the $\nu$(SH) band. The doublet structure of this band and the dependence of the relative intensities of its components on concentration and temperature were explained by the self-association of the acids with formation of SH...S bonds. Self-association of this type is assumed for both phosphorodithioic[96] and diphenylphosphinodithioic[97] acids. On the other hand, cryoscopic measurements have shown[98] that phosphorodithioic acids exist in benzene solutions as monomers. Presumably the decomposition of the self-associated species in this system is caused by the formation of complexes by the acid with the solvent (benzene). There is at present no doubt about the possibility of the formation of hydrogen bonds of the type SH...$\pi$.

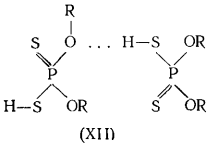
Many workers[99,100] believe that the doublet structure of the $\nu$(SH) band is due to the presence of two rotational isomers with intramolecular hydrogen bonds between the SH groups and the oxygen atoms of the substituent or the sulphur atom in the P=S group.

Quantitative studies on the hydrogen bonds in the self-associated species of phosphorodithioic acids have been carried out by NMR and infrared spectroscopy. Thus a study has been made[101,102] of the hydrogen bond strengths in the self-associated species of a number of phosphorodithioic acids and in their complexes with dioxan. The authors[101,102] suggested the cyclic structure



(XI)

for phosphinodithioic acids and the linear dimeric structure

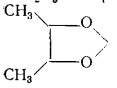


(XII)

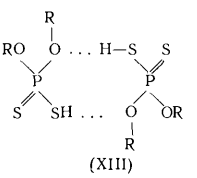
for the self-associated species of phosphonodithioic and phosphorodithioic acids. We may note, however, that the conclusion concerning the preferential formation of structure (XII), reached[101] on the basis of a comparison of the values of $\nu$(SH) for self-associated species and complexes with dioxan as well as the hypothesis that the proton-accepting capacity of the oxygen in the RO substituent is greater than that of the thiono-sulphur in the P=S group appear to have little justification. One should also note that the same workers[102] believe that the thiophosphoryl group in phosphinic acids gives rise to more stable associated species than those produced by the oxygen of the substituent in phosphonic and phosphoric acids.

An NMR study has been made[103] of the self-association of dithio-derivatives of phosphorus-containing acids. In agreement with previous results[101,102], it was shown that the main type of equilibrium in solutions of these acids in carbon tetrachloride or cyclohexane is monomer $\rightleftharpoons$ dimer. The value of $\Delta H$ for self-association obtained by infrared spectroscopic (Table 6) and NMR methods (Table 7) agree satisfactorily when account is taken of the experimental error.

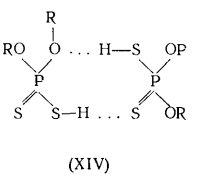
Table 6. The spectroscopic characteristics and strength of the hydrogen bonds formed by organophosphorus dithio-acids $R_1R_2PSSH$ in their self-associated species and in their complexes with dioxan.

| $R_1$ | $R_2$ | Self association | | Complex with dioxan | |
|---|---|---|---|---|---|
| | | $\nu_{SH...S(O)}$, cm$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $\nu_{SH...O}$, cm$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ |
| n-$C_3H_7$ | n-$C_3H_7$ | 2405 | 3.2 | 2445 | 2.0 |
| $CH_3$ | $C_6H_5$ | 2405 | 3.4 | 2440 | — |
| $CH_3$ | $CH_3O$ | 2460 | 2.1 | 2470 | — |
| $CH_3$ | $C_2H_5O$ | 2460 | 2.1 | 2470 | — |
| $CH_3$ | n-$C_3H_7O$ | 2460 | 2.4 | 2470 | — |
| $CH_3$ | iso-$C_3H_7O$ | 2460 | 2.0 | 2470 | — |
| $C_2H_5$ | $C_2H_5O$ | 2460 | 2.3 | 2460 | 1.8 |
| $C_2H_5O$ | $C_2H_5O$ | 2460 | 2.1 | 2460 | 1.5 |
|  | | 2460 | 2.4 | 2450 | 1.8 |

The stability of the complexes (XI) of phosphinodithioic acids varies in the range 2.6–3.4 kcal mole$^{-1}$. Consequently the energy of the SH...S=P hydrogen bond is close to 1.5 kcal mole$^{-1}$. As already mentioned, in phosphonodithioic and phosphorodithioic acids, both thiono-sulphur and oxygen atoms in the substituent can behave as electron donors. For this reason, these acids can give rise to the following structures apart from complexes of types (XI) and (XII):



(XIII)



(XIV)

The conclusion[101,102] that the open-chain dimers (XII) are formed preferentially by phosphonic and phosphoric acids is inconsistent with thermodynamic data[101–103]. Thus the energy of the SH...O hydrogen bond between dithio-derivatives of phosphorus-containing acids and dioxan is 1.5–1.8 kcal mole$^{-1}$.[101] On the other hand, the strength of the bond of the same type but with the oxygen atom of the substituent at the phosphorus atom should be smaller, since in this case the electron-donating capacity of the oxygen atom is reduced owing to the effect of the $p\pi - d\pi$ conjugation[106,107]. Table 7 shows that the bond energy in the self-associated phosphonic and phosphoric acid species varies from 2.7 to 4.3 kcal mole$^{-1}$. Clearly

a structure of type (XII) with a single SH...O hydrogen bond cannot alone account for the observed heats of complex formation. On the other hand, cyclic structures of types (XI), (XIII), and (XIV) are consistent with experimental data. We therefore suggest that phosphonodithioic as well as phosphinodithioic acids form mainly cyclic dimeric self-associated species in solution in inert solvents. This conclusion is further confirmed by the similarity of the values of $\Delta S$ for self-association obtained for complexes of all three types of acids (Table 7).

**Table 7.** The spectroscopic and thermodynamic characteristics of the hydrogen bond in the self-association species of the acids $R_1R_2PSSH$.

| $R_1$ | $\tau_0$, p.p.m. | $\Delta\tau_C$, p.p.m. | $K^{40°}$, (mole fraction)$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. | $pK_a^*$ | $-\Sigma\sigma_\Phi^{**}$ |
|---|---|---|---|---|---|---|---|
| $C_2H_5$ | 8.07 | 2.75 | 1.4 | 2.7 | 8.0 | 5.06 | 2.202 |
| $C_6H_5$ | 7.67 | 1.33 | 1.0 | 2.6 | 8.3 | 3.48 | 1.184 |
| $CH_3$*** | 7.42 | 2.00 | 1.9 | 3.0 | 8.2 | 3.16 | 1.179 |
| n-$C_4H_9O$ | 7.42 | 1.43 | 1.8 | 3.6 | 10.3 | — | 0.822 |
| n-$C_5H_7O$ | 7.40 | 1.48 | 2.0 | 3.5 | 9.8 | — | 0.630 |
| iso-$C_4H_9O$ | 7.34 | 1.27 | 1.4 | 3.5 | 10.5 | — | 0.600 |
| iso-$C_5H_7O$ | 7.50 | 1.45 | 2.9 | 3.6 | 9.7 | 2.94 | 0.582 |
| $C_2H_5O$ | 7.30 | 1.58 | 1.1 | 2.7 | 8.2 | 2.84 | 0.425 |
| $C_6H_5O$ | 5.67 | 2.00 | 14.0 | 4.3 | 8.5 | 2.41 | 0.122 |

* Determined in 100% alcohol[104].
** Overall $\sigma$ constants[105].
*** $R_2 = C_2H_5O$, in the remaining cases $R_1 = R_2$.

When data for the self-association of mono- and di-thio-derivatives of phosphorus-containing acids are compared, sharp differences are discovered[108]. The self-associated species of the monothio-derivatives have a trimeric cyclic structure formed by OH...O hydrogen bonds, while the dithio-acids give rise to cyclic dimers with SH...S and SH...O bonds. It was noted that, when oxygen is replaced by sulphur, both the electron-donating and the proton-donating capacity of the hydrogen bond are reduced. The sharp differences between the values of $K$, $\Delta H$, and $\Delta S$ for the self-associated species investigated are therefore based not only on the differences in the numbers of the hydrogen bonds forming the complexes but also in their properties.

## 3. HYDROGEN BONDS AND RAPID PROTON EXCHANGE REACTIONS INVOLVING SH GROUPS

It was shown previously[55,109-111] that the initial stage of the proton transfer reaction between molecules or ions is the formation of an intermediate reaction complex in which the reactions centres of the interacting species are brought closer together by hydrogen bonds, which ensures the most favourable mutual orientation of the centres for the reaction. The increase of the strength of the hydrogen bond in the intermediate complex leads to a decrease of the height and width of the potential barrier to the reaction, which facilitates proton transfer via both the classical mechanism and as a result of the tunnel effect. These are also the causes underlying the observed correlations between the kinetic and activation parameters of rapid proton exchange reactions and the thermodynamic characteristics of the hydrogen bond between the exchanging reactants[55].

However, the dependence of the mechanism of the rapid proton exchange reactions on the structure of the complexes and the properties of the hydrogen bond between the exchanging components has still been inadequately investigated. This problem has been solved in a number of studies[54,59,120-122] for reactions involving SH, COOH, and COSH groups. Reactions of this type occupy an important place in various biochemical processes[123].

The kinetics and mechanism of the rapid proton exchange between the SH groups in a series of substituted thiophenols and the COOH group of acetic acid, catalysed by sodium acetate, have been investigated[54,120] by NMR. It was established that the rate-limiting stage of the reaction involves proton transfer from the thiophenol to the acetate ion in the bimolecular complex formed by hydrogen bonds:

$$PhSH \ldots {}^-OAc \rightleftarrows PhS^- \ldots HOAc. \qquad (3)$$

The increase of the rate constant and the decrease of the activation energy with enhancement of the electron-accepting capacity of the substituents in the thiophenol ring (Table 8) are consistent with the proposed exchange mechanism (3).

**Table 8.** The kinetic and activation parameters of the fast proton exchange reaction between ArSH and AcOH catalysed by sodium acetate.

| Substituent | $10^{-2}\,k^{40°}$, litre mole$^{-1}$ s$^{-1}$ | $E$, kcal mole$^{-1}$ | lg $A$ |
|---|---|---|---|
| 2,5-$(CH_3)_2$ | 4.3 | 10.1 | 9.7 |
| 4-$OCH_3$ | 10.5 | 9.5 | 9.7 |
| H | 16.2 | 9.3 | 9.7 |
| 4-Cl | 49.0 | 8.9 | 9.9 |
| 2,5-$Cl_2$ | 169.8 | 8.8 | 10.4 |

It is of interest to compare these data with the results of studies on the proton exchange between thiophenols and methanol in an alkaline medium[124] which proceeds in the trimolecular complex

$$ArSH \ldots \underset{|}{\overset{CH_3}{O}}H \ldots {}^-SAr \qquad (XV)$$

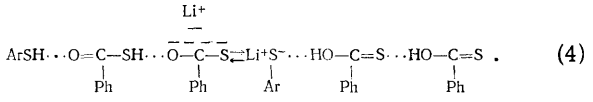
and its rate is limited by proton transfer from the thiophenol to the alcohol. The activation energy is in this case much more sensitive to the influence of the substituents in the thiophenol ring than in reaction (3). This can be explained by the levelling of the strengths of the AH...B hydrogen bonds involving a strong electron donor (for example $B = OH^-$ or $AcO^-$) and differing in the strengths of the proton donors, like the differences between the acid strengths in highly basic solvents. The activation energies for the exchange reaction involving such hydrogen bonds, which depend on the strength of the latter, are therefore also levelled.

The proton exchange between the SH and COOH groups in thiolactic acid $CH_3CH(SH)COOH$, between 1-methylethanethiol and acetic acid[121], and in mercaptoacetic acid $HSCH_2COOH$[122] takes place in a binary complex of type (3)

when the process is catalysed by sodium acetate. The values of $k$, $E$, and $\lg A$ are listed below:

| Compound | $10^{-2}k$, litre mole$^{-1}$ s$^{-1}$ | $E$, kcal mole$^{-1}$ | $\lg A$ |
|---|---|---|---|
| Thiolactic acid | 3.6 (42° C) | 11.8 | 10.7 |
| 1-Methylethanethiol | 0.1 (46° C) | 14.2 | 10.8 |
| Mercaptoacetic acid | 7.1 | 12.4 | 8.5 |

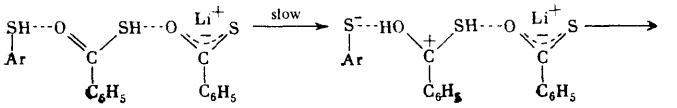
The proton exchange between a series of thiophenols and thiobenzoic acid, differing sharply from acetic acid in its proton- and electron-donating properties, has been investigated[59] and it has been established that, when the process is catalysed by lithium thiobenzoate, its rate-limiting stage involves proton transfer in the trimolecular complex formed by hydrogen bonds:



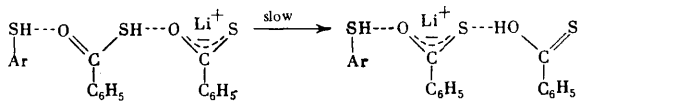
(4)

This complex arises as a result of the association of the dimers $C_6H_5SH\cdots O{=}C(SH)C_6H_5$ (III) present in the system with lithium thiobenzoate, since trimolecular collisions of thiophenol, acid, and catalyst molecules are unlikely. The formation of the complex or its decomposition cannot limit the rate of exchange, since they are rapid reactions involving the formation or dissociation of hydrogen bonds.

The data obtained for the influence of substituents on the kinetics of reaction (4) provided evidence in support of a detailed exchange mechanism. Three schemes are possible: single-stage synchronous transfer of two protons [reaction (4)] and two-stage ionisation schemes [reactions (5) and (6)], in the slow stage of which the thiobenzoic acid or catalyst molecule is protonated:



(5)



(6)

Scheme (6) is inconsistent with the influence of substituents on the rate of reaction, since the rate of the slow stage in this scheme should not depend on the substituents in the thiophenol ring. On the other hand, mechanisms (4) and (5) are consistent with experimental data. Furthermore, a quantitative relation has been observed between the kinetic parameters of the exchange reaction and the thermodynamic characteristics of the hydrogen bond in the dimeric species formed by thiophenols with thiobenzoic acid (Tables 3 and 9). This relation presupposes proton transfer in the slow stage via the S–H...O=C hydrogen bond [see scheme (5)].

We may note that a considerable similarity between the kinetics and mechanisms of the rapid proton exchange reactions of thiophenols with thiobenzoic acid[59] and methanol[124,125] has been observed. In both cases, the rate of reaction is described by a third-order kinetic equation, the substituents in the thiophenol ring have the same type of influence, and even the corresponding catalytic rate constants and activation energies are similar. Presumably, such analogy is due to the similarity of the slow stages in the above processes—proton transfer via the SH...O hydrogen bond in accordance with a type (5) mechanism.

Table 9. The kinetic and activation parameters of the fast proton exchange reaction between substituted thiophenols and thiobenzoic acid catalysed by lithium thiobenzoate.

| Substituent | $10^{-3}\,k^{40°}$ litre mole$^{-1}$ s$^{-1}$ | $E$, kcal mole$^{-1}$ | $\lg A$ |
|---|---|---|---|
| 2,5-$(CH_3)_2$ | 4.6 | 8.7 | 9.8 |
| 4-$OCH_3$ | 13.6 | 8.0 | 9.7 |
| 4-$CH_3$ | 13.1 | 7.8 | 9.6 |
| H | 20.9 | 7.8 | 9.8 |
| 2,5-$Cl_2$ | 140.0 | 4.8 | 8.5 |

In contrast to the above similarity, the exchange of thiophenols with thiobenzoic acid differs as regards kinetics and mechanism from the seemingly analogous proton exchange reaction between thiophenols and acetic acid. The weak hydrogen bond between thiophenol and acetic acid and the marked tendency of the latter to undergo self-association cause the alkali-catalysed rapid proton exchange involving the SH and COOH groups to proceed via the bimolecular mechanism (3), the acetic acid molecule not being involved in the slow stage. On the other hand, the stronger hydrogen bond between thiophenol and thiobenzoic acid and the much smaller (compared with acetic acid) tendency of the latter towards self-association explains why the proton exchange between the SH and COSH groups take place in a trimolecular hydrogen-bonded complex.

Thus the data examined in this section constitute undoubted proof that the properties of the hydrogen bond between the exchanging components determine not only the kinetics but also the characteristics of the mechanism of rapid proton exchange.

## 4. THE ELECTRON-DONATING CAPACITY OF SULPHUR COMPOUNDS

The proton- and electron-donating properties of the hydrogen bond formed by the SH groups of mercaptans, thiophenols, and thiocarboxylic acids, as well as the thio-derivatives of phosphorus-containing acids were examined above. Other types of sulphur compounds, for example sulphides $R_2S$, thioketones $R_2C{=}S$, phosphine sulphides $R_3P{=}S$, etc. do not have a mobile proton but can nevertheless form hydrogen bonds as electron donors by virtue of the lone electron pairs of the bivalent sulphur atom.

Convincing evidence for the association of sulphur compounds of this type with various proton donors has been compiled in the literature[12]. For example, the OH...S,[126-128] OH...S=P,[129] OH...S=C,[130,131] NH...S,[132] and CH...S[133]

bonds have been discovered. The electron-donating properties of the hydrogen bonds formed by amines, ethers, and sulphides (thioethers) with phenols and alcohols have been compared[134-140].

The values of $\Delta H$ quoted in Table 10 show that the electron-donating capacity of the hydrogen bonds formed by amines is twice as great and that of the bonds formed by ethers approximately 1.5 times as great as that of the bonds involving sulphides.

**Table 10.** Hydrogen bond strengths in the complexes of amines, ethers, and sulphides with alcohols and phenols.

| Electron donor | $-\Delta H$, kcal mole$^{-1}$ | Electron donor | $-\Delta H$, kcal mole$^{-1}$ |
|---|---|---|---|
| $(CF_3)_3COH$ [calorimetry (Ref.134)] | | $p$-$ClC_6H_4OH$ [i.r. (Refs.137-139)] | |
| $(C_2H_5)_3N$ | 14.3 | $(C_2H_5)_3N$ | 9.5 |
| $(C_2H_5)_2O$ | 8.3 | $(C_4H_9)_2O$ | 6.3 |
| $(C_2H_5)_2S$ | 7.0 | $(C_2H_5)_2S$ | 5.0 |
| $p$-$CH_3C_6H_4OH$ [i.r. (Ref. 137, 138)] | | $(CF_3)_2CHOH$ [i.r., calorimetry (Ref.137, 140)] | |
| $C_5H_5N$ | 7.8 | $(C_2H_5)_3N$ | 11.5 |
| $(C_4H_9)_2O$ | 5.9 | $(C_2H_5)_2O$ | 7.2 |
| $(C_2H_5)_2S$ | 4.3 | $(CH_2)_4S$ | 5.8 |
| $(CH_2)_4S$ | 4.6 | $C_3H_7OH$ [GLC (Ref.136)] | |
| $C_6H_5OH$ [i.r. (Ref.137, 138)] | | $(C_8H_{17})_2CH_3N$ | 5.1 |
| $(C_2H_5)_3N$ | 9.1 | $(C_8H_{17})_2O$ | 3.8 |
| $(C_3H_9)_2O$ | 6.0 | $(C_8H_{17})_2S$ | 2.4 |
| $(C_4H_9)_2O$ | 6.0 | $C_4H_9OH$ [GLC (Ref.136)] | |
| $(C_2H_5)_2S$ | 4.6 | $(C_8H_{17})_2CH_3N$ | 5.3 |
| $p$-$FC_6H_4OH$ [i.r. (Ref.137, 139)] | | $(C_8H_{17})_2O$ | 3.8 |
| $(C_2H_5)_3N$ | 9.0 | $(C_8H_{17})_2S$ | 2.8 |
| $(C_2H_5)_2O$ | 5.6 | $(CH_3)_3COH$ [GLC (Ref.136)] | |
| $(C_2H_5)_2S$ | 4.7 | $(C_8H_{17})_2CH_3N$ | 4.0 |
| $m$-$FC_6H_4OH$ [i.r. (Ref.138)] | | $(C_8H_{17})_2O$ | 3.1 |
| $(C_4H_9)_2O$ | 6.0 | $(C_8H_{17})_2S$ | 2.0 |
| $(C_2H_5)_2S$ | 5.0 | | |

The data obtained have been analysed[136] with the aid of the Drago relation[141]

$$-\Delta H = E_A\ E_B + C_A\ C_B, \qquad (7)$$

where the empirical parameters $E_A$ and $C_A$ refer to the proton donor and $E_B$ and $C_B$ refer to the electron donor. The values of $E_A$ and $E_B$ characterise the ability of the donor and acceptor to enter into an electrostatic interaction, while $C_A$ and $C_B$ determine the contribution to the overall bond energy by the donor–acceptor (covalent) forces. Calculation of the contributions of the electrostatic ($-\Delta H_E = E_A E_B$) and donor–acceptor ($-\Delta H_C = C_A C_B$) interactions to the overall energy of the hydrogen bond showed that, when dioctyl ether, methyldioctylamine and dioctyl sulphide are involved in association with aliphatic alcohols, the contributions of the electrostatic forces to the overall energy of the hydrogen bond are 83, 56, and 34% respectively. Consequently, according to Pearson's classification[142], ethers are "hard" bases, sulphides are "soft" bases, while amines are "hard-soft" bases.

The electron-donating capacities of ethers and sulphides in relation to alkyl halides have been compared[143]. The data obtained by gas–liquid chromatography (GLC) are difficult to interpret in terms of the hypothesis that complexes are formed in this system only via the C–H...O and C–H...S hydrogen bonds. Thus the stabilities of the complexes formed by chloroform with di-n-octyl ether and di-n-octyl sulphide are 2.38 and 1.93 kcal mole$^{-1}$ respectively. These values agree with the usual hypothesis that the electron-donating capacity in the hydrogen bond decreases on passing from oxygen to sulphur[12,55]. On the other hand, the complex of bromoform with the ether ($-\Delta H$ = 2.17 kcal mole$^{-1}$) proved to be less stable than that with the sulphide ($-\Delta H$ = 2.28 kcal mole$^{-1}$). Furthermore, the replacement of chloroform by bromoform leads to a decrease of the stability of the ether complex in accordance with the reduced proton-donating capacity of bromoform relative to chloroform[144-147], while the opposite behaviour applies to the sulphide—the bromoform complex is more stable than the chloroform complex. In order to account for the above findings, the authors[143] assume that in the association of halogenoalkanes with ethers and particularly with sulphides complexes with charge transfer of the $n \rightarrow \sigma^*$ type[148] between the oxygen or sulphur atoms (n-electron donor) and halogen atoms (electron acceptor) are formed in addition to the hydrogen bond. The contribution of the charge-transfer interaction increases and the tendency towards the formation of hydrogen bonds diminishes on passing from the ether to the sulphide and from chloroform to bromoform. Possibly the classic electrostatic interaction, which may be enhanced with increase of atomic polarisability on passing from O to S and from Cl to Br, plays an important stabilising role for such relatively weak "contact" complexes[149,150].

The hydrogen bonds between phenylacetylene and ethers and sulphides have been investigated[133] by NMR and infrared spectroscopy. The formation constants of the 1 : 1 complexes formed by sulphides are approximately five times smaller than those of the complexes formed by ethers.

**Table 11.** The thermodynamic characteristics of the hydrogen bonds formed by chloroform, phenol, and ethanol with certain sulphides and disulphides.

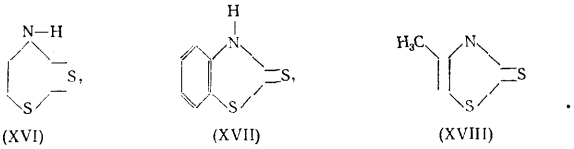
| Electron donor | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. | Electron donor | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|---|
| $Cl_3CH$ [NMR (Ref.151)] | | | $C_6H_5OH$ [i.r. (Ref.153)] | | |
| $(CH_3S)_2$ | 0.93 | 7.0 | $(CH_3S)_2$ | 2.30 | 6.2 |
| $(C_3H_9)_2S$ | 1.70 | 9.0 | $(C_4H_9)_2S$ | 4.90 | 16.6 |
| $(CH_2)_4S$ | 2.30 | 10.9 | $C_2H_5OH$ [i.r. (Ref.153)] | | |
| $Cl_3CH$ [NMR (Ref.152)] | | | $(CH_3S)_2$ | 1.50 | — |
| $(CH_3)_2S$ | 1.50 | — | $(C_4H_9)_2S$ | 2.60 | — |
| $(C_2H_5)_2S$ | 2.10 | — | | | |

The electron-donating capacities in the hydrogen bonds of sulphides and disulphides may be compared on the basis of the available data[151-153] (Table 11). It is striking that the strength of the hydrogen bond diminishes approximately by a factor of two on passing from sulphides to disulphides. The chemical bond between two sulphur atoms weakens their electron-donating properties. This observation was made for the first time by Epshtein and Zhdanova[153], but has not been explained. The present author believes that the cause of the weakening of the electron-donating capacity of disulphides may be as follows. The multiplicity of the chemical bonds between two sulphur atoms may increase, because, apart from a single $\sigma$ bond, there is a possibility of interaction of the $\pi$-type between the $3p$ orbital of the lone electron pair of one atom and the vacant $3d$ orbital of another, which is suitable as

regards symmetry. Such interaction must lead to an increase of the degree of delocalisation of the 3*p* electrons and hence to a decrease of the orbital electron density. This entails a decrease of the capacity of the 3*p* orbital of the lone electron pair of the sulphur atom for overlapping with the 1*s* orbital of the hydrogen atom of the proton donor, which leads in its turn to the weakening of the hydrogen bond noted above. An increase of the amount of double bond character in S–S in disulphides is indicated by the data quoted in Foss's paper[154].

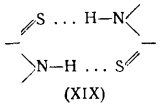
Hydrogen bonds involving the electron-donating C=S, P=S, and As=S groups have been investigated[155-161]. The abilities of certain enaminothiones to form hydrogen bonds has been compared in an infrared spectroscopic and NMR study[155] with those of the corresponding oxo-analogues. It was observed that the efficiency of the thiono-group as an electron donor may be less effectively reflected in an intermolecular hydrogen bond than in the case of the carbonyl group. The opposite is true of intramolecular conjugated chelate systems, which has been attributed to the 6π-electron stabilisation of the chelate, including the expansion of the orbital of the sulphur atom.

Hydrogen bonds of type N–H...S=C have been discovered[157] in the self-associated species of the heterocyclic thioamides (XVI)–(XVII):



(XVI) (XVII) (XVIII)

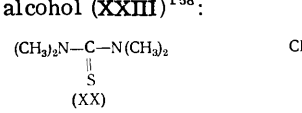
According to X-ray diffraction data[162], 2-mercaptobenzothiazole (XVII) forms centrosymmetric cyclic dimers with a short hydrogen bond. The infrared spectra of the thioamides (XVI)–(XVIII) hardly change on passing from crystals to a dilute solution in carbon tetrachloride. The cyclic dimeric structure of the associated species



(XIX)

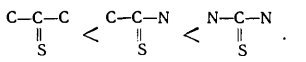
probably persists also in carbon tetrachloride solution. The intensity of the ν(NH...S) bands and the values of $\Delta\nu = \nu(HN) - \nu(NH...S)$ show that the strength of the hydrogen bond in complexes of type (XIX) increases in the sequence (XVI) < (XVII) < (XVIII). This conclusion is consistent with the observed dimerisation constants, which are 88, 570, and 5540 litre mole$^{-1}$ for complexes (XVI), (XVII), and (XVIII) respectively, and the results of a study[163] of the influence of hydrogen bonds on the ultraviolet spectra of the same compounds.

The OH...S=C hydrogen bond has been investigated calorimetrically in relation to the association of tetramethylthiourea (XX) and *NN*-dimethylthioacetamide (XXI) with alcohols—hexafluoroisopropyl alcohol (XXII) and trifluoroethyl alcohol (XXIII)[158]:

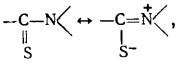


(XX) (XXI)

The energies of the OH...S=C hydrogen bond in the associated species formed by compound (XX) with compounds (XXII) and (XXIII) are 6.5 kcal mole$^{-1}$ ($\Delta\nu$ = 445 cm$^{-1}$) and 4.6 kcal mole$^{-1}$ ($\Delta\nu$ = 290 cm$^{-1}$), while the energies of the bond of the same type in the complexes formed by compound (XXI) with compounds (XXII) and (XXIII) are 6.0 kcal mole$^{-1}$ ($\Delta\nu$ = 430 cm$^{-1}$) and 4.3 kcal mole$^{-1}$ ($\Delta\nu$ = 280 cm$^{-1}$). According to the literature[164], the bond energies in the complexes formed by phenol with alkylthioureas are 4–4.8 kcal mole$^{-1}$. Comparison of Sherry and Purcell's data[158] with those of Singh et al.[44] showed that the electron-donating capacity of sulphur increases in the sequence



This is probably associated with the increasing contribution of the electrostatic interaction to the energy of the OH...S=C hydrogen bond in the above series owing to the greater contribution of the dipolar structure in thioamides



than in thioketones.

The electron-donating capacity of sulphur in the P=S and As=S groups has been investigated by infrared spectroscopy and calorimetry in a number of studies[158-160] (Table 12). The enthalpies of formation of the hydrogen bond with phenol have shown that the electron-donating capacity of the As=S group is only slightly greater than that of the P=S group and much smaller than that of the As=O group with similar substituents.

**Table 12.** The hydrogen bond strengths and the ν(OH) band shifts in the complexes formed by phenol and fluorinated alcohols with thio-derivatives of phosphorus-containing acids, phosphine sulphides, and arsine sulphides and oxides.

| Electron donor | Δν, cm$^{-1}$ | −ΔH, kcal mole$^{-1}$ | Electron donor | Δν, cm$^{-1}$ | −ΔH, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| | $C_6H_5OH$[159] | | | $CF_3CH_2OH$[158] | |
| $(C_2H_5)_3P=S$ | 321 | 5.9 | $(C_4H_9)_3P=S$ | 273 | 4.4 |
| $(C_2H_5O)_2C_6H_5P=S$ | 261 | 5.1 | $(C_8H_{17})_3P=S$ | 272 | 4.3 |
| $(C_2H_5O)_3P=S$ | 196 | 4.6 | $(C_6H_5)_3P=S$ | 200 | — |
| $(C_2H_5S)_3P=S$ | 191 | 4.6 | | $C_6H_5OH$[160] | |
| $(C_6H_5Cl_2P=S$ | 186 | 4.3 | $(C_2H_5)_3As=S$ | 369 | 6.2 |
| | $(CF_3)_2CHOH$[158] | | $C_6H_5(C_2H_5)_2As=S$ | 343 | 5.9 |
| $(C_4H_9)_3P=S$ | 423 | 6.3 | $(C_6H_5)_2C_2H_5As=S$ | 321 | 5.7 |
| $(C_8H_{17})_3P=S$ | 414 | 5.9 | $(C_6H_5)_3As=S$ | 296 | 5.5 |
| $C_6H_5)_3P=S$ | 312 | 4.6 | $(C_6H_5)_3P=S$ | 241 | 4.9 |
| | | | $C_6H_5(C_2H_5)_2As=O$ | 711 | 8.6 |

The empirical parameters $E_B$ and $C_B$ [see Eqn. (7)] for the sulphur-containing bases investigated have been calculated[158]. As was to be expected, the parameters found for S donors differ significantly from the corresponding characteristics of "hard" oxygen- and nitrogen-containing donors, namely in the case of sulphur the parameters $C_B$ are greater and the $E_B$ are smaller. This implies that the covalent contribution to the strength of the hydrogen bond involving an S donor plays a decisive role. This conclusion is consistent with results[136] according to which S donors are classified as "soft" bases.

## III. VARIATION OF THE PROTON- AND ELECTRON-DONATING CAPACITIES IN SERIES OF COMPOUNDS OF THE SAME TYPE FORMED BY GROUP V–VII ELEMENTS

### 1. GROUP V ELEMENTS

The electron-donating properties in the hydrogen bonds formed by compounds of Group V elements, with the exception of nitrogen, have been very little investigated. Nevertheless, the available literature data[165,166] make it possible to trace certain regularities in the variation of the electron-donating capacities of analogous nitrogen, phosphorus, arsenic and antimony compounds. In the studies quoted, the association of pyrrole, phenol, and methanol with the electron donors $(C_2H_5)_3Y$ (Y = N, P, As, or Sb) was investigated and it was found that all the compounds form hydrogen bonds with the proton donors. Antimony and even arsenic exhibit semimetallic properties, but form hydrogen bonds nevertheless. There is probably a significant contribution of the *p* or *d* orbitals to that of the free electron pair of antimony, imparting to the latter directional properties, which are required in the formation of the hydrogen bond.

According to the data in Table 13, the electron-donating capacity in the N–H...Y (Y = N, P, As, or Sb) hydrogen bond decreases in the sequence $(C_2H_5)_3N > (C_2H_5)_3P > (C_2H_5)_3As > (C_2H_5)_3Sb$. This might have been expected, since the fundamental properties change in the same direction[167] and the formation of the hydrogen bond is the first stage in the acid-base interaction with proton transfer[168].

**Table 13.** Characteristics of the hydrogen bonds formed by pyrrole and phenol with $R_3Y$.

| Y | $\Delta\nu$, cm$^{-1}$ | $K^{30°}$, litre mole$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|
| | | Pyrrole, N–H...Y | | |
| N | 310 | — | — | — |
| P* | 216 | 1.53 | — | — |
| P | 166 | 0.89 | 3.0 | 10.0 |
| As | 101 | 0.37 | 2.5 | 10.0 |
| Sb | 65 | 0.23 | — | — |
| | | Phenol, O–H...Y | | |
| N | 556 | 90.00 | 9.1 | — |
| P | 333 | 4.50 | 4.3 | 11.0 |
| As | 219 | 1.01 | 3.4 | 11.0 |
| Sb | 155 | 0.43 | 2.9 | 11.0 |

*R = n-$C_4H_9$, in the remaining cases R = $C_2H_5$.

The significant discrepancy between the very large change in basicity and the relatively small change in electron-donating capacity in the $R_3Y$ series has been discussed[165]. For example, the difference between the basicities of $(C_2H_5)_3P$ and $(C_2H_5)_3As$ amounts to 5 p$K$ units, while the association constant changes only by a factor of 2.5. There exist two alternative explanations of the variation of the basicity in the series of analogous compounds of the elements belonging to the same Group: either in terms of the Gibbs rehybridisation theory[169] or in terms of the theory of electron correlation repulsion[167]. Both theories are based on allowance for the electronic configuration of the central atom (the reaction centre of the base) in the proton transfer. According to Gurka and Taft's results[170], the formation of the hydrogen bond can be regarded as only partial proton transfer, since the electronic configuration of the central atom changes in this process to a much lesser extent than on protonation. Hence follows the small change in electron-donating capacity on formation of the hydrogen bond.

As will be seen below, there are other explanations in the literature of the insignificant change in electron-donating capacity on transition from, say, phosphorus to arsenic or from sulphur to selenium, based, in particular, on the examination of the contributions of various mechanisms to the redistribution of electron density between the proton donor and electron donor on complex formation.

The nature of the changes in electron-donating capacity in the O–H...Y[166] and N–H...Y[165] (Y = N, P, As, or Sb) bonds is the same. The values of $\Delta\nu$, $K$, and $\Delta H$ (Table 13) show that the electron-donating capacity of Y in the O–H...Y bond diminishes in the sequence N > P > As > Sb. The greatest changes in the above quantities occur in the transition from nitrogen to phosphorus. Arsenic and antimony are characterised by similar electron-donating capacities. This may be associated with the increase of the polarisability of the orbital of the free electron pair on passing to heavier elements in Group V, which leads to an increase of the contribution of dispersion forces to the energy of the hydrogen bond. At the same time the charge-transfer interaction may be intensified, since the ionisation potential of Y diminishes.

It is noteworthy that the Badger–Bauer rule[171] holds for the A–H...Y hydrogen bonds (Y is a Group V element), since there is a linear correlation between $\Delta\nu$ and $\Delta H$.

The proton-donating capacities of compounds with X–H (X = N, P, or As) groups have been investigated only for X = N. There have been no direct experimental studies on the properties of the X–H...B hydrogen bond with X = P or As. There are only indirect data which suggest that, on passing from amines to phosphines or from ammonium to phosphonium compounds, the proton-donating capacity of X–H falls. Such studies include those of the rapid proton exchange between trimethylphosphonium ions and water[172] or between dimethylphenylphosphonium ions and methanol[173]. The results of these studies have been examined in detail in a review[55] and compared with those for the analogous reactions involving N–H bonds.

A sharp decrease of proton-donating capacity on passing from N–H to P–H is indicated by the *ab initio* calculations[27] of the energy of the hydrogen bond in the ammonia and phosphine complexes with the hydrides of the electronegative elements in the Second and Third Periods. For example, $-\Delta H$ = 4.07 kcal mole$^{-1}$ for the complex $H_2N$–H...$OH_2$, while for the complex $H_2P$–H...$OH_2$, $-\Delta H$ is only 1.06 kcal mole$^{-1}$.

The problem of the type of change in proton-donating capacity on passing from P–H to As–H still remains unresolved.

### 2. GROUP VI ELEMENTS

The first quantitative studies on the relative electron-donating capacities in the hydrogen bonds formed by analogous compounds of Group VI elements include those of West and coworkers[174,175], where the thermodynamic characteristics of the hydrogen bonds between phenol and the electron donors $(n\text{-}C_4H_9)_2Y$ or $(t\text{-}C_4H_9)_2Y$ (Y = O, S, Se or Te) were determined by infrared spectroscopy. It

was shown for the first time that the atoms of heavy Group VI elements behave as electron donors in the formation of the OH...Se and OH...Te hydrogen bonds.

The replacement of oxygen by sulphur or selenium lowers significantly the strength of the hydrogen bond with phenol (Table 14). The maximum difference between the values of $\Delta H$ is observed on passing from oxygen to sulphur.

Table 14. Characteristics of the hydrogen bonds between phenol and dibutyl chalcogenides $R_2Y$[175] (the results of West et al.[174] are given in brackets).

| Y | $\Delta\nu$, cm$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|
| O | 278 | 5.71 (5.98) | 15.5 (11.8) |
| S | 254 | 4.19 (4.26) | 13.5 (9.0) |
| Se | 240 | 3.69 (3.72) | 14.9 (7.6) |
| Te | 220 | — | — |
| O* | — | 7.31 | 22.0 |
| S* | — | 4.87 | 12.2 |

*R = t-$C_4H_9$, in the remaining cases R = n-$C_4H_9$.

It is striking that the values of $\Delta H$ found by West and coworkers[174,175] are virtually the same, while the values of $\Delta S$ diverge significantly. According to Pimentel and McClellan[1], values of $-\Delta S$ in the range 8–12 e.u. are the most probable for hydrogen bonds having average energies between 4 and 6 kcal mole$^{-1}$. The values of $\Delta S$ quoted in the second study by West et al.[175] are apparently too low (i.e. their absolute values are too high), while the earlier results[174] are more correct. The measured values of $\Delta\nu$ agree with the results of later investigations[176].

Table 15. The spectroscopic and thermodynamic characteristics of the hydrogen bonds formed by phenol and indole with diethyl chalcogenides $(C_2H_5)_2Y$.

| Y | $\Delta\nu$, cm$^{-1}$ | $\Delta k/k$ | $K^{40°}$, litre mole$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|---|
| | | Phenol, O-H...Y | | | |
| O | 274 | 0.146 | 4.50 | 5.63 | 14.9 |
| S | 251 | 0.134 | 0.80 | 3.35 | 11.1 |
| Se | 236 | 0.126 | 0.62 | 3.15 | 11.1 |
| Te | 213 | 0.114 | 0.50 | — | — |
| | | Indole, N-H...Y | | | |
| O | 155 | 0.860 | 1.72 | — | — |
| S | 136 | 0.760 | 0.72 | — | — |
| Se | 132 | 0.740 | 0.69 | — | — |
| Te | 130 | 0.730 | 0.48 | — | — |

Note. $\Delta k/k \simeq 2\Delta\nu/\nu_0$ is the relative change in the force constant of the O–H or N–H bond on formation of the hydrogen bond[178].

The hydrogen bonds formed by phenol and indole with diethyl ether and its sulphur, selenium and tellurium analogues have been investigated by NMR and infrared spectroscopy[177]. It was found that the N–H group in indole and the O–H group in phenol form hydrogen bonds not only with oxygen and sulphur but also with selenium and tellurium. Chojnowski and Brandt[177] attempted to analyse the results (Table 15) in order to determine which type of interaction—electrostatic or charge-transfer—makes the main contribution to the energy of the hydrogen bond. It was suggested that the contribution of the electrostatic interaction to the A–H...$Y(C_2H_5)_2$ hydrogen bonds (A–H is a constant moiety and Y = O, S, Se or Te) should decrease on passing from oxygen to tellurium, since the negative charge on the electron-donating atom diminishes in the same sequence, but the contribution of charge transfer to the overall bond energy should then increase, since the ionisation potential of Y diminishes.

Table 15 shows that all the characteristics of the complex-formation reactions ($\Delta\nu$, $\Delta k/k$, $K$, and $\Delta H$) decreases from oxygen to tellurium. Consequently the electron-donating capacity of Y in the hydrogen bond diminishes in the sequence O > S > Se > Te.

Since $\Delta k/k \simeq b^2$, where $b$ is the coefficient defining the contribution of the state with electron transfer to the overall wave function of the complex[179,180], i.e.

$$\psi = a\varphi(AB) + b\varphi(A^-B^+), \qquad (8)$$

the observed decrease of $\Delta k/k$ and hence of the coefficient $b$ [Eqn. (8)] from oxygen to tellurium implies a decrease of the contribution to the overall energy of the hydrogen bond due to the charge-transfer interaction. It is believed[177] that the interaction of this type is not of decisive importance in the formation of hydrogen bonds, since the increase of the H...Y bond length from oxygen to tellurium causes a greater decrease of its strength than the postulated increased influence of charge transfer on $\Delta H$ as the ionisation potential of Y diminishes[181].

According to Pogorelyi et al.,[182] butyl chalcogenides form hydrogen bonds not only with the proton-donating OH and NH groups but also with the mercapto-group of thiophenol. As was to be expected, the strength of the SH...Se and SH...Te bonds is lower than that of the OH...Se and OH...Te bonds. The values of $\Delta H$ for the complexes investigated (Table 16) diminish in the sequence O > S > Se > Te.

Table 16. The thermodynamic parameters of the hydrogen bonds formed by 2,6-di-t-butylphenyl (ArOH) and thiophenol with di-n-butyl chalcogenides $(n\text{-}C_4H_9)_2Y$.

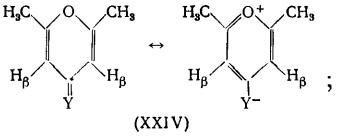
| Y | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|
| | $C_6H_5SH$ | | ArOH | |
| O | 2.7 | 10.3 | 3.8 | 13.2 |
| S | 2.4 | 8.1 | 3.3 | 11.7 |
| Se | 2.3 | 8.1 | 3.3 | 12.0 |
| Te | 2.1 | 7.9 | 3.1 | 12.2 |

The observed[175-177,182] decrease of the electron-donating capacity of Group VI elements with increase of $n$ (the principal quantum number of the orbital of the free electron pair of Y) is probably an indication that the main contribution to the energy of the A–H...Y hydrogen bond (Y = O, S, Se, or Te) comes from the redistribution of the charge owing to the overlapping of the 1$s$ orbital of the bridging hydrogen atom with the $np\sigma$ orbital of Y.[181] With

increase of $n$, the $p$ electrons become more diffuse, and their orbital density decreases, with a consequent decrease of the capacity of the corresponding orbitals for overlapping and there is an appreciable intensification of the repulsion forces between A and Y due to the inner electrons of Y.

However, the above treatment does not rule out another explanation—the decrease of $\Delta H$ in the sequence O > S > Se > Te may be caused by the weakening of the electrostatic interaction, since the negative charge diminishes from oxygen to tellurium.

In this connection, the results of a study of hydrogen bonds involving 2,6-dimethyl-4-pyrone and its thio- and seleno-analogues are of interest[183-185]:



(XXIV)

Y=O, S, or Se .

Compounds of the type of the pyrone (**XXIV**) differ from dialkyl chalcogenides by the presence of an appreciable negative charge, localised on the electron-donating centre—the exocyclic oxygen, sulphur, or selenium atom[184], which may affect the relative contributions of different types of interactions to the hydrogen bond energy.

Table 17 shows that the results obtained by the NMR[185] and infrared spectroscopic[184] methods agree satisfactorily. For both phenol and methanol, the strength of the hydrogen bond decreases in the sequence pyrone > thiopyrone > selenopyrone. In conformity with its greater proton-donating capacity, phenol forms more stable complexes than methanol.

Table 17. The spectroscopic and thermodynamic characteristics of the hydrogen bonds in the association complexes of 2,6-dimethyl-4-pyrone and its thio- and seleno-analogues with methanol and phenol.

| Proton donor | $\tau_0$, p.p.m. | $\tau_C$, p.p.m. | $K^{40°}$, litre mole$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|---|
| | | Pyrone, OH...O | | | |
| $CH_3OH$ | 4.15 | 3.87 | 4.3 | 4.8 | 12.1 |
| $C_6H_5OH$ | 4.15 | 3.76 | 7.4 | 5.5* | 10.5* |
| | | Thiopyrone, OH...S | | | |
| $CH_3OH$ | 3.26 | 3.07 | 0.9 | 3.6 | 11.6 |
| $C_6H_5OH$ | — | — | — | 4.8* | 4.5* |
| | | Selenopyrone, OH...Se | | | |
| $CH_3OH$ | 2.89 | 2.67 | 1.0 | 3.1 | 9.7 |
| $C_6H_5OH$ | — | — | — | 3.9* | 4.8* |

Note. $\tau_0$ and $\tau_C$ are the chemical shifts of the $-H\beta$ protons of the pyrone derivatives investigated in the monomer and complex respectively.
*Infrared spectroscopy; NMR was used in the remaining cases.

The dependence on $n$ of $\Delta H$ for the hydrogen bonds between different proton donors and bases where the electron-donating centres are Group VI elements is similar for the pyrones (**XXIV**) and dialkyl chalcogenides. The strength of the hydrogen bond and hence the electron-donating capacity decrease with increase of $n$. The present author believes that these data demonstrate that the mechanism of the redistribution of electron density owing to charge transfer from the highest occupied orbital of the electron donor to the antibonding $\sigma$ orbital of the A–H bond does not play a decisive role in the formation of the hydrogen bond between the atoms of Group VI elements, regardless of the structure of the electron donor molecule.

Thus the electron-donating properties of Group VI elements are determined mainly by the overlapping between the 1$s$ (H) and $np$ (Y) orbitals. This conclusion is confirmed by the correlation between the strength of the hydrogen bonds formed by ethers and sulphides with the integral for the overlap of the orbital of the $np$ electrons of the oxygen and sulphur atoms with the 1$s$ orbital of the bridging hydrogen atom[186].

Together with the redistribution of the charge via the orbital overlapping mechanism, there is also a change in the contribution to $\Delta H$ by the electrostatic interaction. The negative charge on the heteroatom decreases approximately by a factor of two on passing from oxygen to tellurium in dialkyl chalcogenides[177]. On the other hand, in pyrones the negative charge increases somewhat when oxygen is replaced by sulphur[187] and possibly by selenium. This does not, however, lead to an increase of $\Delta H$ in the above series as a result of the increasing contribution of the electrostatic interaction, probably because of the increase of the atomic radius of Y.

Egorochkin et al.[188] inferred a change in the electron-donating capacity of chalcogens in the compounds $[(C_2H_5)_3M]_2Y$ (M = Si, Ge or Sn) from the value of $\Delta\nu$(C–D) i.e. from the shift of the C–D band of deuterochloroform on complex formation. According to $\Delta\nu$ measurements, the electron-donating capacity of Y in the $[(C_2H_5)_3Si]_2Y$ series diminishes in the sequence Te > Se > S > O, which is the exact reverse of the series quoted above for chalcogen–carbon compounds. In the series with M = Ge or Sn, the general sequence in terms of decreasing electron-donating capacity, i.e. O > Te > Se > S, also differs from the series for carbon compounds. According to the authors[188], the complete or partial inversion of the electron-donating capacity series for chalcogens on passing from carbon compounds to compounds of its electronic analogues can be accounted for by the effects of the $p\pi - d\pi$ conjugation between M and Y, which leads to a decrease of the electron-donating capacity of Y. The capacity of chalcogens for $p\pi - d\pi$ conjugation with the elements of the carbon subgroup diminishes in the sequence O > S > Se > Te and the capacity of Group IV elements for such conjugation varies in the sequence Si > Ge > Sn. If this is the case, then the electron-donating capacity of oxygen linked to silicon should diminish to the greatest extent owing to the $p\pi - d\pi$ conjugation.

Table 18. The spectroscopic and thermodynamic characteristics of the hydrogen bonds formed by 2,6-di-t-butylphenol (ArOH), thiophenol, and selenophenol with pyridine[195].

| Proton donor | Bond | $\tau_0$, p.p.m. | $\Delta\tau$, p.p.m. | $K^{40°}$, (mole fraction)$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|---|---|
| ArOH | O—H ... N | 5.17 | 3.20 | 3.0 | 5.0 | 14 |
| PhSH | S—H ... N | 6.85 | 3.12 | 1.2 | 3.2 | 10 |
| PhSeH | Se—H ... N | 8.62 | 4.42 | 2.5 | 3.4 | 9 |

The present author believes that the decrease of the electron-donating capacity of $(R_3M)_2Y$ on replacement of, say, M = C by M = Si with Y constant can be accounted for with the aid of the concept of the $p_\pi - d_\pi$ conjugation. On the other hand, the series based on the variation of the electron-donating capacity of Y for different M proposed by Egorochkin et al.[188] and their treatment appear to be doubtful. Firstly, these series have been established only on the basis of the $\Delta\nu$(C–D), which reflect only the change in the strength of the C–D bond on complex formation and may not be correlated with the energy of the hydrogen bond (for a more detailed treatment, see below). For this reason, the basicity series can be established reliably only by measuring the thermodynamic characteristics of the hydrogen bond. Furthermore, the series proposed by Egorochkin et al.[188] conflict with other data[189,190] for hydrogen bonds involving the compounds $R_3P{=}Y$ (Y = O, S, Se or Te). The latter studies established on the basis of determinations of $\Delta H$ that the sequence based on the variation of the electron-donating capacity of chalcogens linked to phosphorus agrees fully with the corresponding series for carbon compounds, i.e. O > S > Se > Te. We may note that the effect of the $p_\pi - d_\pi$ conjugation in the P=Y bond should be greater than in the Si–Y bond, since the increase of nuclear charge from silicon to phosphorus causes a contraction of the atomic *d* orbitals of phosphorus and this leads in its turn to an improvement of the conditions for $d-p$ overlapping[191]. Thus, there are at present no adequate grounds for the assumption that the sequence based on the variation of the electron-donating capacity in the hydrogen bonds of chalcogens in their compounds with silicon is different from that in compounds with carbon or phosphorus.

The situation is different in rigid systems, such as, for example, the intramolecular hydrogen bond. We examined above studies from which it follows that, on formation of hydrogen-bonded chelates, sulphur can behave as a more effective electron donor than oxygen. However, there are insufficient data to extend this series to selenium compounds let alone tellurium compounds.

The intramolecular hydrogen bond in 3-methyl-1-phenyl-4-phenylaminomethylene-5-pyrazolone and in its thio- and seleno-analogues has been investigated by NMR[192]. The measured values of $\tau_{NH...Y}$ and $J_{NH-CH}$ (the spin–spin interaction constants) suggest[192] that the strength of the N–H...Y (Y = O, S, or Se) intramolecular hydrogen bond, giving rise to six-membered conjugated chelate rings, increases in the sequence O < S < Se. The construction of planar models enabled the authors of the above study to conclude that the geometry of the selenium derivative is more favourable from the standpoint of the formation of a hydrogen bond than that of the oxygen and sulphur analogues. The model for selenopyrazolone demonstrates an almost linear disposition of atoms in the N–H...Se fragment and hence the most effective overlapping of the 1*s* orbital of the hydrogen atom with the pure *p* orbital of the lone electron pair of selenium. Possibly the increase of the strength of the intramolecular hydrogen bond in the sequence O < S < Se is also due to the molecular geometry, which is more favourable for the formation of the bond.

The strength of the intermolecular hydrogen bond in the cyclic dimers of 2-pyridone and its thio- and seleno-analogues increases, as expected, in the opposite sequence: O > S > Se.[193] Planar models of these complexes show that the ring strain in the dimer increases on replacement of oxygen by sulphur and even more so on its replacement by selenium.

The proton-donating capacity in the X–H...B (X = O, S, Se, or Te) hydrogen bond in chalcogen compounds has been very little studied. It has only been firmly established (see, for example, Zuika and Bankovskii[12]) that, on passing from oxygen compounds to the analogous sulphur compounds the proton-donating capacity of X–H is sharply reduced. This is associated with the increase of the overlap integral $\int_{X-H} = \psi_{1s(H)}.\psi_{np(X)}.d\tau$ and of electron density at the bridging hydrogen atom when X = O is replaced by X = S, which entails a decrease of the residual capacity for overlapping of the 1*s*(H) orbital[61,194]. Furthermore, the replacement of O by S leads to a decrease of the dipole moment of the X–H bond and hence to a decrease of the contribution of the electrostatic interaction to the overall energy of the hydrogen bond. When these explanations are extended to selenium and tellurium compounds, one may expect that the proton-donating capacity will decrease in the sequence OH > SH > SeH > TeH. However, no experimental confirmation of this hypothesis has so far been obtained. There has been only one relevant study[195] where the hydrogen bonds formed by 2,6-di-t-butylphenol, thiophenol, and selenophenol with pyridine were investigated. It was found, contrary to expectation, that selenophenol forms with pyridine an even stronger hydrogen bond than does thiophenol, although, judging from the values of $\tau_0$, the electron density at the hydrogen atom in the X–H bond increases monotonically in the sequence OH < SH < SeH (Table 18).

The present author suggests that the observed sequence based on the variation of the proton-donating capacity, namely OH > SH < SeH, can be accounted for on the basis of the following postulates. According to Lippincot and Schroeder[196], the heat of formation of the X–H...B hydrogen bond can be represented by the sum

$$\Delta H = Q_{X-H} + Q_{X\ldots B} + Q_{H\ldots B},$$

where $Q_{H...B}$ is the exothermic heat of formation of the new bond, $Q_{X-H}$ the endothermic heat of extension of the X–H bond, and $Q_{X...B}$ the endothermic heat of interelectron repulsion arising when the atoms X and B approach one another. On passing from oxygen to sulphur and to selenium, $Q_{H...B}$ falls, while $Q_{X...B}$ increases for the reasons described above. These changes reduce $\Delta H$ in the above sequence. Since the strength of the X–H chemical bond diminishes on passing from oxygen to selenium, $Q_{X-H}$ decreases in the same direction, which may result, depending on the magnitude of the effect, in an increase of $\Delta H$. The influence of the weakening of the X–H bond formed by the proton donor on $\Delta H$ is probably particularly important for strong ionising electron donors, such as, for example, nitrogen-containing bases, since partial or complete proton transfer

$$X{-}H\ldots N \rightleftarrows X\ldots H\ldots N \rightleftarrows X^-\ldots H{-}N^+,$$

accompanied by a significant change in the length of the X–H bond, is most probable in such systems. Whereas the change in $\Delta H$ on passing from phenol to thiophenol is probably determined mainly by the changes in $Q_{H...B}$ and $Q_{X...B}$, the influence of the low strength of the Se–H bond on $\Delta H$ becomes appreciable for selenophenol. Such joint influences of all three effects on $\Delta H$ can in fact explain why thiophenol and selenophenol form hydrogen bonds of similar strength with the same electron donor.

### 3. GROUP VII ELEMENTS

In early studies[197-200], the changes in electron-donating capacity in the hydrogen bonds of halogen compounds were inferred from the values of $\Delta\nu$(OH) for phenol or methanol. It was assumed that the Badger–Bauer rule[171] is valid for the O–H...Y system for any Y. Measurements of $\Delta\nu$(OH) showed that the electron-donating properties are enhanced in the sequence F < Cl < Br < I. However, analysis of the thermodynamic characteristics of hydrogen bonds of different types showed[1,201] that the Badger–Bauer rule is applicable only to a limited range of related compounds.

The data in Table 19 are completely inconsistent with the earlier conclusion concerning the sequence of the changes in the proton-accepting capacity of the covalently bound halogen. Quantities such as $-\Delta H$ and $-\Delta F$ (the free energy change) decrease in the sequence F > Cl > Br > I, while the values of $\Delta\nu$ vary in the opposite sequence. According to the literature[201,202], $\Delta F$ for the intramolecular hydrogen bond in 2,6-dihalogenophenols decreases in the sequence Cl > Br > F > I. However, the results of Baker and Kaeding[201] and Richards and Walker[202], on the one hand, and West et al.,[174] on the other, are not inconsistent, since mainly steric factors influence the changes in $\Delta F$ in systems with intramolecular hydrogen bonds.

Table 19. The thermodynamic and spectroscopic characteristics of the hydrogen bonds formed by phenol with cyclohexyl halides[174].

| Electron donor | $\Delta\nu$, cm$^{-1}$ | $-\Delta H$, kcal mole$^{-1}$ | $-\Delta F^{25°}$, kcal mole$^{-1}$ | $-\Delta S$, e.u. |
|---|---|---|---|---|
| Cyclohexyl fluoride | 53 | 3.13 | 1.31 | 6.1 |
| Cyclohexyl chloride | 66 | 2.21 | 0.87 | 4.5 |
| Cyclohexyl bromide | 82 | 2.05 | 0.85 | 4.0 |
| Cyclohexyl iodide | 86 | 1.72 | 0.82 | 3.0 |

West et al.[174] put forward a qualitative explanation of the absence of correlation between $\Delta H$ and $\Delta\nu$ in many instances. $\Delta H$ is known to reflect the total energy of the A–H...Y–R interaction, i.e. the H...Y bond strength; $\Delta\nu$ represents a measure of the weakening of the A–H bond only. Consequently, for a constant proton donor A–H, $\Delta\nu$ may be correlated with $\Delta H$ for small changes in the electron donor molecule, i.e. in R, but such correlation need not necessarily persist when Y is altered or even when the degree of hybridisation of the electrons in Y is changed.

The results of West et al.[174] were confirmed by NMR and infrared spectroscopic measurements[203] of the association constants of phenol with n-hexyl fluoride, n-butyl chloride, n-butyl bromide, and n-butyl iodide. Although there are certain quantitative discrepancies between the values of $K$ determined by different methods, nevertheless the sequence based on the variation of the proton-accepting capacity of alkyl halides (F > Cl > Br > I) remains unchanged. The values of $\Delta H$ for the association of phenol with $C_6H_{11}F$ (0.9 kcal mole$^{-1}$) and $C_6H_{11}Cl$ (0.5 kcal mole$^{-1}$), which were determined calorimetrically[204], proved to be smaller by a factor of 3–4 than the $\Delta H$ for the same systems calculated from infrared spectroscopic data[174]. For the O–H...X (X = F or Cl) bonds, the absolute value of $\Delta H < 1$ kcal mole$^{-1}$ should probably be regarded as too low, since a weaker proton donor (chloroform) forms with carbon tetrachloride C–H...Cl bonds having $-\Delta H \simeq 1.5$ kcal mole$^{-1}$.[205]

The intramolecular O–H...X (X = halogen) bonds in *o*-substituted halogenophenols and the influence of these bonds on the position of the *cis–trans* equilibrium have been studied in a number of investigations[206-210]. The values of $\Delta H$ obtained[210] show that the strength of the intramolecular hydrogen bond decreases in the sequence F (1.63) = Cl (1.63) > Br (1.53) > I (1.32) for the gas phase, and in the sequence Cl (1.62) > Br(1.57) > I (1.45) ≥ F (1.44) for cyclohexane solutions. According to Tiensung Lin and Fishman[209], the values of $\Delta H$ for the gas phase are approximately twice as large, although a similar sequence persists: Cl (3.41) > Br (3.13) > I (2.75). The behaviour of fluorine[210], which forms virtually the strongest hydrogen bond in the gas phase and the weakest in solution, is the most remarkable. According to Carlson and Fateley[210], the sequence of halogens based on the variation of their electron-donating capacity in the gas phase is consistent with the sequence which would be expected from the size and electronegativities of the halogens. On the basis of its electronegativity alone, fluorine should form a stronger bond than chlorine, but the smaller size of the fluorine atom causes some decrease in bond strength, since the OH group is unable to approach sufficiently closely for optimum overlapping of the 1*s*(H) and 2*p*(F) orbitals. In inert solvents, *o*-fluorophenol forms the least stable intramolecular hydrogen bond, which indicates the highest *trans* : *cis* ratio. The *trans*-isomer is probably stabilised in this case by the preferential formation of intermolecular hydrogen bonds, since the electron-donating capacity of fluorine is a maximum in the series of halogens.

The relative proton-donating capacities of hydrogen halides have been investigated[211-214]. It was found for solutions in aromatic hydrocarbons that the relative shift $\Delta\nu/\nu$ of the X–H bond on formation of a hydrogen bond with a standard electron donor diminishes from HF to HI.[211] The ratio of the band intensities of the bound and free H–X molecules increases in the same sequence. On this basis, it was concluded that the stability of the hydrogen-bonded complexes is determined by the acidity of HHal and that the relative band shift does not characterise the stability of this complex. A similar claim was made by workers[212] who measured the frequencies of the complexes formed by HF, HCl and HBr with dioxan. However, other results[213,214], obtained from measurements of $\Delta H$ for the hydrogen bonds between HX and benzene, carbon tetrachloride, ketones, and ethers in carbon tetrachloride solutions and in the gas phase, cast doubt on these conclusions[211,212]. It was found that the energy of the hydrogen bond formed by HX with all the electron donors enumerated above is a maximum for HF, decreasing on passing to HCl and still more on passing to HBr. For example, in the case of acetone $-\Delta H$ for HF, HCl, and HBr is 8.4, 6.1, and 5.7 kcal mole$^{-1}$ respectively. The energy of the X–H... B hydrogen bond and the relative frequency shift were found to vary in parallel.

Thus the strength of the hydrogen bond formed by the proton donors X–H (X = F, Cl, Br, or I) with a specified acceptor decreases with increasing acidity of the hydrogen halide, which is probably due to the decrease of the residual capacity for overlapping of the 1*s*(H) orbital as the electronegativity of the halogen diminishes. It is noteworthy that, according to Shchepkin[214], the maximum change in the energy of the X–H... B bond occurs on passing from HF to HCl. When HCl is replaced by HBr, the change is much smaller. In the series of proton

donors PhXH (X = O, S, or Se) the small differences between the $\Delta H$ for the heavy atoms can probably be explained by the weakening of the X–H bond, which is said[196] to compensate to some extent the decrease in $\Delta H$ owing to the reduction of the residual capacity for overlapping of the 1*s*(H) orbital in the same direction.

Thus the electron-donating capacity of R–X and the proton-donating capacity of X–H decrease in the sequence F > Cl > Br > I, the maximum difference between these properties being observed on passing from fluorine to chlorine.

## IV. CERTAIN GENERAL PROBLEMS OF THE HYDROGEN BOND

The sum total of the data discussed in previous sections makes it possible to establish certain general regularities in the variation of the proton- and electron-donating capacities in the hydrogen bonds formed by analogous compounds of Group V–VII elements. An attempt will also be made to determine wherever possible the factors which play a decisive role in the variation of the properties of the A–H...Y, X–H...B, and X–H...Y hydrogen bonds (where A–H and B are standard proton and electron donors and X and Y are a series of elements belonging to a single Group or Period).

For the A–H...Y hydrogen bonds, the electron-donating capacity of Y, belonging to the given Group, diminishes on passing to heavier elements: N > P > As > Sb; O > S > Se > Te; F > Cl > Br > I. The greatest differences between the electron-donating capacities are observed on passing from the elements in the Second Period to those in the Third Period, i.e. between nitrogen and phosphorus, between oxygen and sulphur, and between fluorine and chlorine, while for heavier elements the differences are much less pronounced. We may note that even elements such as antimony, tellurium, and iodine, which are of the metallic or semimetallic type, are capable of forming hydrogen bonds as electron donors. Proton-accepting capacity can probably be regarded as virtually the exclusive property of the free electron pair and there is at present no reason to deny the possession of this property by still heavier atoms such as those of bismuth, polonium, and astatine.

According to modern ideas[10,181], the main contribution to the formation of the hydrogen bond comes from the electrostatic interaction, the repulsion of electron clouds, and the redistribution of electron density. The latter involves the overlapping of the 1*s*(H) and *np*(Y) orbitals and charge transfer from the highest occupied orbital of the proton acceptor Y to the antibonding $\sigma$ orbital of the proton donor A–H. The data obtained for the decrease of the electron-donating capacity in Groups V–VII on passing to heavier elements suggest that the main contribution to the hydrogen bond energy is made by the overlapping of the 1*s*(H) and *np*(Y) orbitals. With increase of $n$, $p$ electrons become more diffuse and their orbital density diminishes; together with the interelectron repulsion, which increases in the same direction, this causes a decrease of the capacity for overlapping of the *np*(Y) orbital. From the standpoint of the model of charge-transfer complexes, the opposite behaviour would be observed—the electron-donating capacity of Y should increase with increase of $n$, since this entails a diminution of the ionisation potential.

We may note that the role of charge transfer in the hydrogen bond is the most controversial problem. This model is attractive, because it involves the inclusion of hydrogen-bonded complexes in the general class of donor–acceptor complexes. However, the correlation between the ionisation potentials of Y and the thermodynamic characteristics of association by hydrogen bonding is limited[1]. The most important experimental argument against the charge-transfer model of the hydrogen bond is the absence of the charge-transfer band from the spectra of hydrogen-bonded complexes[215]. Analysis of the infrared spectra with the aid of the vibronic theory[178,216], based on Mulliken's ideas[180], also showed[166] that charge transfer does not play a decisive role in the formation of the hydrogen bond by the elements of the same Group as electron donors.

As already stated, the effect of charge transfer may reduce merely to a decrease of the difference between the heats of association of neighbouring members of the Group as the ionisation potential is reduced. The increase of the polarisability of the electrons in Y with increase of $n$, resulting in an increase of the contribution of dispersion interaction, may play the same role.

The fastest decrease of proton-accepting capacity with increasing atomic number has been observed in a series of electron donors belonging to Group V. Chojnowski[166] explains this by the fact that the greatest differences between the hybridisations of the free electron pair orbital are characteristic of Group V elements. This follows from a comparison of the valence angles in the corresponding alkyl derivatives: 109° for $(CH_3)_3N$, 100° for $(CH_3)_3P$, and 96°C for $(CH_3)_3As$ in Group V and 111° for $(CH_3)_2O$ and 105°C for $(CH_3)_2S$ in Group VI. These data show that the increase of the amount of $s$ character of the free electron pair orbital, resulting in a decrease of its capacity for overlapping[217,218], is faster in Group V than in Group VI. If one assumes by analogy that the amount of $s$ character increases at the lowest rate in Group VII, one can understand the small change in electron-donating capacity on passing from chlorine to bromine and iodine.

We shall now consider how the electron-donating capacity changes in the A–H...Y hydrogen bonds for Y belonging to different Groups in the same Period. It was established previously[1] that the electron-donating capacity of the elements in the Second Period decreases in the sequence N > O > F, i.e. with increase of the electronegativity of Y. The data in Tables 13–15 and 19 suggest that this tendency in the variation of the electron-donating capacity is maintained in the Third, Fourth, and possibly Fifth Periods (P > S > Cl; As > Se > Br; Sb > Te > I), although the differences for neighbouring numbers of the series gradually diminish with increasing number of the Period. Calculations of the hydrogen bond energy[27] and the H...Y bond populations[219] showed, in agreement with experimental data, that the electron-donating capacity of Y decreases in the sequences P > S > Cl and Se > Br.

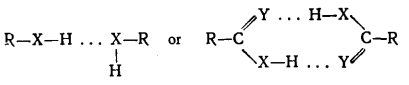
Thus the available data suggest that the electron-donating capacity of Group V–VII elements in the same Period decreases with increasing electronegativity, in contrast to the series of electron donors in a single Group. Consequently the electrostatic interaction is not of decisive importance in the formation of hydrogen bonds even with "hard" bases such as oxygen and fluorine compounds. The proton-accepting capacity of the elements in a single Period is probably determined by the redistribution of charge between the molecular fragments of the complex AH...Y owing to the overlapping of the 1*s*(H) and *np*(Y) orbitals and as a result of charge transfer from the *np*(Y) orbital of the proton acceptor to the antibonding $\sigma$ orbital of the A–H bond of the proton donor. On passing from nitrogen to fluorine, from phosphorus to chlorine, etc., the number of free electron pairs of the atom Y increases,

which leads to an intensification of the interelectron repulsion [176] in A...Y and impairment of the conditions for the overlapping of the 1*s*(H) and *np*(Y) orbitals. Furthermore, the increase of the ionisation potential in the same direction hinders charge transfer to the antibonding $\sigma$ orbital of the A–H bond. The joint operation of the above factors can account for the observed decrease of the electron-donating capacity within the limits of the same Period on passing to heavier elements.

We shall now consider how the proton-donating capacity changes in the X–H...B hydrogen bond, although, as we have seen, there are very few literature data for the elements in the Third, Fourth, and Fifth Periods. Nevertheless, one can assume that, for elements of the same Group or Period, the following series based on decreasing proton-donating capacity are valid: NH > PH, OH > SH ≃ SeH, FH > ClH > BrH > IH, FH > OH > NH, and ClH > SH > PH. [27]

The proton-donating capacity of the XH group is known [2] to be determined mainly by the tendency of the H atom in this group to accept electrons from the B atom, using the residual capacity for overlapping of the 1*s*(H) orbital. This capacity should increase with decrease of the overlap integral of the X–H bond [60], i.e. with increase of the degree of dissociation of the hydrogen atom as a proton. With increase of the electronegativity of the X atom, the overlap integral for the X–H bond diminishes, which entails an increase of the proton-donating capacity of the X–H group. Furthermore, the dipole moment of the X–H bond and hence also the contribution of the electrostatic interaction to the hydrogen bond energy increase with increasing electronegativity of X. These factors are in fact responsible for the increase of the proton-donating capacity of X–H on passing to heavier elements in the Period and to lighter elements in the Group. It is noteworthy that, within the limits of the same Period, the acidity and proton-donating capacity of X–H are the same, since the X–H bond energy and the degree of dissociation of the hydrogen atom as a proton vary in opposition. On the other hand, within the limits of a single Group, the bond energy and the degree of dissociation vary in parallel, which gives rise to the inverse relation between acidity and proton-donating capacity.

We shall now consider how the properties of the hydrogen bond are affected by the simultaneous variation of the proton- and electron-donating capacities of the interacting molecules. Such a situation arises in self-association processes:



when the substituent is altered. Electron-accepting substituents, for example, increase the proton-donating capacity of the X–H group but reduce the electron-donating capacity of X or Y. The overall effect of the substituent will depend on the relative contributions of the electron donor and proton donor to the hydrogen bond energy. Three cases are possible: (a) the contribution of the electron donor is greater than that of the proton donor and the introduction of electron-donating substituents strengthens the bond; (b) the contribution of the proton donor plays a decisive role and electron-accepting substituents strengthen the hydrogen bond; (c) the increase (decrease) of the proton-donating capacity of the X–H group is compensated by the decrease (increase) of the electron-donating capacity of X or Y and the strength of the hydrogen bond should not then depend on the nature of the substituent.

Analysis of the experimental data enabled the author of this review to put forward certain hypotheses of a general type [85]. Thus it has been established that the strength of hydrogen bonds in self-associated species of substituted anilines increases following the introduction of electron-donating substituents [220]: the tendency of mercaptans towards self-association is more pronounced than that of thiophenol [15]; the degree of self-association of phenols increases in the sequence *p*-chlorophenol < *p*-fluorophenol < *p*-cresol [221] and the stability of the self-associated species increases on passing from ethyl alcohol to t-butyl alcohol [94]. All these data lead to the conclusion that, in series of compounds forming hydrogen bonds of the type NH...N, SH...S, OH...O, and probably in general "homoquantum" bonds of the type X–H...X′ (where X and X′ are atoms of elements belonging to the same Period), the variation of the hydrogen bond strength is determined mainly by the variation of the properties of the electron donor.

On the other hand, in series of compounds associated via "heteroquantum" bonds of the type X–H...Y (where X and Y are elements belonging to different Periods), the variation of the stability of the associated species is presumably determined by the variation of the properties of the atom whose electrons, involved in the formation of the hydrogen bond, are characterised by a larger principal quantum number. Thus the variation of $\Delta H$ for the S–H...O bond should be determined by the variation of the proton-donating capacity of the SH group and for the NH...P bond by the variation of the electron-donating properties of the phosphorus atom under the influence of substituents. The latter hypothesis explains the type of influence of substituents on the stability of self-associated species of thiobenzoic acids [85], the ratio of the quantities $\rho$ [Eqns. (1) and (2)] for the association of thiophenols with acetophenones [52], and the shift of the thiol–thione equilibrium [88] under the influence of substituents.

Since the influence of substituents reduces the electronic polarisation of the reaction centre of the molecule, an explanation of the essential physical features of the empirical rule which has been formulated [85] is provided by calculations, involving complete neglect of differential overlapping (CNDO/2), of the charge shifts [222] in the molecular fragments of the HSH...$OH_2$ and HOH...$SH_2$ complexes [195]. These complexes provide one of the simplest examples of "heteroquantum" hydrogen bonds. It was found that the charge shift in the $H_2O$ molecule functioning as either an electron or proton donor is zero or many times smaller than the charge shift in the $H_2S$ molecule. This can be accounted for by the fact that, on passing from oxygen to sulphur, the deformability and polarisability of the electron clouds increase. The above results show that, on formation of the "heteroquantum" hydrogen bonds SH...O and OH...S, the maximum charge shift occurs precisely in the fragments of the complex where a change in properties is stated [85] to have a decisive influence on the change in bond energy. Consequently the greater sensitivity of the energy of a "heteroquantum" hydrogen bond to changes in the properties of the atom with the higher principal quantum number of the valence electrons can be explained by the fact that the maximum charge shift on formation of the hydrogen-bonded complex occurs in the molecular fragment with this atom.

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# Vibrational Spectra of Free Radicals

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A survey of results obtained on the vibrational spectra of simple free radicals, polyatomic neutral radicals, and polyatomic radical-ions is accompanied by 141 references.

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## I. INTRODUCTION

The vigorous development of the chemistry and physics of free radicals during recent years is due to their important role as intermediate species in many chemical reactions and biological processes. Simple free radicals have been detected in the spectra of planets, comets, and stellar objects. Many problems of structural and theoretical chemistry, as well as chemical kinetics, are solved by means of free radicals. Such questions as the structure of electron shells and their modification under the influence of perturbations, the mechanisms of chemical reactions and physical processes causing magnetic relaxation of nuclei, etc. can be settled. Interest in free radicals arises also from their widespread application in many fields of science and technology. They are used as paramagnetic probes and spin labels in the physical chemistry of polymers, biophysics, and molecular biology. Stable free radicals act as inhibitors of the degradation of polymeric materials in technology. Many of them are employed in magnetometers and radio-frequency lasers.

Detailed studies have been made of the chemical properties, electron spin resonance spectra, and electronic spectra of free radicals, and their electronic structure has been calculated by quantum-chemical methods. The Nobel Prize was awarded in 1971 for a long series of investigations on the electronic spectra of simple radicals (Herzberg's monograph[1]). However, little work has been done on the vibrational spectra, which give valuable information both for identifying free radicals and for determining their electronic structure. The vibrational spectra of simple radicals have been more fully studied. Two reviews[2,3] have covered the literature on their infrared spectra up to 1971. The data given in most papers on the vibrational spectra of polyatomic radicals are fragmentary and non-systematic. Only quite recently have the first publications appeared in which the problem of interpreting vibrational spectra for several neutral and charged polyatomic radicals has been posed and more or less solved, and their force field has been estimated.

The present Review examines the literature on the vibrational spectra of neutral and charged polyatomic free radicals, as well as recent publications on the spectra of simple radicals not covered in the 1971 reviews by Andrews and by Milligan on the infrared spectra of simple radicals stabilised in neutral rigid matrices. Papers on the spectra of polyatomic radical-ions have been divided into three groups. The first comprises those with qualitative descriptions of spectra and an approximate assignment of one of two bands. The second group combines investigations on the variation of several characteristic frequencies in series of radical-ions of similar structure. The third group consists of recent papers giving an interpretation of the vibrational spectra of several stable radical-ions based on the calculation of normal vibrations, as well as an estimate of their force field and a comparison of the force constants with parameters of their electronic structure.

## II. VIBRATIONAL SPECTRA OF SIMPLE FREE RADICALS

Simple free radicals comprising a few atoms are very unstable owing to their very great chemical activity, so that the recording of their vibrational spectra presents considerable difficulties. Since their lifetime is very short ($10^{-3}$–$10^{-5}$ s), two approaches have been made to determining the vibrational spectra of such radicals: (1) the free radicals were fixed in rigid, inert matrices, which lowered their reactivity and lengthened their lifetime to such an extent that the usual instruments could be used; or (2) an infrared spectrometer having a scanning time $< 1$ ms was used. Since the production of such an instrument is a complex technical task, accomplished not long ago[4,5], the matrix isolation of free radicals has become widely used. The possibility of thereby obtaining infrared spectra of free radicals, as well as unstable molecules and ions, was demonstrated by Pimentel and his coworkers, and this method was developed and perfected in his own laboratory. Details of the method of matrix isolation have been given in the reviews[2,3], together with a discussion of procedures for obtaining simple radicals and identifying them from their spectra. In almost all the above studies the reliability of the assignment was improved by investigating every possible isotopic variety of the radicals and comparing the spectra of radicals prepared in different ways.

The reviews give results on the infrared spectra of methyl and halogenomethyl radicals, as well as radicals obtained by adding a third atom to a diatomic molecule (e.g. HCO, HalCO, HalOO, HOO), halogenated radicals (e.g. OF, OCl, CF, CCl, $NF_2$), radicals obtained by the photolysis of silane and halogenated silanes, and several others. Much of the work covered in the reviews was in a stage of further development, as is indicated by the appearance of communications on continued investigations of the infrared spectra of the radicals mentioned[2,3]. Thus a higher concentration of the $HO_2$ radical has been obtained[6] than in previous work. The spectra of four compounds of

formula $DO_2$ differing in isotopic composition with respect to oxygen have been reported for the first time. Calculation of the vibrations of $HO_2$ having various isotopic compositions confirmed the previous assignment of the 1389-$cm^{-1}$ band to the deformation vibration of OOH, but the 1101-$cm^{-1}$ band to the O–O stretching vibration. A bond angle of 105 ± 5° gave good agreement with experiment for $DO_2$. The relatively low force constant of the O–H bond in $HO_2$ and the near equality of the force constants of the O–O bonds in $HO_2$ and $O_2$ are compatible with the close similarity of their electronic structures, evident in the location of the corresponding electron transitions in the same spectral range. A recent analysis[7] of the vibrational spectra of peroxyl and deuteroperoxyl obtained in various ways reveals a positive isotopic shift of the $\nu_3$ vibration (1101 and 1123 $cm^{-1}$ for $HO_2$ and $DO_2$ respectively) and a negative shift for $\nu_2$ (1389 and 1020 $cm^{-1}$). Analysis of the spectral data for isotopically substituted derivatives of the $HO_2$ radical led to the conclusion that the oxygen atoms were not equivalent, which showed that the radical has an unsymmetrical structure.

The frequency of the out-of-plane deformation vibration of the methyl radical (611 $cm^{-1}$) differs significantly from the harmonic approximation. Riveros showed[9] that this discrepancy is consistent with the planar structure of the radical established from electron spin resonance data if the anharmonicity of the out-of-plane motion is taken into account. This success led Smith and Andrews[10] to use perturbation theory to calculate the anharmonic potential function of the ground state for out-of-plane deformations in the series of radicals $CH_2X$ (where X = Cl, Br, I). The calculated potentials were compared with the harmonic functions, and employed to confirm the observed isotope shifts. With $CH_3$ and $CH_2X$ the quartic anharmonic constants make a significant contribution to the potential energy, so that the harmonic force constants are considerably too low. Subsequently these workers extended the range of halogenomethyl radicals studied by infrared spectroscopy, by investigating the tri-,[11] di-,[11] and mono-iodomethyl[12] radicals. The 1106-$cm^{-1}$ band in the spectrum of $CHI_2$ was assigned to oscillation of the HCI angle, and the 716-$cm^{-1}$ band to an antisymmetric stretching vibration of the C–I bonds. With $CDI_2$ these vibrations give bands at 850 and 653 $cm^{-1}$ respectively. The 693-$cm^{-1}$ band of the $CI_3$ radical is attributed to stretching of the C–I bonds. The spectrum and the force field of $CH_2I$ were compared with the corresponding characteristics of the other monohalogenomethyl radicals. All three iodomethyl radicals show an unusually large force constant of the C–I bond in comparison with the value for $sp^3$-hybridised carbon atoms. It was considered that the change in hybridisation from $sp^3$ to $sp^2$ was insufficient to explain this observation, and $\pi$-bonding of the $\pi(p-p)$ and $\pi(p-d)$ type was assumed.

Milligan and his coworkers[13] examined the infrared spectra of the two halogenated methyl radicals $CClF_2$ and $CCl_2F$, and established that, as in $CHCl_2$ and $CCl_3$, the carbon–chlorine bond in $CCl_2F$ is considerably stronger than in stable molecules. Considering the possibility that the bond is strengthened by the presence of $\pi(p-d)$ interaction, these workers point out that such interaction will be considerable with a planar or almost planar structure, but a non-planar structure has been established for trichloromethyl.

One of the few studies demonstrating the possibility of applying yet another method of vibrational spectroscopy to unstable free radicals is an investigation of the Raman spectrum of the OF radical obtained photolytically on exposure in an argon matrix to a laser source[14]. The results support the assignment based on the infrared spectrum.

Investigation of the Raman spectra of the $NF_2$ radical in the gaseous state at high temperatures (up to 250°C)[15] is equally interesting from the point of view of technique. The frequencies of the completely symmetrical vibrations $\nu_1 = 1074$ $cm^{-1}$ and $\nu_2 = 572$ $cm^{-1}$ agree well with the corresponding frequencies in the infrared spectrum of the gaseous state.

The frequencies of the free radical NCN observed in the infrared spectrum in different matrices have been given[16–18] as $\nu_2 = 423$ $cm^{-1}$ and $\nu_3 = 1475$ $cm^{-1}$. The 2672-$cm^{-1}$ band detected at high concentrations of the radical was interpreted[19] as $\nu_1 + \nu_3$, which yielded $\nu_1 = 1197$ $cm^{-1}$.

The spectrum of the CNN radical in a matrix contains the bands[20] $\nu_2 = 393$ $cm^{-1}$, $\nu_1 = 1241$ $cm^{-1}$, and $\nu_3 = 2847$ $cm^{-1}$. From the estimated force constants it was concluded that the CN bond was almost triple, and the NN bond almost double. Vibration frequencies of the diazomethyl radical HCNN and its deuterated analogue were given[21] without interpretation. The bands at 1756, 1158, and 392 $cm^{-1}$ were attributed[22] to the dicyanomethylene free radical $C_3N_2$. These wave-numbers are close to those calculated for a linear molecule having the force constants of molecules of similar structure.

Use of a multiple-pass gas cell to give an optical path of 80 m yielded an infrared band at 1360 $cm^{-1}$, assigned[23] to an antisymmetric vibration of the symmetrical nitrate free radical $NO_3$ in the gas phase. The corresponding band of the planar nitrate ion lies at 1315 $cm^{-1}$.

Milligan and Jacox[24] observed the infrared bands $\nu_2 =$ 1499 $cm^{-1}$ and $\nu_3 = 3220$ $cm^{-1}$ for the $NH_2$ radical, displaced to 1496 and 3215 $cm^{-1}$ respectively for $^{15}NH_2$. A band at 1321 $cm^{-1}$ was detected in the spectrum of NDH, and $ND_2$ was characterised by a band at 1110 $cm^{-1}$. Investigating the infrared spectrum of NHF and its isotopic analogues, these workers[25] interpreted the observed two fundamental frequencies as $\nu_2 = 1432$ $cm^{-1}$ and $\nu_3 = 1000$ $cm^{-1}$.

Ogilvie[26] has recently revised the earlier interpretation[27] of the infrared spectrum of the HNO radical, and has suggested a new assignment of bands after comparing the geometrical parameters of the radical with the frequencies: he attributes the band at 2719 $cm^{-1}$ to N–H vibration, and that at 2043 $cm^{-1}$ to N–D, corresponding to the greater lengths of these bonds.

The infrared emission spectrum of the OH free radical has been determined by Murphy[28] for the fundamental and overtone regions. The fundamental band proved to be weaker than had been expected. The relative probabilities of the transitions were determined from the intensity ratio of fundamental and overtone bands, and hence the dipole moment function $\mu(R)$OH was calculated.

All three fundamental frequencies—$\nu_1 = 985$ $cm^{-1}$, $\nu_2 =$ 496 $cm^{-1}$, and $\nu_3 = 1042$ $cm^{-1}$—were observed with the $SO_2^-$ radical-anion stabilised as a charge-transfer complex with caesium and other alkali metals in an argon matrix[29]. The isotopic data indicate that interaction between $SO_2^-$ and $Cs^+$ is slight, so that all vibrational frequencies of normal and isotopic $SO_2^-$ can be calculated in good agreement with experiment without regard to the influence of the caesium ion. The slight splitting of the principal frequencies suggested that the oxygen atoms were not equivalent. Estimates by these workers indicate an $SO_2^-$ bond angle of ~ 160°, while the SO bond was considerably weaker than in $SO_2$, owing to the addition of the nineteenth valency electron to an orbital that was bonding for the terminal oxygen atoms and antibonding for the SO bonds.

The infrared spectra of the halogen dihalides have been investigated in a matrix[30-32]. The 696-$cm^{-1}$ band in the spectrum of the free radical $HCl_2$ has been assigned[30] to the $\nu_3$ vibration; the corresponding band in $DCl_2$ is at 464 $cm^{-1}$. Examination of the infrared absorption spectrum of the $HBr_2$ radical gives[31] $\nu_3 = 727$ $cm^{-1}$ and $\nu_1 = 165$ $cm^{-1}$, and indicates a linear structure ($D_{\infty h}$ symmetry) as for $HCl_2$. The spectrum of the radical $HI_2$, also interpreted[32] on the hypothesis of $D_{\infty h}$ symmetry, gave $\nu_3 = 682$ $cm^{-1}$ and $\nu_1 = 121$ $cm^{-1}$. The potential functions of all three radicals contain a large quartic term, which governs the anharmonicity of the H–Hal vibrations. Inspection of the force constants indicates that the hydrogen bonds are as strong in the $HHal_2$ radicals as in the $HHal_2^-$ ions. Comparison of the force constants in the series of hydrogen dihalides and the corresponding ion leads to the conclusion that the contribution of the quartic term to the potential function is larger for the radicals than for the ions. In the case of the ions the contribution of the anharmonic term diminishes with increase in size of the halogen atom, a tendency that is even more marked in the neutral radicals. Thus removal of an electron from a non-bonding orbital in $HHal_2^-$ has little effect on the hydrogen bond, but a marked effect in increasing the anharmonicity of the potential function. From the results for the above three radicals it was suggested[31] that $HF_2$ should be stable.

The spectra of the free radicals $CO_2^-$, $CCl_3$, and $CH_3CO$ have been recorded[33] in a rotating cryostat enabling infrared and e.s.r. spectra to be determined on the same specimen. Those of the first two radicals were obtained to check the technique; the spectrum of the acetyl radical, obtained for the first time, was investigated in greater detail. The 1796-$cm^{-1}$ band was assigned to a vibration of the carbonyl group; the 958-$cm^{-1}$ band was interpreted as due to a carbon–carbon stretching vibration.

Flash photolysis in the vacuum ultraviolet has recently been used[34] to obtain the radicals $C_3$, $C_3H$, $C_3H_2$, and $C_3H_3$ isolated in a matrix, as well as the allyl radical, and a preliminary assignment of the infrared bands has been made.

Pimentel et al.[35] obtained the infrared spectrum of the methyl radical in the gaseous state for the range of out-of-plane vibrations (450–740 $cm^{-1}$), using their method of rapid scanning spectroscopy. The observed frequencies (607 and 603 $cm^{-1}$ for $CH_3$, 561 and 558 $cm^{-1}$ for $CH_2D$, and 461 $cm^{-1}$ for $CD_3$) are close to those of the matrix-isolated radical and its deuterated derivatives, and were assigned to out-of-plane deformation vibrations of umbrella type. The lower frequency was due not to inversion of a pyramidal molecule but to a vibrationally excited methyl radical. The potential function of the out-of-plane vibration was calculated on the hypothesis that the radical had a planar structure. The anharmonicity was described by a quartic term, and could not be neglected in the case of $CD_3$.

In concluding this Section we may note the procedure suggested by Johnston et al.[36] for observing the infrared spectra of free radicals, based on the method of molecular modulation. Intense flash photolysis gives a fairly high concentration of radicals, with which, owing to fast reactions, it is often possible to observe not the species formed initially but their reaction products. The proposed method enables spectra of free radicals to be obtained at the very low concentrations obtainable with moderate light intensities. The photolysing light is switched on and off periodically, which slightly modulates the concentration of the radicals formed and of other intermediate products. The periodic variation in the concentration of unstable compounds, by slightly varying the absorption, modulates the intensity of the transmitted infrared beam. When the spectrum is scanned, the modulated intensity is obtained only within regions characteristic of the radicals or other short-lived products. Measurements of the phase shift during molecular modulation can be used to estimate the lifetime of the radical. Compounds are in general identified from the position and the form of the infrared bands. But when the spectrum is unknown or the bands overlap, the method permits identification of the absorbing substance as initial reactant, intermediate compound, or secondary product from the magnitude of the phase shift.

The radical ClO, formed photolytically from gaseous chlorine and oxygen, was detected in the gas phase from the absorption spectra and the phase shifts found in this work; the frequency 942 $cm^{-1}$ is consistent with the value for the matrix-isolated radical. Analysis of the phase shifts of the infrared absorption led to assignment of the 1127-$cm^{-1}$ band to the $HO_2$ radical obtained by photolysis of ozone in the presence of hydrogen peroxide (1101 $cm^{-1}$ in the case of matrix isolation). This method, though technically complicated, may give valuable information on short-lived radicals, especially at very low concentrations.

## III. VIBRATIONAL SPECTRA OF POLYATOMIC FREE RADICALS

Little use of vibrational spectroscopy has been made in studying neutral radicals obtained by the homolytic cleavage of bonds. Karagonis[37] was one of the first to employ the infrared spectrum to determine the structure of the triphenylmethyl radical. From the number of infrared-active vibrations it was concluded that a planar structure was the most probable. No features of a radical character have been detected[38] in the infrared spectra of several perchlorodi(and tri)phenylmethyl radicals, merely a slight bathochromic shift in the frequency of the benzene ring ~ 1500 $cm^{-1}$. An analysis of the vibrational structure of the luminescence spectra of three arylmethyl radicals has been given[39] without assignment of the vibrational frequencies.

A series of papers contain data on the infrared spectra of phenoxy-radicals[40-50]. With 2,4,6-tri-t-butylphenoxyl[40,41] the hydroxyl band of the phenol at ~ 2.7 μm disappears, and the band appearing at 6.4 μm is assigned to the $\nu$(C–O*) vibration (where the asterisk denotes the unpaired electron). From the position and number of carbon–oxygen stretching bands[41-45,48] it was concluded whether the phenoxy-radicals were present in monomeric or dimeric form. The same bands were examined in elucidating structure of the 2,2-bis-(3,5-di-t-butyl-4-hydroxyphenyl)propane diradical[47].

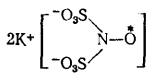
A systematic investigation of the infrared spectra of stable phenoxy-radicals and related molecules has been made[51-53] in order to reveal the influence of the unpaired electron on the force field of the molecule. The infrared spectra of three phenoxy-radicals—2,4,6-tri-t-butylphenoxyl[52], 2,6-di-t-butyl-4-(2,6-di-t-butylquinobenzyl)phenoxyl (galvinoxyl), and 3,3′,5,5′-tetra-t-butylindophenoxyl[53]—have been interpreted. The most significant difference between the spectra of radicals and related molecules (initial phenols and molecules of quinonoid structure) is observed in the region containing carbon–oxygen and cyclic carbon–carbon stretching vibrations. The main

features of the force field of the phenoxy-radicals have been determined, and the changes in the spectra of the radicals in comparison with those of the related molecules were shown to be due mainly to change in the force field, not in the geometrical structure. Analysis of the modes of vibration of phenols, radicals, and quinonoid molecules indicates that the same coordinate makes the predominant contribution to the comparable vibrations. Hence the frequency shifts observed in the phenol–radical–quinonoid sequence are due to change in the force constants, not in the modes of vibration (Table 1). Thus it was suggested[52, 53] that the effect of the unpaired electron on the infrared spectra could be estimated by comparing the force constants of radicals and related molecules. The changes in the frequencies of out-of-plane deformation vibrations of cyclic carbon–hydrogen bonds and in the carbon–oxygen bond intensities for the series of compounds indicate a decrease in the $\pi$-electron densities on the carbon atoms forming carbon–hydrogen bonds and also an increase in polarity of the CO bond.

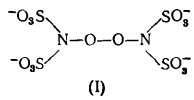
**Table 1.** Force constants ($10^6$ cm$^{-2}$) of ring carbon–carbon bonds and of carbon–oxygen bonds in phenol, the phenoxy-radical, and quinonoid molecules.

| Bond | Phenol | Phenoxyl | Cyclohexadienone | Quinone |
|---|---|---|---|---|
| Q″ q | 7,00 | 13,88 | 16,02 | 16,18 |
| Q Q | 10,04 | 11,46 | 13,95 | 13,85 |
| Q′ Q′ | 10,04 | 8,66 | 7,85 | 7,85 |
| Q″ Q″ | 10,04 | 9,76 | 6,77 | 7,85 |

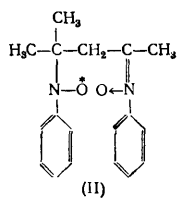
Infrared spectroscopy has been used to elucidate the structure of several nitroxide radicals[3, 54–61]. In the case of Frémy's salt



frequencies have been tentatively assigned to group vibrations for both monomeric and dimeric forms[54, 55]: the stretching frequency of the N–O* bond was assigned to the frequencies 1620 and 1260 cm$^{-1}$ in the two forms. Analysis of the infrared spectrum led to choice of (I) for the structure of the dimer.



(I)



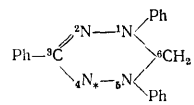
(II)

From an investigation of the infrared spectra of Benfield's radical (II), its derivatives substituted in an aromatic ring, and the initial compounds, Tüdos et al.[56] concluded that the main difference between the spectra of radicals and initial compounds is disappearance of the hydroxyl band at ~ 3300 cm$^{-1}$. They detected no other spectral features characteristic of radicals.

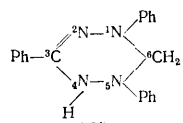
Piperidine nitroxide free radicals were also characterised by their infrared spectra[57–60]. The range 1300–1400 cm$^{-1}$ was studied[58] with the aim of detecting the $^{14}$N–O* bond, whose stretching frequency is 1373 ± 7 cm$^{-1}$.[60] The vibration frequency of the $^{15}$N–O* bond was also determined[60], as ~ 1353 cm$^{-1}$.

The band at 7.43 $\mu$m in the spectrum of the dimethoxydiphenylnitroxide free radical was assigned[61] to $\nu$(N–O*). The estimated force constant of this bond (8 mdyn Å$^{-1}$) is intermediate between the values for single and double bonds.

Several workers[62–64] have used infrared spectroscopy to study the verdazyls, a new class of uncharged stable radicals prepared not long ago. Kuhn and Trischmann[62] assigned the vibrations of the benzene rings in 1,3,5-triphenylverdazyl (III) and in 1,5-diphenylverdazyl, but the vibrations of the heterocycle remained almost unassigned. Qualitative examination of the infrared spectrum suggested that the radical was more symmetrical than the original leuco-base (IV), and the N–H stretching band near 3400 cm$^{-1}$ had disappeared. A fairly complete assignment of the infrared spectra of the verdazyl (III) and its derivatives substituted in one aryl ring was based[63] on the analogy with formazans investigated previously. The 1340-cm$^{-1}$ band was attributed to an NN-stretching vibration in the heterocycle. Other workers[64] assign an intense band at 1145 cm$^{-1}$ to this vibration in the verdazyl (III), and the 1340-cm$^{-1}$ band to a CN-stretching vibration in an *N*-phenyl group.



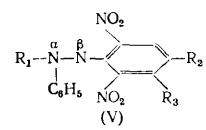
(III)



(IV)

The same paper reports the assignment of the infrared spectra of the initial leuco-base (IV), its analogue deuterated in the heterocycle, and the verdazyl cation (III), and changes in the spectrum accompanying one-electron cation-radical interconversions are traced. The spectra of the leuco-base (IV) and the radical (III) differ significantly in the frequencies of stretching vibrations of the tetrazole ring, whereas the vibration frequencies of the benzene rings remain unchanged. The spectrum undergoes appreciable changes when charged structures are formed from the radical. The frequency of the 1165-cm$^{-1}$ band due to an NN-stretching vibration rises in the spectrum of the cation, whereas that of the 1197-cm$^{-1}$ band due to the $C_{(6)}N$-stretching vibration falls, relative to those of the corresponding vibrations of the radical (1145 and 1208 cm$^{-1}$); the 1266-cm$^{-1}$ band due to vibration of the $C_{(3)}N$ bond hardly shifts. The vibration frequencies of the phenyl rings undergo little change on formation of the ion. From the frequency shifts of the $C_{(3)}N$- and NN-stretching vibrations for the cation it was assumed[64] that a considerable proportion of the positive charge was localised on the $N_{(1)}$ and $N_{(5)}$ atoms, which is consistent with the quantum-chemical calculation of the $\pi$-electron structure of the triphenylverdazyl cation.

Investigation of the infrared spectra of a series of free radicals of hydrazine type having the general formula



(V)

and of the initial hydrazines has revealed[61,65] changes in the spectra due to redistribution of electron density resulting from the appearance of the unpaired electron. The 3300-$cm^{-1}$ band due to NH-stretching vibrations has disappeared from the infrared spectra of stable hydrazyl radicals, and a series of characteristic frequencies are lower than in the original compounds. The strong bands at 1620 and 1600 $cm^{-1}$, assigned to skeletal vibrations of the picryl residue and of the monosubstituted benzene ring attached to the $\alpha$-nitrogen atom respectively, have diminished in frequency by 20 $cm^{-1}$, which is attributed to increasing conjugation resulting from the appearance of the unpaired electron on the $\beta$-nitrogen atom. The presence of the unpaired electron explains also the appearance of a new band of medium intensity in the range 1210–1250 $cm^{-1}$, assigned to stretching vibrations of the central fragment $\rangle N-N^{*}-$.

The infrared spectrum of propene adsorbed on zinc oxide at 125°C shows[66] detachment of a hydrogen atom from the methyl group and the appearance of a band at 1545 $cm^{-1}$, assigned to vibrations of CC bonds with order 1.5 in the allyl radical. The force constant of this bond was estimated as 7.54 mdyn $Å^{-1}$.

The vibrational spectrum of the benzyl radical, formed by the flash photolysis of toluene or an $\alpha$-monohalogenated derivative, was obtained by analysing the vibrational structure of the luminescence[67-73] and absorption[74,75] spectra. Emission spectra of the benzyl radical with well resolved vibrational structure were obtained both for the gas phase by means of a long-path cell[69] and for the radical trapped in various matrices at low temperatures[67,68]. The spectra of deuterated analogues of the benzyl radical were also given[70,71], and the vibrational frequencies were interpreted by analogy with toluene. More recently[72] the luminescence and absorption spectra of the benzyl and *o*-, *m*-, and *p*-fluorobenzyl radicals have been obtained in an adamantane matrix, and an analysis was given of the vibrational structure of the spectra of all these radicals. The vibrational frequencies of the benzyl radical agreed well with those obtained earlier. The infrared spectrum of the benzyl radical deposited with a neon matrix on caesium bromide and calcium fluoride windows at the temperature of liquid helium was given[73] without assignment.

The force constants of the benzyl radical were calculated[76] by means of a calibration curve from the bond orders obtained by the Hückel method and also by the self-consistent field method to a semi-empirical approximation allowing for electronic–vibrational interaction[77]. The latter were used[78] in calculating the frequencies and the forms of the normal planar vibrations of the benzyl radical, the equilibrium bond lengths of the radical being obtained by the Pariser–Parr method with variation of the resonance integral $\beta$ specified as a power function of the bond order. The satisfactory agreement between calculated and observed frequencies permits the hope that quantum-chemical estimation of bond lengths and force constants could be applied to solving the vibrational problem for free radicals. Comparison of the vibrational spectra of isoelectronic radicals—phenoxyl and benzyl—indicates that the force constants of the ring have changed more in the former than in the latter radical relative to the initial molecules[52] (Tables 1 and 2).

Quasi-line luminescence spectra have been used to provide the vibrational frequencies of radicals obtained by the photodissociation of durene[79,80], xylenes[81], ethyltoluenes[82-84], and diethylbenzenes[85]. Assignment of the frequencies of the radicals was based on analogy with the vibrational spectra of the initial molecules and of related paramagnetic species.

The vibrational frequencies 630, 1010, and 1600 $cm^{-1}$ observed[86] in the luminescence spectrum of the diphenylmethylene diradical are closely similar to those of benzene (606, 992, and 1600 $cm^{-1}$).

Table 2. Force constants ($10^6$ $cm^{-2}$) of carbon–carbon bonds in toluene and the benzyl radical.

| Bond | Toluene | Benzyl |
|---|---|---|
| Q″ q | 6.77 | 8.13 |
| Q Q | 10.04 | 10.06 |
| Q Q′ | 10.04 | 9.52 |
| Q′ Q″ | 10.04 | 9.90 |
| q | | |

A vibrational structure has recently been given[87] for the fluorescence and phosphorescence spectra of the $\alpha$-indanyl free radical obtained by the $\gamma$-radiolysis of indane frozen in a neutral matrix at 77 K, and assignment of several vibrational frequencies has been attempted by analogy with indane.

The infrared spectrum of the exceptionally stable perchlorodiphenylaminyl radical has been given[88] without any attempt at interpretation.

## IV. VIBRATIONAL SPECTRA OF RADICAL-IONS

Radical-ions provide a convenient model for elucidating the influence of an unpaired electron on the force field of a molecule, since the matrices of the kinematic coefficients of a neutral molecule and of a radical derived from it should not differ greatly (the masses are the same, and the distances would not change markedly). The main changes in the vibrational frequencies are therefore determined by variation in the force constants. Until recently only the infrared spectra of radical-ions had been investigated. The first communications on the Raman spectra and the resonance Raman spectra have appeared only during recent years as a result of improvement in the method of obtaining the former spectra and the use of lasers for their excitation.

Papers on the vibrational spectra of radical-ions can be divided roughly into three groups. The most numerous group contains spectra and their qualitative description with an approximate assignment of one or two bands[61,89-101]. The second group[102-126] combines investigations of the frequency shifts in certain characteristic vibrations in a series of radical-ions of similar structure and correlations of these shifts with the variation of the parameters of the electron structure. The third group[127-137] comprises only the most recent publications, which give a fairly complete interpretation of the vibrational spectra of radical-ions based on calculation of the normal vibrations, together with an estimate of the force field and a comparison of the force constants with the parameters of the electronic structure.

Research on the infrared spectra of free radical-ions began in 1954–1955 with the work of Kainer and Otting[61,89], who obtained the spectra of various nitrogen-containing

radical-cations and compared them with those of the corresponding neutral molecules to establish the spectral variation on passing from molecules to radical-cations. The appearance of the unpaired electron in the radical salts of secondary and tertiary *para*-substituted arylamines leads to a marked strengthening of bands in the region of 6.25 μm due to stretching vibrations of the phenyl rings and of the band at 8.5 μm due to CH-deformation vibrations[61]. These effects are considerably weaker in the spectrum of pentaphenylpyrrole perchlorate, but the bands at 6.92 and 7.11 μm have become much more intense[61]. The spectrum of pyocyaninium perchlorate exhibits marked strengthening of the CH bands at 3.3 and 3.4 μm, with the appearance of two bands, at 2.90 and 2.95 μm, attributed to vibrations of OH and NH bonds respectively. With pyocyanin perchlorate it is impossible to distinguish $\nu$(OH) from $\nu$(NH) on the basis of the 3.1-μm band, owing to the bridge between the nitrogen and oxygen atoms[61].

A spectral investigation was made[89] on the radical-ions obtained by reaction between the electron-donating *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) and electron-accepting halogenated *p*-benzoquinone derivatives. The spectrum of the radical-anions shows a decrease in the $\nu$(C=O) frequency to 6.5 μm (from 6 μm for the neutral molecule). The spectrum of the cation is characterised by weakening of the $\nu$(CH) and $\gamma$(CH) bands at 3.5 and 12.3 μm, with a marked shift in the $\delta(CH_3)$ band to 7.55 μm, while resembling the spectrum of the cation in the radical salt with the inorganic perchlorate anion (Wurster's blue).

A series of papers by Matsunaga[90-96], containing the infrared spectra of radical salts, must also be included in the first group. He examined the infrared spectra of the anions in the sodium and potassium salts of tetrachloro-*p*-benzoquinhydrone, *p*-biphenoquinhydrone, and tetrachloro- and tetrabromo-*p*-biphenoquinhydrone[90]. Using an approximate relation between the force constant and the bond order together with an empirical dependence of $\nu$(C=O) on the force constant, this worker calculated bond orders $P(C{=}O)$ and force constants for the radical-anions.

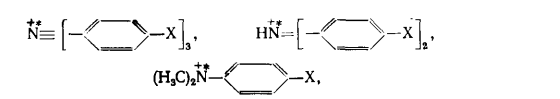
The radical-cations in salts of phenothiazine with iodine and bromine have similar spectra, differing markedly from that of the original molecule[91,92]. The infrared spectra of the radical-cations of dibenzophenothiazine remain unchanged on replacement of chloride by bromide, iodide[93], and also perchlorate anions: i.e. the spectra of the radicals are determined mainly by the absence of an electron from the highest filled orbital and are independent of the nature of the gegenion. The same conclusion applies also to the infrared spectra of the radical salts of phenoxazine, phenoselenazine, and benzophenothiazines with iodine and bromine[94]. Examination of the infrared spectra of the radical-cations of these compounds with halogenated derivatives of *p*-benzoquinone as anions shows[95] that the nature of the radical-cations remains the same with organic and with inorganic anions. From the displacement of the carbonyl band in the spectra of the anions it was concluded that this function loses ~ 30% of its double-bonded character, and the ring loses its quinonoid structure. This explains the marked difference between the infrared spectra of the radical-anions and those of the neutral molecules. The spectra of such radical-anions of semiquinones also resemble those in the alkali-metal salts. The presence of similar semiquinone radical-anions was observed[96] in the infrared spectra of complexes of dibenzophenothiazine with dichlorodicyano-*p*-benzoquinone, of 5,6 : 11,12-bisdithionaphthacene with *o*-chloranil, and of ferrocene with tetrachloro-*p*-biphenoquinone. The radical compounds investigated in this series of papers by Matsunaga have attracted attention as organic semiconductors, and their infrared spectra have been studied in parallel with their electrical conductivity.

In solutions with different gegenions the infrared spectrum of the radical-anion of 7,7,8,8-tetracyanoquinodimethane (TCQM) exhibits a bathochromic shift of $\nu(C{\equiv}N)$ (from 4.50 μm in the neutral molecule to 4.55–4.60 μm in the radical-anion[97]). Comparison of the infrared spectra of the radical salts $[TCQM]^-Li^+$ and $[TMPD]^+ClO_4^-$ recorded in Nujol with the spectrum of $[TMPD]^+[TCQM]^-$ indicates[98] that in the last salt both components are present in ionic form. Raman and infrared spectra have been obtained[99] for radical-ion complexes of tetracyanoquinodimethane with various cations; the spectra were not interpreted, but characteristic intense bands in the range 1100–1300 $cm^{-1}$ were noted.

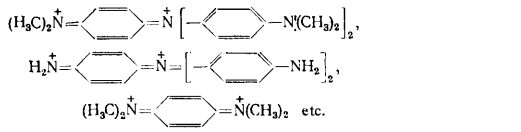
The infrared spectra in Nujol and hexachlorobutadiene of the radical salts—triphenylammonium bromoantimonate, triphenylmethyl chlorostannate, tri-*p*-tolylammonium chloroantimonate, tri-*p*-tolylmethyl hexafluoroniobate, and tri-*p*-tolylammonium hexafluorotantalate—were given[100] without interpretation.

On examining a series of radical-anions obtained from alkylnitrobenzenes with alkali metals in dioxan, Nakai[101] found that the most significant difference between the spectra of the radical-anions and those of the neutral molecules was the enhanced intensity of the band due to antisymmetric nitro-stretching vibrations.

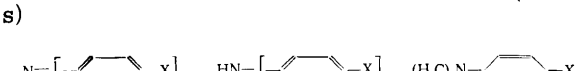
The second group comprises more detailed investigations[102-104] of the infrared spectra of several di- and triarylamine radical-cations



(X = $N(CH_3)_2$, $NH_2$, $OCH_3$, F, Cl, NOH, $NOCH_3$) and quinonedi-imine dyes (doubly charged cations)



With certain simplifications a relation was established[102] between the bond order calculated in the Hückel approximation and the stretching frequencies of the bonds attaching the benzene ring to the substituent and to the nitrogen atom in the arylamine radical salts, which explained the rise in these frequencies observed in the cations relative to the neutral molecules. The spectra of the above radicals and dyes were assigned[103,104] on the basis of an interpretation of those of the initial neutral molecules (leuco-bases)



Comparison of the infrared spectra indicates that singly and doubly charged cations are related in structure. Conversion of a radical into a dye does not produce such a marked change in structure as does that of the leuco-base into the radical. The changes observed in the spectra of radicals and dyes relative to those of the leuco-bases suggest that the positive charge appearing on the central nitrogen atom of the cation leads to displacement of the electrons of the lone pairs of the nitrogen, oxygen, and fluorine substituents in the CN, CO, and CF bonds, which are thereby strengthened. The consequent redistribution

of electron density changes the force constants of the CC bonds in the benzene ring. Thorough investigation of $\nu$(C–N) in radicals and dyes, together with data for many other compounds, indicated[104] that the CN bond orders had levelled out.

Savitskii and Kuznetsov[105] have since examined the infrared spectra of the Wurster salts of *p*-phenylenediamine (pPDA), *NN*-dimethyl-*p*-phenylenediamine (DMPD), and *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD). The spectra of the radical salts were assigned by analogy with those of the initial amines and on the basis of the isotopic frequency displacements in the deuterated compounds. The range of skeletal vibrations undergoes the most considerable changes in the spectra of the radical salts in comparison with the initial amines, the frequencies tending to rise presumably owing to the more quinonoid character of the nitrogen–carbon skeleton. In the case of $[pPDA]^+$ and $[DMPD]^+$ hydrogen bonds of the anions (bromide and iodide) and amino-groups of the cations are involved in formation of the crystalline state, with a decrease in the paramagnetism of these salts. In the paramagnetic salt $[TMPD]^+$ the crystalline state is formed without the involvement of hydrogen bonds, obviously owing to steric hindrance.

Radical-anions of conjugated polycyclic hydrocarbons are obtained in high yields and are quite stable in a vacuum, which make them convenient subjects for investigation by infrared spectroscopy. Kachkurova[106–108] examined the infrared spectra of the radical-anions of naphthalene, anthracene, naphthacene, and pentacene, obtained in a vacuum by interaction with a metallic potassium mirror in oxolan. Assignment of the observed bands was facilitated by recording also the spectra of deuterated analogues. The frequencies showed a general tendency to fall on radicalisation, which was attributed to the presence of the unpaired electron in an antibonding orbital, weakening all the bonds in the radical with a decrease in force constants and increase in bond lengths. The frequency shift of the out-of-plane CH-deformation vibrations was especially large. It decreased with increase in the number of rings in the hydrocarbon, owing to the diminished electron density on the carbon atoms. With naphthacene and pentacene dianions could be obtained[108,109]. The effect on certain vibrations of the successive addition of two extra electrons could be traced by comparing the spectra of dianions and monoanions. A further fall in a series of frequencies with increase in the electron density on the ring carbon atoms is observed in the dianion spectra. The frequency shift of out-of-plane CH vibrations is larger for naphthacene than for pentacene, since the extra electron is distributed among a larger number of aromatic rings.

A preliminary assignment of several infrared bands and Raman lines of the radical-anion of naphthalene, observed by other workers[110], is consistent with Kachkurova's results[106,107].

Examination of the structure of the electronic absorption spectra of the radical-cations of naphthalene, anthracene, and phenanthrene in vitreous boric acid[111] gave the ring CC-stretching frequencies as respectively 1485, 1411, and 1356 $cm^{-1}$, with a fall in frequency in comparison with the neutral molecules. The infrared spectrum of the radical-cation of polyfluorinated naphthalene[112] also showed the disappearance of bands in the range 1600–1670 $cm^{-1}$, assigned to ring carbon–carbon vibrations, with the appearance of bands at ~ 1550–1590 $cm^{-1}$. As in the case of the radical-anions[106,107], such fall in frequencies is caused by weakening of the bonds.

The infrared and Raman spectra of the radical-anion of anthracene, obtained as a solid film by coprecipitation of anthracene and potassium vapours in a vacuum, have been investigated[113]. Films having different ratios of potassium to anthracene ($\frac{1}{2}$, 1, and 2) were identified from the vibrational and electronic spectra. Certain frequencies exhibit irregular behaviour, although in general transfer of the extra electron loosens the bonds. It was therefore considered urgently necessary to analyse the force constants both for a real interpretation of the spectra and for a quantitative estimate of the effect of the extra electron. Such irregularity in the frequency shifts was not observed by Kachkurova[106,107], obviously owing to the impossibility of observing the complete spectrum of anthracene dissolved in oxolan.

Resonance intensification of certain bands in the Raman spectrum of the radical-anion and the dianion of anthracene has been observed[114] in oxolan. According to a preliminary assignment no large differences are evident between the solid state and the solution, but the normal coordinates and results for deuteriated compounds must be examined to establish the correctness of the assignment. Later the same workers[115] observed the resonance form of the Raman spectrum of the radical-anion of biphenyl in oxolan. Assignment of the bands was based on analogy with neutral biphenyl. Both positive and negative displacements of the bands were observed. The higher stretching frequency of the central bond was associated with an increase in its order.

The radical-anions of several aromatic nitriles—benzonitrile, 1- and 2-cyanonaphthalene, *p*-cyanobiphenyl, 9-cyanophenanthrene, 1-cyanopyrene, 9-cyanoanthracene, etc.—obtained both by reaction of the nitriles with alkali metals in oxolan[116] and by cathodic reduction in dimethyl sulphoxide[117], showed a fall in the frequency of out-of-plane CH-deformation vibrations on radicalisation. The smallness of the change in polarity of the CH bonds can be judged from the almost identical intensities of these bands in the initial nitriles and in the radical-anions. Radicalisation entails weakening of CC valency bonds and hence a fall in frequency in the region of 1600 $cm^{-1}$ with an increase in intensity. The nitrile-stretching bands $\nu$(C≡N) were the most sensitive to the change in structure of aromatic nitriles on reduction. In the radical-anions their frequencies had fallen by 95–140 $cm^{-1}$, while the half-widths had increased from 7–9 to 22–45 $cm^{-1}$. The accompanying increase in the integral intensities of the nitrile bands was about tenfold.

The fall in frequency of the nitrile group on the appearance of a further electron in an antibonding orbital of a nitrile dianion[118] is 50% greater than with the singly charged anion. The half-width increases to 50–70 $cm^{-1}$, while the integral intensity is around hundredfold that observed for the neutral molecule. Such sensitivity of the C≡N vibration to variation in electronic structure gave rise to a broad investigation of the behaviour of nitrile bands on the formation of radical-anions from a number of aromatic nitriles[119,120]. The change in frequency of this vibration gives an indication of the change in order of the C≡N bond and also in its force constant: the shift in $\nu$(C≡N) correlates with the decrease in the calculated bond orders $P$(C≡N). The intense $\nu_{as}$(C≡N) band of aromatic radical-anions containing two nitrile groups is accompanied by the appearance of a weak $\nu_s$(C≡N) band at a higher frequency, not allowed in neutral molecules for reasons of symmetry, but active in radical-anions[119] owing to the unsymmetrical disposition of the gegenion.

The infrared bands of radical-anions of $^{15}N$-substituted nitriles[120] exhibit smaller isotopic displacement than in the case of the neutral molecules, which indicates that CC bonds adjacent to a nitrogen atom make a greater contribution to the vibrational energy. Inspection of the vibrations of radical-anions containing two nitrile groups leads to the conclusion that conversion of a molecule into a radical produces a considerable increase in vibrational interaction between the separated C≡N groups. The interaction force constant has been estimated on the basis of a simple vibrational model (N≡C–C...C–C≡N) as $F_{CN,CN} \simeq 0.3$ mdyn Å$^{-1}$. The main factor increasing vibrational interaction in the radical-anions is the great mobility of the unpaired electron in the antibonding orbital.

The carbonyl-stretching frequency provides a convenient indicator of change in the electronic structure of the group. It can be used[121,122] to determine the density $\rho$ of the unpaired electron on the carbonyl group in radical-anions of ketones. The displacement of the carbonyl band in the spectrum of the radical relative to its position in the neutral molecule is described by the equation

$$\Delta\nu(C=O) = A\rho, \qquad (1)$$

where $A = 250$ cm$^{-1}$ is a constant, roughly half the difference in frequency between double and single carbonyl bonds. A similar dependence extends to the nitrile and sulphonyl groups. An attempt to obtain a similar relation for the aryl group was unsuccessful, which the Reviewers regard as normal in view of the complicated form of the ring-stretching vibrations. Formula (1) is extremely useful for assigning the $\nu$(C=O) frequencies of the reduced forms of carbonyl compounds. In particular, this relation formed a guide in interpreting[123] the $\nu$(C=O), $\nu$(C=C), and $\nu$(C≡N) bands in the infrared spectra of the dianion and the radical-anion of biscarbodicyanocyclobutadiene studied in solution in dimethyl sulphoxide. The carbonyl bands showed that the frequency for the radical-anions was on the average ~ 35 cm$^{-1}$ lower than in the neutral molecule, with an additional fall of ~ 43 cm$^{-1}$ on further reduction to the dianion. The density of the unpaired electron on the carbonyl group in the radical-anion estimated by means of formula (1) is 0.17. The nitrile frequencies also fall on passing from the neutral molecule to the radical-anion and the dianion.

The magnitude and the direction of the frequency shifts of the carbonyl bands in the infrared spectra of the radical-anions and dianions of benzophenone, fluorenone, phenanthraquinone, and anthraquinone in polar solvents, on the application of Eqn. (1), give about the same order of magnitude of electron density on the carbonyl group[124] as does calculation to the Hückel approximation. The diminution in double-bonded character of the carbonyl bond with the accumulation of negative charge on the antibonding orbital is reflected in a change in the force constants calculated from the orders of the bonds and their self-polarisabilities by means of the formula of Coulson and Longuet-Higgins.

The infrared region of the carbonyl and aryl frequencies (1800–1500 cm$^{-1}$) has been examined following the reduction of several diketones on a metallic mirror in oxolan[125]. From the change in these frequencies and in the colour of the solution it was concluded that reduction of the diketones took place in two stages.

In the infrared spectrum of the dianion of tetraphenylethylene[126] the aryl frequency is 36 cm$^{-1}$ lower than in that of the neutral molecule, while $\nu$(C=C) is not observed. The large shift in the aryl frequency together with nuclear magnetic resonance data and quantum-chemical calculations of the electron density suggested an almost planar structure for the dianion and strong delocalisation of antibonding electrons.

In contrast to radical-anions in solution, stable radical-anions in the solid phase give a sufficiently complete spectrum for more reliable interpretation and estimation of the force field. Such investigations have recently been made for the radical-anions of chloranil ($p$-QCl$_4$)[127], bromanil ($p$-QBr$_4$),[128,129] 2,5-dibromo-3,6-dichloro-$p$-benzoquinone ($p$-QBr$_2$Cl$_2$),[130] and tetracyanoethylene[131,133–135]. All these compounds show significant differences between the spectra of the neutral molecules and those of the radical-anions, probably because of differences in their intramolecular force fields. The influence of the crystal field on the vibrational frequencies was assumed to be small and was disregarded. The radical-anions of the halogenated derivatives of $p$-benzoquinone were closely similar. In all three compounds the appearance of an unpaired electron in the lowest antibonding orbital was associated with a considerable fall in the stretching frequencies of the C=O and C=C bonds. In a force field this causes a decrease in the force constants of the C=O, C=C, and C–Br bonds (and also of the C–Cl bond in $p$-QBr$_2$Cl$_2$) with an increase in the force constant of the C–C bond (Table 3).

**Table 3.** Force constants (mdyn Å$^{-1}$) of the neutral molecules $p$-QBr$_2$, $p$-QCl$_2$, and $p$-QBr$_2$Cl$_2$ and of the corresponding radical-anions*.

| Bond | Neutral molecules | | | Radical-anions | | |
|---|---|---|---|---|---|---|
| | $p$-QCl$_4$[127] | $p$-QBr$_4$[128] | $p$-QBr$_2$Cl$_2$[130] | $p$-$\dot{Q}\bar{C}l_4$[127] | $p$-$\dot{Q}\bar{B}r_4$[128] | $p$-$\dot{Q}\bar{B}r_2Cl_2$[130] |
| C=O | 9.7 | 9.62 | 9.62 | 7.3 | 7.10 | 7.10 |
| C=C | 6.6 | 6.67 | 6.67 | 6.1 | 6.26 | 6.26 |
| C–C | 3.0 | 2.96 | 2.96 | 3.5 | 3.33 | 3.33 |
| C–Br | — | 2.63 | 2.63 | — | 2.17 | 2.17 |
| C–Cl | 2.67 | — | 2.67 | 2.67 | — | 2.45 |

*Q = benzoquinone.

Variation of the diagonal force constants was used to obtain the force field of the radical-anions from that of the neutral molecules. Force constants can be expressed in terms of bond orders and self-polarisabilities by means of the relation of Coulson and Longuet-Higgins. For the homopolar C=C and C–C bonds the self-polarisability term is small, which is apparent in a linear dependence of force constants on bond orders. The bond orders $P$(C=C) and $P$(C–C) estimated from known force constants agree with the results of quantum-chemical calculations for $p$-benzoquinone. For the C=O bond the order does not agree as well with those calculated quantum-chemically, but the tendency for $P$(C=O) to decrease on passing from a neutral molecule to the radical-ion is maintained here. Bond lengths obtained from the bond orders estimated in this way also agree with those calculated quantum-chemically: the C=O and C=C bonds become longer, but the C–C bonds become shorter.

The distribution of spin density has been obtained[132,129] from infrared-spectral data for the radical-anions of chloranil and bromanil on the hypothesis that the coefficients of the atomic orbitals remain the same in the molecular orbitals of the radical-anions as in the neutral molecules. The resulting spin densities are closely similar in

magnitude to those calculated from the hyperfine splitting constants on oxygen-17 in the electron spin resonance spectrum of the radical-anion of *p*-benzoquinone.

The decisive factor in the infrared frequency differences between neutral molecules and radical-anions is the difference in electronic structure[127-132]. Some difference between the bond orders obtained from the infrared spectra and calculated quantum-chemically may be due to frequency shifts under the influence of the crystal field, whose effect may be different for molecules and for radicals. Furthermore, the matrices of the kinematic coefficients of radical-anions and neutral molecules are not strictly identical, which also may make some contribution to the frequency shifts. Therefore the sets of force constants for radical-anions[127,128,130] are not the only ones possible. But the main conclusions on the electronic structure were based on an analysis of the change in the stretching frequencies, and the above effects can be neglected to a first approximation.

The infrared spectrum of the radical-anion of tetracyanoethylene proved especially interesting[131,133-135]. Apart from the C≡N stretching bands at 2208 and 2183 $cm^{-1}$, displaced to significantly lower frequencies than in the neutral molecule (2262 and 2230 $cm^{-1}$), and a very intense band at 1371 $cm^{-1}$, the spectrum of the radical-anion exhibited no appreciable absorption in the range 600–1300 $cm^{-1}$, where the most intense bands of the neutral molecule are located: only extremely weak bands are present at 1187 and 970 $cm^{-1}$, corresponding to the intense bands at 1155 and 959 $cm^{-1}$ due to C–C stretching vibrations in the neutral molecule. Since the 1371-$cm^{-1}$ band could have no other origin, it was assigned to a completely symmetrical vibration of the C=C bond (in the Raman spectrum of the neutral molecule $\nu$(C=C) = 1573 $cm^{-1}$).

Table 4. Force constants (mdyn $Å^{-1}$) of tetracyanoethylene and its radical-anion.

| Bond | Neutral molecule | | Radical-anion | |
|---|---|---|---|---|
| | Ref.131 | Ref.135 | Ref.131 | Ref.135 |
| C=C | 6.31 | 6.59 | 4.00 | 4.54 |
| C–C | 4.80 | 5.32 | 5.23 | 5.68 |
| C≡N | 16.84 | 17.04 | 15.70 | 16.34 |

The activation theory of Ferguson and Matsen and the hypothesis[134] of vibronic interaction have been used[131,133] to explain such activation of a completely symmetrical vibration in the infrared spectrum and the deactivation of antisymmetric vibrations of C–C bonds. The spectrum of the radical-anion of tetracyanoethylene has been interpreted on these assumptions, an analysis of the planar normal coordinates has been made, and the force constants of the bonds have been estimated in the Ursey–Bradley potential function of a simple field. Table 4 demonstrates the good agreement among results obtained by different workers. It shows that the extra electron in the lowest antibonding orbital of tetracyanoethylene decreases the force constants of the C=C and C≡N bonds and increases that of the C–C bond, so that this bond becomes stronger than C=C. The parallel variation in bond orders estimated from infrared spectral data is consistent with the results of quantum-chemical calculations. Investigation of the resonance Raman spectrum of the radical-anion of tetracyanoethylene[135] confirms the validity of the hypothesis of vibronic interaction and supports the earlier assignment of the infrared spectrum.

Recent conclusions[136,137] on the infrared and Raman spectra of the chloranil anion are consistent with previous results[127], although the inadequacy of varying only diagonal force constants on passing from neutral molecule to radical-anion is noted here. The infrared spectrum of the tetracyanoquinone radical-ion[137] is described satisfactorily by the force field obtained by varying the diagonal force constants of the bonds and the interaction constants of the bonds in the neutral molecule. The change in the latter constants is attributed to rearrangement of the quinonoid ring in the direction of a benzenoid structure.

The possibilities of resonance Raman spectroscopy for investigating free radicals has been demonstrated[138] in a study of the anions and dianions of several aromatic compounds (anthracene, biphenyl, terphenyl, diphenylbutadiene, perylene, and benzophenone). The differences observed in the spectra are larger on passing from the molecule to the anion than from the anion to the dianion. The appearance of several new bands with the charged forms is attributed to change in the selection rules under resonance conditions of excitation. Examination of such spectra is promising for systems having the strongest vibronic interactions, such as free radicals and multicharged ions possessing mobile electrons.

Investigation by the same workers[139] of the resonance Raman spectra of negative and positive mono- and di-ions of naphthacene revealed a considerable change in intensity on passing from neutral molecules to ionic forms, and established that the spectra were influenced mainly by the magnitude of the charge, not its sign.

A brief communication on the resonance Raman spectrum of the radical-cation of *p*-phenylenediamine[140] notes the high concentration sensitivity and the possibility of excluding the interfering effect of the solvent as advantages of the method. The spectrum is interpreted on the assumption of a cation-radical structure with the carbon–nitrogen bonds partly double-bonded in character.

A quite recent careful investigation[141] of the infrared and Raman spectra of the 7,7,8,8-tetracyanoquinodimethane radical salt $Cs_2(TCQM)_3$ and its deuterated derivatives, when compared with the results of X-ray diffraction, leads to the very interesting conclusion that the organic compound is present as two radical-anions and one neutral molecule.

Thus this survey of the literature provides evidence of the usefulness of applying methods of vibrational spectroscopy to investigate the changes of electronic structure involved in the conversion of molecules into radicals.

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# Radical Reactions of Aromatic Polyfluoro-compounds

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The review is devoted to the reactions of aromatic polyfluoro-compounds mainly with alkyl and aryl radicals. Certain features of the behaviour of compounds of this class in radical reactions are examined and the reaction mechanisms are discussed in those cases where they differ significantly from those in the corresponding reactions of non-fluorinated compounds. The bibliography includes 101 references.

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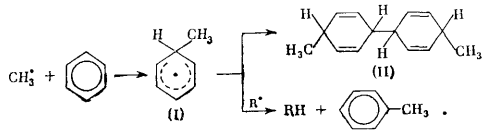
## I. INTRODUCTION

Aromatic polyfluoro-compounds have been the object of continuous attention of research workers during the last 10–15 years, after convenient and easy methods for their synthesis were discovered. The data accumulated so far on the chemistry of such compounds permit the conclusion that their reactions with each of the main types of reagents (nucleophiles[1,2], electrophiles[3], and carbenes[4-9]) open general pathways to the synthesis of polyfluoro-compounds of fundamentally new structural types. In this sense, the radical reactions of aromatic polyfluoro-compounds, the study of which has been vigorously developing in recent years, constitute a striking example of the influence of fluorine atoms on the nature of the product formed and on the reactivity of aromatic compounds.

In the present review attention has been concentrated on the reactions of aromatic polyfluoro-compounds with alkyl and aryl radicals. In addition, the reactions with certain other radicals as well as photochemical and thermal reactions involving a free-radical mechanism are discussed.

## II. REACTIONS WITH ALKYL RADICALS

In contrast to homolytic arylation reactions of non-fluorinated aromatic compounds, widely described in a number of reviews and monographs[10,11], the radical alkylation reactions have not been surveyed. In order to be able to compare subsequently the available data on the action of alkyl radicals on aromatic polyfluoro-compounds and on their non-fluorinated analogues, it is useful to consider briefly the results of studies of the interaction of non-fluorinated compounds and alkyl radicals. The reactions of aromatic compounds with methyl and trifluoromethyl radicals in both liquid and gaseous phases have been studied in greatest detail. The mechanism adopted, discussed here in relation to the reaction of the methyl radical with aromatic compounds, involves the addition of the radical in the first stage with formation of a σ complex of type I:




(1)

(2)

It is assumed that direct abstraction of hydrogen from the aromatic ring with formation of the phenyl radical does not occur, since biphenyls were not detected in the reaction products[12]. Calculation has also shown that the abstraction of hydrogen from the σ complex (I) [Eqn. (2)] is energetically more favourable than the direct abstraction of hydrogen from the aromatic ring (64 and 100 kcal respectively)[13].

**Table 1.** The relative rates of methylation and phenylation of compounds of the type $C_6H_5X$.

| Relative rate | X | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | H | F | I | Br | $CH_3$ | $t\text{-}C_4H_9$ | $C_6H_5$ | $OC_6H_5$ |
| Methylation (Ref.14) | 1 | 1.51 (2.2)* | 2.11 (4.2) | 3.87 (3.6) | 1.46 | 0.68 | 7.47 | 4.89 |
| Phenylation (Ref.16) | 1 | 1.03 | 1.06 | 1.29 | 1.23 | 0.64 | 2.94 | — |

* The data of Heilman et al.[17] are indicated in brackets.

Comparison of the relative rates of methylation and arylation of benzene and its derivatives (Table 1) shows that $CH_3^{\cdot}$ is more selective than $C_6H_5^{\cdot}$, which may be attributed to the low reactivity of the intermediate σ complex (I) formed. The latter factor results in a significantly different subsequent fate of the σ complexes formed when alkyl or aryl radicals add to aromatic compounds. The σ complexes produced by the addition of alkyl radicals accumulate in the medium and vanish, dimerising in the vapour phase [Eqn. (1)], or react with the radicals of the medium, giving rise to methylbenzenes [Eqn. (2)], [14,15] while the σ complexes produced by the addition of aryl radicals disproportionate preferentially with formation of the corresponding biaryls[10].

In the reactions of aromatic compounds with sources of methyl radicals, the methylation products can be identified, while the formation of dimers of type (II) in most cases merely postulated on the grounds of general considerations[12,14,18]. Only one communication[12] reports the identification by gas–liquid chromatography (GLC) in the mixture of products of the reaction of benzene with $CH_3^{\cdot}$ of 2,2′-, 2,4′-, and 4,4′-dimethylbiphenyls, which might have been formed on dehydrogenation of the corresponding dimers. Other alkyl radicals, such as $C_2H_5^{\cdot}$, iso-$C_3H_7^{\cdot}$, and n-$C_3H_7^{\cdot}$, exhibit a reactivity in relation to aromatic

compounds analogous to that of the methyl radical, which can be inferred from the identical ratios of the isomeric alkyl derivatives obtained in the reaction of $C_6H_5Cl$ with $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$,[19] and from the relative rates of addition of the ethyl[20], isopropyl[21], and n-butyl[22] radicals to aromatic compounds.

The study of the reactions of the trifluoromethyl radical with aromatic compounds showed that, as in the reaction with the methyl radical, the differences between the processes in the gas and liquid phases are insignificant[23] and that the main process is addition to the ring[24,25]. It has been found that $CF_3^{\cdot}$ is more reactive than $CH_3^{\cdot}$, which is in all probability due to its pronounced electrophilic properties (for example the rates of addition of $CH_3^{\cdot}$ and $CF_3^{\cdot}$ to benzene relative to their addition to iso-octane are 0.4 and 7.1 respectively)[26]. The relative rates of addition of $CF_3^{\cdot}$ to substituted benzenes (Table 2) also show that the trifluoromethyl radical is electrophilic.

Table 2. The relative rate constants $k_{rel}$ for the addition of the trifluoromethyl radical to substituted benzenes $C_6H_5X$.[27]

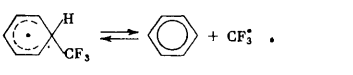
| X | H | $CH_3$ | $OCH_3$ | I | Br | Cl | F | $CF_3$ | $CCl_3$ | $NO_2$ | CN |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $k_{rel}$ | 1 | 1.43 (1.65)* | 1.93 (2.80) | — (1.65) | 0.89 (0.77) | — (0.65) | 0.35 (0.48) | 0.26 (0.30) | 0.36** — | — (0.45) | — (0.4) |

* The data of Szwarc and coworkers[28] are indicated in brackets.
** Data of Giles and Whittle[29].

The data in Table 2 show that the aromatic ring is activated with respect to the addition of the trifluoromethyl radical by electron donors and deactivated by electron acceptors. The halogens can be arranged in the following sequence in terms of the extent to which they hinder the addition to the compounds $C_6H_5Hal$: $I > Br > Cl > F$. The deactivating affect of electron-accepting substituents such as $CF_3$ and $CCl_3$ proved to be weaker than expected. The influence of other substituents resembles qualitatively the observed influence in the reactions of substituted benzenes with electrophiles and differs from the influence of these substituents in the reactions with methyl and phenyl radicals. However, the much lower dependence, compared with heterolytic reactions, of the rate of the addition reaction on the nature of the substituent in $C_6H_5X$, noted for all homolytic reactions, persists under these conditions in the reactions of aromatic compounds with the trifluoromethyl radical[11,15,30].

Fundamental differences in the behaviour of other fluorine-containing alkyl radicals in reactions with aromatic compounds have not been observed[31].

An interesting observation was made in a study of the reaction of $CF_3^{\cdot}$ and $C_2F_5^{\cdot}$ with aromatic compounds at different temperatures. When the addition of the trifluoromethyl radical to benzene at 65°C is irreversible in both gaseous and liquid phases, then at 140–150°C [32,33] (and for the perfluoroethyl radical at 110°C)[31] the process becomes reversible:



Proceeding now to the consideration of the reactions of aromatic polyfluorocompounds with alkyl radicals, we may note in the first place the appreciably reduced rate of addition of the trifluoromethyl radical to compounds of the $C_6H_nF_{6-n}$ ($n = 0-6$) series with increase of the number of fluorine atoms (Table 3).

Table 3. The Arrhenius parameters* of the reactions involving the addition of the trifluoromethyl radical to aromatic compounds[27].

| Compound | $10^{11} \cdot k_1/k_2^{1/2}$ ** | $E_1 - \frac{1}{2}E_2$ | $10^{8} \cdot A_1/A_2^{1/2}$ |
|---|---|---|---|
| $o$-$C_6H_4(CH_3)_2$ | 44.9 | 4.4 | 29.0 |
| $C_6H_5CH_3$ | 16.9 | 4.9 | 25.0 |
| $C_6H_5CF_3$ | 3.05 | 5.8 | 18.0 |
| $C_6H_5Br$ | 10.5 | 6.7 | 210 |
| $C_6H_6$ | 11.8 | 5.4 | 39.0 |
| $C_6H_5F$ | 4.14 | 4.0 | 1.6 |
| $o$-$C_6H_4F_2$ | 2.90 | 4.7 | 3.1 |
| $m$-$C_6H_4F_2$ | 2.12 | 4.9 | 3.06 |
| $p$-$C_6H_4F_2$ | 3.10 | 4.1 | 1.4 |
| 1,2,4-$C_6H_3F_3$ | 1.40 | 5.0 | 2.2 |
| 1,3,5-$C_6H_3F_3$ | 0.782 | 4.5 | 0.62 |
| 1,2,3,4-$C_6H_2F_4$ | 1.03 | 5.8 | 5.5 |
| 1,2,4,5-$C_6H_2F_4$ | 0.985 | 4.1 | 0.42 |
| $C_6HF_5$ | 0.679 | 5.1 | 1.26 |
| $C_6F_6$ | 0.484 | 5.8 | 2.8 |
| $C_6F_5CF_3$ | 0.525 | 4.6 | 0.53 |
| $p$-$C_6F_4(CF_3)_2$ | 0.143 | 4.2 | 0.069 |
| $C_6F_5CH_3$ | 0.991 | 3.7 | 0.24 |
| $C_6F_5Br$ | 0.767 | 5.2 | 2.0 |

* The kinetic method is based on the determination of the decrease of the yield of the radical recombination product relative to an internal standard (CO for the generation of the trifluoromethyl radical from hexafluoroacetone) when an aromatic substrate capable of combining with the radical is added to the reaction mixture.
** $k_1$ is the rate constant for the addition of $CF_3^{\cdot}$ to the aromatic compound and $k_2$ the rate constant for the dimerisation of trifluoromethyl radicals.

In a theoretical consideration of the addition of radicals to aromatic compounds, it is usual to assume that the changes in the rate constants are caused mainly by the changes in the activation energies for the reactions. The explanation of the deactivation of the aromatic ring by fluorine atoms in terms of electron repulsion effects or the dipolar influence of the medium also presupposes a change in activation energies. However, the data in Table 3 show that the activation energies are actually very close for all substituted benzenes, while the activation entropy (the $A$ factor) depends significantly on the number and nature of substituents.

Evidently the replacement of hydrogen atoms by fluorine in the reaction centre of the aromatic compound can influence both the activation energy and entropy of the radical addition reaction. Szwarc and coworkers[34] quote data showing that the activation entropies for hexafluorobenzene and benzene differ very little, while according to the data of Whittle and coworkers[27] the $A$ factor for aromatic polyfluoro-compounds is lower by a factor of approximately ten than for benzene derivatives without fluorine atoms. The reversibility of the addition of the trifluoromethyl radical to aromatic compounds at high temperatures (150°C for benzene and 180°C for hexafluorobenzene)[34] introduces some uncertainty into both sets of results.

Nevertheless findings such as the similarity of the ratios of the rate constants for the addition of $CF_3^{\cdot}$ to $C_6H_6$ and $C_6F_6$, obtained by Szwarc and Whittle in the temperature range 24–80°C ($k_{C_6H_6}/k_{C_6F_6} = 20$), and the observed decrease of the $A$ factor for the addition of the trifluoromethyl radical to a series of other polyfluorobenzenes (Table 3) suggest that the change in activation entropy observed by Whittle and coworkers is greater than the possible experimental error and is therefore more reliable than the data of Szwarc and coworkers. The decrease of the activation entropy for the addition of the trifluoromethyl radical occurring in the presence of substituents at the reaction centre may be a result of a partial restriction of the rotation of the trifluoromethyl group about the C–$CF_3$ axis in the transition state.

For compounds of the type $C_6F_5X$ with X = H as the standard substituent, the same effects of the substituents are observed in the addition reaction of the trifluoromethyl radical (Table 4) as for the benzene derivatives $C_6H_5X$ (Table 2).

Table 4. The relative rate constants $k_{rel}$ for the addition of the trifluoromethyl radical to compounds of the type $C_6F_5X$.[27]

| X | H | F | Br | Cl | $CF_3$ | $CH_3$ |
|---|---|---|---|---|---|---|
| $k_{rel}$ | 1 | 0.71 | 1.13 | 1.12* | 0.77 | 1.46 |

* The rate constants were calculated from the ratios $k_{C_6H_5Cl}/k_{C_6H_6} = 0.065$ [29] and $k_{C_6F_5H}/k_{C_6H_6} = 0.058$.[27]

Interesting observations have been made on the mode and ease of abstraction of hydrogen from aromatic fluorocompounds by the trifluoromethyl radical[27]. As fluorine atoms accumulate in the $C_6H_nF_{6-n}$ molecule, the abstraction of hydrogen becomes increasingly more difficult, but the addition of $CF_3^{\cdot}$ is hindered at the same time, in agreement with the earlier hypothesis that the abstraction of hydrogen in the reactions of aromatic compounds with alkyl radicals is most likely to occur from σ addition complexes of these radicals rather than directly from the ring. When the benzene ring contains a substituent such as the $CH_3$ group, hydrogen is abstracted from the latter in $C_6F_5CH_3$ with much more difficulty than in $C_6H_5CH_3$, which can be explained by the greater strength of the C–H bond in pentafluorotoluene.

The abstraction of a bromine atom is observed in the reactions of benzene derivatives such as $C_6H_5Br$ and $C_6F_5Br$ with the trifluoromethyl radical, which can be inferred from the formation of $CF_3Br$. It is then found that bromine is abstracted from bromopentafluorobenzene approximately six times more readily than from bromobenzene, but the rate constants for these reactions cannot be calculated, since there exist two alternative mechanisms of the abstraction of bromine: (1) directly from the aromatic ring and (2) from the intermediate σ complex in which $CF_3^{\cdot}$ has added to the carbon atom linked to bromine. The observations of Whittle and coworkers[27] tend to support the second mechanism. Firstly, the rate of formation of $CF_3Br$ [and $CH_3Br$?] from both $C_6F_5Br$ and $C_6H_5Br$ does not change appreciably with temperature and, secondly, the activation energies for the two reactions are less than 2 kcal mole$^{-1}$, while that for the abstraction of hydrogen is approximately 5 kcal mole$^{-1}$. Despite the low activation energy, the elimination of bromine from $C_6H_5Br$ proceeds much more slowly than that of hydrogen, probably due to steric factors, which may play a more important role in the abstraction of bromine located in the geminal position with respect to the $CF_3$ group in the σ complex than in the abstraction of hydrogen from the analogous σ complex. In contrast to the reactions of $C_6H_5Br$ and $C_6F_5Br$, an appreciable elimination of the chlorine atom was not observed in the reaction of the trifluoromethyl radical with $C_6H_5Cl$ and $C_6F_5Cl$ even at 110–120°C.[29] The calculated activation energy for the elimination of the chlorine atom is approximately 13 kcal mole$^{-1}$. On the other hand, iodine is abstracted very rapidly from $C_6H_5I$ and $C_6F_5I$ by the trifluoromethyl radical, the rate of abstraction from pentafluoroiodobenzene being approximately four times greater than from iodobenzene.

When $CF_3^{\cdot}$ interacts with pentafluorobenzaldehyde[35], the hydrogen atom is abstracted with formation of trifluoromethane and a pentafluorobenzoyl radical, which recombines with $CF_3^{\cdot}$ to form octafluoroacetophenone:

$$C_6F_5CHO + CF_3^{\cdot} \xrightarrow{h\nu} C_6F_5CO^{\cdot} + CF_3H\ ;$$
$$C_6F_5CO^{\cdot} + CF_3^{\cdot} \rightarrow C_6F_5COCF_3\ .$$

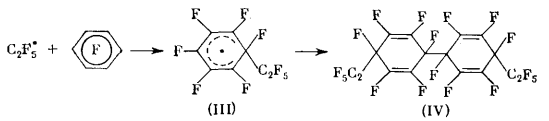
The activation energy for the abstraction of the hydrogen atom from pentafluorobenzaldehyde is higher than for benzaldehyde (8.6 and 4.6 kcal mole$^{-1}$ respectively), but the yield of octafluoroacetophenone is significantly higher than that of acetophenone in the corresponding reaction of benzaldehyde. According to the authors[35], the latter factor may be a result of the low stability of the non-fluorinated benzoyl radical (the dissociation energy of the $C_6H_5$–CO bond is only 28 kcal mole$^{-1}$), which readily dissociates with formation of $C_6H_5^{\cdot}$ and CO. On the other hand, it may be that the high yield of octafluoroacetophenone is due to the high reactivity of the pentafluorobenzoyl radical [cf. the reaction of $C_6F_5I$ with $Ni(CO)_4$, see Section V below], which reacts with the trifluoromethyl radical before dissociating with formation of $C_6F_5$ and CO.

It is of interest to compare the results of the study of the interaction of benzene and hexafluorobenzene with the chlorodifluoromethyl radical generated from 1,3-dichlorotetrafluoroacetone on photolysis[36]. The significant differences between the temperature dependences of the rates of formation of the products of the addition of $CF_2Cl^{\cdot}$ to $C_6H_6$ and $C_6F_6$ observed by the authors were interpreted in terms of the different stabilities of the corresponding σ complexes (up to 100°C for $C_6H_6CF_2Cl^{\cdot}$ and up to 250°C for $C_6F_6CF_2Cl^{\cdot}$).

The fact that the elimination of fluorine atoms was not observed in any of the reactions of aromatic polyfluorocompounds with fluorine-containing alkyl radicals may serve as evidence that the main pathway in the reaction of the σ complexes produced by the addition of the radicals to aromatic polyfluoro-compounds involves their dimerisation. We already noted previously that, in the vast majority of the reactions investigated, with both non-fluorinated and fluorinated reagents, dimeric products could not be isolated and the conclusions concerning the mechanism of the reaction of the σ complexes resulting from the addition of alkyl radicals to fluorinated and non-fluorinated aromatic compounds were based on kinetic data. In a study of the reaction of hexafluorobenzene with the perfluoroethyl radical generated from perfluoropropionyl peroxide, the isomeric compounds (IV)—the dimers

of the σ complex produced by the addition of $C_2F_5^{\cdot}$ to $C_6F_6$ (III)—were recently isolated[37] as the main reaction products:

$$(C_2F_5COO)_2 \xrightarrow{\Delta} 2C_2F_5^{\cdot} + 2CO_2 ;$$



(III) (IV)

The difference in the behaviour of benzene and hexafluorobenzene in their reactions with nitromethane at 550°C is noteworthy[38]. The main product of the reaction of benzene is biphenyl, while the remaining products consist to the extent of 80% of nitrogen compounds (aniline and *N*-methylaniline)[39]; on the other hand, the reaction with $C_6F_6$ yields mainly pentafluorotoluene and pentafluorophenol, the ratio of which varies with the molar ratio of the reactants (Table 5).

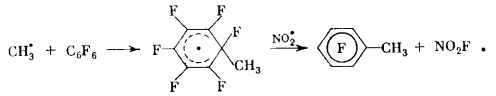
Table 5. The proportions of the products of the reaction of $C_6F_6$ with $CH_3NO_2$ (determined as percentages by GLC relative to one mole of $C_6F_6$).

| Reaction product | Nitromethane (no. of moles) | | Reaction product | Nitromethane (no. of moles) | |
|---|---|---|---|---|---|
| | 1 | 0.1 | | 1 | 0,1 |
| $C_6F_5CH_3$ | 37.5 | 60.0 | $C_6F_5CHO$ | 6.6 | 4.6 |
| $C_6F_5OH$ | 33.0 | 3.0 | $C_{12}F_{10}$ | 6.8 | 2.9 |
| $C_6F_5OCH_3$ | 5.9 | 12.7 | unknown products | 10.2 | 16.8 |

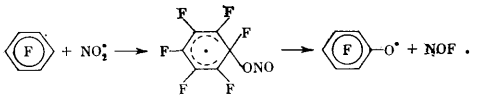
The observed difference between the products of the reactions of nitromethane with benzene and hexafluorobenzene may be attributed to a certain amount of nucleophilic character of the methyl radical, as a result of which its attack on $C_6F_6$, which is sensitive to nucleophiles[2], becomes the preferred pathway. Possibly the degree of such preference reflects the difference between the bond dissociation energies $D(C_6F_5-CH_3) - D(C_6H_5-CH_3) = 25$ kcal mole$^{-1}$.[40] The following mechanism is proposed for the formation of the main product of the reaction of $CH_3NO_2$ with $C_6F_6$. At a high temperature nitromethane decomposes into two radicals:

$$CH_3NO_2 \rightarrow CH_3^{\cdot} + NO_2^{\cdot} .$$

The methyl radical adds to hexafluorobenzene with formation of a σ complex, from which a fluorine atom is abstracted by the $NO_2^{\cdot}$ radical:



The methyl radical apparently reacts with hexafluorobenzene so fast that there is not sufficient time for the abstraction of a hydrogen atom from nitromethane, as happens in the reaction with benzene. The role of $NO_2^{\cdot}$ in the two reactions is likewise different. The radical abstracts hydrogen from benzene, giving rise to the phenyl radical responsible for the formation of biphenyl in the phenylation of benzene or during dimerisation. Fluorine is apparently abstracted to only an insignificant extent from $C_6F_6$, since only very small amounts of decafluorobiphenyl are formed. The $NO_2^{\cdot}$ radical is most likely to play the main role in the formation of pentafluorophenol in the reaction with $C_6F_6$:



The pentafluorophenoxy-radical probably abstracts hydrogen from nitromethane, forming pentafluorophenol.

The alternative mechanism of the formation of pentafluorophenol via pentafluoronitrobenzene or possibly indirectly via pentafluorophenyl nitrite (without the preliminary dissociation of nitromethane as in the formation of phenols from different aromatic nitro-compounds at a high temperature[41]) is probably ruled out owing to the absence of $CH_3F$ from the reaction products.

Pentafluoroanisole may be formed in the reaction of hexafluorobenzene with nitromethane as a result of the attack on $C_6F_6$ by the methoxy-radical formed in the nitro-nitrite rearrangement or in the recombination–dissociation of nitromethane:

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow CH_3O^{\cdot} + NO^{\cdot}$$
$$\downarrow$$
$$CH_3^{\cdot} + NO_2^{\cdot} .$$

The preferential elimination of fluorine relative to that of hydrogen in the reactions with the methyl radical generated from nitromethane at high temperatures is clearly seen in the interaction of *p*-difluorobenzene with nitromethane[38]. The main product of this reaction is fluorophenol and the ratio of the yields of the products of the abstraction of fluorine and hydrogen atoms is 33 : 1.

The higher reactivity of hexafluorobenzene relative to benzene was also noted in a study of the reactivity of polyfluorinated unsaturated compounds with respect to the methyl radical generated from acetyl peroxide[43] (Table 6).

Table 6. The affinities of unsaturated compounds and their fluorinated analogues for the methyl radical[42].

| Compound | $C_6H_6$ | $CH_2=CH-CH=CH_2$ | $C_6F_6$ | $CF_2=CF-CF=CF_2$ |
|---|---|---|---|---|
| $k_1/k_2$* | 0.4[15] | 2900[43] | 3.1 | 900 |

*$k_1$ is the rate constant for the addition of $CH_3^{\cdot}$ and $k_2$ the rate constant for the abstraction of hydrogen from the solvent by $CH_3^{\cdot}$.

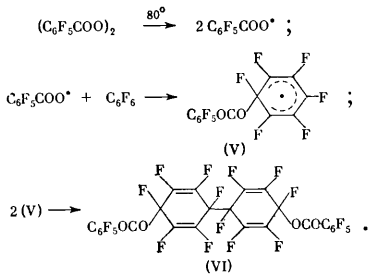
The above reactions of alkyl radicals with aromatic polyfluoro-compounds reveal certain characteristic features of the behaviour of these compounds. In the first place, one should note the higher reactivity of aromatic polyfluoro-compounds with respect to nucleophiles. No less important is the conclusion that the fluorine-containing radical σ-complexes are more stable, which follows from a comparison of the dissociation temperatures of such complexes, formed by the addition of alkyl radicals to benzene and hexafluorobenzene.

## III. REACTION WITH ARYL RADICALS

The data described in the previous Section showed that the available information about the reactions of a large set of aromatic polyfluoro-compounds with alkyl radicals

concerns mainly the process kinetics and there are almost no data concerning the synthetic possibilities of the reactions. In the studies on the interaction of aromatic polyfluoro-compounds with aryl radicals, there has been a more successful combination of investigations on these different lines, which make it possible to discover both the quantitative relations governing the behaviour of aromatic polyfluoro-compounds in these reactions as well as interesting synthetic reactions. Mainly aroyl peroxides have been used as the sources of aryl radicals in the reactions investigated, since it was observed that hexafluorobenzene does not react, for example, with the pentafluorophenyl radicals generated from $C_6F_5NHNHNH_2$[44] in the presence of oxidising agents, or from $C_6F_5I$ on photolysis[45], or with a source of $C_6F_5^{\cdot}$ such as $C_6F_5N(NO).COCH_3$, which might have been expected to be effective by analogy with the non-fluorinated compound[46].

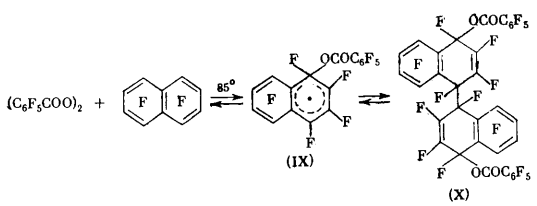
In the decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene at 80°C, 4,4′-di(benzoyloxy)perfluoro-1,1′,4,4′-tetrahydrobiphenyl (VI), resulting from the dimerisation of the σ complex (V) formed by the addition of the pentafluorobenzoyloxy-radical to $C_6F_6$, is the main reaction product (60%).[47,48]



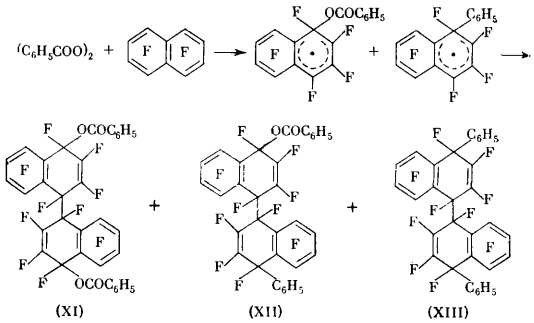
Apart from compound (VI), 3–5% of perfluorophenyl benzoate (VII) and 5–7% of tetrafluorobiphenyl (VIII) are produced. English chemists[49,50] were unable to isolate in a similar reaction any products other than compounds (VII) and (VIII).

The principal characteristics of this reaction are the virtual absence of the products of homolytic substitution and the preferential involvement of pentafluorobenzoyloxy-radicals in the reaction. We may recall that non-fluorinated reagents give rise mainly to biphenyls under these conditions. Compounds (VII) and (VIII), which are formed in insignificant amounts, can be regarded either as a result of the reaction of the radicals generated from pentafluorobenzoyl peroxide (for example the dimerisation of $C_6F_5^{\cdot}$ or the recombination of $C_6F_5^{\cdot}$ and $C_6F_5COO^{\cdot}$) or as products of the reaction of these radicals with hexafluorobenzene.

The interaction of octafluoronaphthalene (OFN) with pentafluorobenzoyl peroxide leads to results analogous to those obtained in the reaction with hexafluorobenzene. The main product at 85°C (in acetonitrile) is the dimer (X) of the σ complex resulting from the addition of the pentafluorobenzoyloxy-radical to the 1-position of OFN (IX):[51]

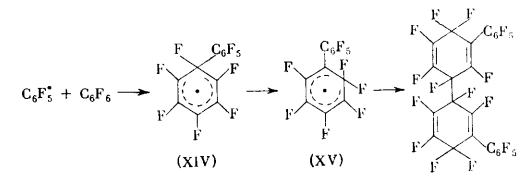


The reaction of OFN with the non-fluorinated benzoyl peroxide under the same conditions[51] probably yields a mixture of the dimers (XI), (XII), and (XIII):



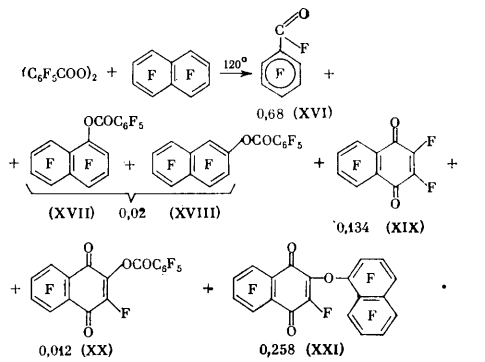
The involvement of both benzoyloxy- and phenyl radicals in this reaction, in contrast to the reactions with pentafluorobenzoyl peroxide, indicates a significant influence of the introduction of the fluorine atoms into the peroxide molecule on the nature of its decomposition (this problem will be discussed below).

The exclusive involvement of the pentafluorophenyl radical in the reaction of $C_6F_6$ with $(C_6F_5COO)_2$ is observed only at high temperatures. Thus a mixture of isomeric dimers of the σ complex formed by the addition of the pentafluorophenyl radical to hexafluorobenzene is produced at 200°C.[48] The structure of these dimers, confirmed by their spectroscopic characteristics and their defluorination to perfluoro-*m*,*m*′-quaterphenyl, shows that the reaction probably involves the dimerisation of the σ complex (XV), formed as a result of the migration of the fluorine atom in the initial σ complex of type (XIV):

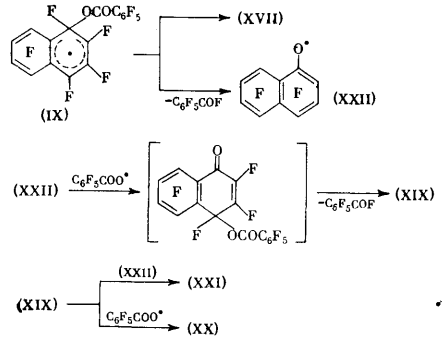


The driving force of the migration of the fluorine atom in the σ complex (XIV) is probably the considerable increase of the stability of the rearranged σ complex (XV) as a result of the possibility of the involvement of the pentafluorobenzene ring in the delocalisation of the unpaired electron.

It is of interest that an increase of temperature in the reaction of pentafluorobenzoyl peroxide with OFN does not lead to the formation of products with participation of the pentafluorophenyl radical. At 120°C this reaction already proceeds via a completely unusual pathway[65], resulting in the formation of a mixture of products in which 2-(1′-naphthoxy)perfluoro-1,4-naphthoquinone (XXI) predominates:



The formation of the naphthoquinone derivatives (XIX), (XX), and (XXI), which has no analogies in the familiar reactions of aroyl peroxides with naphthalene and its derivatives, is attributed to the following reactions:



The radical σ complex (IX) can, on the one hand, lose a fluorine atom and be converted into typical homolytic substitution products–perfluorobenzoyloxynaphthalenes, and, on the other hand, it can split off pentafluorobenzoyl fluoride (XVI) to give a new radical, i.e. the heptafluoronaphthoxy-radical (XXII), which is responsible for the subsequent reactions leading to the formation of compounds (XIX), (XX), and (XXI). This pathway to the stabilisation of the σ complex (IX) is probably due to the presence of the fluorine atom and the benzoyloxy-group in the geminal unit, which is confirmed by the formation of compounds (XIX) and (XXI) when OFN reacts with benzoyl peroxide at 85 °C in the absence of an inert solvent[53]. Hexafluoronaphthoquinone derivatives are formed in this reaction together with homolytic substitution products and the products of the reaction of benzoyl peroxide without the involvement of a fluorinated substrate (Table 7).

Table 7. The results of the interaction of benzoyl peroxide with octafluoronaphthalene (the yields are expressed in moles per mole of peroxide; peroxide : OFN = 1 : 4; 30 h).

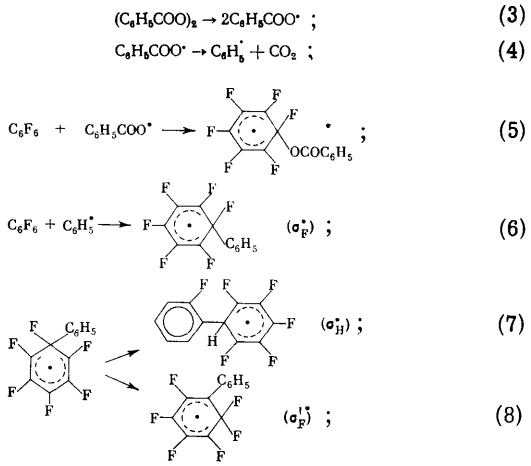
| Compound | Reaction temperature | |
|---|---|---|
| | 85° | 110° |
| 1-Benzoyloxyheptafluoronaphthalene | 0.045 | 0.019 |
| 2-Benzoyloxyheptafluoronaphthalene | 0.037 | 0.012 |
| 1-Phenylheptafluoronaphthalene | 0.104 | 0.287 |
| 2-Phenylheptafluoronaphthalene | 0.031 | 0.120 |
| 3,5,6,7,8-Pentafluoro-2-(heptafluoro-1'-naphthoxy)-1,4-naphthoquinone (XXI) | 0.056 | 0.019 |
| Hexafluoro-1,4-naphthoquinone | 0.022 | 0.018 |
| Benzoyl fluoride | 0.515 | – |
| Biphenyl | 0.051 | 0.094 |
| Phenyl benzoate | 0.566 | 0.048 |

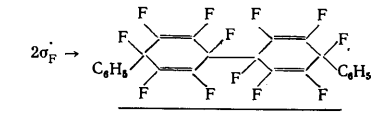
The data in Table 7 show that a change in reaction temperature has only an insignificant effect on the qualitative composition of the reaction products, but does influence appreciably their quantitative proportions. With increase of temperature, the yield of phenylheptafluoronaphthalenes increases, as has been observed in the reaction of naphthalene with benzoyl peroxide[54]. The proportions of the isomers remain almost unchanged as the temperature is altered and indicate the greatest sensitivity of the α-position in the OFN molecule to radical attack, in agreement with the calculated radical localisation energy of OFN.

It is very remarkable that the reaction of OFN with $(C_6H_5COO)_2$ involves the homolytic substitution of a fluorine atom, which constitutes at the same time the preferred process. This may imply that the absence of products of the homolytic substitution of fluorine atoms in reactions of OFN and $C_6F_6$ with $(C_6F_5COO)_2$ is not solely due to the great strength of the C–F bond in the initial aromatic polyfluoro-compounds [$D(C_6F_5–F)$ = 140 kcal;[55] $D(C_6H_5–H)$ = 102 kcal [56]], but is also associated with the nature of the radical.

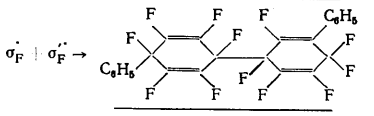
For example hexafluorobenzene reacts with $(C_6H_5.COO)_2$ [57–61] and some of its substituted derivatives[62] to form homolytic substitution products. High yields (60–80%) of the corresponding pentafluorobiphenyls were obtained in the reactions with benzoyl peroxide itself and its 3-methyl derivative but, after the introduction of electron-accepting substituents (3-chloro-, 3-bromo-, and 4-nitro-) into the peroxide molecule, the yields of the arylation products are appreciably reduced, particularly in the case of the nitroderivative of the peroxide. Williams and coworkers[62] used this mode of reaction as a basis for the conclusion that the mechanism of the arylation of aromatic polyfluoro-compounds is similar to the familiar mechanism of the arylation of non-fluorinated aromatic compounds and involves the formation of biaryls either via the disproportionation of the corresponding σ complexes or via the elimination of a fluorine atom from the latter by any radical present in the mixture.

However, a detailed study of the kinetics and products of the reaction of hexafluorobenzene with benzoyl peroxide led to the abandonment of disproportionation as a pathway to the formation of biaryls and a new mechanism was postulated for this reaction, based on the involvement of benzoic acid as a defluorinating agent. The mechanism, which also includes stages common to the reactions of non-fluorinated compounds, is given below[59–61] (the compounds which were islated from the products of this reaction are underlined):

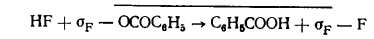




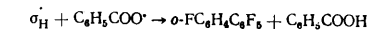
(13)



(14)



(15)



(16)



(17)

The first stages in this mechanism [stages (3) and (4)] are well known and require no explanation. Like the subsequent addition of the radicals to the substrate [Eqns. (5) and (6)], they are analogous to the stages of the interaction of aroyl peroxides with other aromatic systems. The stage involving the rearrangement of the initially formed σ complex ($\sigma_F^{\cdot}$) with migration of the fluorine atom to the unsubstituted cyclic compound [Eqn. (7)] and the subsequent reaction with benzoyl peroxide [Eqn. (9)] of the rearranged σ complex ($\sigma_H^{\cdot}$) explain in the simplest manner the formation in this reaction of small amounts of 2,2′,3,4,5,6-hexafluorobiphenyl (XXIII) and benzoic acid. The formation of compound (XXIII) was also observed in the high-temperature (600°C) reaction of hexafluorobenzene with nitrobenzene (mass-spectrometric data)[41,63], for which a radical mechanism has been proposed.

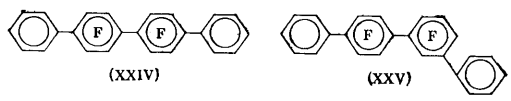
Stages (9) and (10) reflect the contribution of the induced decomposition of benzoyl peroxide to the reaction, which follows also from the analysis of the kinetic parameters of the reaction[61]. The rearrangement [Eqn. (8)] of the σ complex ($\sigma_F^{\cdot}$) with migration of the fluorine atom to a neighbouring position (a 1,2-shift), competing with the rearrangement [Eqn. (7)] to a σ complex ($\sigma_H^{\cdot}$) probably takes place to a greater extent, as can be seen from the yields of the products of dimerisation with participation of the rearranged σ complex ($\sigma_F^{\prime\cdot}$).[59]

Defluorination of the σ complex ($\sigma_F^{\cdot}$) with participation of benzoic acid [Eqn. (11)] is one of the main stages of the reaction. It leads to the formation of pentafluorobiphenyl and is a pathway to the regeneration of the benzoyloxy-radical and a source of HF. The absence of benzoic acid, an effective defluorinating agent, is probably the reason for the low yields of pentafluorobiphenyl in the reactions of hexafluorobenzene with other sources of phenyl radicals, such as phenylazotriphenylmethane[64] and $C_6H_5N=NOC_5H_{11}$.[65] The important role of benzoic acid is demonstrated by the increase of the yield of pentafluorobiphenyl when the decomposition of phenylazotriphenylmethane is carried out in hexafluorobenzene in the presence of benzoic acid[64].

The proposed mechanism for the interaction of hexafluorobenzene with benzoyl peroxide includes several pathways to the generation of benzoic acid. Apart from stage (9) mentioned above, reaction (15) and to a lesser extent reaction (16) merit attention. The required amounts of esters may be formed in subsequent reactions of the σ complex produced by the addition of the benzoyloxy-radical to hexafluorobenzene [Eqn. (5)] or via reactions (10) and (17). Since pentafluorophenyl benzoate, the formation of which may be expected when the substrate undergoes aroyloxylation initiated by reaction (5), is absent from the reaction products, all the esters are probably formed in radical–radical reactions. The most significant contribution apparently comes under these conditions from the ester $\sigma_F$–$OCOC_6H_5$, the formation of which includes the recombination of two radicals present at high steady-state concentrations.

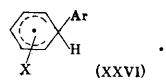
It is of interest that the combination of stages (10), (11), and (15) ultimately leads to the formation of pentafluorobiphenyl and heptafluorodihydrobiphenyls†, i.e. to the products which can be formed also by the disproportionation of the σ complex ($\sigma_F^{\cdot}$).

The abandonment of disproportionation as one of the stages of the process was dictated by the following considerations. The disproportionation is a single-stage reaction and requires that the radical–radical combination processes resulting in dimers should not take place preferentially. However, since dimerisation and disproportionation are kinetically equivalent, the rate being equal to $k[\sigma_F^{\cdot}]^2$, the process with the lower activation energy, namely dimerisation, is the most probable, ruling out the elimination of a fluorine atom. The contribution of the dimerisation processes [Eqns. (13) and (14)] varies as a function of the reaction conditions and the yields of the dimers vary from 3 to 50%.[59] The formation on defluorination of the mixture of dimers of compounds (XXIV) and (XXV) (octafluoroquaterphenyls) confirms the rearrangement of the σ complex ($\sigma_F^{\cdot}$) formed initially to the σ complex ($\sigma_F^{\prime\cdot}$) with 1,2-migration of the fluorine atom[59]:




The results of the interaction of benzoyl fluoride with substituted aromatic polyfluoro-compounds are presented in Table 8, which includes for comparison also data for certain non-fluorinated compounds.

The transition state in the arylation of simple benzene derivatives ($C_6H_5X$) is generally believed to have a structure intermediate between that of the ground state and that of a σ complex of type (XXVI):




It is assumed that the unpaired electron is delocalised over the entire ring, including the substituent. Such delocalisation with participation of the substituent determines to a large extent the observed mode of substitution in homolytic arylation. In aromatic polyfluoro-systems ($C_6F_5X$), there is a choice between two structures in which the substituent involved in delocalisation is X or F, which may lead to differences in the isomeric composition of the arylation products $C_6F_5X$ and $C_6H_5X$.

The proportions of the isomeric biphenyls in the reactions of benzoyl peroxide with chloro- and bromo-pentafluorobenzenes are analogous to those observed in the

† The heptafluorodihydrobiphenyls were not isolated, but it was postulated that they are converted into pentafluorobiphenyl during the treatment of the reaction products, since it has been shown that the distillation of the mixture of products under severe conditions (300°/760 mmHg instead of 100°/15 mmHg) results in an increase of the yield of pentafluorobiphenyl almost by a factor of 1.5 and to the same decrease of the yield of an unidentified tarry residue[66].

non-fluorinated series, which may be a result of the similar efficiencies of chlorine, bromine, and fluorine atoms in the delocalisation of the unpaired electron in the corresponding σ complexes. The isomeric composition of the pentafluorobenzene phenylation products shows that substitution in the 1- and 3-positions takes place most readily, which apparently corresponds to a greater ease of formation of the corresponding σ complexes which are stabilised by the involvement of three fluorine atoms in the resonance, in contrast to σ complexes formed when the 2- and 4-positions are attacked. The greater ease of substitution of hydrogen compared with fluorine is probably also determined by the difference between the mechanisms of the aromatisation of the corresponding σ complexes[68]. For the same reasons as in the case of $C_6F_5H$, the 3-position is the most reactive in $C_6F_5CF_3$. The additional decrease of the reactivity of the 2-position is attributed to steric factors and the relatively greater reactivity of the 3-position relative to the 4-position is thought to be due to the presence of three fluorine atoms involved in the stabilisation of the σ complexes formed in the former case and of two such atoms in the latter[68].

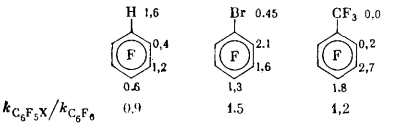
Table 8. The ratio of the isomers formed in the phenylation of aromatic compounds at 80°C (determined as percentages by GLC).

| Compound | Isomeric composition of phenylation products | | |
|---|---|---|---|
| | 2- | 3- | 4- |
| $C_6F_5Cl$[66] | 44.1 | 35.0 | 20.9 |
| $C_6H_5Cl$[67] | 50.1 | 31.6 | 18.3 |
| $C_6F_5Br$ *[66,68] | 43.6 (45.0) | 39.0 (36.0) | 17.4 (14.0) |
| $C_6H_5Br$[69] | 49.3 | 33.3 | 17.4 |
| $C_6F_5CF_3$[68] | 5.0 | 71.0 | 24.0 |
| $C_6F_5H$ **[68] | 15.0 | 45.0 | 11.0 |
| $C_5F_5N$[66] | 47.7 | 22.1 | 30.3 |
| $C_6H_5N$[70] | 54.0 | 32.0 | 14.0 |

* The data of Bolton et al.[68], according to which approximately 5% of the product resulting from the substitution of the bromine atom is also formed, are indicated in brackets.

** The formation of 29% of the product of the substitution of a hydrogen atom was also noted.

The partial rate factors for attack in different positions in $C_6F_5X$, determined by comparing the composition of the reaction products and the relative rate constants obtained from competition experiments with equimolar amounts of $C_6F_6$ and $C_6F_5X$, are indicated below[68]:

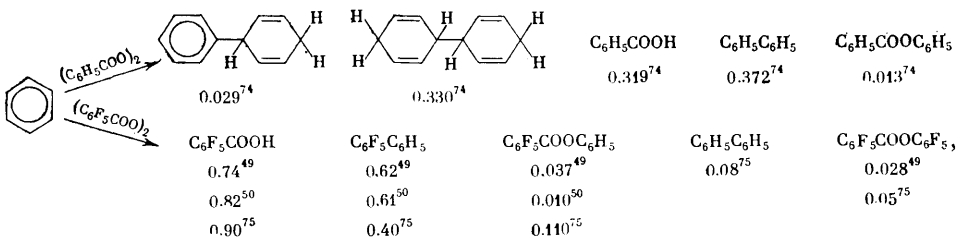


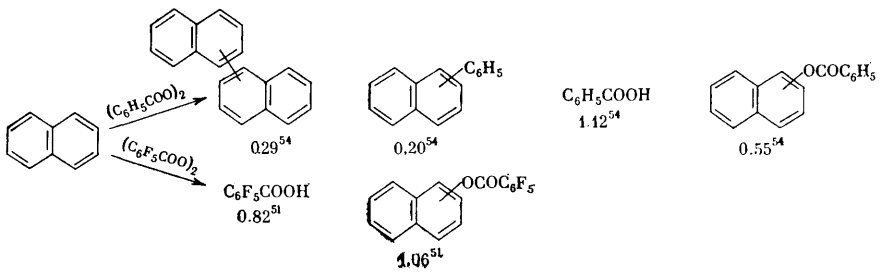

The relative rates of arylation of aromatic polyfluoro-compounds shown here differ from those obtained previously from the competing reactions of each substrate with benzene (for example $k_{C_6F_5Br}/k_{C_6F_6} = 1.0$).[11] This discrepancy is probably determined by the fact that, when benzene is used as the standard, the atoms substituted and the mechanisms of their substitution are different, and in addition there is a possibility of the formation of complexes by the mixture components[71]. For this reason, the results obtained from the competing reactions with $C_6F_6$ are more reliable[68].

It has already been stated that the high reactivity of the *meta*-position in all the compounds $C_6F_5X$ can be explained by the formation of a σ complex having three fluorine atoms capable of involvement in delocalisation. However, attack on the hexafluorobenzene itself also involves the formation of a σ complex with three stabilising fluorine atoms and yet the partial rate factors for attack in the *meta*-position are greater than unity for all the substrates. Such anomalous activation of the *meta*-position is believed to be a result of the formation of complexes of different stabilities by the precursor of the phenyl radical and the aromatic polyfluoro-substrate[68].

The greater ease of substitution of a hydrogen atom compared with a fluorine atom has been demonstrated for the reactions of $C_6F_5H$ with the phenyl radical[68]. Similar results were obtained for certain other substituted aromatic polyfluoro-compounds containing fluorine and hydrogen atoms in the molecule simultaneously. For example, the interaction of 1,2,4,5-tetrafluorobenzene[72] and 2,3,4,5,6-pentafluorobiphenyl[73] with the pentafluorophenyl radical, generated from $C_6F_5I$ on photolysis or thermal decomposition, leads to the formation in high yields only of products resulting from the substitution of hydrogen atoms: 2,2′,3,3′,4,5,5′,6,6′-nonafluorobiphenyl and three isomeric decafluoroterphenyls (14% of the *o*-isomer, 49.7% of the *m*-isomer, and 36.3% of the *p*-isomer) respectively.

In order to estimate the influence of fluorine atoms on the reactivity of aromatic polyfluoro-compounds in radical reactions, it is necessary to compare the above data for the interaction of hexafluorobenzene and octafluoronaphthalene with benzoyl and pentafluorobenzoyl peroxides with the results of the corresponding reactions of benzene and naphthalene presented in the scheme below (the yields are quoted in mole per mole of the peroxide):






The known increase of the yield of benzoyloxylation products relative to the yield of phenylation products in the case of highly reactive substrates[76] and of the formation of products of the reaction of the peroxide without the involvement of the aromatic substrate when the reactivity of the latter is low[77] may be adopted as a basis for a qualitative comparison. Analysis of all the results presented from this standpoint justifies the assumption that the reactivities of hexafluorobenzene and octafluoronaphthalene in reactions with aroyl peroxides are greatly reduced compared with those of non-fluorinated substrates. Thus, benzoyloxation products are absent in the reaction of hexafluorobenzene with benzoyl peroxide (they are formed in the corresponding reaction of benzene) and considerable amounts of biphenyl are produced. The formation of the products of the conversion of benzoyl peroxide itself (biphenyl and phenyl benzoate) is also observed in the reaction of OFN, although the relative contributions of the benzoyloxylation and phenylation processes remain the same as in the reaction of benzoyl peroxide with naphthalene.

The decrease of the reactivity of aromatic polyfluoro-compounds is characterised quantitatively by the ratio of the rates of phenylation of benzene and hexafluorobenzene found from the competing reactions of the latter with benzoyl peroxide: $k_{C_6F_6}/k_{C_6H_6} = 0.44$.[68] The reduced reactivity of aromatic polyfluoro-compounds may be caused by the influence of the fluorine atoms both in the stage involving the addition of the radical with formation of the $\sigma$ complex and in the stage where the $\sigma$ complex is stabilised by the elimination of a fluorine atom. The series based on the relative reactivities of aromatic compounds with respect to electrophilic benzoyloxy-radicals ($C_6H_5OCH_3 > C_6H_5CH_3 > C_6H_6 > C_6H_5Cl > C_6H_5NO_2$)[79,80] shows that electron-accepting substituents in the substrate hinder benzoyloxylation. On the other hand, regardless of the electronic nature, all the substituents facilitate phenylation, as shown by the following series of relative rates of phenylation of benzoyl peroxide[30]: $C_6H_6$ (1); $C_6H_5F$ (1.03); $C_6H_5Cl$ (1.06); $C_6H_5NO_2$ (2.94); 1,3,5-$C_6H_3Cl_3$ (3.68). Comparison of these two series shows that the influence of fluorine atoms in the substrate on the first stage—the addition of the radical with formation of a $\sigma$ complex—should be of the opposite types for the phenyl and benzoyloxy-radicals. However, experimental results show that the reactivity of aromatic polyfluoro-compounds is reduced both relative to the electrophilic benzoyloxy-radical and relative to the neutral phenyl radical. The latter fact may be due to the steric shielding of the reaction centre by the *ortho*-fluorine atoms, which prevent attack by phenyl radicals. An example of the influence of steric shielding of the reaction centres by the *ortho*-fluorine atoms on the reactivity is provided by the reduced reactivity of pentafluorobenzaldehyde relative to benzaldehyde in nucleophilic reactions involving the carbonyl group[81].

The influence of fluorine atoms in aromatic substrates on the stage involving the stabilisation of radical $\sigma$-complexes reflects the formation of dimerisation products of these complexes in the reactions of hexafluorobenzene and octafluoronaphthalene with benzoyl and pentafluorobenzoyl peroxides. This influence may be associated with the difference between the C–H and C–F bond dissociation energies[55,56], with the increased stability of the fluorinated radical $\sigma$ complexes, and also with the greater stability of the fluorinated dimers.

As already mentioned, one of the characteristics of the reactions of aromatic polyfluoro-compounds with aroyl peroxides is that, in the reactions of both hexafluorobenzene and octafluoronaphthalene with pentafluorobenzoyl peroxide under mild conditions (80–85°C), products involving the participation of the pentafluorobenzoyloxy-radical are formed preferentially. This may be caused by the influence of fluorine atoms on the reactivity of the radicals, which is manifested by an enhancement of their electrophilic properties.

Kurz and Pellegrini[80] showed that the benzoyloxy-radical is electrophilic and that the introduction of electron-accepting substituents into the peroxide molecule enhances the electrophilic properties of the benzoyloxy-radicals formed on its decomposition. The enhancement of the electrophilic properties of the pentafluorobenzoyloxy-radical can be explained satisfactorily by the overall inductive electron-withdrawing effect of the pentafluorophenyl group, resembling the effect of the 2,4-dinitrophenyl residue[82]. The enhanced electrophilic properties of the pentafluorobenzoyloxy-radical are reflected in a higher degree of $\alpha$-substitution in the reaction of naphthalene with pentafluorobenzoyl peroxide: the ratio of the $\alpha$- and $\beta$-naphthyl pentafluorobenzoates in this reaction is 10:1,[51] while in the reaction of naphthalene with benzoyl peroxide it is 2.7:1[54] (the $\alpha$-position in naphthalene is known to be most reactive in electrophilic reactions). The more marked electrophilic properties of the pentafluorobenzoyloxy-radical compared with the benzoyloxy-radical apparently lead to its increased reactivity in reactions with aromatic substrates. On the other hand, the high steady-state concentration of pentafluorobenzoyloxy-radicals, which can also indirectly reflect the influence of fluorine atoms on the reactivity of fluorinated radicals, may play a significant role in the preferential formation of benzoyloxylation products.

Kinetic data for the decomposition of benzoyl and pentafluorobenzoyl peroxides in benzene and hexafluorobenzene (Table 9)[83] show that pentafluorobenzoylperoxide is less resistant to unimolecular thermal decomposition than is benzoyl peroxide, since the rate constant for its decomposition in both benzene and hexafluorobenzene is greater than for the non-fluorinated peroxide. The reduced stability of the fluorinated peroxide may be associated, for example, with the appearance of an additional Coulombic repulsion between the *ortho*-fluorine

atoms in the benzene ring of the peroxide. The possibility of such a field effect has been used by Blomquist and Buselli[84] to account for the higher rate of decomposition of *ortho*-substituted symmetrical peroxides compared with their *meta*- and *para*-analogues. On the other hand, the ease of decomposition of pentafluorobenzoyl peroxide may be a result of the increased stability of the pentafluorobenzoyloxy-radical, which is confirmed by the kinetics of the decomposition of benzoyl and pentafluorobenzoyl peroxides in the absence of solvents[78]. The rate constant for the formation of $CO_2$ in the decomposition of benzoyl peroxide is greater than in the decomposition of pentafluorobenzoyl peroxide ($36.5\times10^{-2}$ and $10.1\times10^{-2}$ $min^{-1}$ respectively), i.e. pentafluorobenzoyloxy-radicals are more resistant to decarboxylation. The higher stability of pentafluorobenzoyloxy-radicals may be caused by the more effective delocalisation of the unpaired electron with participation of the benzene ring. All these factors taken together may promote a higher steady-state concentration of pentafluorobenzoyloxy-radicals.

Table 9. Kinetic parameters of the benzoyl and pentafluorobenzoyl peroxide decomposition reactions in benzene and hexafluorobenzene (80°C; initial peroxide concentration between 0.024 and 0.24 M).[83]

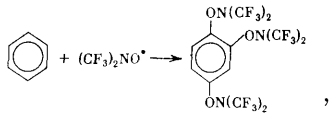
| Peroxide | $(C_6H_5COO)_2$ | | $(C_6F_5COO)_2$ | |
|---|---|---|---|---|
| Substrate | $C_6H_6$ | $C_6F_6$ | $C_6H_6$ | $C_6F_6$ |
| $10^3k$, $min^{-1}$ | 2.9 | 1.5 | 8.6 | 2.5 |
| $E$, kcal $mole^{-1}$ | 30 | 34 | 29 | 31 |
| $\lg A$ | 16 | 18 | 16 | 17 |

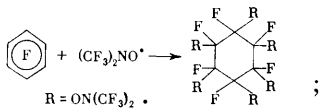
Evidently the pentafluorophenyl radical is also electrophilic, which is clearly illustrated by data for its interaction with substituted benzenes[65,85]. Thus the relative rate of the pentafluorophenylation of chlorobenzene is lower than that of its phenylation (0.72 and 1.06 respectively). However, the ratio of the degree of substitution in the *ortho*- and *para*-positions to the dgree of substitution in the *meta*-position is greater for pentafluorophenylation than for phenylation: $(o- + p-)/m- = 3.9$ and 2.9 respectively. In the reaction of the pentafluorophenyl radical with nitrobenzene, the electrophilic nature of the radical is manifested by an appreciable increase of the degree of substitution in the *meta*-position: $(o- + p-)/m- = 9.2$ ($C_6H_5^{\cdot}$) and $(o- + p-)/m- = 0.87$ ($C_6F_5^{\cdot}$). On reaction with 1,2,4,5-tetrafluorobenzene, the pentafluorophenyl radical generated from pentafluoroiodobenzene on photolysis of thermal decomposition gives a high yield of 2, 2′,3,3′,4,5,5′,6,6′-nonafluorobiphenyl, reacting at the site of the maximum electron density, which also indicates the electrophilic nature of the pentafluorophenyl radical[72].

The electrophilic properties of the pentafluorophenyl radical explain the high yield of biphenyls in the corresponding reactions of pentafluorobenzoyl peroxide and other sources of the pentafluorophenyl radical with benzene[75] and its derivatives[45,65,85,86]. On the other hand, the absence of pentafluorobenzene in these reactions and the fairly severe conditions under which the pentafluorophenyl radical reacts with hexafluorobenzene suggest a reduced reactivity of this radical, which may be attributed to the shielding of the radical reaction centre by the *ortho*-fluorine atoms.

## IV. OTHER REACTIONS

Hexafluorobenzene reacts with the bis(trifluoromethyl)-nitroxy-radical, combining with two, four, or six $(CF_3)_2NO$ residues, depending on the reaction conditions[87]. Under analogous conditions, the reaction of $(CF_3)_2NO^{\cdot}$ with benzene leads to the formation of the 1,2,4-trisubstituted product only[88]:

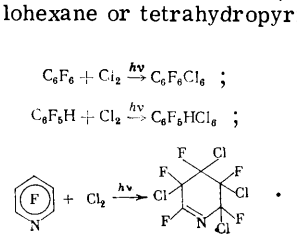




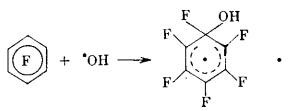

Addition takes place exclusively in the reactions of this radical with other aromatic polyfluoro-compounds. Thus the number of $(CF_3)_2NO$ groups with which the fluoro-compound combines is four for pentafluoropyridine[89], two, four, or six for chloropentafluorobenzene, four for octafluorotoluene, two, four, or six for pentafluorobenzoic acid, four or six for pentafluorobenzaldehyde, two or six for pentafluorophenol, and two, four, or six for pentafluoroaniline[90].

When perfluorodiphenylacetylene reacts with hexafluorodimethylnitrogen oxide, it is possible to identify only decafluorobibenzoyl (in 25% yield), but the unidentified reaction products include compounds containing the $(CF_3)_2NO$ group[91].

When chlorine is allowed to act on hexafluorobenzene[92], pentafluorobenzene[93], or pentafluoropyridine[89] under irradiation, it combines with the substrate, forming the corresponding cyclohexane or tetrahydropyridine derivatives:

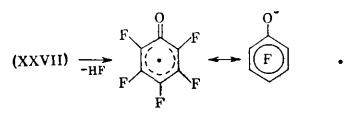


The interaction of fluorinated benzenes (1,2,3,4-$C_6H_2F_4$, $C_6F_5H$, and $C_6F_6$) with $e_{aq}^-$ and $^{\cdot}OH$ in aqueous solutions under pulse radiolysis and $\gamma$-irradiation[94] leads in the former case to the generation of the pentafluorophenyl radical and other fluorinated radicals with almost quantitative elimination of the fluoride anion: $C_6F_6 + e_{aq}^- \rightarrow C_6F_5^{\cdot} + F^-$, and in the latter case results in the addition of $^{\cdot}OH$ with formation of the $\sigma$ complex (XXVII):

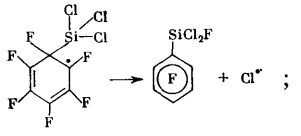


(XXVII)

The $\sigma$ complex (XXVII) is unstable, since a fluorine atom and the OH group are attached to the same carbon atom, but can be stabilised by the elimination of HF and the formation of a new radical:



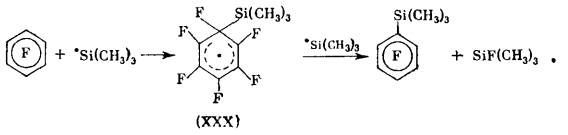
A photochemical interaction of the type of substitution takes place between hexafluorobenzene and trichlorosilane[95]. The reaction results in the formation of dichlorofluoro(pentafluorophenyl)silane (XXIX) as the main product together with *o*-, *m*-, and *p*-disubstituted compounds. It is suggested that the formation of compound (XXIX) is associated with a rearrangement in the σ complex (XXVIII) formed initially followed by the stabilisation of the new σ complex as a result of the elimination of a chlorine atom which initiates the reaction:



(XXVIII) (XXIX)

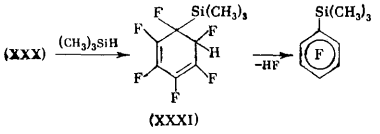
$$Cl^{\cdot} + SiHCl_3 \rightarrow HCl + {}^{\cdot}SiCl_3 .$$

The photochemical reaction between hexafluorobenzene and trimethylsilane proceeds in a somewhat different manner, yielding preferentially pentafluorophenyltrimethylsilane, which indicates the stabilisation of the σ complex (XXX), [analogous to the σ complex (XXVIII)] as a result of the abstraction of a fluorine atom by a second trimethylsilyl radical[95]:



(XXX)

Nor can one exclude the possibility that pentafluorophenyltrimethylsilane is formed in the dehydrofluorination of the adduct (XXXI):



(XXXI)

Irradiation of a solution of $C_6F_6$ in cyclohexane[96] leads to a fairly complex mixture of products in which it is possible to identify cyclohexylpentafluorobenzene, pentafluorobenzene, decafluorobiphenyl, and a compound with the overall formula $C_{18}H_{22}F_4$, which is most probably dicyclohexyltetrafluorobenzene. The nature of the products shows that a free-radical process takes place in all probability. It is evident that the initial dissociation of hexafluorobenzene into a fluorine atom and a pentafluorophenyl radical is unlikely not only because $C_6F_6$ is resistant to irradiation in the absence of hydrocarbons but also owing to the high C–F bond energy in $C_6F_6$.[55] The process probably proceeds via the following mechanism:

$$C_6F_6 \xrightarrow{h\nu} C_6F_6^{*}; \quad C_6F_6^{*} + HR \rightarrow C_6F_6^{\cdot} + HF + R^{\cdot} \rightarrow C_6F_5R;$$

$$2C_6F_5^{\cdot} \rightarrow C_{12}F_{10} \xrightarrow[RH]{h\nu} \text{high-molecular weight products;}$$

$$C_6F_5^{\cdot} + C_6F_6 \rightarrow C_{12}F_{11}^{\cdot} \rightarrow C_{12}F_{10}; \; C_6F_5^{\cdot} + RH \rightarrow C_6F_5H + R^{\cdot}; \; 2R^{\cdot} \rightarrow R_2.$$

A mechanism involving the formation of the pentafluorophenyl radical is postulated for the reaction of $C_6F_5I$ with $Ni(CO)_4$,[97] the main products of which are decafluorobiphenyl, decafluorobenzophenone, and pentafluorobenzene when it is carried out in dimethylformamide. The pentafluorophenyl radical may be formed as a result of the direct reaction of pentafluoroiodobenzene with nickel tetracarbonyl {in the decomposition of the complex $[C_6F_5Ni^{I}(CO)_n]$} or as the product derived from the pentafluorobenzoyl radical formed initially. The following reaction mechanism is most probable:

$$C_6F_5I + Ni(CO)_4 \rightarrow [C_6F_5CONi(I)(CO)_n] + (3-n)\,CO;$$

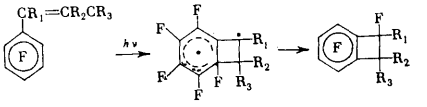
(XXXII)

$$(XXXII) \xrightarrow{-[NiI(CO)_{n+1}]^{\cdot}} C_6F_5^{\cdot}; \; C_6F_5^{\cdot} + RH \rightarrow C_6F_5H + R^{\cdot}; \; 2C_6F_5^{\cdot} \rightarrow C_6F_5C_6F_5;$$

$$C_6F_5^{\cdot} + CO \rightleftarrows C_6F_5CO^{\cdot}; \; C_6F_5CO^{\cdot} + C_6F_5^{\cdot} \rightarrow C_6F_5COC_6F_5.$$

The absence of decafluorobibenzoyl from the reaction products [bibenzoyl is the sole product of the reaction of $C_6H_5I$ with $Ni(CO)_4$] [98] demonstrates a high reactivity of $C_6F_5CO^{\cdot}$, which is present at a low concentration and reacts with the medium before dimerisation. In the analogous reaction with $Ni(CO)_4$, bromopentafluorobenzene is less reactive and hexafluorobenzene is recovered unchanged from the reaction mixture.

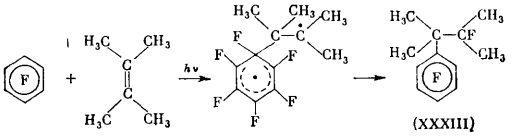
In a study of the gas-phase photolysis of polyfluorinated alkenylbenzenes, they were found to be converted into fluorine-containing benzocyclobutenes with migration of a fluorine atom from the aromatic ring to the side chain. The proposed mechanism of the photochemical rearrangement involves the intermediate formation of biradicals[99]:



(a) $R_1=R_2=R_3=F$; (b) $R_1=R_2=R_3=H$; (c) $R_1=F$, $R_2=R_3=H$; (d) $R_1=CH_3$, $R_2=R_3=H$; (e) $R_1=R_2=H$, $R_3=CH_3$.

The migration of the fluorine atom may occur as a sigmatropic, 2,3-shift concerted with the cyclisation process or following the latter, although the authors[99] do not rule out the possibility of repeated sigmatropic 1,5-shifts of the fluorine atom.

The photolysis of hexafluorobenzene in the presence of 2,3-dimethylbut-2-ene yields mainly compound (XXXIII), the formation of which is probably associated with the migration of a fluorine atom from the ring to the side chain in the intermediate biradical[100]:

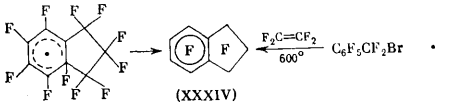


(XXXIII)

The reaction of a number of substituted aromatic polyfluoro-compounds with tetrafluoroethylene at a high temperature, giving rise mainly to the formation of perfluoroindan (XXXIV), which has been described recently[101] is of interest. The mechanism proposed by the authors includes the intermediate formation of the perfluorobenzyl radical (the way in which it is generated in this reaction is still obscure):

$$C_6F_5X \xrightarrow[600-700^{\circ}]{CF_2=CF_2} C_6F_5CF_2^{\cdot} \xrightarrow{CF_2=CF_2} C_6F_5CF_2CF_2CF_2^{\cdot} \rightarrow$$

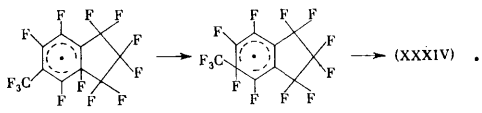
$$X = OH,\ SH,\ OCH_3,\ NH_2$$



(XXXIV)

Compound (XXXIV) is the main product also in the reaction of perfluoro-*p*-cresol and perfluoro-*p*-thiocresol with tetrafluoroethylene, which the authors attribute to the isomerisation of the intermediate σ complex (XXXV) to the σ complex (XXXVI) via a sigmatropic 1,3-shift of a fluorine

atom with subsequent elimination of the $CF_3$ group from the σ complex formed:



(XXXV) (XXXVI)

The possibility of the involvement of the perfluorobenzyl radical in these reactions has been confirmed by the formation of compound (XXXIV) (again in 80% yield) during the joint pyrolysis of tetrafluoroethylene with perfluorobenzyl bromide, which is a source of $C_6F_5CF_2^{\cdot}$.[101]

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# Advances in the Chemistry of the Acetals of Acid Amides and Lactams

V.G.Granik, A.M.Zhidkova, and R.G.Glushkov

Data on the chemistry of the acetals of acid amides and lactams published during the period between 1969 and 1974 are surveyed. The reactions of the acetals of acid amides and lactams with various nucleophiles and electrophiles are considered, particular attention being devoted to the possibility of using such amide and lactam acetals in the synthesis of heterocyclic compounds which are of interest both chemically and biologically.
The bibliography includes 89 references.

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## I. INTRODUCTION

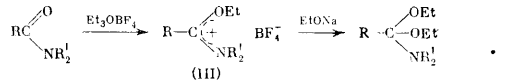
During the last two decades, the chemistry of acid amides and latcams has become enriched in new data associated primarily with the study and utilisation for synthetic purposes of "activated forms" of these compounds. Such "activated forms" include iminoesters [1], lactim ethers [2], complexes of acid amides with alkylating and acylating agents [3-6], keten *ON*-acetals [7,8], aminals [9,10], and extremely readily available at the same time very highly reactive compounds which Meerwein called the acetals of acid amides [11,12].

The acetals of acid amides were obtained for the first time in 1956 [11], but their properties were not described in detail until 1961. [12] In recent years, the chemistry of these compounds has been developing so vigorously that the review [13] published in 1969 no longer reflects the advances achieved in this field.

The present review surveys data on the chemistry of amide acetals published during the period between 1969 and 1974. Earlier studies are discussed only in those instances where this is required for the description of new material or when relevant studies were not considered in the review mentioned above [13].

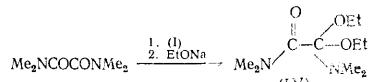
## II. THE SYNTHESIS OF THE ACETALS OF ACID AMIDES AND LACTAMS

One of the most general methods for the synthesis of the acetals of acid amides and lactams involves the interaction of amides or lactams with alkylating and acylating agents followed by the treatment of the resulting complexes with alkali metal alkoxides [13]. The most frequently used alkylating agents are triethyloxonium fluoroborate (I) and dimethyl sulphate (II). Although a quantitative comparison of the reactivities of these alkylating agents in the synthesis of amide acetals has not so far been made, one should note an important qualitative difference between them, consisting in the fact that the interaction of acid amides with compound (I), in contrast to the reaction with compounds (II), proceeds irreversibly [14]. The study of the alkylation of acid amides by compound (I) has been shown [14] that the steric effects of the substituents in the amides do not have an appreciable influence on the reactions; an exception to this rule is provided by those cases where the steric hindrance is accompanied by a significant destabilisation of the cation (III):

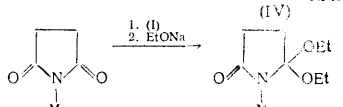


(III)

Thus $Cl_3CCON(CH_3)_2$, in which the amide group is linked to the extremely bulky and highly electronegative trichloromethyl group, does not react with compound (I). In those instances where the molecule contains two amide functional groups, the "acetalisation" of both is possible only in the presence of bridging groups between them [15]. Thus only the monoacetals (IV) and (V) can be synthesised from the bisdimethylamide of oxalic acid [14] and *N*-methylsuccinimide [16] with the aid of compound (I):

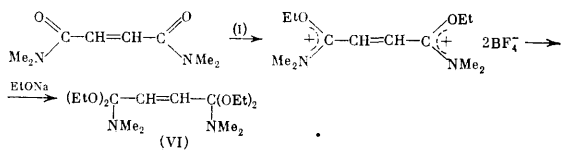


(IV)



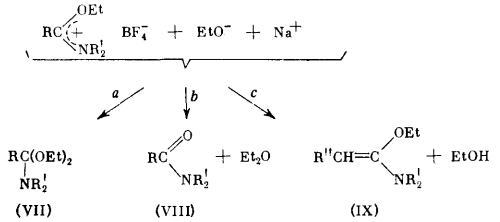
(V)

The separation of the amide groups by the -HC=CH- bridge ensures the possibility of the formation of the bisacetal (VI) [14]:



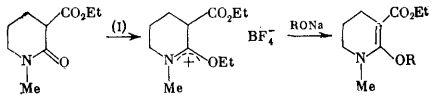
(VI)

The interaction of the intermediate complexes (III) with sodium alkoxides [14] can proceed in three ways depending on the nature of the substituent R: (a) the formation of the amide acetal (VII); (b) the regeneration of the initial amide (VIII); (c) the formation of the $\alpha$-alkoxyenamine (IX):



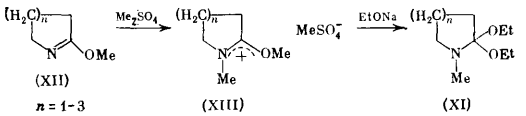
(VII) (VIII) (IX)

Reaction *a* should proceed most readily. This process involves the simplest ion association, since its activation energy is apparently significantly lower than in cases *b* and *c* and the acetal (VII) should be formed rapidly, provided that, for example, the steric hindrance to attack by the alkoxide anion is not too great. If R is a bulky substituent such as the t-butyl or dichloromethyl group, the reaction is directed via the thermodynamically favourable pathway *b* with formation of stable molecules such as the amide (VIII) and an ether. Finally, if R is a relatively small and highly electron-accepting group, a proton may be abstracted from the $\alpha$-position (relative to the amide group) and the $\alpha$-alkoxyenamine (IX) may be formed. One should note that the synthesis of enamines of type (IX) had also been observed earlier when 2-ethoxy-3-ethoxycarbonyl-1-methyl-3,4,5,6-tetrahydropyridinium fluoroborate (X) was treated with sodium alkoxide [17]:



(X).

A new version of the synthesis of lactam acetals (XI) involves the use of lactim ethers (XII) as the starting materials [18,19]:

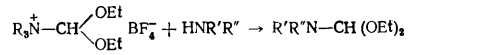


(XII) (XIII) (XI)

$n = 1$-3

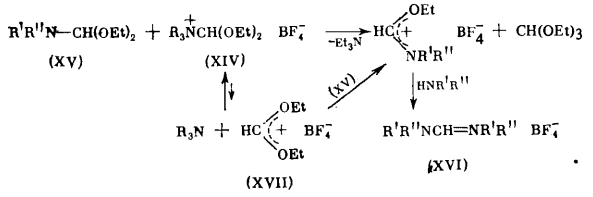
The study of the alkylation of compound (XII) by dimethyl sulphate using the method of competing reactions with analysis of the reaction mixtures by gas–liquid chromatography (GLC) showed that the rate of formation of the complexes (XIII) depends significantly on the size of the ring in compound (XII): the highest rate of alkylation is observed for *O*-methylbutyrolactim (XII, $n = 1$) and the lowest for *O*-methylcaprolactim (XII, $n = 3$). Examination of the *N*-alkylation of lactim ethers with the aid of molecular models showed that the difference between the rates of reaction is determined mainly by conformational factors [19].

New methods for the synthesis of acid amide acetals include the interaction of dialkyoxymethylammonium salts (XIV) with secondary amines [20]:



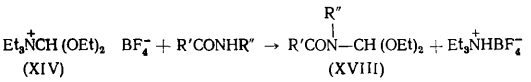
(XIV) (XV)

The acetals (XV) can react further with the salts (XIV) to form an orthoformate ester and amidinium salts (XVI):



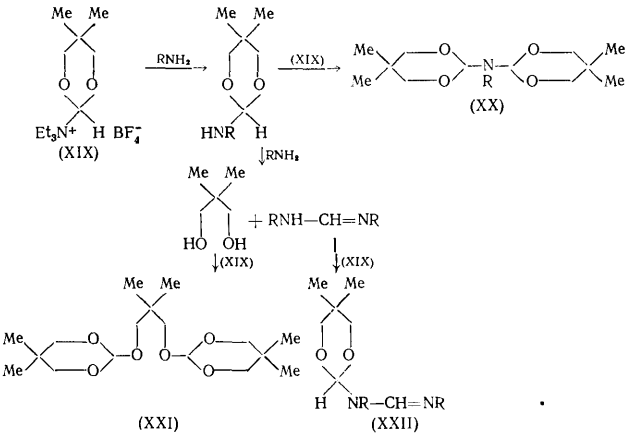
(XV) (XIV) (XVII) (XVI)

It has been suggested [20] that the above side reactions occur owing to the dissociation of the dialkyoxmethylammonium salts (XIV) into a tertiary amine and a dialkoxycarbonium salt (XVII), which reacts with the acetal (XV). This is confirmed by the finding that an excess of the corresponding tertiary amine, which displaces the equilibrium towards compound (XIV), leads to an appreciable increase of the yield of the acetals (XV). *N*-Acylamidoacetals (XVIII) have been obtained by the reaction of the salts (XIV) with acid amides [21]:



(XIV) (XVIII)

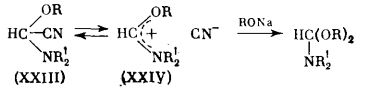
The reaction of dialkoxymethylammonium salts (XIX) with primary amines proceeds in an interesting manner and the following mechanism has been proposed [22]:



(XIX) (XX) (XXI) (XXII)

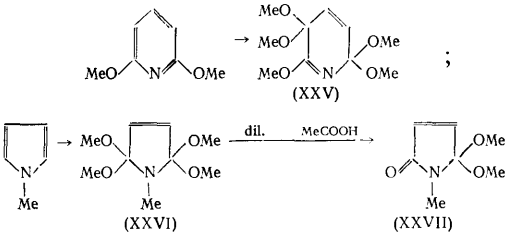
When the molar ratio of the salt (XIX) and the amine is 2 : 1, the main reaction product is the bisacetal (XX), while in the presence of an excess of the amine mainly the amidine-acetals (XXII) are formed, compound (XXI) having also been isolated as a side product.

A new method of synthesis of amide acetals, consisting in the interaction of $\alpha$-dialkylamino-$\alpha$-methoxyacetonitriles (XXIII) with sodium alkoxide has been published recently [28]. The reaction evidently proceeds via a stage involving the dissociation of compound (XXIII) with subsequent attack by the alkoxide anion on the cation (XXIV):



(XXIII) (XXIV)

In addition, the synthesis of the acetals of unsaturated lactams (XXV)–(XXVII) in the anodic oxidation of pyrrole and pyridine derivatives in methanol has been described [24]:

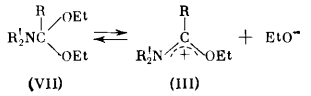


(XXV) (XXVI) (XXVII)

## III. THE PROPERTIES AND REACTIONS OF THE ACETALS OF ACID AMIDES AND LACTAMS

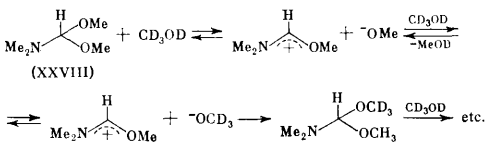
The structure of amide acetals, represented by formulae (VII) and (XI), does not justify the assumption that these compounds can be highly reactive in relation to nucleophiles [25] and electrophiles.

In 1961, Meerwein et al.[12] and subsequently also other investigators[13,26] showed that solutions of the acetals of acid amides and lactams are conducting. This phenomenon can be explained by the fact that amide acetals dissociate in solution into an ambident cation (III) and an alkoxide anion. It must be emphasised that the alkoxide anion is capable of interacting, for example, with compounds having an active methylene group, forming carbanions and therefore facilitating the nucleophilic addition reaction



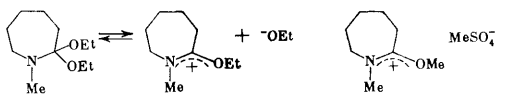
(VII) (III)

This treatment is nowadays generally accepted[13] and provides a satisfactory explanation of the properties of amide acetals. In particular, the only explanation of the readily cccurring exchange of the hydrogen atoms of the *O*-methyl groups of the dimethyl acetal of dimethylformamide (XXVIII) for deuterium in the presence of an excess of $CD_3OD$ is its preliminary dissociation[27]:



(XXVIII)

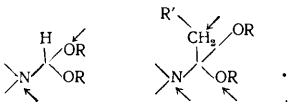
An attempt has been made[26] to estimate quantitatively by the polarographic method the degree of dissociation of the diethyl acetal of *N*-methylcaprolactam (XII, $n = 3$). Comparison of the polarographic behaviour of this acetal and the methyl sulphate complex of *N*-methylcaprolactam (XIII) showed that the content of the ambident cation (XXIX) in methanol solution does not exceed 0.3%:



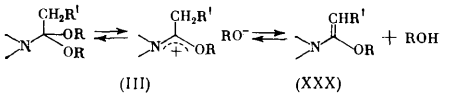
(XII) $n=3$ (XXIX) (XIII)

Bearing in mind the high reactivity of cations of this type in relation to reagents bearing a negative charge or having a lone electron pair, one may conclude that even the above insignificant degree of dissociation is sufficient to ensure the interaction of the acetals with various nucleophiles.

Investigations have shown that there are significant differences between the acetals of dimethylformamide, on the one hand, and their homologues and the acetals of lactams with the extremely reactive $CH_2$ groups in the $\alpha$-positions, on the other. Thus electrophiles can attack only the nitrogen atom in the acetals of dimethyl-formamide or the $RO^-$ anion formed following the dissociation of the acetal. On the other hand, together with the processes described above, the acetals of homologous amides as well as lactam acetals can undergo also reactions involving the $\alpha$-$CH_2$ groups (alkylation, acylation, etc.).

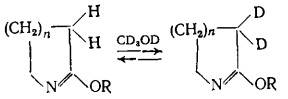


The ability of amide and lactam acetals to undergo $\alpha$-*C*-alkylation (acylation) has been explained[13,28,29] by the fact that the ambident cation (III) can interact with the alkoxide anion, the process involving the abstraction of a proton from the activated $\alpha$-$CH_2$ group in the cation (III) and the formation of an $\alpha$-alkoxyenamine (XXX), which readily reacts with electrophiles like other enamines[30]:



(III) (XXX)

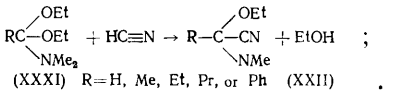
This hypothesis is supported also by data indicating a considerable mobility of the $\alpha$-protons in lactim ethers[31]:



## 1. REACTIONS OF AMIDE AND LACTAM ACETALS WITH NUCLEOPHILES

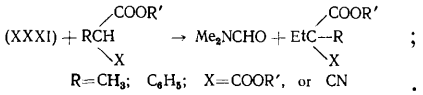
### a. Reactions of the Acetals Via Activated CH, $CH_2$, and $CH_3$ Groups

Numerous studies have been made on the reactions of amide and lactam acetals with compounds having activated methyl, methylene, or methylidyne groups[13,14,32-50]. The interaction of amide acetals with anhydrous hydrocyanic acid is accompanied by the substitution of [one of] the alkoxy-groups of the acetal by the cyano-group with formation of $\alpha$-alkoxyaminonitriles (XXIII)[32]:



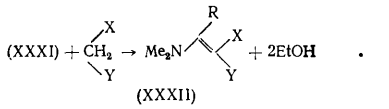
(XXXI) R=H, Me, Et, Pr, or Ph (XXII)

On the other hand, when the acetals react with C–H acids such as ethyl- or phenyl-malonic and cyanoacetic esters, the latter undergo *C*-alkylation[32]:



R=$CH_3$; $C_6H_5$; X=COOR', or CN

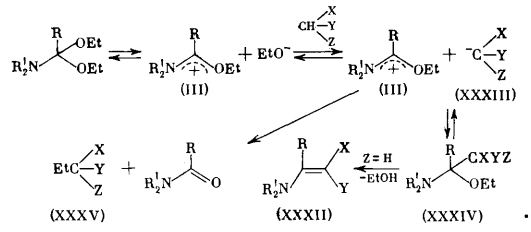
When compounds with active methylene or methyl groups are made to react with amide or lactam acetals, a third type of interaction takes place involving the formation of enamines (XXXII)[13]:



(XXXII)

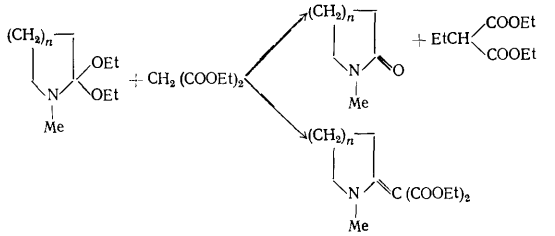
Bredereck et al.[32] believe that the first step in the interaction of amide acetals with compounds having activated CH or $CH_2$ groups involves the abstraction of a proton from the latter and the formation of the anion (XXXIII). The reaction of the anion (XXXIII) with the ambident cation (III) can proceed via the irreversible association of (III) and (XXXIII) with formation of compound (XXXIV). Subsequently, depending on the structure of the anion (XXXIV), the enamine (XXXII) (with Z = H) may be formed or *C*-alkylation may take place, which

results in the formation of compound (XXXV), and the corresponding amide:



In the presence of the weakly stabilised anion (XXXIII) (for example, $^-C{\equiv}N$), the addition product (XXXIV) is thermodynamically more favourable and the equilibrium is displaced towards its formation. On the other hand, when the anion is stabilised by conjugation, compound (XXXIV) is present in the equilibrium mixture in only a small amount; if one of the substituents (X, Y or Z) is a hydrogen atom, conditions are created for the elimination of an alcohol with formation of an enamine (XXXII). Simultaneously with this process (but more slowly), the cation (III) may alkylate the anion (XXXIII) with formation of the *C*-alkyl derivative (XXXV). When the anion does not contain a hydrogen atom, the latter process becomes dominant and the main reaction product is compound (XXXV). Thus, by postulating the equilibrium (XXXIII) ⇌ (XXXIV), one can account for the possible reactions occurring when amide acetals react with CH acids. However, one must stipulate the case where the formation of compound (XXXIV) is prevented by steric factors. Under these conditions, the only reaction pathway becomes *C*-alkylation† with formation of compound (XXXV).

It follows from the above mechanism that the formation of the enamine (XXXII) must be accompanied by *C*-alkylation. Indeed, a study of the reaction of lactam acetals[33-35] with malonic ester showed that the process proceeds in two ways, C–C condensation predominating:

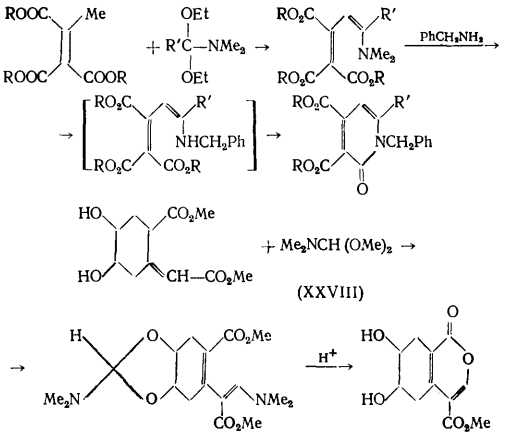


(XI), $n$=1–3

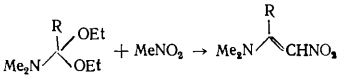
A study of the reactions of lactam acetals (XI) with compounds having active methylene or methyl groups[33-35] established that the rate of reaction depends both on the size of the lactam ring and on the strength of the CH acid: the highest reactivity is shown in this process by the diethyl acetal of *N*-methylbutyrolactam (XI, $n$ = 1), the increased mobility of the hydrogen atoms in the $CH_2XY$ group promoting a higher reaction rate.

†The initial amide and an ether may be formed in a side reaction (see above).

The ability of amide acetals to react readily with compounds having active $CH_2$ or $CH_3$ groups has been used in new syntheses of 2-pyridones[36] and condensed $\alpha$-pyrones[37]:



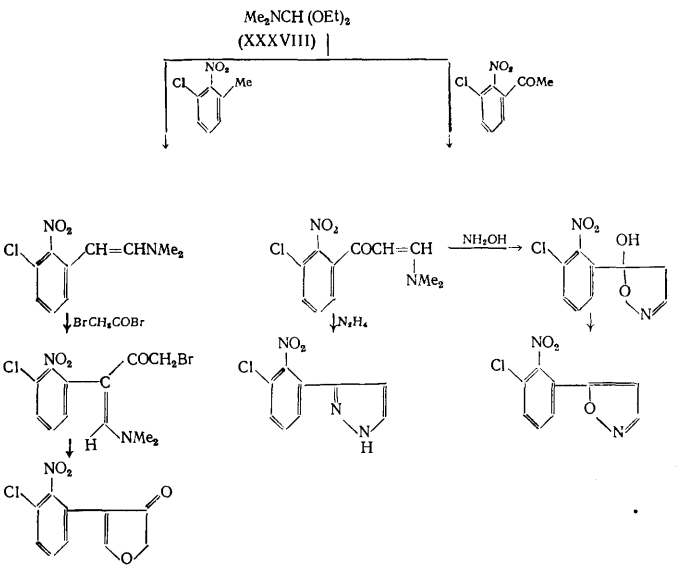
Bredereck et al.[14] compared the reactivites of the acetals (XXXVI) and (XXXVII) in condensation with nitromethane:



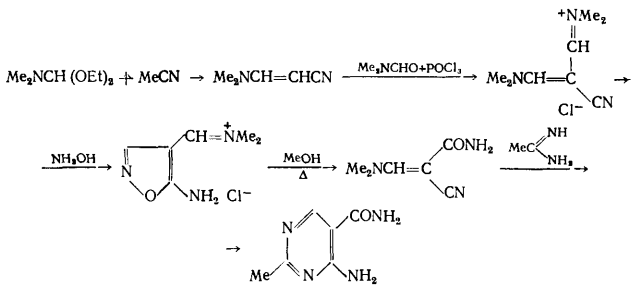
(XXXVI), R=$CONMe_2$ ;
(XXXVII), R=$CO_2Et$ .

Whereas in the first case the reaction proceeds with a yield of 96% (80°C, 1 h), in the second the yield does not exceed 37% even after prolonged heating (80°C, 5 h). According to the authors, this difference between the reactivities of the acetals (XXXVI) and (XXXVII) is due to the much greater destabilising effect of the $CO_2Et$ group compared with that of the $CONMe_2$ group.

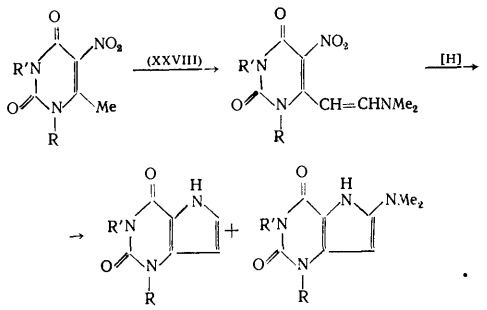
The diethyl acetal of dimethylformamide (XXXVIII) has also been used in the synthesis of pyrrolnitrin analogues[38]:



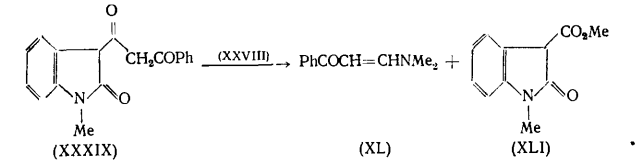
Isoxazole and pyrimidine derivatives have been synthesised from the acetal (XXVIII) [39]:



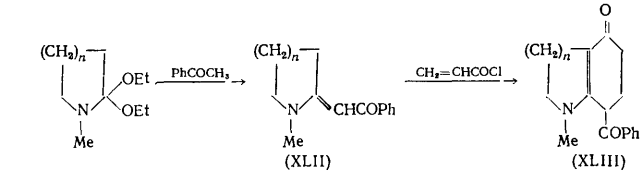
as well as pyrrolo[3,2-*d*]pyrimidines [40]:



The reaction of the acetal (XXVIII) with 3-benzoylacetyl-1-methyloxindole (XXXIX) proceeds in a very unusual manner. The C–C bond is ruptured with formation of *NN*-dimethylaminomethyleneacetophenone (XL) and 3-methoxycarbonyl-1-methyloxindole (XLI) [41]:



The interaction of the lactam acetals (XI) with acetophenone led to the synthesis of the enaminoketones (XLII) from which a new synthesis of hydrogenated derivatives of indole, quinoline, and benzazepine (XLIII) was achieved by reaction with acryloyl chloride [42]:



(XI), $n = 1-3$ .

A series of studies on the reactions of amide acetals with nitromethane derivatives [43], acetonitrile [44,45], malonic ester [46], and β-benzoylpropionic ester [47] have been published in recent years. They involved the synthesis of a number of substituted enamines, which can be used as the starting materials for the preparation of various heterocyclic compounds (see, for example, Spencer et al. [48]).

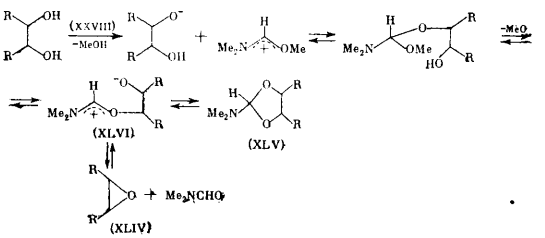
The above data permit the conclusion that lactam acetals react more smoothly with nucleophiles than do amide acetals [25]. A clear example is provided by the finding that lactam acetals react readily with phenylacetic ester, giving satisfactory yields [25,49], while the diethyl acetal of *NN*-dimethylacetamide could not be made to undergo this reaction [50].

### b. Reactions with Alcohols and Mercaptans

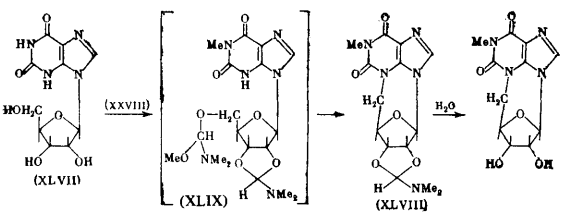
One of the methods for the synthesis of amide acetals involves the transesterification of the dimethyl acetal of dimethylformamide (XXVIII) with alcohols [13]. Compound (XXVIII) and other amide acetals react similarly with alkanethiols and arylalkanethiols, forming the thioacetals of acid amides [51]:

$$Me_2NCH(OMe)_2 + 2RSH \rightarrow Me_2NCH(SR)_2 + 2MeOH .$$

The reaction of amide acetals with alcohols constitutes the basis of a new method for the synthesis of epoxy-compounds (XLIV). [52] The process mechanism is consistent with the usual concepts concerning the interaction of amide acetals with alcohols:

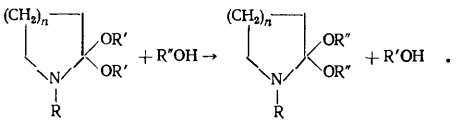


It is seen from the above mechanism that the reaction may involve the formation of cyclic amide acetals (XLV). One of the main factors determining the nature of the products formed is the configuration of the initial diol. For example, the reaction of the acetal (XXVIII) with *cis*-cyclohexanediol results in the formation of the cyclic acetal [XLV, R,R = $-(CH_2)_4-$] only, while its *trans*-isomer is converted smoothly into the epoxy-compound (XLIV). The cyclic acetal (XLVIII) has also been obtained in the reaction of xanthosine (XLVII) with the dimethyl acetal of dimethylformamide (XXVIII) [53]:



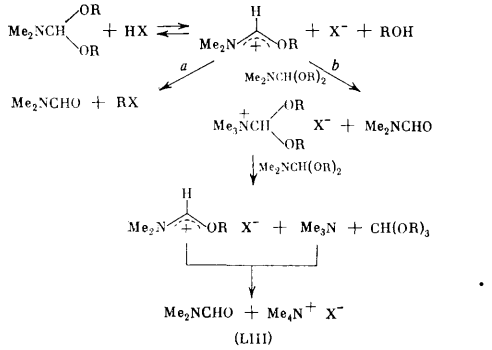
The above mechanism shows that the amide acetal (XXVIII) reacts not only with the vicinal secondary hydroxyls but also with the primary hydroxy-group. Owing to the high polarisation of the $O-CH_2$ group in the intermediate bisamide acetal (XLIX), the xanthine fragment undergoes intramolecular *N*-alkylation with formation of the cyclonucleoside (XLVIII). This is accompanied by the *N*-methylation of xanthosine by the acetal (XXVIII) (see above).

It is noteworthy that lactam acetals are readily transesterified by alcohols, like amide acetals[54,55]:

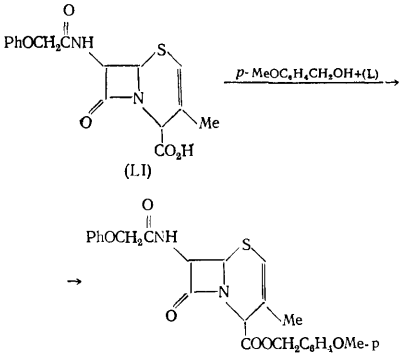


c. Reactions with Phenols and Carboxylic Acids

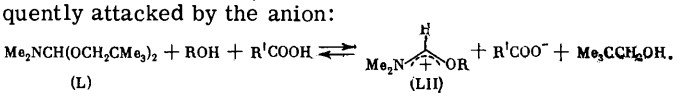
The esterification of carboxylic acids and phenols in their reactions with amide and lactam acetals takes place even more readily than the *C*-alkylation of compounds having an acid $CH_2$ group (see above)[12,33-35,55-57]. When the molecule contains a phenolic hydroxyl and a carboxy-group, the alkylation proceeds very selectively at the carboxy-group[56,57]. Despite its apparent simplicity, the reaction of amide acetals with carboxylic acids may be accompanied by a series of side processes[56]:



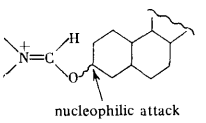
The relative contributions of the main process *a* and the side reactions *b* depend to a large extent on the nature of the substance alkylated HX.[58] Thus, in the interaction of the dimethyl acetal of dimethylformamide (XXVIII) with phenol, the reaction proceeds almost exclusively via pathway *a*. The reaction with picric acid proceeds mainly via pathway *b*. Similar behaviour has been observed also for a series of carboxylic acids: the formation of methyl benzoate predominates in the reaction involving benzoic acid, while only tetramethylammonium trifluoroacetate was isolated in the reaction with trifluoroacetic acid. However, the acidity of HX is not the only factor determining the mode of the process. The concentration of the reactants plays an important role in these processes. Thus, when solutions of the reactant are diluted and the steady-state concentration of compound (XXVIII) is reduced, it is possible to increase sharply the yield of alkylation products[56]. It was found that the rate constant for the esterification of *p*-nitrobenzoic acid by the dimethyl acetyl of *N*-formylpyrrolidine is almost twice as high as the rate constant obtained when compound (XXVIII) is used in this reaction. The dineopentyl acetal of dimethylformamide (L) has been used successfully in the alkylation of carboxylic acids[13]. Its employment for this purpose is based on the fact that derivatives of neopentyl alcohol are capable of undergoing $S_N2$ reactions to only a very slight extent[56]. As an example, one may quote the esterification of $\Delta^2$-diacetoxycephalosporin (LI), which proceeds under mild conditions[59]:



The mechanism of the esterification reaction with the aid of comopund (L) provides for the intermediate formation of the cation (LII), in which the residue R is subsequently attacked by the anion:



Naturally, when the residue R contains in this instance an asymmetric centre linked to the oxygen atom, the nucleophilic attack should involve an inversion of configuration ($S_N2$ mechanism). Epimerisation of this kind has been achieved for a series of derivatives of 3$\alpha$-hydroxycholestane and androstane[56]:




This method can probably be used for the inversion of configuration also in other optically active alcohols.

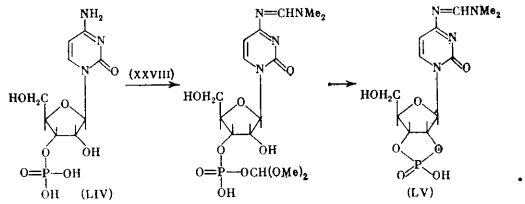
d. Reactions of Amide Acetals with Other Acid Compounds

The study of the interaction of the acetal (XXVIII) with other acid agents[58] confirmed that there is a definite (although not direct) relation between the mode of reaction and the acid $pK_a$. The study of the reaction of compound (XXVIII) with amides has shown that, as a rule, both pathways *a* and *b* (see above) operate and that pathway *a* is fully inhibited only in the reaction with $Tos_2NH$. A similar behaviour has been observed for hydrochloric and phosphorus-containing acids (alkylation and the formation of quaternary salts are both observed to some extent). When toluene-*p*-sulphonic acid or $HClO_4$ are used in the reaction with compound (XXVIII), the only products are the corresponding NNN'N'-tetramethylformamidinium salts (LIII).

e. Reactions with Phosphorus-Containing Compounds

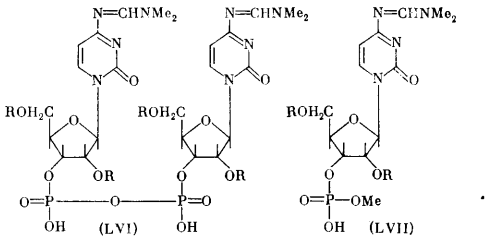
The interaction of the dimethyl acetal of dimethylformamide with nucleoside phosphates is a special case of reactions of compound (XXVIII) with OH and CH acids. When the aglycone of the nucleoside phosphate contains the $NH_2$ group, as, for example, in cytidine phosphate

(LIV), the reaction via the phosphate group is accompanied in this case also by condensation via the 4-amino-group[60]:

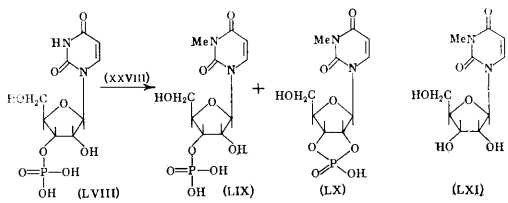


The mechanism of the formation of compound (LV) has been represented as one involving the activation of the P–O bond with subsequent closure of the five-membered ring.

The study of this reaction in other systems[60] showed that in all cases cyclic compounds of type (LV) are formed. Thus the reaction constitutes a convenient method for the synthesis of compounds containing only one unprotected OH group in the 5′-position. It is noteworthy that, in those cases where the OH groups in the 2′- and 5′-positions had been protected beforehand, the reactions of ribonucleoside phosphates with compound (XXVIII) lead to the formation of pyrophosphates (LVI) and the methyl esters (LVII) as the side products (the main reaction involves the protection of the 4-amino-group of the pyrimidine base):

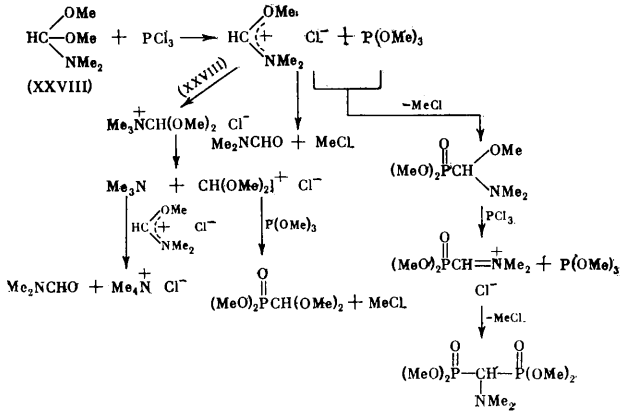


When the neopentyl acetal (L) is used in reactions with aminonucleoside phosphates, the condensation proceeds selectively via the $NH_2$ group, without involving the hydroxy-groups. It was noted that dephosphorylation with formation of compound (LX) is observed in the interaction of uridine phosphate (LVIII) with compound (XXVIII) in addition to the *N*-methylation of compound (LIX) and the cyclisation of the phosphate group at the 2′-hydroxy-group in compound (LX)[60]:

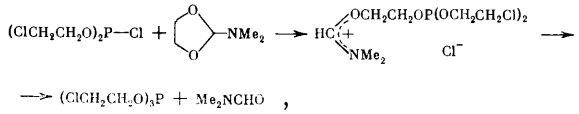


Furthermore, certain reactions of amide acetals with diribonucleoside phosphates may involve the dissociation of internucleotide linkages[61].

The reactions with phosphorus halides and with the esters of phosphorus-containing acids occupy a special place in the chemistry of amide acetals[62–64]. The following mechanism has been proposed for the reaction of the acetal (XXVIII) with $PCl_3$[62]:



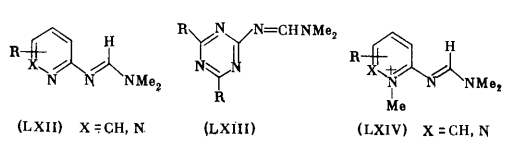
The reactions of amide acetals with other chlorophosphines have also been described[63]:



as well as the reactions with phosphite esters and phosphine oxides[63,64].

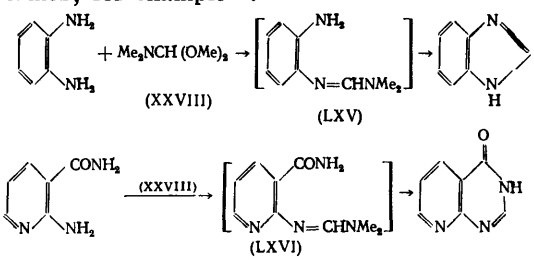
## f. Reactions with Amines

The synthesis of amidines from amide and lactam acetals has been investigated in fair detail[13]. A number of studies on the reactions of lactam acetals with aniline derivatives[25,55,65–68] and heterocyclic[60,69–73] and aliphatic[74,75] amines have been published in recent years. The interaction of amide and lactam acetals with amines constitutes a simple and convenient approach to the synthesis of various amidines, which is particularly important in connection with the fact that a number of substances exhibiting a high biological activity have been discovered in recent years among representatives of this class of compound (see, for example, Refs. 76–78). A series of 6-formamidinopenicillanic acids have been obtained by the reaction of amide acetals with aminopenicillanic acid[74]. It has been shown that animal-esters can be obtained by the interaction of compound (XXVIII) with secondary amines[75]. Various aminoheterocycles have also been successfully made to react with acetals, which led to the synthesis of the heterocyclic amidines (LXII)–(LXIV)[70]:



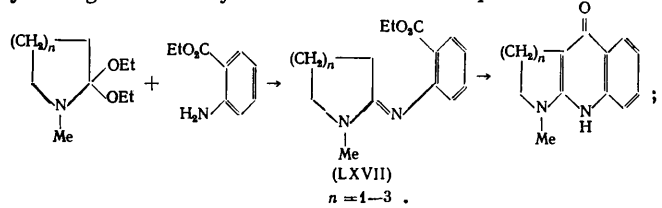
Amide acetals have been used successfully in recent years also as cyclising agents in the synthesis of various heterocyclic compounds. Thus, on heating with the dimethyl acetal of dimethylformamide, *o*-diamines or

*o*-aminocarboxamides form condensed imidazoles of pyrimidines, for example [70]:

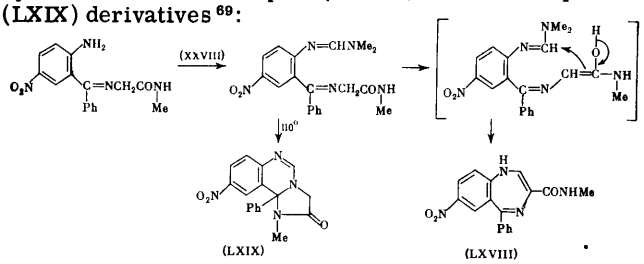


The reaction probably proceeds via the intermediate formation of the amidines (LXV) and (LXVI).

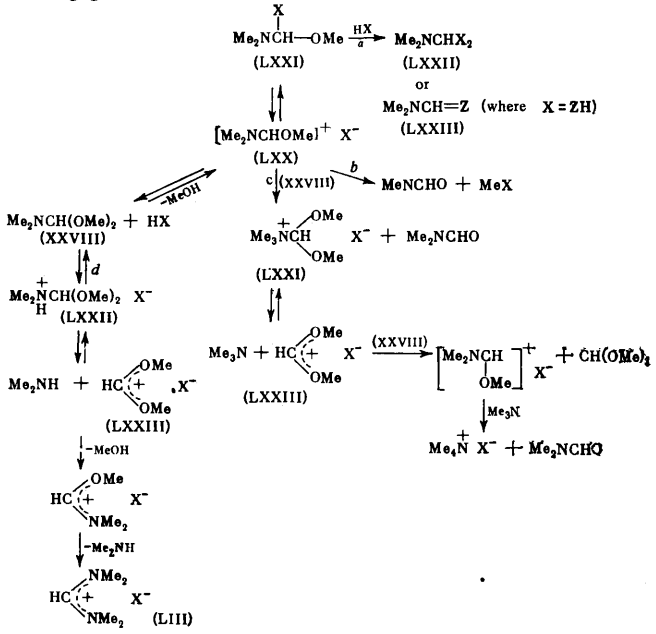
When lactam acetals react with an anthranilate ester, the corresponding amidines (LXVII) are again formed, cyclising to the tricyclic derivatives of 4-quinolone [66]:



The acetal (XXVIII) has been used successfully in the synthesis of benzodiazepine (LXVIII) and imidazoquinazoline (LXIX) derivatives [69]:



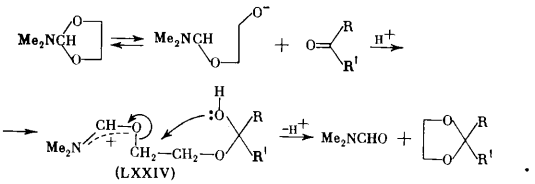
The data presented above show that the majority of studies on the reactions of amide and lactam acetals with nucleophiles are based on the interaction of amide acetals with compounds containing active C–H, O–H, S–H, and N–H groups. These reactions can be represented by the following general mechanism [58]:



As mentioned above, one of the main factors determining the mode of the process (pathways *a*–*d*) is apparently the acidity of the initial HX. Pathway *a* is characteristic of weak acids, such as HC≡CR or AlkOH [with formation of compound (LXXII)] or $H_2O$, $RNH_2$, and $RR'CH_2$ [with formation of compound (LXXIII)]. The reactions of ArOH or certain carboxylic acids proceed mainly via pathway *b*. Stronger acids ($CF_3COOH$, $Tos_2NH$, and picric acid) react via pathway *c*. Finally, pathway *d* is characteristic of sulphonic acids and $HClO_4$.

### g. Reactions with Aldehydes and Ketones

As mentioned above, amide and lactam acetals condense with compounds having activated $CH_2$ or $CH_3$ groups (including ketones [13]) with formation of enaminocarbonyl compounds. However, amide acetals are also capable of reacting with aldehydes and ketones via another mechanism—with formation of the corresponding acetals and ketals [56]:



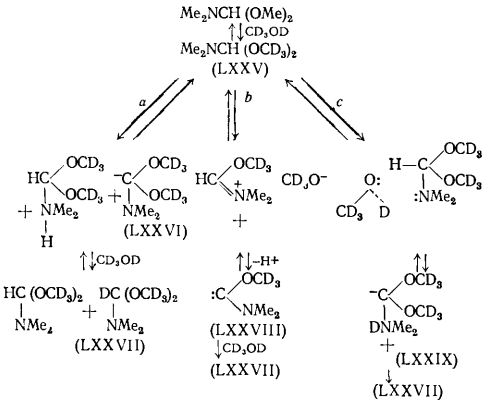
The reaction of compounds with a highly polarised carbonyl group (for example $CCl_3CHO$) is possible also in the absence of acid catalysis. It must be emphasised that the intermediate compound is sterically hindered. This factor makes it possible to use amide acetals as selective agents for the protection of keto-groups. For example, in the steroid series this process proceeds readily via the carbonyl group in the 3-position without affecting the keto-groups in the 17- and 20-positions [56].

## 2. REACTIONS OF AMIDE AND LACTAM ACETALS WITH ELECTROPHILES

### a. Reactions Involving Dimethylformamide Acetals

The simplest reaction of amide acetals with electrophiles is deuterium exchange. It was noted previously that, in solution of the dimethyl acetal of dimethylformamide (XXVIII) in deuteromethanol, the protons of the *O*-methyl groups of the acetal are rapidly exchanged for deuterium [27]. It is of interest that the formyl proton of the acetal is exchanged for a deuteron, albeit more slowly. This process requires a detailed examination, since many features observed in the study of this phenomenon proved to be common also to the reactions of dimethylformamide acetals with other electrophiles. A mechanism has been proposed [27] for the deuteration of amide acetals via the intermediate formation of carbenes. Three possible

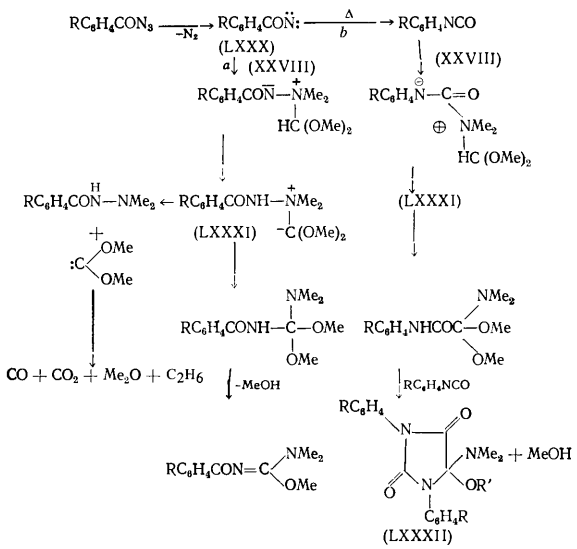
mechanisms of the deuterium exchange (pathways *a–c*) were examined in another investigation[79]:



Mechanism *a*, which provides for the abstraction of the formyl proton already in the first stage with formation of the anion (LXXVI), is unsuitable for the following reasons: under the conditions governing the formation of the deuteroacetal (LXXVII), orthoesters, in which the overall $-I$ effect of the alkoxy-groups is greater than in amide acetals, do not undergo deuterium exchange, and even chloroform is deuterated under these conditions more slowly than compound (LXXV). Mechanism *b*, according to which the intermediate is the carbene (LXXVIII), conflicts with the finding that the complexes $[MeOCH{=}NMe_2]X^-$ (where X = $MeSO_4^-$ or $BF_4^-$) do not undergoe deuterium exchange.

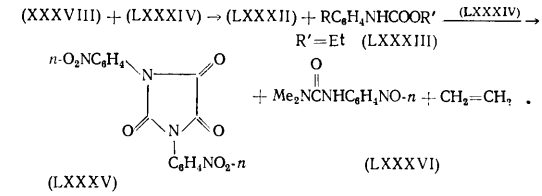
The "ylid" mechanism *c* is supported by the following data: (1) the enhancement of the electron-donating properties of the *N*-alkyl residues leads to an increase (up to a certain limit) of the rate of deuterium exchange; (2) the enhancement of the acid properties of the deuterating agent accelerates the deuterium exchange (the deuterium exchange proceeds to the extent of 25% after 196 s in $CD_3OD$ and after 705 s in t-BuOD); (3) the presence of strong bases in the system retards the deuterium exchange owing to a competing reaction.

Bedereck et al.[80] proposed mechanisms for the thermal and photochemical reactions of the acetal (XXVIII) with benzoyl azides:

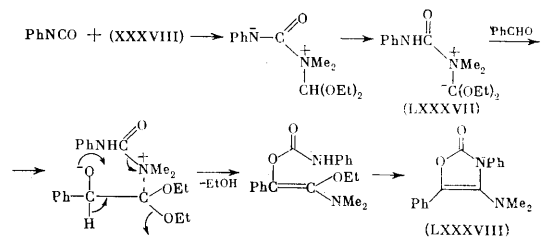


According to this mechanism, the intermediate nitrene (LXXX) interacts under mild conditions with the acetal (XXVIII), this being followed by a rearrangement to the ylid (LXXXI), from which the final reaction products are formed (photochemical reaction—pathway *a*). On heat treatment (pathway *b*), the nitrene (LXXX) rearranges to the isocyanate, which reacts further with compound (XXVIII). In this case, the synthesis on the *ON*-acetal of parabanic acid (LXXXII, R′ = Me) is also preceded by the formation of the ylid (LXXXI).

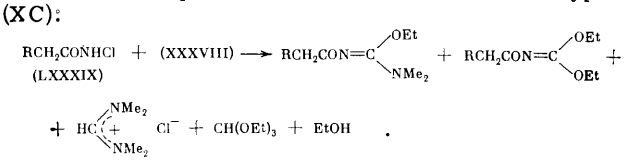
The mechanism of the reactions of amide acetals with isocyanates has been demonstrated in relation to the diethylacetal of dimethylformamide [compound (XXXVIII)].[81] It was found that, as in the thermal reaction with benzoyl azides, the main products are the *ON*-acetal (LXXXII, R′ = Et) and the carbamic ester (LXXXIII, R′ = Et). The highly reactive *p*-nitrophenyl isocyanate (LXXXIV, R = *p*-$NO_2$) reacts further, forming derivatives of parabanic acid (LXXXV), urea (LXXXVI), and ethylene:



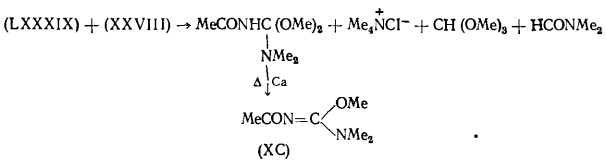
To demonstrate the intermediate formation of the ylid (LXXXVII), this reaction was carried out in benzaldehyde, a preliminary test having established that the latter does not react either with the dimethylformamide acetal (XXXVIII) or with the *ON*-acetal (LXXXII, R′ = Et). The product isolated in this reaction was 4-dimethylamino-3,5-diphenyloxazolin-2-one (LXXXVIII), for the formation of which the following mechanism has been proposed:



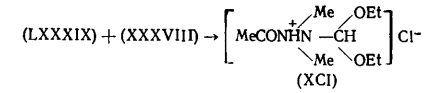
The interaction of the diethyl acetal of dimethylformamide (XXXVIII) with *N*-halogenoamides, *N*-halogenoureas, and *N*-halogenourethanes (LXXXIX)[82] proceeds with formation of multicomponent mixtures of substances, in which the main products are keten *ON*-acetals of type (XC):



It is of interest that, when the dimethyl acetal of dimethylformamide (XXVIII) is used in the reaction, the nature of the side products changes:

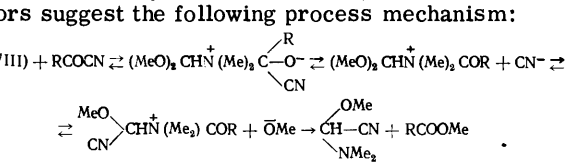


By allowing the acetal (**XXXVIII**) to react with *N*-chloroacetamide (**LXXXIX**, R = H), Bredereck et al.[83] succeeded in isolating the intermediate (**XCI**):



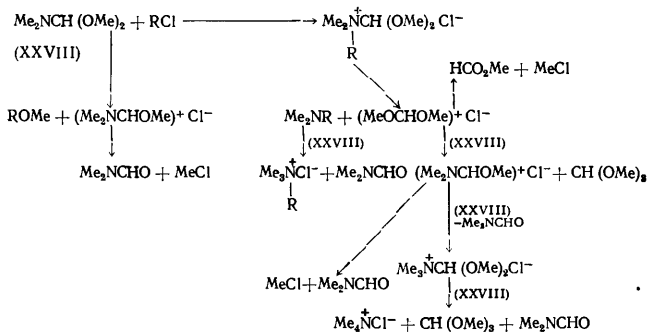
On the basis of the structure of the salt (**XCI**) and the probable formation of the ylid (**LXXXI**) from the latter, the authors suggested that the conversion of the ylid into the final product (**XC**) proceeds via an $S_E1$ or an $S_Ni$ mechanism.

The reaction of the dimethyl acetal of dimethylformamide (**XXVIII**) with an acyl cyanide leads smoothly to the formation of α-dimethylamino-α-methoxyacetonitrile [84]. The authors suggest the following process mechanism:



The reaction of acyl cyanides with orthoesters proceeds with a much lower yield even under much more severe conditions.

A detailed study of the reactions of the dimethyl acetal of dimethylformamide (**XXVIII**) with alkylating and acylating agents has been published recently[85]. It was shown that the alkylation proceeds exclusively via the nitrogen atom of the amide acetal, while the ratio of the *O*- and *N*-acylation products depends significantly on the nature of the acyl halide used. The authors proposed the following general reaction mechanism:

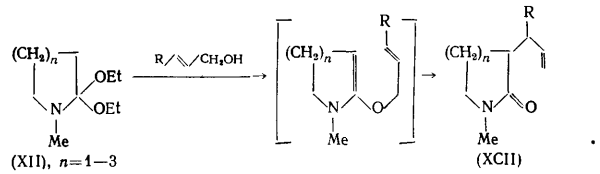


Experimental data led to the conclusion that the reactivity of acyl halides in the *O*-acylation of the amide acetal (**XXVIII**) increases in the sequence

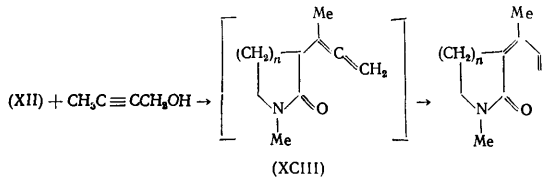
$$AlkCOCl < ArCOCl < RSO_2Cl < (RO)_2P(=O)Cl \sim R_2PCl \sim R_3SiCl .$$

b. Reactions of the Homologues of the Dimethylformamide Acetal and Lactam Acetals

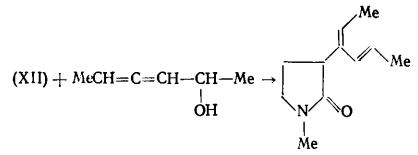
The introduction of alkyl or acyl groups in the α-positions of amides and lactams is known to proceed with difficulty as a rule. In this connection, a convenient method for the synthesis of α-alkyl(acyl)amides or α-alkyl(acyl)lactams is provided by the interaction of the corresponding amide or lactam acetals with alkylating or acylating agents. Thus the reaction of lactam acetals with unsaturated alcohols leads to the formation of 3-allyllactams (**XCII**) [54]:



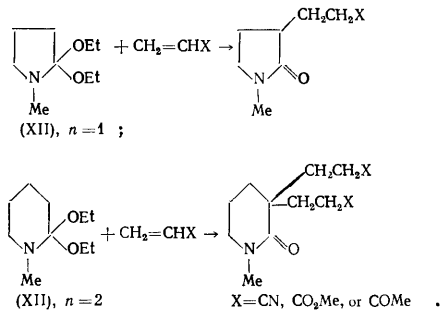
The conjugated lactam (**XCII**) has been synthesised by the reaction of compound (**XII**, $n = 1$) with butynol. When the acetal of *N*-methylcaprolactam was used in this reaction, the intermediate allene (**XCIII**) could be isolated:



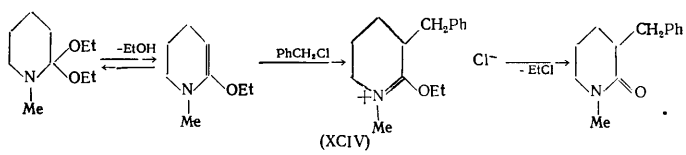
The reaction with allenes proceeds similarly[54]:



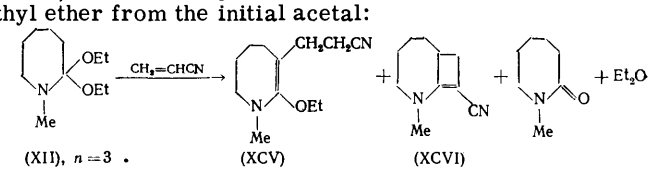
The reactions of lactam acetals with compounds such as acrylonitrile have been investigated in fair detail[29]. It has been shown that, when compound (**XII**, $n = 1$) interacts with $CH_2$=CHX (where X = CN, $CO_2Me$, or COMe), only the products of monosubstitution in the 3-position of the lactam ring are formed, while compound (**XII**, $n = 2$) forms 3,3-disubstituted lactams under these conditions:



Alkylation of compound (**XII**, $n = 2$) with benzyl chloride leads to a monoalkylation product. Such specificity of the benzylation of compound (**XII**) has been explained[29] by the ability of the intermediate immonium salt (**XCIV**) to split off ethyl chloride:

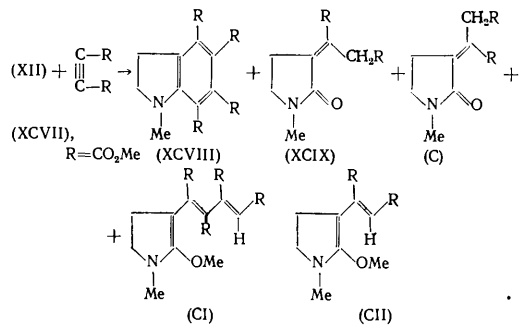


The diethyl acetal of *N*-methylcaprolactam (**XII**, $n = 3$) reacts with acrylonitrile[35], forming the $\alpha$-alkoxyenamine (**XCV**), the cyclic product (**XCVI**), and *N*-methylcaprolactam, the last compound as a result of the elimination of ethyl ether from the initial acetal:



(XII), $n=3$ . (XCV) (XCVI)

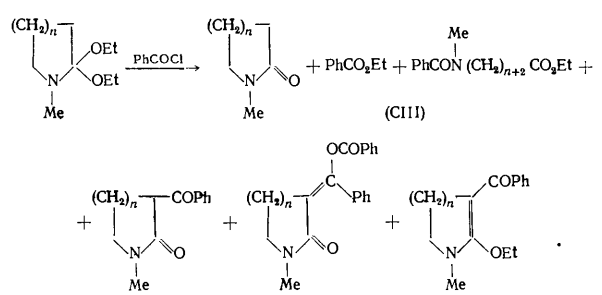
When the acetal (**XII**, $n = 1$) was allowed to react with the acetylenedicarboxylate ester (**XCVII**), a number of substances, (**XCVIII**)–(**CI**), were isolated[86]:



(XCVII), R=$CO_2$Me (XCVIII) (XCIX) (C) (CI) (CII)

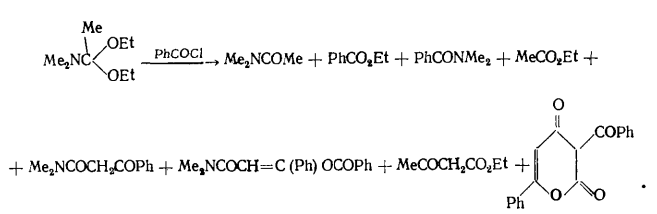
It was shown that the primary product of this reaction is the enamine (**CII**), which is converted into the isomers (**XCIX**) and (**C**) under mild conditions, for example in chromatography on silica gel, while on heating with the ester (**XCVII**) it gives rise to the indoline (**XCVIII**).

Among the reactions of amide and lactam acetals with electrophiles, those with benzoyl chloride have been investigated in greatest detail[28,35,87,88]. As was to be expected, these reactions proceed unambiguously with formation of *C*-, *N*-, and *O*- acylation products:

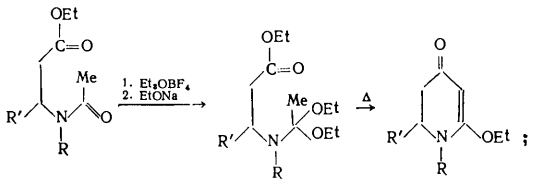


(CIII)

The benzoylation of the dimethylacetamide acetal (**CIV**) proceeds in an even more complex manner; its mechanism has been examined in detail[88]:

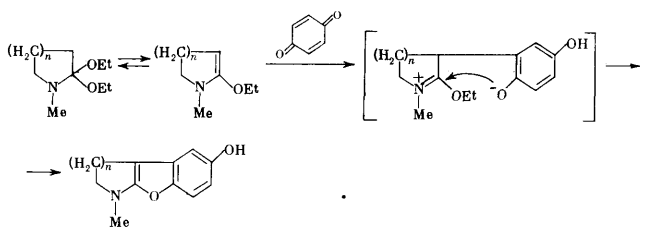


The ability of amide acetals to react with electrophiles has been used in the synthesis of heterocyclic compounds, for example for the preparation of 2,4-dioxopiperidine derivatives[50]:



R=Me, R′=H, or (RR′)=$-(CH_2)_4-$ .

It has been found recently that lactam acetals condense readily with *p*-benzoquinone, cyclising subsequently to condensed benzofurans[89]:



Thus the data described show that the discovery of amide and lactam acetals, a new class of organic compounds, initiated a new field in organic chemistry, which is of great promise from both synthetic and theoretical points of view. There is no doubt that the scope of the applications of amide acetals in organic synthesis is far from exhausted and that the chemistry of these exceptionally reactive compounds will continue to attract the attention of many organic chemists.

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# α-Cyanoacetylenes

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The problems of the synthesis, physical properties, and reactivities of α-acetylene nitriles are discussed. The bibliography includes 200 references.

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## I. INTRODUCTION

α-Cyanoacetylenes are nowadays of considerable interest not only because of the wide variety of their chemical properties and synthetic possibilities, but also because of their ability to give rise to ultrahigh flame temperatures on combustion in oxygen or ozone [1]. Furthermore, cyanoacetylene has been detected in cosmic space [2-6] and it has been suggested that it was involved in the prebiological synthesis of important nitrogen compounds [7,8] (purines and pyrimidines).

However, no reviews have been published hitherto on the physical and chemical properties of these interesting compounds. This paper is the first attempt at a consideration and a systematic account of the available literature data on this problem.

## II. METHODS OF PREPARATION OF α-CYANOACETYLENES

α-Cyanoacetylenes were first detected in 1909 by Moureu, who also proposed a method for the synthesis of cyanoacetylene (CA), dicyanoacetylene (DAC), dicyanodiacetylene (DCDA), and other α-cyanoacetylenes [9-11]:

$$RC{\equiv}C{-}COOH \xrightarrow[H_2SO_4]{CH_3OH} RC{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} \rightarrow RC{\equiv}C{-}CONH_2 \xrightarrow[-H_2O]{P_2O_5} RC{\equiv}C{-}C{\equiv}N \quad .$$

Since then, this method has been used fairly frequently in laboratory practice for the synthesis of small amounts of CA, DCA, and other substituted α-cyanoacetylenes [9-15]. Later many investigators [16-26] attempted to modify Moureu's method without altering its essential features. Thus Blomquist and Winslow [17] synthesised DCA in the following way:

$$HOOC{-}CH(Br)CH(Br)COOH \xrightarrow{KOH} HOOC{-}C{\equiv}C{-}COOH \rightarrow \xrightarrow[H_2SO_4]{CH_3OH} H_3COOC{-}C{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} \rightarrow H_2NOC{-}C{\equiv}C{-}CONH_2 \xrightarrow{P_2O_5} N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N \quad .$$

At 215°C and 2 mmHg, the diamide is dehydrated in 15 min, the yield of DCA amounting to 37%. Cookson et al. [22] succeeded in raising the yield of DCA to 40% by lowering the dehydration temperature of the diamide to 200°C. CA can also by synthesised under laboratory conditions by dehydrating the oxime of propargyl aldehyde with acetic anhydride [27].

The only method for the synthesis of DCDA consists in the treatment of the copper(I) derivative of propiolonitrile with aqueous potassium hexacyanoferrate(III).[11] Brockman [28] investigated the reaction in detail, but a high yield of DCDA was not achieved:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[NH_4OH]{CuCl} CuC{\equiv}C{-}C{\equiv}N \xrightarrow[36\%]{K_3Fe(CN)_6;6^\circ;C_6H_6} N{\equiv}C{-}(C{\equiv}C)_2{-}C{\equiv}N \quad .$$

Other investigators [1,19,21] were also unable to make significant improvements to the method of synthesis of DCDA.

In the 1960s, various investigators [29-46] began to develop vigorously fundamentally new, in the main high-temperature methods for the synthesis of CA and DCA. Thus the possibility of synthesising CA from acetylene [29,30] or acetonitrile [31] on contact in the gas phase with hydrogen cyanide or dicyanogen at temperatures in the range 770 to 975°C has been demonstrated in a number of United States patents. Acrylonitrile and other impurities are formed together with CA, the yield of the latter increasing as the temperature is raised, while the yield of acrylonitrile falls. In order to determine whether or not acrylonitrile is an intermediate in the formation of CA, separate experiments were undertaken on the pyrolysis of acrylonitrile at 770° and 935°C. It was found that the yield of CA should be much lower if acrylonitrile were an intermediate. A simple radical reaction mechanism was therefore proposed:

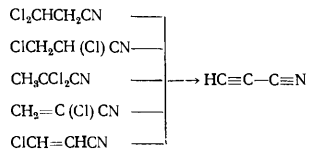
$$\left.\begin{matrix} HC{\equiv}\dot{C} + HC{\equiv}N \\ N{\equiv}\dot{C} + HC{\equiv}CH \end{matrix}\right\rbrace \rightarrow HC{\equiv}C{-}C{\equiv}N + \dot{H} \quad .$$

It is suggested that the reaction is initiated by the acetonitrile present in an amount of 0.04% in the initial hydrogen cyanide:

$$CH_3CN \rightarrow \dot{H} + CH_2CN; \quad \dot{H} + HC{\equiv}CH \rightarrow HC{\equiv}\dot{C} + H_2 \quad .$$

When a mixture of hydrogen cyanide and acetonitrile vapours with an inert gas is passed through a quartz tube at 700-900°C with a contact time of 5-0.01 s, malonodinitrile, acrylonitrile, and dicyanogen are formed preferentially. At 900-1100°C, CA is formed in 18% yield, but the main product is dicyanogen [31]. Comp [32] obtained CA in yields up to 95% by the non-catalytic reaction of acetylene with dicyanogen at 800-900°C. A satisfactory yield of CA is obtained when acetylene is highly diluted with dicyanogen and an inert gas. Substituted acetylenes react with dicyanogen under analogous conditions. Dehydrogenation of propionitrile and β-phenylpropionitrile over metal oxides at 600-800°C leads to CA and β-phenylpropiolonitrile, but the yield of the desired products has not been stated [33]. The formation of CA was

also noted when acetylene was added to active nitrogen, the yield of hydrogen cyanide, dicyanogen, and CA passing through a maximum as the supply of acetylene to the reaction zone was increased[34]. Morita and Hashimoto[35,36] recently synthesised CA by the pyrolytic cleavage of halogen-containing nitriles in a quartz tube in a stream of nitrogen, at 1000°C and a pressure of approximately 25 mmHg in the system. The yield of CA was 68–73%, depending on the initial nitrile:

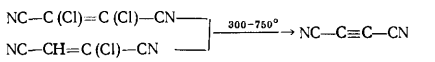



A more detailed study of the process showed that, apart from CA, monochloroacrylonitriles and acrylonitrile are formed as impurities[37]. The addition of carbon tetrachloride accelerates the pyrolysis of dichloropropionitriles and suppresses the formation of acrylonitrile. The addition of even small amounts of β-chloropropionitrile, which is converted under these conditions into acrylonitrile, leads to a sharp decrease of the yield of CA and increases the content of monochloroacrylonitriles. According to the authors[37], these data indicate that the dehydrochlorination processes under consideration have a radical mechanism. When αα'β-trichloropropionitrile, αβ-dichloroacrylonitrile, and ββ'-dichloroacrylonitrile are pyrolysed, chlorocyanoacetylene (CCA) is formed in a high yield[37].

The gas-phase interaction of acrylonitrile and chlorine at 500–1200°C and a reduced pressure (10–100 mmHg) leads to CA without an admixture of side products[38,39].

Alkyl-substituted homologues of CA may be obtained in high yields from the corresponding lithium acetylides and chlorocyanogen[40] and aryl-substituted derivatives (yield 38%) may be synthesised from phenylethynyl bromide and copper cyanide[47] or from sodium phenylacetylide and dicyanogen[48].†

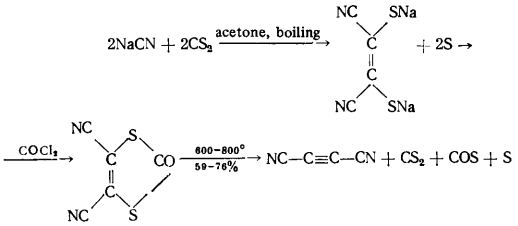
A method for the synthesis of DCA by the pyrolysis of the dichloro-derivative or its mixture with the monochloro-derivative of but-2-ene-1,4-dicarbonitrile at 300–750°C has been developed in the USA[41]:




The reaction is carried out in a pyrolysis reactor using an inert carrier gas, in particular helium (0.02–20% of the volume of the mixture). However, the pyrolysis products interact with one another so readily that the problem of their rapid separation arises even at a reduced temperature.

Zavitzanos[42,43] proposed a method for the synthesis of DCA directly from carbon and nitrogen. The latter is passed over a graphite cylinder heated to 2100–2700°C. Apart from DCA, the reaction products contain dicyanogen and DCDA. It was found that the rate of formation of DCA increases rapidly as the reaction temperature is raised from 2400 to 2700°C.

Ciganek and coworkers[40,45] obtained DCA by the pyrolysis of 4,5-dicyano-1,3-dithiol-2-one vapour:




DCA can be obtained on a preparative scale from tetracyanoethylene (yield up to 72%).[45]

DCA is also formed in the retrodiene cleavage of dimethyl 5,6-dicyano-oxabicyclo[2,2,2]hepta-2,5-dienedicarboxylate.[46] Other attempts at the synthesis of DCA, for example by the reaction of bromocyanogen with LiC≡CLi, were unsuccesful[49].

## III. PHYSICAL PROPERTIES

CA is a mobile, volatile, and readily inflammable liquid boiling at 42.5°C, easily converted on cooling into crystals melting at 5°C, which are quite stable on storage at a low temperature (−70°C).[37] There is an infinite parallel arrangement of linear chains in CA crystals owing to the formation of hydrogen bonds or charge-transfer complexes[50]. The CA vapour is highly irritant to mucous membranes and has a lachrymatory effect. On storage in air, CA rapidly darkens and on combustion in oxygen gives rise to a bright colourless flame (like acetylene). CA is sparingly soluble in water and readily soluble in alcohol and acetone. Its solutions become rapidly coloured brown.

DCA is a colourless transparent liquid boiling at 76.5°C, which crystallises[45], forming crystals melting at 20.5°C. The study of the crystal structure of DCA showed that it forms monoclinic crystals at 5°C, belonging to the space group $C_{2h}^5$–$P2_1/a$. Precision [X-ray] photography established that the unit cell contains two molecules and has the following dimensions: $a = 8.93$, $b = 6.04$, $c = 3.86$ Å, and $\beta = 99°20'$.[51]

Under the usual conditoins, DCA is a toxic and volatile substance. It is potentially explosive in the pure state and in concentrated solutions, while its dilute solutions in inert solvents are stable. Pure DCA rapidly darkens in air, because it is sensitive to the presence of oxygen, but can be stored almost indefinitely in dry ice.

DCDA sublimes in the form of fine white crystals, melting at 64.5°C, which are extremely volatile and unstable[19]. However, DCDA specimens may be stored *in vacuo* or in nitrogen at room temperature. After storage for three months, an appreciable amount of DCDA was found to have sublimed from the initial specimen[19]. Even at 100°C, only partial decomposition of DCDA is observed. DCDA solutions in $CS_2$, $CCl_4$, $CHCl_3$, furan, and hexane slowly acquire an amber colour, but in cyclohexane these changes are rapid. The solution in toluene becomes slowly coloured blue, while in benzene the same colour is acquired instantaneously.

DCDA has an irritant smell and is a powerful lachrymatory agent. The physical properties of members of the series $N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$, where $n = 0$–2, agree fairly well with the general relations governing the variation of the boiling point, melting point, and density with increasing molecular weight in a homologous series. The temperature variation of DCA and DCDA vapour pressures is significantly linear for both solid and liquid states.

†A method for the introduction of the cyano-group into bromo-substituted acetylenic alcohols by their reaction with copper cyanide was reported recently[200].

DCA and DCDA are of interest for the attainment of ultrahigh temperatures, since, on combustion in a suitable amount of oxygen, they form mainly endothermic products—CO and $N_2$. The possibility of achieving very high combustion temperatures, actually higher than in the combustion of dicyanogen, is associated with this fact[52]. Kirshenbaum and Grosse[53] found that, when DCA is burnt in oxygen, a temperature of approximately 5260 K is developed at 1 atm and 5750 K at 40 atm. It was expected that the replacement of molecular oxygen by ozone would give a temperature of 5520 K at 1 atm. Such temperatures were indeed subsequently attained[54]. (The temperature of the DCDA flame was not investigated owing to the difficulty of obtaining a sufficient amount of the latter.)

In connection with the foregoing, the heats of formation of cyanoacetylenes, measured for the first time by Moureu[11], are of interest. Subsequently Armstrong and Marantz[55] determined more accurately the heat of combustion of DCA and reported the corrected value[56] $\Delta H^\circ_{298}$(comb.) = −495.5 ± 0.2 kcal mole$^{-1}$ for the liquid substance and the heats of formation $\Delta H^\circ_{298}$(form.) of liquid and gaseous DCA calculated from it—119.6 and 126.5 kcal mole$^{-1}$ respectively.

There have been numerous studies on other physicochemical properties of α-cyanoacetylenes. The infrared spectra of CA[21,57-66], DCA, and DCDA have been investigated and discussed in detail in a collected volume[67]. The infrared spectra of CA and its deuterated derivative have been investigated in the gaseous and crystalline states (at 77 K) and measurements have been made of the integral intensities of the following absorption bands assigned on the basis of the calculation of the normal vibration frequencies: 3327 (2607) cm$^{-1}$ for the CH(CD) stretching vibrations, 2272 (2251) cm$^{-1}$ for C≡C, 2077 (1956) cm$^{-1}$ for C–N, and 863 cm$^{-1}$ for C–C (in the gase phase)[68]. Analysis of the spectra led to the conclusion that molecules of this type have a linear structure. Using the observed vibration frequencies and applying the system of valence force coordinates, Miller and Hannan[59] calculated the force constants of the C≡N ($16 \times 10^5$–$17.5 \times 10^5$ dyn cm$^{-1}$) and C–C ($6.0 \times 10^5$–$7.5 \times 10^5$ dyn cm$^{-1}$) bonds in DCA.

The infrared spectra of DCDA[21] were measured in the range 35–4000 cm$^{-1}$ in the vapour phase and in solution in carbon tetrachloride and carbon disulphide, while the Raman spectra were obtained for solutions in carbon tetrachloride, hexane, furan, and toluene. The absorption bands, assigned to the C≡N [2235 cm$^{-1}$ (Raman), 2266 cm$^{-1}$ (i.r.)] and C≡C [2183 cm$^{-1}$ (Raman), 2057 cm$^{-1}$ (i.r.)] stretching vibrations, do not interact with one another, in contrast to the two C–C vibrations with $\Sigma g^+$ symmetry. The C–C stretching vibrations give rise to a smiple intense band in the infrared spectrum in the region of 717 cm$^{-1}$.

The thermodynamic functions of DCDA have been calculated[64] for the range 200–2000 K in terms of the rigid rotator approximation. The bond polarisabilities and the average moleculer polarisability in the ground electronic state were determined using a potential δ-function. Derivatives of molecular polarisability have been calculated for fully symmetrical vibrations. The force constants of the C≡N, C≡C, and C–C bond vibrations have been obtained: $16.823 \times 10^5$, $15.614 \times 10^5$, and $6.753 \times 10^5$ dyn cm$^{-1}$ for the central bond, and $6.357 \times 10^5$ dyn cm$^{-1}$ for the bonds adjoining C≡N. The force constants have also been obtained from the overall valence-force field[65]. Moffat and Knowles[66] described a method for the calculation of various thermodynamic characteristics of dicyanogen, DCA, and DCDA: entropy, heat capacity, internal and free energy, and enthalpy (the last three quantities are determined from the dissociation energy of the molecule calculated from the heats of combustion and formation), etc.

There is extremely limited information about the rotational spectra of α-cyanoacetylenes. Westenberg and Wilson[69] analysed the purely rotational spectra of several CA and deuterated CA isotopic series in the microwave region and calculated the H–C (1.057 Å), C≡C (1.203 Å), C–C (1.382 Å), and C≡N (1.157 Å) bond lengths.

The dielectric constants of CA were determined[70] in the range 8850–9500 MHz in the gas phase at 42°C, the molecular polarisation remaining constant at 278 cm$^{-3}$. The molecular polarisation of CA at 9400 MHz is the same as at low frequencies. Measurements have been made of the $I = 1 \leftarrow 0$ and $I = 2 \leftarrow 1$ rotational transitions in the ground vibrational state[71]. Some of the lines in the rotational spectra of CA in the microwave range are quoted for the first time in the "Strelets V2" source book[3-5,72,73].

Information about the difference between the energies of the ground and excited electronic states was obtained from the electronic spectra of α-cyanoacetylenes. The spectrum of gaseous CA has many closely spaced weak bands in the range 230–260 nm.[74] The bond lengths and angles in the CA molecule have been determined from rotational spectroscopic data. The same workers[75] investigated the diffuse absorption band of CA in the gas phase in the range 200–230 nm, but its vibrational structure could not be analysed. In other investigations[76,77], the CA spectrum was obtained with a high resolution and the bands were analysed. The ionisation potential of CA has been calculated as 11.6 eV from the observed Rydberg series. Subsequently Dibeler et al.[78] measured mass spectrometrically the ionisation potentials of CA, DCA, and DCDA, which are respectively 11.6, 11.4, and 11.4 eV.

Connors et al.[79] investigated the absorption spectrum of gaseous CA in the range 105–200 nm. The first transition (61 000–66 000 cm$^{-1}$), having two main bands at 62 000 and 64 500 cm$^{-1}$, was assigned to the $\nu_2'(\sigma^+)$ or $\nu_3'(\sigma^+)$ excitation and the transition at 69 000 cm$^{-1}$ was assigned to the internal valence shell. The peak at 71 100 cm$^{-1}$, separated from the first band by 2100 cm$^{-1}$, can be regarded as due to the $\nu_2'(\sigma^+)$ or $\nu_3'(\sigma^+)$ active vibrations.

The spectra of DCA[80] in iso-octane solution and in the gas phase showed that the DCA molecule remains planar in the excited state and that its $D_{\infty h}$ nuclear configuration is preserved. DCA exhibits an intense absorption[79] in the range 150–165 nm, giving rise to three peaks separated by 2150 cm$^{-1}$, which may be assigned to the symmetrical $\nu_1'(\sigma_g^+)$ or $\nu_2'(\sigma_g^+)$ vibration. The Rydberg series (8100 to 92 440 cm$^{-1}$) has also been isolated.

The DCDA spectrum[79] in the range 105–200 nm has a more complex structure. The very intense transition in the range 175–190 nm was assigned to the $\nu_1'(\sigma_g^+)$ or $\nu_2'(\sigma_g^+)$ symmetrical vibration; in addition, three Rydberg series, giving a first ionisation potential of approximately 11.2 eV (90 300 cm$^{-1}$), were observed. A continuous absorption spectrum of gaseous DCDA[81] was also obtained in the range 230–310 nm. The fundamental characteristics of the transition suggest that the molecule is linear in both ground and excited states.

Calculations of the relative intensities in the photoelectronic spectra of CA and DCA have been published[82] and the magnetic rotation of DCA has been reported[83,84].

Analysis of the normal coordinates of CA[85,86] made it possible to determine the distribution of potential energy with respect to bonds and valence angle vibrations. Since

the application of the usual symmetry coordinates to DCA [87] leads to unduly high force constants, another set of symmetry coordinates has been proposed in which the -C-C≡C-C- chain is regarded as a system of three strongly interacting oscillators [88]. The normal DCDA coordinates have also been analysed [89] and the symmetry coordinates for the $\sigma^{+}_{g}$ and $\sigma^{+}_{u}$ symmetry types of the $L_{\infty}\omega$ group have been set up.

## IV. REACTIVITIES

α-Cyanoacetylenes are capable of entering into various chemical reactions involving both the C≡C and the C≡N bond. They are particularly reactive in reactions with nucleophiles owing to the conjugation of the triple bond with the electron-accepting cyano-group.

### 1. Hydration

The problem of orientation in the reactions involving addition to the conjugated triple bonds is naturally of considerable interest. It has been shown, for example, that diacetylene can combine with one or two water molecules, forming acetylacetylene or diacetyl respectively [90]. On the other hand, when CA is treated with 98% sulphuric acid at 20°C and then with ice, it does not undergo any changes, while chlorocyanoacetylene (CCA) gives a 75% yield of β-chloropropiolamide under these conditions [91]. Treatment of CA with sulphuric acid under controlled conditions (at 35–40°C) gave a 20% yield of propiolamide [92].

α-Aminocyanoacetylenes are readily hydrated in an aqueous solution of THF in the presence of hydrochloric acid, cyanoacetamides (I) being isolated in almost quantitative yield [93]:

$$R_2NC{\equiv}C{-}C{\equiv}N \rightarrow \underset{(I)}{R_2NCOCH_2C{\equiv}N}$$

R=Me, or Et .

CA behaves quite differently in aqueous THF in the presence of the hydrated form of Dowex-1 anion-exchange resin. Sasaki and Shoji [94] showed that di-(β-cyanovinyl) ether (II) is then formed in a yield of up to 60%:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[\text{Dowex-1}]{THF,\ H_2O} \underset{(II)}{N{\equiv}C{-}CH{=}CHOCH{=}CHC{\equiv}N} \quad .$$

Thus, depending on the reaction conditions, water can add to α-acetylenes in different ways.

CA and CCA can enter into the Ritter reaction forming the corresponding propiolamides (III) in a yield of 10 to 80%: [91,95]

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow{R^{+}} HC{\equiv}C{-}\overset{+}{C}{=}NR \xrightarrow{H_2O} \underset{(III)}{HC{\equiv}C{-}CONHR} \quad ;$$

R= t-$C_4H_9$, $(C_6H_5)_2C(COOH)$, $(CH_3)_2C(CH_2Cl)$, $C_{11}H_{17}$, $C_{11}H_{15}$, or $C_6H_{11}$.

The extension of this reaction to more complex systems makes it possible to obtain heterocyclic compounds containing the ethynyl group. Thus the reaction of 2-methylpentane-2,4-diol with CA or CCA in sulphuric acid leads to 2-ethynyl- or 2-chloroethynyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines. [96] Under these conditions, DCA and DCDA give rise to resins, which are difficult to treat.

### 2. The Addition of Alcohols and Phenols

The base-catalysed addition of methanol and ethanol to CA proceeds very readily already at 10°C, two moles of the alcohol being added with formation of ββ-dialkyoxypropionitrile (V) in 50–78% yield [18]. In the presence of KCN or potassium carbonate, it is possible to obtain a mixture of β-ethoxyacrylonitrile (IV) and diethoxypropionitrile (V):

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow{ROH} \underset{(IV)}{ROCH{=}CHC{\equiv}N} \rightarrow \underset{(V)}{(RO)_2CHCH_2C{\equiv}N} \quad .$$

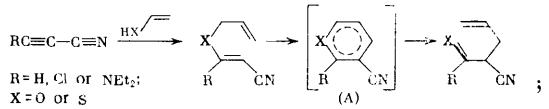
CA reacts similarly wtih glycols, 2-cyanomethyl-1,3-dioxolan and 2-cyanomethyl-1,3-dioxan being obtained from ethylene glycol and 1,3-propylene glycol respectively. The yields of the products were not indicated [18].

The addition of lower alcohols to CCA proceeds without catalyst at room temperature with formation of 3-alkoxy-3-chloroacrylonitrile: the reaction with allyl alcohol gave the Claisen rearrangement product (VI): [93]

$$ClC{\equiv}C{-}CN \xrightarrow{CH_2{=}CHCH_2OH} NC{-}C{\equiv}COCH_2CH{=}CH_2 \rightarrow$$

$$\xrightarrow{CH_2{=}CHCH_2OH} NC{-}CH{=}C(OCH_2CH{=}CH_2)_2 \rightarrow \underset{(VI)}{NC{-}CH(CH_2CH{=}CH_2)C(=O)CH_2CH{=}CH_2} \quad .$$

The reaction of cyanodiethylaminoacetylene with allyl alcohol in the presence of $BF_3$ etherate at room temperature gives rise to 2-cyano-*N*Λ-diethylpent-4-enamide. Sasaki et al. [93] proposed in such cases the mechanism of the Claisen rearrangement involving an intermediate with a quasi-cyclic structure (A):




CCA reacts with lower alcohols in the presence of sodium alkoxides, forming ββ-dialkoxyacrylonitriles (VII): [97]

$$ClC{\equiv}C{-}C{\equiv}N \xrightarrow[ROH]{NaOR} \underset{(VII)}{(RO)_2C{=}CHC{\equiv}N} \quad .$$

As shown by Moureu [11], DCA also interacts very readily with alcohols in the presence of alkaline agents, the reactivity of the alcohol decreasing with increasing length of its alkyl group. Winterfeldt et al. [98] investigated the stereochemistry of this reaction and showed that it leads to a mixture of *cis*- and *trans*-products (VIII) (yield 50 to 52%) in the proportions 4 : 1:

$$NC{-}C{\equiv}C{-}CN \xrightarrow{ROH} \underset{(VIII)}{NC{-}CH{=}C(OR)CN} \quad ;$$

R=Me, iso-Pr, or t-Bu

When piperidine is used at 0°C, the reaction proceeds stereospecifically (*cis*-adduct, 59% yield), while at 20°C a 9 : 1 mixture of the *cis*- and *trans*-adducts is obtained (yield 52%).

The addition of phenol to CA in the presence of sodium phenoxide proceeds sluggishly and leads to a mixture of monoadducts (IX) and diadducts (X), from which only the latter could be isolated [99]:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow{PhOH} \underset{(IX)}{PhOCH{=}CHC{\equiv}N} \rightarrow \underset{(X)}{(PhO)_2CHCH_2C{\equiv}N} \quad .$$

Having applied this reaction to halogenophenols, Miller [20] developed a method for the synthesis of halogeno-β-phenoxyacrylonitriles (IX) (in a yield of approximately 70%), which have found applications as agents effective against apple scab and as soil fungicides, insecticides, and herbicides.

### 3. The Addition of Thiols

Sasaki et al.[93] showed that the addition of propene-2-thiol to CA in the absence of a catalyst proceeds very slowly, while in the presence of sodium methoxide the reaction is accelerated and leads to a mixture of *cis*- and *trans*-β-allylthioacrylonitriles (XI) in 46% yield:

$$HC\equiv C-C\equiv N + HSCH_2CH=CH_2 \rightarrow \underset{(XI)}{H_2C=CHCH_2SCH=CHCN}$$

Like allyl alcohol, propene-3-thiol reacts with CCA and cyanodiethylaminoacetylene, forming the products of the Claisen rearrangement, for example (XII):

$$ClC\equiv C-C\equiv N + HSCH_2CH=CH_2 \rightarrow NC-CH=C(SCH_2CH=CH_2)_2 \rightarrow$$

$$\rightarrow NC-\underset{\underset{CH_2CH=CH_2}{|}}{\overset{S}{\overset{\|}{C}}}-SCH_2CH=CH_2$$

(XII)

Welle and Brandsma[40] investigated the addition of propyne-3-thiol to alkyl-α-cyanoacetylenes and found that in hexamethylphosphoramide the reaction is exothermic and proceeds without catalyst, terminating in essence at the stage of the product (XIII), which has the *cis*-configuration when R = H:

$$RC\equiv C-C\equiv N + HC\equiv C-CH_2SH \xrightarrow{20^\circ} \underset{(XIII)}{HC\equiv C-CH_2SC(R)=CHC=N} \rightarrow (HC\equiv C-CH_2S)_2C(R)CH_2C\equiv N;$$

(XIV)

R = H, or Alk .

Thiophenol readily reacts with CA in the presence of sodium methoxide on cooling, the yield of β-phenylthiolacrylonitrile (XV) reaching 75%. ββ-Di(phenylthio)-propionitrile (XVI) was obtained together with the adduct (XV) under analogous conditions in the presence of an excess of thiophenol[99]:

$$HC\equiv C-C\equiv N \xrightarrow[MeONa]{PhSH} \underset{(XV)}{PhSCH=CHC\equiv N} \rightarrow \underset{(XVI)}{(PhS)_2CHCH_2C\equiv N} .$$

CA reacts just as readily with *p*-methylbenzenethiol (at a reduced temperature in methanol solution in the presence of sodium *p*-methylbenzenethiolate), forming exclusively the *cis*-adduct in 100% yield[100,101]. Truce and Wolf[102] discovered a new reaction involving the addition of toluene-*p*-sulphonyl iodide to acetylenes, which proceeds stereoselectively and leads to the *trans*-adduct (XVII):

$$NC-C\equiv CH + n\text{-}CH_3C_6H_4SO_2I \rightarrow \underset{(XVII)}{\overset{NC}{\underset{I}{}}\!\!>C=C<\!\!\overset{SO_2C_6H_4CH_3\text{-}n}{\underset{H}{}}}$$

The reaction begins even when the components are mixed in the cold and is strongly accelerated by ultraviolet light.

### 4. The Addition of Amines, Hydrazines, and Their Derivatives

α-Cyanoacetylenes readily react with a wide variety of amines. Murahashi et al[99] obtained β-piperidinoacrylonitrile by the exothermic reaction of CA with piperidine in benzene. According to the same workers[99], the analogous reaction with aniline leads to the monoadduct (XVIII) and the diadduct (XIX):

$$HC\equiv C-C\equiv N + PhNH_2 \rightarrow \underset{(XVIII)}{PhNHCH=CHC\equiv N} \rightarrow \underset{(XIX)}{(PhNH)_2CHCH_2CN} .$$

In a later study by Sasaki et al.[103], the monoadduct (XVIII) was not obtained and the yield of (XIX) was 65%. It was shown[103] that the 1 : 1 products of the addition of cyclic secondary amines (morpholine, pyrrolidine, piperidine, aziridine, and imidazole) to CA have the *trans*-configuration. The reaction of CA with other amines proceeds similarly[104-107], the monoadducts, with both the *cis*- and *trans*-configurations, having been isolated. CA reacts with aqueous 28% ammonia solution, giving rise to β-aminoacrylonitrile.[99] The addition of ammonia and amines to DCA was first reported by Moureu and Bongrand[11], who showed that ammonia and primary and secondary amines interact vigorously with 2-cyano-1-phenylacetylene and DCA with formation of β-aminoacrylonitriles, which readily hydrolyse to β-ketonitriles (XXI):

$$RC\equiv C-CN \xrightarrow{NHR^1R^2} \underset{(XX)}{RC(NR^1R^2)=CHCN} \xrightarrow{H_2O} \underset{(XXI)}{RCOCH_2CN} ;$$

R = Ph, or CN .

Since compounds (XX) have not been characterised, Weis[108] repeated this investigation and found that 1-arylamino-1,2-dicyanoethylenes are formed quantitatively when DCA reacts with primary aromatic amines, while in the reaction with aliphatic amines the reaction mixture chars.

Sasaki et al.[109] investigated the possibility of synthesising ynamines by the reaction of CCA with secondary amines. It is known[67] that α-halogenoacetylenes enter into nucleophilic substitution reactions with trialkylamines and (mainly) into addition reactions involving the C≡C bond with secondary amines. The presence of the cyano-group in CCA suggests an increase in the reactivity of the chlorine in nucleophilic substitutions, so that treatment of CCA in ether with sodamide makes it possible to obtain malonodinitrile (XXII) in a satisfactory yield[109]:

$$NC-C\equiv CCl + NaNH_2 \rightarrow \underset{(B)}{[H_2NC\equiv C-CN]} \rightarrow \underset{(XXII)}{NC-CH_2CN} .$$

It has been suggested that the amine (B) is an intermediate in the reaction and is converted into the nitrile (XXII) as a result of prototropic isomerisation. Secondary amines (dimethylamine, diethylamine, piperidine, morpholine, and pyrrolidine) react with CCA to give the corresponding cyanoynamines (XXIII):

$$NC-C\equiv CCl + HNR_2 \rightarrow \underset{(XXIII)}{NC-C\equiv CNR_2} .$$

A higher yield of compound (XXIII) is achieved when the reaction is carried out at −50°C with a twofold excess of the amines. The ynamines (XXIII) readily undergo acid hydrolysis, being converted into cyanoacetamides in almost quantitative yield. They also readily react with amines, alcohols, and other compounds[109].

The interaction of CCA with allylamine[93] proceeds in a more complex manner—with formation of compound (XXIV):

$$NC-C\equiv CCl \xrightarrow{H_2NCH_2CH=CH_2} \underset{(XXIV)}{NC-CH=C(NHCH_2CH=CH_2)(NCH_2CH=CH_2)(NHCH_2CH=CH_2)} .$$

Depending on the conditions in the reaction between CCA and diallylamine, compound (XXV) or (XXVI) is obtained[93,109]:

$$\underset{(XXV)}{NC-C\equiv CN(CH_2CH=CH_2)_2}; \quad \underset{(XXVI)}{NC-CH=C[N(CH_2CH=CH_2)_2]_2} .$$

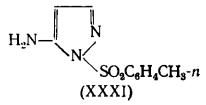
Hydrazines and semicarbazides are stronger bases and nucleophiles than amines, and can therefore react with CA

via both the triple bond and via the nitrile group or can simultaneously attack both reaction centres. For example, hydrazine hydrate in ethereal solution reacts with CA to form 1,2-di-(β-cyanovinyl)hydrazine (XXVII), while thiosemicarbazide in methanol at 20°C gives rise to β-thiosemicarbazidoacrylonitrile (XXIX)[99]:

$$\underset{\text{(XXVII)}}{NC{-}CH{=}CHNHNHCH{=}CHCN};\quad \underset{\text{(XXVIII)}}{NC{-}CH{=}CHNHNH_2};$$
$$\underset{\text{(XXIX)}}{NC{-}CH{=}CHNHNHCSNH_2};\quad \underset{\text{(XXX)}}{PhNHNHCH{=}CHCN}\ .$$

Under other conditions, CA reacts with hydrazine hydrate to give a 3 : 1 mixture of compound (XXVII) and β-cyanovinylhydrazine (XXVIII). CA and phenylhydrazine, taken in equimolar proportions in ether at −40°C, react to form a 1 : 1 adduct having the *trans*-configuration (XXX).[99]

The attempt to cyclise compounds (XXVIII) and (XXX) by heating in protic or aprotic solvents were unsuccessful[92]. However, CA reacts with tosylhydrazine to form 5-amino-1-*p*-tosylpyrazole (XXXI) in approximately 50% yield and only 23% of the non-cyclic product[97]:



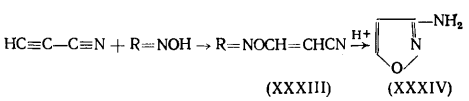
(XXXI)

5-Amino-1-arenesulphonylpyrazoles, which are used as analgesics, diuretics, and chemotherapeutic agents, have been obtained by the same reaction (in benzene at 90°C).[110]

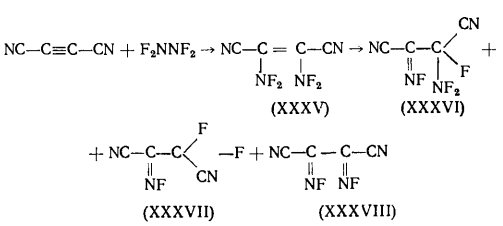
A solution of semicarbazide in methanol reacts with CA via the following mechanism and gives a 99% yield of cyanoacetaldehyde semicarbazone (XXXII):[97]

$$HC{\equiv}C{-}C{\equiv}N + H_2NNHCONH_2 \xrightarrow{MeOH} (MeO)_2CHCH_2CN \rightarrow \underset{\text{(XXXII)}}{NC{-}CH_2CH{=}NNHCONH_2}\ .$$

Alkylideneiminoxyacrylonitriles (XXXIII), which readily cyclise to 3-aminoisoxoazole (XXXIV), have been obtained by the reaction of CA with alkanone oximes[111]:




Tetrafluorohydrazine adds to DCA under more severe conditions (140°C, 5 h), which can probably be accounted for by the decrease of the nucleophilic reactivity of hydrazine when fluorine atoms are introduced into its molecule[112]. Bisdifluoroamino-1,2-dicyanoethylene (XXXV) is probably formed initially and then isomerises to the final dinitrile (XXXVI) (yield 33%) and disproportionates to side products of this reaction, namely (XXXVII) (12%) and (XXXVIII) (15):




3-Aminoisoxazole was obtained by the condensation of DCA with *N*-hydroxyurethane[113] and was then converted into 3-sulphanilamidoisoxazole, which exhibits bactericidal activity.

### 5. Halogenation and Hydrohalogenation

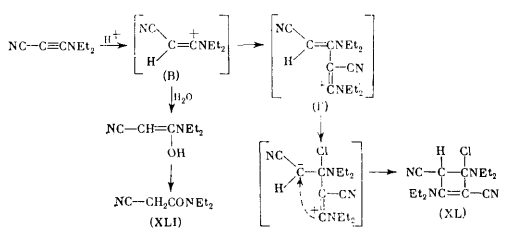
The addition of bromine and iodine to CA in alkaline solutions of KBr and KI proceeds with low yields of trihalogenoacrylonitriles[114]. Like other acetylenes, CA is readily halogenated with a high degree of selectivity at 30–60°C in alcoholic and aqueous alcoholic solutions of copper(II) chloride and bromide, forming αβ-dibromo-αβ-dichloro- and tribromo-derivatives of acrylonitrile[115,116].

Bromocyanoacetylene is halogenated under similar conditions. The halogenation of CA in methanol solutions of a mixture of $CuCl_2$ and $CuBr_2$ leads to the formation of α-bromo-β-chloroacrylonitrile. In aqueous solutions of the corresponding hydrogen halides and copper(I) halides at 30–35°C, CA readily gives rise exclusively to *cis*-β-halogeno-derivatives of acrylonitrile (XXXIX),[117] in agreement with the generally accepted ideas concerning the electron shift in CA:

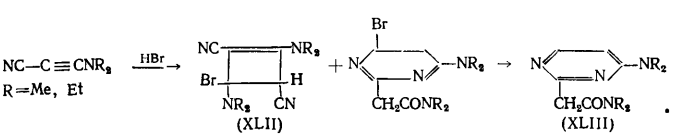
$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[CuHal]{HHal} \underset{\text{(XXXIX)}}{CHHal{=}CHCN}\ .$$

The hydrohalogenation of bromocyanoacetylene and iodocyanoacetylene proceeds under analogous conditions. The addition of HCl to CA in sulphuric acid in the presence of boron trifluoride etherate leads to ββ-dichloropropionitrile[91]. In research designed to synthesise Little's model of a one-dimensional organic superconductor, the products of the addition of HBr and ICN to DCA were used to introduce 1,2-dicyanovinyl groups into azo-, cyanine, and merocyanine dyes[24].

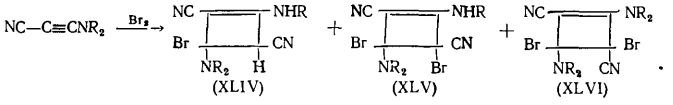
Aminocyanoacetylenes behave quite differently in the presence of hydrogen halides[118,119]. Sasaki[118] established that the reaction of cyano-*NN*-diethylaminoacetylene in solution in methylene chloride at 0–5°C with gaseous hydrogen chloride leads to the cyclobutene (XL) in 85% yield. The mechanism of the formation of this cyclobutene apparently involves the initial protonation of the ynamine with formation of the intermediate (C), which reacts further with the nucleophilic centre of the initial compound and gives rise to the intermediate (D):




The latter is rapidly attacked by the chloride anion with subsequent cyclisation to the cyclobutene (XL). The analogous reaction in the presence of small amounts of water leads exclusively to the cyanoacetamide (XLI). The addition of hydrogen bromide to the initial ynamine at 0°C proceeds in two ways with formation of products (XLII) and (XLIII):



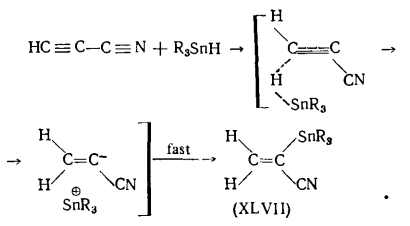
When these ynamines were allowed to react with bromine, cyclobutene derivatives (XLIV)–(XLVI) were again obtained in proportions which depend on the amount of bromine employed[118]:



(XLIV) (XLV) (XLVI)

## 6. The Reactions of α-Cyanoacetylenes with Metal Compounds

CA reacts exothermically with tin monohydrides via the *trans*-addition mechanism, which has been confirmed by experiments with deuterated transalkylstannanes[120–122]:



(XLVII)

The reaction is of second order overall: in terms of their influence on its rate, the substituents R in tin hydrides can be arranged in the following sequence: pH ≪ Me < Et, iso-Bu[121,123]. Lead hydrides[124] can also react with CA, but in this case a mixture of compounds (XLVIII)–(L) is formed:

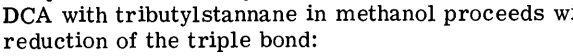
$H_2C{=}C(PbR_3)CN$; $R_3PbCH{=}CHCN$; $R_3PbCH{=}CHCN$

(XLVIII), 50% (XLIX), 45%, *cis*- (L), 5%, *trans*-

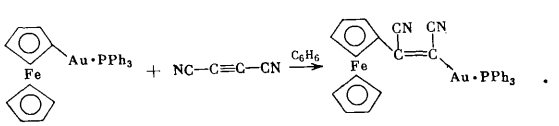
The stereochemistry of this process was not investigated in detail; it was suggested that compounds (XLVIII) and (XLIX) are formed via the *trans*-addition mechanism, while compound (L) is obtained as a result of the rearrangement of compound (XLIX) in the presence of the initial lead hydride[124].

Leusink, Noltes, and coworkers observed the exchange of hydride hydrogen between organic derivatives of tin and lead. When $R_3PbOAc$ and $Ph_3SnH$ are mixed in THF at −80°C and then treated with CA, a 3 : 7 mixture of products (XLVIII) and (XLIX) is formed[125].

Quintard and Pereyre showed[126] that the reaction of DCA with tributylstannane in methanol proceeds with the reduction of the triple bond:

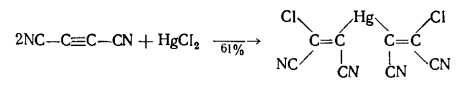


Nesmeyanov and coworkers[127] investigated the reactivity of the complex of ferrocenylgold with triphenylphosphine in relation to tetracyanoethylene and DCA. It was found that DCA is inserted (20°C, 15 min) in the C–Au bond with formation of 1,2-dicyano-1-ferrocenyl-2-(triphenylphosphinegold)ethylene (LI) in 76% yield:



(LI)

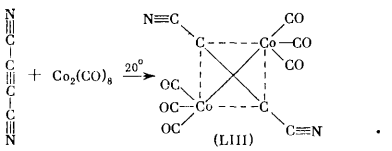
In a saturated aqueous NaCl solution, mercury(II) chloride adds to DCA (5–10°C, 20 min)[108]:



(LII)

It has been shown that in aqueous ethanol the $[Co(CN)_5]^{3-}$ ion forms stable compounds having the composition $K_6[Co_2(CN)_{10}A].2H_2O$ with acetylenes (A) having electron-accepting substituents (such compounds include DCA).[128]

Dickson and Jawhey[129] obtained hexacarbonyl-m-dicyanoacetylenedicobalt (LIII) by the reaction of DCA with dicobalt octacarbonyl in hexane:

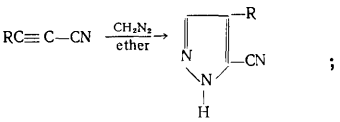


(LIII)

When DCA was allowed to react with $(Ph_3P)_2Ir(CO)Cl$ and nickelocene, complexes were obtained in low yields in which the metal atom is linked by a π-bond with the acetylenic ligand[130].

## 7. 1,3-Dipolar Cycloaddition

Numerous examples of the reactions of alkynes, particularly conjugated alkynes, with various types of dipoles are known[67]. For example, the method of synthesis of 4-R-5-cyanopyrazoles (LIV) is based on the reaction of α-cyanoacetylenes with diazoalkanes[92,131]:

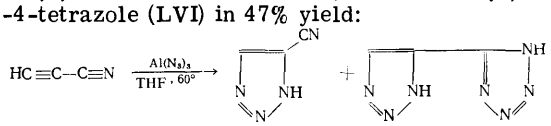


R=H,Cl, or Br (LIV)

Such pyrazoles may be used to synthesise pyrazole-3,5-dicarboxylic acid, which exhibits hypoglycaemic activity.

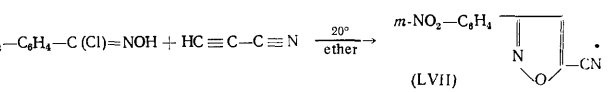
Sasaki et al.[132] described the synthesis of 5-cyano-3-(5-nitrofuryl)pyrazole in 36% yield from CA and 5-nitro-2-furyldiazomethane in ether at 20°C in the presence of triethylamine.

In 1969, Arnold and Thatcher[133] achieved the cyclisation of CA with aluminium azide and obtained a mixture of 4-cyano-1,2,3-triazole (LV) in 32% yield and 5-(1,2,3-triazolyl)-4-tetrazole (LVI) in 47% yield:



(LV) (LVI)

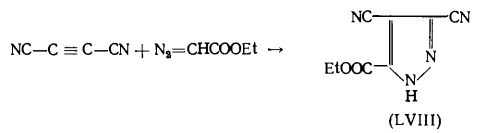
5-Cyanoisoxazole (LVII) has been obtained in 35% yield by the condensation of CA with the chloride of *m*-nitrophenylhydroxamic acid[134]:



(LVII)

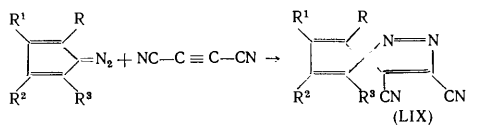
Weis[108] found that the addition of DCA to the *N*-oxide of benzonitrile or diazomethane leads respectively to 4,5-dicyano-3-phenylisoxazole in 81% yield or 3,4-dicyano-*N*-methylpyrazole in 99% yield. Ethyl 3,4-dicyanopyrazole-5-carboxylate (LVIII) has been synthesised from DCA

and ethyl diazoacetate [135] in 40% yield and then converted into 3,4,5-tricyanopyrazole:



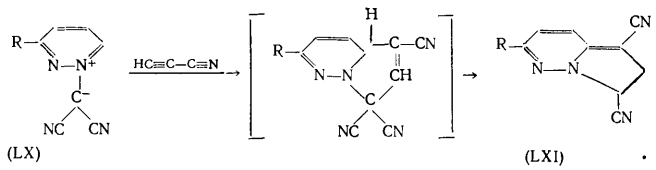
(LVIII)

Various polycyclic adducts can be obtained by the reaction with diazo-compounds. For example, Dürr and coworkers [136,137] achieved the 1,3-dipolar cycloaddition of diazocyclopentadienes to DCA (20°C, 1–2 h) and obtained spiropyrazoles (LIX):



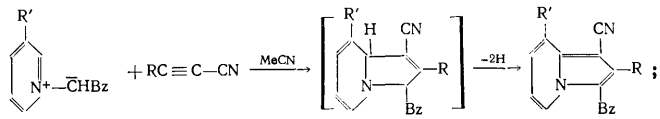
(LIX)

The 1,3-dipolar cycloaddition to CA to *N*-ylids (LX) in acetone (20°C, 4–12 h) results in the formation (in 30 to 80% yield) of pyrrolo[1,2-*c*]pyridazines (LXI):[138]



(LX) (LXI)

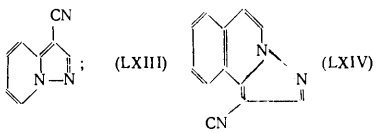
The analogous condensation of DCA with isoquinolinium ylid in dimethylformamide (DMF) leads to 1,2,3-tricyanopyrrolo[2,1-*a*]isoquinoline [139]. Sasaki et al. [140] achieved the 1,3-dipolar cycloaddition of CA and CCA to *N*-ylids and *N*-imines, but the yield of final products did not exceed 5–25%:



(LXII)

R=H, Cl; R′=H, or Me .

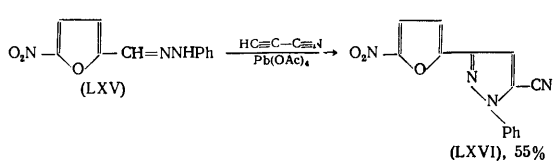
1-Aminopyridinium and 2-aminoisoquinolinium iodides react with CA in DMF (with added $K_2CO_3$) at 20°C, forming respectively 3-cyanopyrazolo[1,5-*a*]pyridine (LXIII) and 1-cyanopyrazolo-[5,1-*a*]isoquinoline (LXIV):



(LXIII) (LXIV)

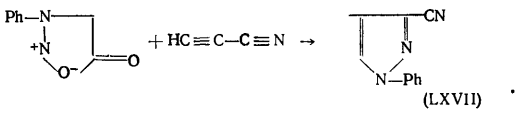
The interaction of pyridinium and triphenylphosphonium 1-cyclopentadienides with CA (−50°C, $N_2$) leads to the corresponding ylids of 1-(2-trans-β-cyanovinyl)cyclopentadiene.

5-Cyano-3-(5-nitro-2-furyl)-1-phenylpyrazole (LXVI) has been synthesised by the condensation of CA with the phenylhydrazone (XLV) in a THF–benzene mixture at 20°C in the presence of lead tetra-acetate [141]:



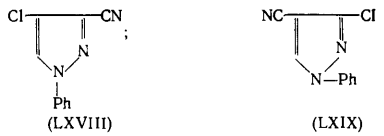
(LXV) (LXVI), 55%

Pyrazole (LXVII) has been obtained in satisfactory yield by the reaction of CA with *N*-phenylsydnone in chlorobenzene at 110°C:



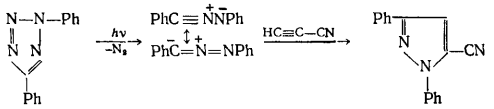
(LXVII)

Under analogous conditions, the reaction with CCA gives a 2:3 mixture of the isomeric pyrazoles (LXVIII) and (LXIX):



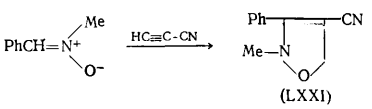
(LXVIII) (LXIX)

Diphenylnitrileimine [92], which was obtained by the ultraviolet irradiation of a solution of 2,5-diphenyltetrazole in THF, readily reacts with CA and yields 5-cyano-1,3-diphenylpyrazole (LXX):



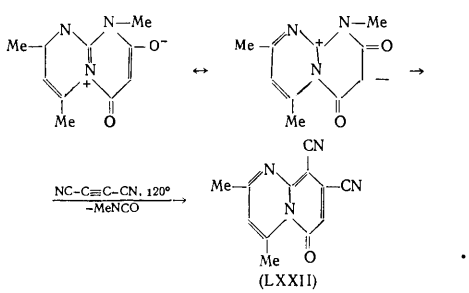
(LXX), 64%

Sims and Houk [142] established that CA reacts with *N*-methyl-*C*-phenylnitrone in benzene at 25°C to form exclusively 4-cyano-2(*N*)-methyl-3-phenylisoxazoline (LXXI), while the reaction with *N*-t-butylnitrone gives a 1:1 mixture of 4-cyano- and 5-cyano-*N*-t-butylisoxazolines:



(LXXI)

DCA enters into a 1,4-cycloaddition reaction as an acetylenic dipolarophile with the anhydro-2-hydroxy-1,6,8-trimethyl-4-oxopyrimido[1,2-*a*]pyrimidinium system [143]—a new heteroaromatic betaine with condensed rings:

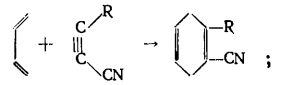


(LXXII)

## 8. α-Cyanoacetylenes in the Diels–Alder Reaction

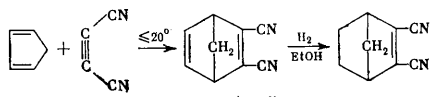
Diene synthesis is one of the convenient methods for obtaining cyclic and heterocyclic systems based on a wide variety of unsaturated compounds. CA and particularly DCA are used fairly frequently nowadays as dienophiles of the acetylenic series. The dienophilic activity of α-cyanoacetylenes is consistent with the fact that the rate of diene synthesis increases following the introduction of electron-donating substituents into the dienes and electron-accepting

substituents into the dienophiles, the reactions proceeding in accordance with the general mechanism



R=H, or CN .

In 1945, Blomquist and Winslow [17] were the first to use DCA as a dienophile in the reaction with one of the commonest reactive dienes—cyclopenta-1,3-diene (CPD)—in order to obtain insecticides having the properties of pyrethrum:

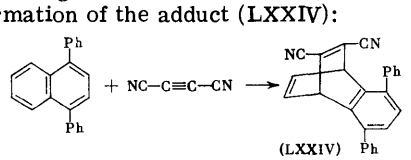


(LXXIII), 83%

The adduct (LXXIII) was also obtained by other workers [22,144]. CA reacts with CPD with much more difficulty than does DCA: thus 1,3-dicyanobicyclo[2,1,2]hepta-1,3-diene is formed in 37% yield in petroleum ether (30°C, 12 h). [99] Subsequently numerous dienes with a wide variety of structures were introduced into diene synthesis with $\alpha$-cyanoacetylenes: butadiene [99,108], isoprene and chloroprene [93], allo-ocimene [145], cyclohexa-1,3-diene [22,108,144], 3-diphenylcyclohexa-1,4-diene [146], cyclo-octatetraene [108], fluorocyclo-octatetraene [147], furan [46,108], thiophen [148-150], benzene [151] and its derivatives (durene, veratrol, m-cresyl methyl ether, arsabenzene) [22,144,151,152], naphthalene and 1,4-diphenylnaphthalene [22,153], anthracene [22,108,154,155], 9,10-diphenylanthracene [156], naphthacene [157], dimethyl- and diphenyl-fulvenes [17,22], bicyclo[2,2,1]heptadiene [22,108], bicyclo[2,2,2]octa-2,5,7-triene [158], *cis*-bicyclo[6,1,0]nonatriene [159,160], spiro[2,6]nonatriene [161], norbornadiene [162], [2,2]paracyclophane [151], ergosteryl acetate [163], [8](2,5)furanophane [164], and 6-chloro-3-cyano-2,4-bis(dimethylamino)-pyridine [165].

Benzene derivatives are relatively inert as dienes in Diels–Alder reactions, but are capable of condensing with DCA, the reaction having been shown by Ciganek [151] to be strongly accelerated by aluminium chloride. Thus, 2,3-dicyanobicyclo[2,2,2]octa-2,5,7-triene is formed in 14% yield in the reaction of benzene with DCA (180°C, 48 h), while in the presence of $AlCl_3$ at 20°C the yield is 63%. The condensation of DCA with hexamethylbenzene (in benzene, 130°C) is much faster than the condensation with unsubstituted benzene and gives a satisfactory yield of the desired product (83%).

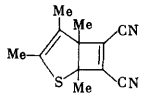
DCA readily condenses with naphthalene [22], anthracene [22,108], and 1,4-diphenylnaphthalene [153], the attack in the last case being directed to the unsubstituted benzene ring with formation of the adduct (LXXIV):



(LXXIV)

On being refluxed with anthracene (100°C, 1 h), DCA gives rise quantitatively to the 1 : 1 9,10-addition product [108], while the 2 : 1 adduct is formed in the reaction with 9,10-diphenylanthracene [156].

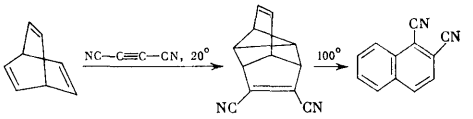
In contrast to benzene, thiophenes do not enter into the Diels–Alder reaction with acetylenes as dienes. In the study of the reaction of DCA and thiophen [148-150], a considerable influence of aluminium chloride on the mode of condensation was discovered. According to Wynberg and Helder [149], this involves a single-stage expansion of the thiophen ring to give thiepin (57% yield). Other workers showed by $^{13}C$ NMR that 2-thiabicyclo[3,2,0]hepta-3,6-diene (LXXV) is formed in this case, i.e. substituted thiophens undergo [2+2]-cyclo addition to DCA: [150]



(LXXV)

The cycloaddition to $\alpha$-cyanoacetylenes of dienes such as norbornadienes [108,162], cyclohexa-1,4-diene [146], or barrelene [158] can be regarded as a kind of extension of the Diels–Alder reaction.

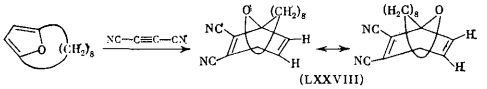
On condensation with DCA [158], barrelene is converted into the naphthalene derivative (LXXVII). The intermediate (LXXVI), isolated at lower temperatures, rearranges to 9,10-dihydronaphthalene, which is converted into the final product in 63% yield:



(LXXVI) (LXXVII)

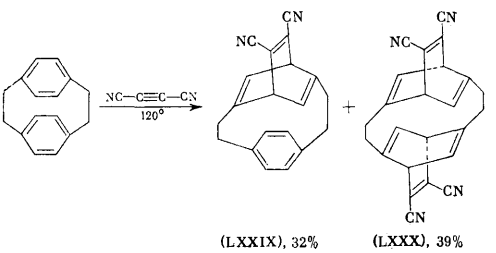
Other cyclopolyenes [147,159-161] condense similarly with DCA.

The Diels–Alder addition of DCA to certain cyclophanes [151,164] leads to unusual tricyclic systems (LXXVIII):



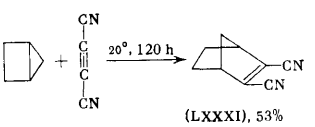
(LXXVIII)

When DCA is heated with [2,2]paracyclophane [151], a mixture of the polycyclic products (LXXIX) and (LXXX) is formed:



(LXXIX), 32% (LXXX), 39%

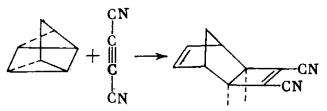
Strained alicyclic systems readily undergo the Diels–Alder reaction with DCA. Thus DCA adds to bicyclo[2,1,0]pentane [166,167] with rupture of the three-membered ring to form the adduct (LXXXI):



(LXXXI), 53%

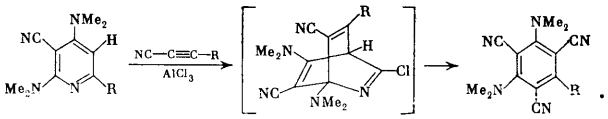
Tricyclo[4,1,0,$0^{3,7}$]heptane [168] reacts with DCA under more severe conditions (70°C, 14 h) to form a 1 : 1 adduct (via a radical mechanism). "Propellerane" or tricyclo-[3,2,1,$0^{1,5}$]octane, synthesised by Gassman et al. [169], reacts very vigorously with DCA at 20°C and somewhat more slowly at −78°C. The reaction of quadricyclane [170] with

DCA in methylene chloride is exothermic and leads to the formation of the 1 : 1 adduct (LXXXII) in 78% yield:



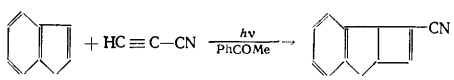
(LXXXII)

On heating in the presence of a small amount of $AlCl_3$, CA reacts with 6-chloro-3-cyano-2,4-bis(dimethylamino)-pyridine[165]. The reaction proceeds via a cyclic intermediate (D) and terminates with formation of 1,3,5-tricyano-2,4-bis(dimethylamino)benzene (LXXXIII):



R = H, Cl (D) (LXXXIII), 4%

When Indene and CA were photolysed[171,172] in benzene in the presence of a sensitiser (acetophenone), cyanocyclobutene (LXXXIV) was obtained in a satisfactory yield:



(LXXXIV)

## 9. Cyanoacetylene in Substitution Reactions

The mobility of the hydrogen atom in CA is caused not only by the very nature of the acetylenic linkage but also by the presence of the electron-accepting cyano-group. Thus the acidity of the acetylenic hydrogen in CA is reflected in its distinct ability to form hydrogen bonds not only with typical basic proton acceptors, but also with the electrons of the triple bond (self-association)[50]. The tendency of CA to undergo substitution reactions is shown primarily in its reaction with metals. Thus copper cyanoacetylide[21] has been obtained as a yellow deposit when a CuCl solution in aqueous ammonia was treated with CA. The attempt to obtain the sodium derivative of CA in liquid ammonia was unsuccessful[25]. Lithium cyanoacetylide[25] has been obtained from butyl-lithium and CA at −70°C. The magnesium bromide derivative of CA (LXXXV) is formed smoothly at a reduced temperature in absolute ether and can react virtually with all reagents capable of involvement in organomagnesium syntheses[173]. In the presence of CuCl, compound (LXXXV) reacts with organic halides, for example with allyl bromide:

$$\underset{\text{(LXXXV)}}{BrMgC\equiv C-CN} + H_2C=CHCH_2Br \xrightarrow{THF,\ Et_2O} \underset{\text{(LXXXVI)}}{H_2C=CHCH_2-C\equiv C-CN}$$

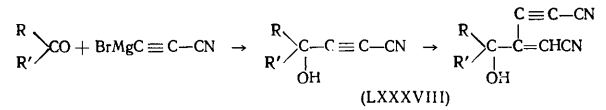
When compound (LXXXV) is treated with phosgene, bromocyanoacetylene is formed, while treatment with ethyl chlorocarbonate results in the formation of 1,6-dicyano-3-ethoxyhex-2-en-4-yne. Acetic anhydride adds to the triple bond of complex (LXXXV) and gives rise to 2,3-diacetyl-3-bromoacrylonitrile. *trans*-Acrylonitriles (LXXXVII) have been obtained by the reactions with epoxyethane and epoxypropane:

$$BrCH_2CHOCH=CHCN$$
$$\quad\quad|$$
$$\quad\quad R$$

(LXXXVII)

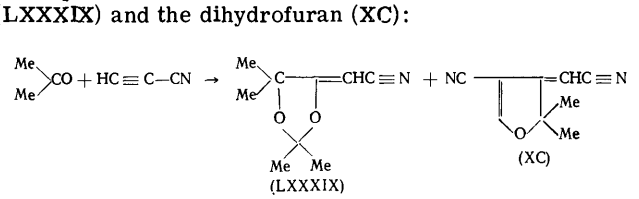
R=H, or Me .

Carbonyl compounds (acetone, cyclohexanone, formaldehyde, etc.) react with compound (LXXXV) to form the corresponding carbinols (LXXXVIII), which can undergo further reactions involving the addition of another CA molecule[173]:



(LXXXVIII)

The reaction of CA with acetone[173] in the presence of a 20% aqueous solution of NaOH leads to the dioxolan (LXXXIX) and the dihydrofuran (XC):



(LXXXIX) (XC)

The magnesium iodide derivative of CA gives cyanoiodoacetylene and not CCA on treatment with toluene-*p*-sulphenyl chloride[25]:

$$IMgC\equiv C-CN + p\text{-}CH_3C_6H_4SO_2Cl \rightarrow IC\equiv C-CN$$

CCA can be obtained only via lithium acetylide:

$$HC\equiv C-CN \xrightarrow{BuLi} LiC\equiv C-CN \xrightarrow[30\%]{Cl_2} ClC\equiv C-CN$$

In contrast to CCA, bromo- and iodo-cyanoacetylenes are obtained by the reaction of CA with bromine or iodine respectively, in aqueous alkaline solutions of KBr and KI in yields of 40–60%[174].

The dimerisation of CA is known[27] to occur in the presence of potassium hexacyanoferrate (III). The same method can be used for asymmetric coupling. Thus, Jones and coworkers[175] described the synthesis of 7-cyanohept-2-ene-4,6-diynol from CA and pent-2-en-4-ynol. The acetylenic compounds are initially converted into copper acetylides and then treated with potassium hexacyanoferrate(III).

It has been shown recently[176] that CA can also undergo the Chodkiewicz condensation, but its use is limited by the occurrence of side reactions and the instability of the products. CA has been used successfully in the synthesis of a natural acetylene analogue (XCI):

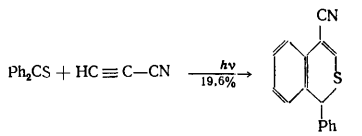
$$NC-C\equiv CH + BrC\equiv C(CH_2)_3OH \xrightarrow{CuCl,\ NH_2OH\cdot HCl,\ EtNH_2} \rightarrow [NC-C\equiv C-C\equiv C(CH_2)_3OH] \rightarrow \underset{\text{(XCI), 9\%}}{NC-C\equiv C-CH=C(CH_2)_3O}$$

5-Aminoisoxazole was isolated as a side product[176].

## 10. Other Reactions of α-Cyanoacetylenes

Apart from those already discussed, a number of non-general reactions of α-cyanoacetylenes have been described.

On being irradiated with light from a sodium lamp, CA undergoes photocycloaddition to diphenyl thione[177] with formation of compound (XCII):

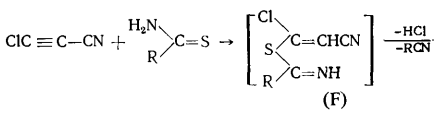


(XCII)

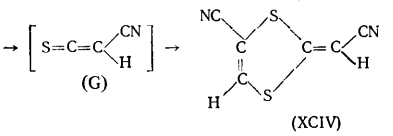
The high-temperature reaction of benzene with CA proceeds with a low conversion (1–2%), benzonitrile and biphenyl having been isolated from the reaction products[178]. When CA was allowed to react with a formate ester[179] in the presence of $HgCl_2$ or $CuCl_2$–$Zn(Ac)_2$, the cyanoacrylate (XCIII) was obtained:

$$HC\equiv C-CN + HCOOR \rightarrow NC-CH=CHCOOR \quad (XCIII)$$

Sasaki et al.[180] found that the reaction of equimolar amounts of CCA and thioacetamide in methanol at 0°C leads to 1,4-dithiofulvene (XCIV). CCA reacts similarly with other thiocarbonyl compounds: thiourea, *NN*-dimethylthiourea, and *N*-phenylthiourea:



(F)



(G)



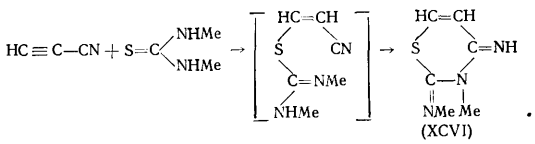
(XCIV)

The authors believe that the reaction begins with nucleophilic attack by the thiocarbonyl group on the triple bond with formation of an intermediate (F), which loses a molecule of hydrogen chloride and RCN, is converted into the unstable thioketen (G), and dimerises to compound (XCIV).

The reaction of CA and methyl- and phenyl-cyanoacetylenes with thiourea and ammonium dithiocarbamate[181] in alcohol proceeds stereospecifically and results in the synthesis of *cis,cis*-thiodiacrylonitriles (XCV):

$$RC\equiv C-CN + H_2NCSNH_2 \text{ or } H_2NCS_2NH_4 \rightarrow NC-CH=C(R)SC(R)=CHCN \quad (XCV)$$

Sasaki et al.[180] found that other thiocarbonyl compounds (thioacetamide and *N*-phenyl-, *N*-methyl-*N'*-phenyl-, and *NN'*-diphenyl-thioureas) react with CA under analogous conditions in methanol or acetone solution to form thiodiacrylonitriles in 70–90% yield. The reaction with *NN'*-dimethylthiourea led to the isolation of 4-imino-3-methyl-2-methylimino-2,3-dihydro-1,3-thiazin (XCVI) in 60% yield:



(XCVI)

Bushby[182] described the reaction between DCA and ethers. On heating for 16 h a mixture of DCA and THF, he obtained tetrahydro-2-furylfumaronitrile (37% yield), the photochemical isomerisation of which leads to the formation of tetrahydro-2-furylmaleonitrile. 1-Ethoxyethylfumaronitrile was obtained similarly in 48% yield from diethyl ether and DCA, while 1,2-dimethoxyethane gave a mixture of 1,2-dimethoxyethylfumaronitrile (6%) and (2-methoxyethoxy)methylfumaronitrile (6% yield).

Reddy and Weis[183] obtained the product of the addition of DCA to triphenylphosphine (in acetonitrile at 25–30°C) having the structure of 1,2,3,4,5,6-hexacyanohexa-2,4-diene-1,6-diylidene-1,6-bistriphenylphosphorane according to revised data[184].

## 11. The Polymerisation of Cyanoethylenes

New polyconjugated systems have been obtained on the basis of CA [185,186], namely polypropiolonitrile and its copolymer with phenylacetylene, which exhibit a high thermal stability and electrical resistance.

A number of workers [187–191] have shown that, at a reduced temperature, CA forms low-molecular-weight polymers under the influence of anionic catalysts. For example, the polymerisation of CA and its copolymerisation with acrylonitrile are initiated by $CH_3ONa$ or KSCN.[189] It is believed that the polymerisation involves the acetylenic linkage, since the polymers readily interact with $H_2O_2$ via the cyano-group, forming amides. In another instance, the polymerisation of CA was initiated by BuLi.[191] The polymerisation of CA in the presence of Ziegler–Natta catalysts[192] leads to a mixture of trimethylsuccinonitrile and polypropiolonitrile in a low yield. It has been established by infrared spectroscopy that polypropiolonitrile has the structure $[-CH=C(CN)-]_n$.

In the presence of initiators of free-radical polymerisation in THF solution, CA forms copolymers with olefinic compounds, for example *N*-vinylcarbazole[193].

Chukhadzhyan and coworkers [194,195] showed that $\pi$-allyl derivatives of nickel are active catalysts of the polymerisation of CA. They believe that the polymerisation proceeds via the triple bond of the acetylenic group; the resulting polymer has a conjugated chain of double bonds with a *trans*-structure, which has been confirmed by infrared spectra and a number of chemical reactions.

The homopolymerisation of DCA was achieved for the first time[196] in the presence of an anionic catalyst, namely butyl-lithium (in heptane–THF at –73°C) and led to the formation of a powdered polymer in 90% yield. The infrared spectra of the latter showed absorption bands characteristic of systems of conjugated bonds with cyano-groups, while the ESR spectrum contained a single narrow signal without a definite structure (the number of unpaired electrons is approximately $10^{18}$ per gram). The polymerisation of DCA in the presence of lithionaphthalene proceeds with a large exothermic heat change, requires large amounts of the catalyst, and results in the formation of oligomers (having molecular weights in the range 400 to 500) soluble in acetone, alcohols, DMF, THF, water, and sulphuric acid and having a resistivity (*in vacuo* at 20°C) of approximately $10^9$–$10^{12}$ $\Omega$ cm.[197]

Byrd[49,198] homopolymerised DCA under free-radical conditions [in the presence of 2-azobisisobutyrodinitrile (ABIBN) for 1400 h at 55°C], the yield of the polymer being 7%. In the copolymerisation of DCA with styrene in THF, acetone, or toluene in the presence of the same catalyst, the conversion reached 80–97%.

Rembaum and Henry[199] proposed a method for the synthesis of the DCA copolymers with various vinyl (5–90 wt.%) compounds: styrene, methyl methacrylate, butadiene, isoprene, isobutene; acrylonitrile, ethylene, and propene. The polymerisation is carried out in polar organic solvents (THF, dioxan, ethyl methyl ketone, etc.) in the presence of ABIBN, benzoyl peroxide, t-butyl hydroperoxide, butyl-lithium, butylmagnesium bromide, and sodionaphthalene (for 10–30 h at 40–70°C and $10^{-5}$ mmHg, yield 70–95%). The resulting copolymers exhibit a moderate thermal stability (they are stable up to 280°C) and are semiconductors, which permits their employment in transistors and solar batteries.

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# Gas-chromatographic Analysis of Metals as Volatile Complexes

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The use of gas-chromatographic methods for analysing metals is considered. Attention is paid mainly to study of the gas-chromatographic properties of compounds of metals with various derivatives of β-diketones as well as complexes with thioketones and derivatives of β-ketoimines. Attempts to separate the rare-earth metals gas-chromatographically are examined, together with highly sensitive gas-chromatographic methods for determining traces of metals (beryllium, aluminium, chromium, etc.). A list of 78 references is included.

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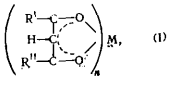

## I. INTRODUCTION

During the period covered by the Review, from the end of 1970 to the beginning of 1975, more than seventy publications appeared on the gas chromatography of volatile compounds of metals, including several reviews[1-7] and one monograph[8]. Certain changes in the general approach to the problem have been noticeable during the past five years. Whereas before 1970 the studies in this field were often in the nature of preliminary investigations, the possibilities of the method have now become clear, and the aims more definite. Most of the papers report comparative investigations of the chromatographic properties of volatile complexes of metals having a common feature (usually either complexes of a series of metals with the same ligand or, in contrast, of a series of ligands with the same metal). The authors have usually tried to find either new volatile complexes, with better properties, of metals that have already been chromatographed, or volatile compounds of metals that had previously proved impossible to chromatograph. Thermogravimetric analysis is widely used to assess the volatility of complexes. Papers on the gas-chromatographic separation of rare-earth metals form a special group. The number of papers on the practical application of the gas chromatography of chelates to the determination of traces of such metals as beryllium, aluminium, chromium, etc. has increased. Finally, a few studies have been made on the specific behaviour of metal chelates in chromatographic columns.

## II. COMPLEXES WITH β-DIKETONES

### 1. Simple β-Diketonates

Many papers have appeared on the further study of metal β-diketonates of the type

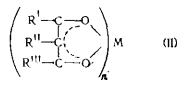


(I)

where $n$ is the charge on the metal ion. The list of complexes investigated has expanded appreciably during recent years. The interest of research workers in the hitherto popular derivatives of hexafluoropentane-2,4-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione diminished somewhat, after which the number of investigations on non-fluorinated β-diketonates increased, especially on derivatives of 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane) $CH_3.C(CH_3)_2.CO.CH_2.CO.C(CH_3)_2.CH_3$. Thermogravimetric analysis has been used[9,10] to study the volatility and investigate the chromatographic behaviour of chelates of this dione with twenty-five metals, including rare-earth elements, nickel(II), cobalt(II), and zinc(II). In a long paper on the investigation of complexes of chromium(III), aluminium(III), iron(III), palladium(II), copper(II), nickel(II), zirconium(IV), rare-earth metals, uranyl(II), and thorium(IV) with various β-diketones, Kuwamoto[11] also paid great attention to chelates with this dione. In particular, thermogravimetric analysis showed that only neodymium(III) and zirconium(IV) among the above metals, as well as sodium, give chelates that decompose partly on sublimation: all the remaining chelates sublime without decomposition. Numerous chelates of metals with pentane-2,4-dione, its hexa- and tri-fluoro-derivatives, and other β-diketones were also studied. The first chromatogram of a zinc(II) chelate with the above tetramethylheptanedione was reported in this paper.

Investigations on the gas-chromatographic properties of complexes of beryllium, aluminium, scandium, vanadyl(II), chromium(III), iron(III), copper(II), and manganese(II) with 1-thienyltrifluorobutane-1,3-dione[12] and of beryllium, aluminium, iron(III), indium, chromium(III), cobalt(III), thorium(IV), and several rare-earth elements with trifluoro-5,5-dimethylhexane-2,4-dione[13] in the main merely confirmed already known laws and gave no fundamentally novel results, apart from the first chromatogram of a chelate of cerium(IV) with the latter dione[13]. The same applies to a detailed examination[14] of chelates of aluminium, gallium, and indium with pentane-2,4-dione and its alkyl derivatives, hexafluoropentane-2,4-dione, 1-phenyltrifluorobutane-1,3-dione, 1-furyltrifluorobutane-1,3-dione, and 1-thienyltrifluorobutane-1,3-dione. The chromatographic behaviour of chelates of several metals—in particular

beryllium, aluminium, chromium, and copper—with alkylated β-diketones of the type



(II)

has been investigated for the first time [11,14,15]. Unfortunately, the replacement of hydrogen by any alkyl as R'' lowers the volatility of the complex and thereby impairs its gas-chromatographic properties, since there is evidently no accompanying improvement in thermal stability. The introduction of fluorinated radicals as R'' might have given more interesting results, but such chelates have not yet been investigated.

## 2. Complexes with Mixed Ligands

Recent years have seen a considerable increase in the number of gas-chromatographic studies of mixed-ligand metal complexes, fluorinated β-diketonates containing also one or two molecules of neutral donors such as dimethylformamide (DMF), dimethyl sulphoxide (DMSO), tributyl phosphate (TBP), diethylamine, etc. The gas-chromatographic behaviour of complexes of nickel(II) and cobalt(II) with trifluoropentane-2,4-dione and dimethylformamide having the composition $ML_2.2DMF$ (where L is a singly charged ligand anion) has been investigated [16]. Quantitative determination of each complex to 0.2 mg proved possible, with separation effected at a relatively low temperature (100°C). The gas chromatography of volatile mixed complexes of zinc $ZnL_2.A$ (where A is a molecule of tri-n-butyl phosphate or tri-n-butylphosphine oxide—TBPO) has also been described [17]. Furthermore, the same paper reported the gas-chromatographic behaviour of mixed chelates of zinc with trifluoropentane-2,4-dione and 4-methylpyridine and with pentane-2,4-dione and 2,2'-bipyridyl. The best results were obtained with the chelate having the composition $ZnL_2.TBPO$.

Investigations have been made on mixed complexes $UO_2L_2.DBSO$ and $ThL_4.DBSO$ formed by uranyl and thorium(IV) with hexafluoropentane-2,4-dione and dibutyl sulphoxide [11] and on complexes of analogous composition with 1,1,1,2,2,6,6,7,7,7-decafluoroheptane-3,5-dione, hexafluoropentane-2,4-dione, and trifluoropentane-2,4-dione with neutral donors (dibutyl sulphoxide, tributyl phosphate, and tributylphosphine oxide). [18] The best results were obtained with hexafluoropentanedione and dibutyl sulphoxide: use of these complexes enabled uranium and thallium at concentrations of 1–120 g litre$^{-1}$ to be determined in solutions with a relative error $< 10\%$. The limiting dilutions for uranium and thorium were respectively 0.6 and 0.4 g litre$^{-1}$.

Jacquelot and Thomas [19] chromatographed mixed complexes $ML_2.2(C_2H_5)_2NH$ of nickel(II) and cobalt(II) with 1-thienyltrifluorobutane-1,3-dione and diethylamine, but the form of the peaks left much to be desired. Furthermore, nickel and cobalt could not be separated, since the two complexes had almost the same retention times. It is interesting that these workers treated the solid carrier with potassium hydroxide to improve the chromatogram. This was probably the first use of this procedure in the gas chromatography of metal chelates.

The properties of complexes of iron(II) and iron(III) with hexafluoropentanedione and tributyl phosphate, as well as their chromatographic behaviour, have been examined in detail [20]. Iron(II) forms a complex $FeL_2.2TBP$, while iron(III) yields $FeL_3$ and $FeL_3.TBP$, with in the latter case one of the hexafluoropentanedione anions ($L^-$) acting as a unidentate ligand. During chromatography the compound $FeL_2.2TBP$ dissociates in the gas phase, but iron(III) present in the complex $FeL_3.TBP$ is reduced in the chromatographic column to iron(II).

Burgett [21] has studied the gas-chromatographic behaviour of complexes $ML_2.2DBSO$ of iron(II), cobalt(II), and nickel(II) with decafluoroheptanedione. He includes results for the chromatographic behaviour of the copper chelate $CuL_2$ with the same ligand. The ion $Cu^{2+}$ does not form complexes having mixed ligands. In the chromatography of small quantities the form of the peaks of all the complexes studied was distorted. The peak of the copper chelate changed form also in the presence of mixed complexes of nickel(II) and cobalt(II).

## 3. Binary Complexes

Studies have been made not only on complexes having mixed ligands but also on volatile binary complexes, which contain more than one identical ligand and ions of two different metals. The latter complexes are usually formed only from fluorinated β-diketones. Belcher et al. [22] showed that, in the presence of excess of the ligand, chelates $ML_3$ of rare-earth metals with fluorinated β-diketones react with alkali-metal cations M' to form complexes $M'ML_4$. The products sublimed in a vacuum without decomposition, but evidently could not be used for gas chromatography. Gurevich et al. [23] prepared volatile complexes $M'CoL_3$ (in which $M' = K^+$, $Rb^+$, $Cs^+$, while L represents a hexafluoropentanedione anion), obtained chromatograms of individual compounds, and effected the gas-chromatographic separation of potassium and rubidium complexes on a stainless-steel column 200 × 0.1 cm containing 1% of Silicone SE-30 on Chromaton N at 250°C. It is interesting that retention of the binary complexes diminished in the sequence from potassium through rubidium to caesium. No mention was made [23] of the possibility of using the resulting complexes for quantitative analysis.

## 4. Separation of Rare-earth Metals

The excellent results obtained when gas chromatography is used to separate compounds of closely similar properties naturally suggest the possible application of this method to solve one of the most difficult problems of analytical chemistry, separation of the rare-earth metals. Volatile complexes of these elements with dipivaloylmethane suitable for use in gas chromatography were first prepared in 1965. [24] Since then researches on the gas-chromatographic properties of various volatile rare-earth β-diketonates have been published regularly, but significant progress in this field has evidently not yet been made. Japanese workers have been responsible for the largest number of papers on the gas chromatography of the rare-earth metals; they have studied complexes with tetramethylheptane-3,5-dione [9–11,25,26], trifluorodimethylhexane-2,4-dione [13], and the latter together with a neutral donor (tributyl phosphate or tri-n-octylphosphine oxide) [27]. Interesting papers on the gas chromatography of mixed-ligand complexes of rare-earth metals have been published by Burgett and Fritz [28–30] and by Sieck and Banks [31].

However, the main task—complete separation of the whole group of rare-earth metals—remains unsolved. Only one case of the separation of chelates of two neighbouring rare-earth metals (complexes of europium and

samarium with dipivaloylmethane)[22], on a column of 2% of a fluorinated silicone oil on Chromosorb G only 45 cm long with temperature programming has been reported. This work was published in 1969, but other workers have evidently been unable to repeat the separation, and publications during recent years represent in most cases the chromatograms of rare-earth metals taken singly, but in some cases as mixtures of two or three elements[25,27-29,31].

Comparison of papers by the same group of workers over several years (1968–1972) shows that the use of complexes with various β-diketones has not yielded any significant improvement in the separation of rare-earth metals[26,27,32]. Recently several investigators have again returned to the study of the dipivaloylmethane complexes, but without especial success[9,10,25]. It is stated[9,10] that a most efficient column is required for the separation of a mixture of lutetium and ytterbium chelates (> 11 000 theoretical plates), whereas 650 theoretical plates are sufficient to separate neodymium and praseodymium chelates. However, despite the availability of such an inefficient column, no attempt was made to achieve even this separation, undoubtedly owing to the additional difficulties encountered in solving the problem. In particular, attempts to improve the efficiency of separation of rare-earth chelates by lengthening the column resulted in broadening of the peaks, so that the separation not only did not improve but even deteriorated. According to other workers[29] the optimum column length is ~ 50 cm. This is probably why columns not longer than 70–75 cm have been used in most attempts at the separation of rare-earth complexes[13,25-27].

## III. VOLATILE COMPLEXES WITH LIGANDS CONTAINING OXYGEN TOGETHER WITH SULPHUR AND WITH NITROGEN

### 1. Derivatives of 4-Thionopentan-2-one

The first research on the gas chromatography of volatile chelates of metals with thioacetylacetone—a ligand containing oxygen and sulphur as donors $CH_3.CS.CH_2.CO.CH_3$—was undertaken by Stephen et al.[33] in 1969. Investigations on these lines have since been continued. In a detailed examination of bivalent compounds of nickel, zinc, cadmium, lead, palladium, platinum, and cobalt with thioacetylacetone Belcher et al.[34,35] found that most of them are monomeric $ML_2$, in contrast to the complexes of these metals with β-diketones, which in most cases are polymeric or hydrated. These workers established that the volatility of the chelates diminished in the sequence

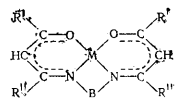
$$\text{nickel} > \text{zinc} > \text{cobalt} > \text{palladium}$$

where only the nickel(II) chelate vaporised completely without decomposition. However, even it was unsuitable for the gas-chromatographic determination of small quantities of the metal. Considerably better gas-chromatographic properties were observed in chelates of several bivalent metals with fluorinated derivatives, e.g. trifluoro-4-thionopentan-2-one[35-37]. Thus chelates of the latter with nickel(II), zinc(II), and cobalt(II) sublimed completely, and those with palladium(II) and platinum(II) by 85% and 65% respectively[36]. These workers were able to separate the nickel, palladium, and platinum chelates on a column comprising 2.5% of Apiezon L on Universal B at 170°C. In a later study[38] the same workers used the nickel(II) complex of trifluorothioacetylacetone for the gas-chromatographic determination of traces of nickel (down to $5 \times 10^{-11}$ g) in alloys, tea, and fats using an electron-capture detector.

Bayer et al.[39,40] investigated the gas-chromatographic behaviour of chelates of nickel(II), palladium(II), and platinum(II) with another sulphur-containing ligand, hexafluoro-4-thionopentan-2-one. The resulting chelates were far more volatile than those with the trifluoro-derivative, and their gas-chromatographic separation was achieved on columns with 1% of SE-30 and with 3% of OV-17 on Chromosorb W at only 80°C. It is interesting that many metals that form very stable chelates with β-diketones (beryllium, aluminium, chromium, etc.) do not react at all with fluorinated β-thioketones such as trifluorothioacetylacetone.

### 2. β-Ketoiminates

The first paper on the gas chromatography of volatile β-ketoiminates of copper(II) and nickel(II) was published in 1967.[41] Since 1971 several interesting studies have appeared by Belcher, Uden, et al.[42-47] Especially promising results were obtained for the bivalent nickel, copper, palladium, and platinum complexes with quadridentate β-ketoimines



where B = $[CH_2]_2$, $[CH_2]_3$, or $CH_2.CH(CH_3)$, R′ = $CH_3$, and R″ = $CH_3$ or $CF_3$. The vapour pressure of such chelates is low, and they had to be chromatographed at high temperatures (up to 250°C), but their thermal stability resulted in almost complete absence of decomposition in the column.

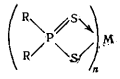
Comparative studies on complexes of copper(II) and nickel(II) with bi- and quadri-dentate β-ketoimines showed that the gas-chromatographic behaviour of the latter was to be preferred, especially in the chromatography of small quantities of the complexes. In particular, the gas-chromatographic determination of copper and nickel in quantities down to $10^{-13}$ g was achieved[46,47]. An interesting fact was revealed by examination of the chelates of these metals with quadridentate ligands containing oxygen and nitrogen. The replacement of terminal alkyl by perfluoroalkyl groups in β-diketones leads in all known cases to an increase in the vapour pressure of the corresponding metal chelates, a rule which is satisfied also for bidentate β-ketoiminates. With quadridentate β-ketoimine complexes (the bivalent copper and nickel complexes were investigated), however, the opposite relation is unexpectedly observed: i.e. the introduction of terminal trifluoromethyl groups into the ligand does not increase but lowers the volatility of the copper(II) and nickel(II) β-ketoiminates[46,47]. No explanation has yet been found for this fact.

## IV. OTHER VOLATILE METAL COMPOUNDS

In 1969 D'Ascenzo and Wendlandt[48] suggested that the gas chromatography of copper, nickel, and zinc could be effected by use of the diethyldithiocarbamates, supposedly possessing adequate volatility. When tested, however, this suggestion proved unfortunate, and was rejected[49]. Barratt et al.,[50] examined the suitability for gas chromatography of volatile beryllium and zinc hydroxyacetates and hydroxypropionates $M_4OR_6$, where R = $CH_3COO^-$ or $C_2H_5COO^-$. They were able to separate the beryllium and

zinc complexes on a glass column with 5% of Apiezon L on Universal B at 150°C. However, the chromatographic properties of the compounds leave much to be desired.

Kleinmann and Neeb[51] chromatographed complexes of gold(I), cadmium(II), and zinc(II) with dialkyldithiophosphines



where R = $CH_3$, $C_2H_5$, and $C_3H_7$. They were able to obtain peaks of the individual complexes and to separate the diethyl-, dipropyl-, and dibutyl-dithiophosphinate complexes of zinc(II) on a glass column with 3% of Silicone OV-225 on Chromosorb W at 220°C. From the form of the peaks the gas-chromatographic properties of these chelates are apparently also far from ideal. Nevertheless, the chromatogram obtained is interesting in demonstrating the kinetic stability of the zinc complexes: otherwise, the chromatogram would have indicated the presence of mixed complexes formed by ligand exchange.

The possibility of the gas-chromatographic determination of certain metals as volatile trimethylsilyl derivatives of anions containing the metal is of interest. Thus a paper on the gas-chromatographic analysis of anions[52] mentions among others the possible determination of the vanadate ion $VO_3^-$. Since many metals—aluminium, chromium, manganese, niobium, tantalum, molybdenum, tungsten, bismuth, lead, tin, etc.—may occur as anions, this raises the hope that new methods may appear for the gas-chromatographic analysis of metals.

Finally, we must note the possibilities that have appeared for the quantitative determination of metals as volatile organometallic compounds. Such compounds had hitherto been regarded as of little interest for the gas-chromatographic analysis of metals, since in most cases quantitative conversion of the metal into the compound could not be achieved. Recently, however, exceptions have appeared to this rule. The first such work was published in 1968 by Bock and Monerjan on the determination of thallium as its cyclopentadienyl derivative[53]. However, as yet this is the only publication on the use of cyclopentadiene derivative in this way. Two interesting papers have appeared on the gas chromatography of several elements—thallium, selenium, tellurium, mercury, arsenic, antimony, bismuth, and tin—as their phenyl derivatives $(C_6H_5)_nM$.[54,55] It is very important that phenyl derivatives of all the above elements (other than thallium) are readily obtained quantitatively by the reaction of phenylmagnesium bromide with diethyldithiocarbamates of the metals in absolute ether. The phenyl derivatives of selenium, tellurium, mercury, arsenic, antimony, and bismuth were separated on a column comprising 5% of Carbowax 20M with added terephthalic acid on Gasochrome Q with a programmed temperature rise from 180 to 220°C (10 deg $min^{-1}$), and also those of thallium, selenium, and tellurium on a column with 3% of Silicone OV-17 on Gasochrome Q under isothermal conditions at 160°C. Further research on these lines may lead to the development of quantitative gas-chromatographic methods of analysis for the above and other elements.

## V. GAS-CHROMATOGRAPHIC ANALYSIS OF TRACES OF METALS

The chief practical value of the gas-chromatographic analysis of volatile compounds of metals consists in the high sensitivity attainable in the determination of chelates of several metals by means of such devices as an electron-capture detector or a microwave emission detector. Gas-chromatographic analysis is comparable in sensitivity with such highly sensitive methods as neutron-activation analysis, mass spectrometry with a spark source, and flameless atomic-absorption spectroscopy, sometimes even surpassing them.

During recent years several papers have been published on the practical application of the gas-chromatographic determination of traces of certain metals as volatile chelates. Descriptions have appeared of the gas-chromatographic determination of beryllium in air[56], terrestrial and lunar rocks and meteorites[57], in the leaves of trees[58], and in various biological materials[59,60], aluminium and chromium in uranium[61], aluminium in sea-water[62] and in polymers[63], nickel in alloys, tea, and fats[38], nickel and copper in biological materials[46], cobalt in vitamin $B_{12}$,[64] and chromium in aqueous solutions[65] and in various biological materials[66-69]. Chelates with trifluoropentane-2,4-dione have been most widely used, but other complexes have also found application[38,46,63,64].

Use of volatile complexes of metals in analysis of traces of elements.

| Element | Ligand | $10^{10}$ x Limit of detection, g | Ref. |
|---|---|---|---|
| Al | trifluoropentane-2,4-dione | 0,009 | 63 |
| | trifluoro-5,5-dimethylhexane-2,4-dione | 0,04 | 63 |
| As | phenyl | 4 | 54 |
| Be | trifluoropentane-2,4-dione | 0,0004 | 57 |
| Co | heptafluoro-7,7-dimethyloctane-4,6-dione | 0,4 | 64 |
| Cr | trifluoropentane-2,4-dione | 0,0025 | 68 |
| | pentane-2,4-dione | 0,03 | 71 |
| Cu | trifluoropentane-2,4-dione | 0,08 | 71 |
| | quadridentate β-ketoimines | 0,001 | 46 |
| Fe | trifluoropentane-2,4-dione | 0,13 | 71 |
| Ga | trifluoropentane-2,4-dione | 0,027 | 71 |
| Ni | trifluoro-4-thionopentan-2-one | 0,5 | 38 |
| | quadridentate β-ketoimines | 0,007 | 46 |
| Pd | trifluoro-4-thionopentan-2-one | 2 000 | 36 |
| Pt | trifluoro-4-thionopentan-2-one | 3 600 | 36 |
| Sc | pentane-2,4-dione | 0,021 | 71 |
| | trifluoropentane-2,4-dione | 0,03 | 71 |
| Th | hexafluoropentane-2,4-dione + tributylphosphine oxide | 8 000 | 18 |
| Tl | cyclopentadiene | 10 000 | 53 |
| U | hexafluoropentane-2,4-dione + tributylphosphine oxide | 12 000 | 18 |
| V | trifluoropentane-2,4-dione | 0,085 | 71 |
| Rare-earth metals | decafluoroheptane-3,5-dione + dibutyl sulphoxide | 200—300 | 28 |

Highly sensitive devices other than the electron-capture detector are beginning to be used for the determination of microquantities of chelates, including mass-spectrometric[70], microwave emission[71-74], and flame-photometric[69] detectors. An atomic-absorption spectrometer with flameless atomisation can be used for the detection of volatile compounds of metals[75]. The Table lists data on the use of metal chelates in quantitative gas-chromatographic analysis.

## VI. BEHAVIOUR OF METAL CHELATES IN A CHROMATOGRAPHIC COLUMN

Volatile complexes of metals are extremely capricious in chromatographic behaviour. Hitherto no objective methods have been available for assessing the suitability of a particular chelate for quantitative gas-chromatographic analysis. The widely used thermogravimetric

analysis permits merely comparison of the relative volatilities of two or more chelates and may indicate whether a given chelate will sublime without decomposition. Quite often a chelate that appears to be "ideal" from thermogravimetric data proves to be unsatisfactory for gas chromatography.

Especially marked departures from "ideality" are observed in work with small quantities of the substance. The literature is full of descriptions of such phenomena as irreversible sorption of the initial portions of chelates in columns[30], distortion of the form of the peak and diminution in the efficiency of the column as the sample becomes smaller[21], redox reactions in the column[20], non-linearity of the calibration curve on dilution of the test solutions (the curve does not pass through the origin)[30,34,38,73], sorption of the chelate by the surface of the liquid phase[30,76], displacement of one sorbed chelate by another[30], anomalous broadening of the chelate peaks with lengthening of the column[29], etc. The anomalous behaviour of chelates in columns has been explained[77] by their dissociation in the liquid phase, a hypothesis apparently supported by the fact that addition of a small quantity of the vapour of the ligand to the carrier gas improves the chromatograms of certain chelates[73,77,78]. Incidentally, surprisingly little attention had been paid until recently to the role of the liquid phase in the chromatography of chelates, although even the unusual fact that metal chelates can in the large majority of cases be satisfactorily chromatographed only on polysiloxane liquid phases and Apiezon L should have interested research workers. Indeed, recent results show that polysiloxanes and Apiezon L are by no means the best liquid phases for the gas chromatography of chelates. Thus the chromatograms of several chelates are considerably improved by use of the liquid phase Dexsil-300 GH based on carboranes[30,47].

Other facts difficult to explain may be mentioned. For example, it is difficult to understand the sharp differences in the sensitivity of a flame-ionisation detector to chelates of rare-earth metals having closely similar properties. Thus the sensitivity of detection of mixed-ligand complexes of erbium and ytterbium with decafluoroheptanedione and dibutyl sulphoxide differs by a factor of 8,[29] whereas that of chelates of neodymium and samarium by a factor of ~ 11![28] Another little understood phenomenon[26] is that the chelate peak gradually diminished on successive admissions to the column of the terbium complex of dipivaloylmethane, and the chromatogram became stable only after several additions of a benzene solution of the dione. The problem of the behaviour of metal chelates in a chromatographic column obviously requires further investigation.

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# Thermotropic Liquid Crystals and Their Applications

E.I.Kovshev, L.M.Blinov, and V.V.Titov

The structure and the physical and physicochemical properties are discussed, with special attention paid to the relation between the chemical structure and the properties of the mesogens. The influence of external factors on liquid-crystalline phases is examined. Various fields of application of liquid crystals are reported, and requirements to be met by such materials are formulated. A list of 210 references is included.

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## I. INTRODUCTION

Many synthetic organic compounds are potentially thermotropic liquid crystals[1]: i.e. over a certain temperature range, on passing into the liquid state, they retain the orientational— and in certain directions sometimes also the translational— long-range order in the disposition of molecules characteristic of crystals. By the end of 1973 more than 5000 organic and organometallic compounds having mesomorphic (liquid-crystalline) properties had been recorded[2], and their number has continually increased. The number of publications on liquid crystals has also grown rapidly during recent years. Thus, according to the publishers LOCUS, about 180 papers in this field appeared during 1968, but in 1973 this had already reached 700. During 1975 about 900 papers and patents were covered in the new journal *Liquid Crystals Abstracts*. Such intensifying interest in liquid crystals is not accidental: just recently the use of thermotropic liquid crystals has made it possible to observe visually changes in temperature[3] of 0.01-0.001 deg, and liquid-crystalline indicators, requiring hardly any energy, have enabled electronic wrist-watches to be placed on the market with an accuracy of a few seconds in a year, as well as pocket electronic calculators. Every year new effects are discovered in liquid crystals, promising great possibilities in science and technology.

The present Review has the aim of acquainting a wide circle of chemists with the fundamental ideas developed during recent years in this interesting and practically important branch of the physics and chemistry of the condensed phase. The greatest attention is paid to the chemical and physical properties of thermotropic liquid crystals that are directly related to their application in

electro-optical devices, although related problems, concerning the fundamental properties of liquid crystals and other fields of application, will be touched on. For further details on individual aspects of thermotropic liquid crystals we may recommend Chistyakov's well known book[4], which gives detailed information on structure, monographs and reviews on the chemistry[5-9], physics, and theory[10,11], electro-optical phenomena[12,13], spectroscopy[14], and thermography[15]. A whole series of short surveys on the most diverse problems of the liquid-crystalline state has been published in a special issue of the *Berichte der Bunsengesellschaft für physikalische Chemie*[16].

## II. STRUCTURE AND GENERAL PROPERTIES

### 1. Classification and Structure

It is now usual to divide thermotropic liquid crystals into three groups—nematic (filamentous), cholesteric, and smectic (soaplike)—although Friedel[17], one of the founders of the nomenclature, not without justification regarded cholesteric as a variety of nematic liquid crystals. The term "smectic" is not specific: this group comprises all liquid crystals that are neither nematic nor cholesteric.

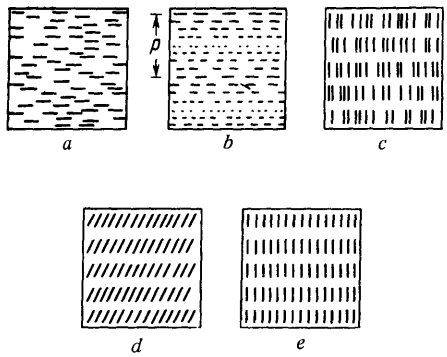



**Figure 1.** Types of thermotropic liquid crystals: *a*) nematic; *b*) cholesteric; *c*)–*e*) smectic; *P*) pitch of helix.

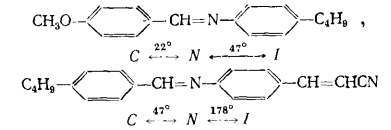
Fig. 1 shows diagrammatically, as rigid rods, the packing of molecules in the various types of liquid crystals.

Formation of the liquid-crystalline state can be observed visually from the melting of the crystalline substance in a capillary. Transition to a homogeneous turbid liquid is then evident, followed at a different temperature by transition from the liquid-crystalline state to an isotropic liquid. A better method is to observe by means of a polarising microscope the change in the phase state of specimens when heated (or cooled). Magnifications of 100–300 are mostly used. The patterns (textures) observed can be used to identify the type of mesophase. The latter method combined with differential scanning calorimetry provides reliable identification of phase transitions, their temperatures, and the heats of transition. Phase transition points can be determined also from the temperature variation of mechanical, optical, electrical, and other properties. The types of mesophases are most reliably determined by X-ray diffraction, but the textures of individual compounds or mixtures are also used for their identification.

#### Nematic liquid crystals

Only orientational order is present in nematic liquid crystals: i.e. the long axes of the molecules forming a unit structure are approximately parallel, with the molecules able to move freely in three directions and rotate about the long axis. A large volume appears as a strongly scattering turbid liquid; in unoriented layers exceeding 0.1 mm in thickness filamentous structures (disinclinations) can be observed under crossed Polaroids; in thinner layers a schlieren texture is evident with characteristic nodes or points of intersection of disinclinations[1]. Marbled, pseudoisotropic, and homogeneous textures are encountered, as well as the filamentous (schlieren) type†. On oriented specimens ("single crystals") homotropic (pseudoisotropic) and homogeneous (planar) textures can be observed according to the direction of the long axes of the molecules (perpendicular or parallel to the walls of the cuvette).

Examples of nematic liquid crystals are *p*-butyl-*p'*-methoxybenzylidenaniline[18] and *p*-*p'*-butylbenzylidenaminocinnamonitrile[19]




(I)

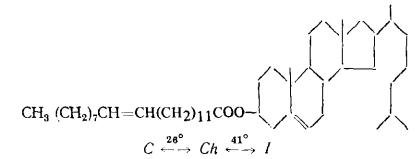



(II)

Here and subsequently *C*, *N*, and *I* denote respectively crystalline, nematic, and isotropic liquid phases, and the numerals above the arrows indicate the temperatures (°C) of the corresponding phase transitions.

#### Cholesteric liquid crystals

Cholesteric liquid crystals are formed by optically active molecules (until recently almost exclusively by esters of cholesterol). Their distinguishing feature is that the direction of the long axes of the molecules in each successive layer, consisting of molecules oriented in parallel and moving freely in two directions, forms a certain angle with the direction of the molecular axes in the preceding layer. A helix is thus formed, whose pitch *P* depends on the nature of the molecules and on external factors (Fig. 1*b*). Such twisting of the molecular axes leads to selective reflection of light, and the wavelength of maximum reflection changes with variation in the pitch of the helix, e.g. owing to slight temperature variation. The oriented layers form a confocal and planar (homogeneous) texture. An example that is colourless in the crystalline and isotropic liquid states, but changes colour (selective reflection) with change in temperature in the liquid-crystalline state, is cholesteryl erucate[20]

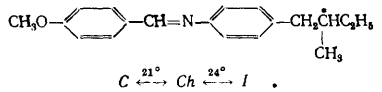



(III)

(*Ch* denotes the cholesteric phase).

†Detailed descriptions and photographs of textures will be found in e.g. Refs. 4 and 9.

Cholesteric liquid crystals include also the so-called "chiral" nematics, which have the structure of typical nematic liquid crystals but exhibit optical activity, e.g. *D*(or *L*)-*N*-*p'*-methoxybenzylidene-*p*-(2-methylbutyl)aniline [21]

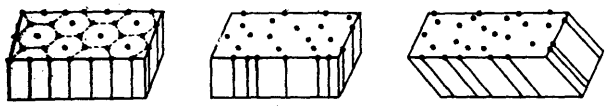


(IV)

$$C \xleftrightarrow{21^\circ} Ch \xleftrightarrow{24^\circ} I \ .$$

Smectic mesophase *A* ($S_A$)

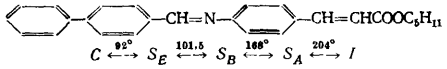
This form comprises layers moving freely relative to one another, whose surfaces are formed by the ends of parallel molecules normal to the surface (Fig. 2*a*). Within a layer the molecules have no translational order: they can move freely in two directions, and rotate about the long axis. The $S_A$ mesophase is the least "organised" among smectic liquid crystals, and may apear in confocal (of fan or polygonal type), homogeneous, or pseudoisotropic textures or as stepped drops. An attempt [22] at a more detailed classification based on crystallographic properties included in particular a variety of the $S_A$ mesophase in which the thickness of the layer was less than the length of a molecule, i.e. in which the molecules were inclined to the plane of the layer and rotated on a cone. The absence of correlation between molecular rotations in different layers leads to a uniaxial crystal as an average structure, in contrast to the biaxial inclined smectic *C*.



*a* *b* *c*

Figure 2. Structure of a layer of a smectic liquid crystal: *a*) $S_A$; *b*) $S_B$; *c*) $S_C$.

The $S_A$ modification occurs at the highest temperature among smectic phases: when heated, it passes into a nematic or a cholesteric mesophase, or else into an isotropic liquid. An example of a liquid crystal of this type is pentyl *p*-*p'*-phenylbenzylidenaminocinnamate [23] at 168–204°C



(V)

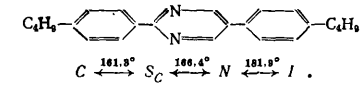
$$C \xleftrightarrow{92^\circ} S_E \xleftrightarrow{101.5} S_B \xleftrightarrow{168^\circ} S_A \xleftrightarrow{204^\circ} I$$

Smectic mesophase *B* ($S_B$)

This is a more ordered phase than $S_A$. The molecules in $S_B$ layers, while remaining mutually parallel and normal to the plane of the layer, form a hexagonal type of packing [24] within the layer (Fig. 2*b*).

Smectic mesophase *C* ($S_C$)

This is analogous to the $S_A$ mesophase, but the mutually parallel long axes of the molecules are inclined at an angle to the surfaces of the layer (Fig. 2*c*). Such a mesophase is formed e.g. by 2,5-di-*p*-butylphenylpyrazine [25]



(VI)

$$C \xleftrightarrow{161.9^\circ} S_C \xleftrightarrow{166.4^\circ} N \xleftrightarrow{181.9^\circ} I \ .$$

As with $S_A$, different varieties of $S_C$ mesophases may exist, differing in the slope of the molecules (>40° for $S_{C1}$ and ≤26° for $S_{C2}$), its temperature dependence, and also the ability to pass into other modifications [22].

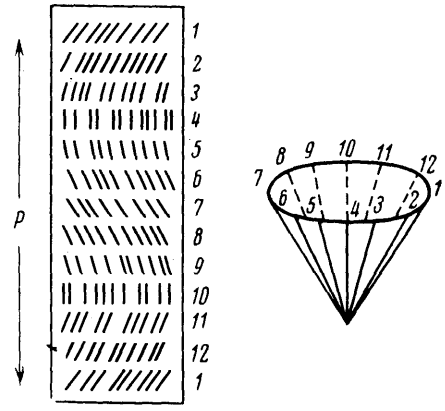
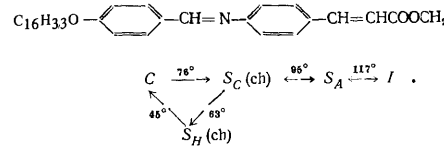



Figure 3. Structure of a ferroelectric *C* smectic, where *P* is the pitch of the "twist". Corresponding numerals on the cone and on the "section" through the layers correspond to the same angle of slope of the molecules.

Liquid-crystalline compounds exhibiting optical activity, e.g. *D*(or *L*)-2-methylbutyl *p*-*p'*-hexadecyloxybenzylidenaminocinnamate [26], are able to form a chiral *C* smectic mesophase $S_C$(ch), in which each successive layer of molecules is turned to a certain angle relative to the preceding layer, so that a twisted structure of pitch *P* is formed (Fig. 3), which with a definite orientation of molecular dipoles possesses ferroelectric properties [26], e.g.



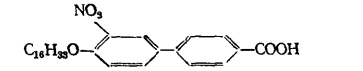
(VII)

$$C \xrightarrow{76^\circ} S_C(ch) \xleftrightarrow{95^\circ} S_A \xrightarrow{117^\circ} I \ .$$

$$S_C(ch) \xrightarrow{45^\circ} S_H(ch) \xleftarrow{63^\circ} S_C(ch)$$

Smectic mesophase *D* ($S_D$)

This mesophase is optically isotropic. X-Ray diffraction reveals no layer structure, but indicates a quasi-cubic lattice. Smectic liquid crystals of this type have been found with only a few compounds, e.g. 4'-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid [27]



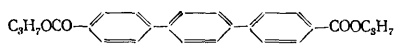
(VIII)

$$C \xleftrightarrow{126.8^\circ} S_C \xleftrightarrow{171.0^\circ} S_D \xleftrightarrow{197.2^\circ} S_A \xleftrightarrow{201.9^\circ} I \ .$$

The $S_D$ mesophase can exhibit not only an isotropic but also a mosaic texture [1].

Smectic mesophase *E* ($S_E$)

The degree of three-dimensional order is extremely high. The molecules in the layers form an orthorhombic lattice [28,29], from which free rotation about the long axis is absent. The $S_E$ mesophase may appear in mosaic and pseudoisotropic textures. Besides the above example (V), a detailed study has been made of the $S_E$ mesophase of dipropyl *p*-terphenyl-4,4″-dicarboxylate [28]

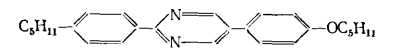



(IX)

$$C \xleftrightarrow{122.0^\circ} S_E \xleftrightarrow{137.1^\circ} S \xleftrightarrow{239.2^\circ} I\ .$$

Smectic mesophases *F* and *G* ($S_F$ and $S_G$)

These mesophases have been studied very little. They both have a layer structure, with an ordered arrangement of molecules in the $S_G$ layers. Schlieren and disrupted confocal textures have been observed for $S_F$, and $S_G$ exhibits a mosaic texture. An example of smectic liquid crystals having both types of mesophase is 5-*p*-pentyloxyphenyl-2-*p*′-pentylphenylpyrimidine [30]




(X)

$$C \xleftrightarrow{79^\circ} S_G \xleftrightarrow{103^\circ} S_F \xleftrightarrow{114^\circ} S_C \xleftrightarrow{144^\circ} S_A \xleftrightarrow{210^\circ} I\ .$$

Smectic mesophase *H* ($S_H$)

This is analogous to the $S_B$ mesophase, but the long axes of the molecules are inclined at an angle to the planes of the layer. As with the $S_C$ mesophase an $S_H$ mesophase formed by optically active molecules has a chiral structure $S_H$(ch) (VII), capable of spontaneous polarisation under the influence of external factors [23].

Plastic crystals

Plastic crystals constitute a special class of mesophase, not included among liquid crystals but sometimes met in the search for liquid-crystalline compounds. They were first characterised by Timmermans [31] in 1935. The molecules forming a plastic crystal were located permanently at the points of a cubic [32] (more rarely a hexagonal) lattice, but are orientationally disordered, with consequent isotropy of the optical properties, so that this type of mesophase was for a long time overlooked by research workers, who used a polarising microscope to define a mesophase. Several plastic crystals (e.g. perfluorocyclohexane) flow under their own weight, but most of them are less plastic, although they can be cut with a knife or extruded through small orifices. A plastic mesophase is formed by several compounds—tetrahedral (tetrachloromethane, silicon tetrafluoride, neopentane), octahedral (tetramethylbutane, hexabromoethane, pivalic acid), cyclic (cyclobutane, cycloheptatriene), bridged (camphor, borneol, tricyclo[2,2,2,2]decane) [33]—as well as several "classical" smectic liquid crystals, e.g. 4′-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid [27].

In spite of the considerable number of studies on the structure and the interconversion of liquid crystals, these problems are still far from a final solution; systematic investigations on the typing of smectic liquid crystals have been undertaken only during recent years [34]. New phenomena are continually being discovered, requiring detailed investigations, e.g. the observation by Vainshtein, Chistyakov, and their coworkers that a smectic mesophase is formed when nematic liquid crystals are mixed [35].

2. Molecular–Statistical Description of the Liquid-crystalline State

The statistical distribution of molecules among orientations is described quantitatively by a series of parameters, the most important of which is that of orientational order (or degree of ordering)

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \qquad (1)$$

introduced by Tsvetkov [36], where $\theta$ is the angle between the axis of an individual molecule in a liquid crystal and the prepared direction of the whole ensemble, and averaging is made over the whole ensemble of molecules (thermal mean). The preferred direction coincides with the optical axis of the liquid single crystal (for nematic liquid crystals, *A* smectics, or a thin layer of a cholesteric liquid crystal) or else with one of the optical axes (sloping smectics *C* and *H*). According to definition $S = 1$ for solid crystals in which the molecules are arranged in parallel, and $S = 0$ for an isotropic liquid phase. In a liquid crystal $0 < S < 1$, and *S* decreases with rise in temperature, as the isotropic phase is approached. The value of the parameter *S* is that it can easily be determined experimentally [37] (from diamagnetic measurements, dichroism, nuclear magnetic resonance spectra, etc.).

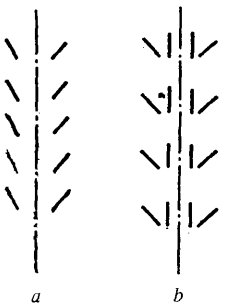



Figure 4. Hypothetical distribution of molecules with preservation of cylindrical symmetry and the same parameter *S*: *a*) dispersion absent; *b*) dispersion takes place.

A more complete statistical description of the molecular distribution is obtained by introducing also the dispersion *D*—a function of $\cos^4\theta$—and additional parameters defined in terms of higher even powers $\cos^n\theta$. The meaning of the parameter *D* can easily be understood by comparing two cylindrical distributions of molecules having the same parameter *S* (Fig. 4). The mean value of $\cos^2\theta$ is the same, but in one case the scatter (dispersion) of the molecules varies relative to the "mean" position shown in Fig. 4*a*.

The question as to which properties molecules should possess for long-range orientational order to be established in a substance occupies a central position in the theory of the liquid-crystalline state. Many attempts have

been made to derive thermodynamic characteristics of liquid crystals from the electronic structure of the molecules. A classification has been given[38] for the levels at which the structure of liquid crystals has been investigated: (*a*) at the simplest level molecules are regarded as rigid rods; (*b*) at the second level molecules are regarded as flat plates, rods with dipoles at an angle to them, or combinations of these two forms; and (*c*) the actual structure of the molecules is considered at the third level. Even at level (*a*) many questions remain unsettled, in particular the evaluation of $S$ for nematic and smectic liquid crystals, the angles of inclination of molecules in smectic $C$, the degree of bonding detween smectic layers, etc. The main problems at level (*b*) are concerned with the ability of molecules to rotate, the ordering of dipoles, etc. Level (*c*) involves the investigation mainly of the conformations of alkyl chains, the orientation of some molecular residues relative to others, internal rotations, etc.

The inadequacy of regarding molecules as rigid rods follows from the extremely graphic experiments on the probing of smectic liquid crystals by means of spin labels[10,39]. If the label belongs to the aromatic skeleton, the degree of ordering $S$ of the molecule is large. For the same label in the alkyl tail $S \to 0$ in effect. Thus the alkyl "tails" seem to be "molten", labile, which explains the "soapiness" of smectic liquid crystals (i.e. the ease of slippage of some layers relative to others).

Even at the first level (*a*), however, extremely important qualitative results have been obtained, mainly for nematic liquid crystals, which in some measure constitute a model system even for other liquid-crystal phases. It was shown in particular[40] that dispersion (van der Waals) forces of attraction between molecules play a decisive part in the organisation of nematic order[41]. The anisotropy of electron polarisability is the most important molecular characteristic governing the tendency of a specific substance to form a liquid-crystalline state. Long rodlike molecules with aromatic and heteroaromatic rings arranged in series are to be preferred in this respect. A favourable factor is the presence of a chain of conjugation along the molecular skeleton, since it will increase the longitudinal component of the polarisability. There is probably no correlation between the presence of a permanent dipole moment in the molecule and the ability of the substance to form nematic liquid crystals[5,41]. The steric factor (the length and the structure of the terminal groups) is also very significant. Theory[40] agrees with experiment in predicting a phase transition of the first kind between nematic and isotropic liquid states, as well as a regular temperature dependence of the parameter of orientational order.

An interesting criterion of the ability of a substance to form a mesomorphic state has been suggested by Ogorodnik[42] on the basis of experiments on the Raman scattering of light. He considers that only compounds that in the solid state form more than one crystalline modification (sometimes metastable) can have a nematic phase. Structural order in the mesomorphic state is then due to the superposition of "solid-crystalline clusters" of a different modification. The general applicability of this principle still lacks experimental verification.

Although the "twistedness" of the structure of cholesteric liquid crystals is due to the chirality (mirror-image asymmetry) of its component molecules, there is no clear correlation between the direction of rotation of the cholesteric helix and the sign of rotation of the individual molecules[43]. Goossens[44] attempted to explain the tendency of these liquid crystals to form a twisted structure in terms of electric dipole–quadrupole interaction between molecules on the basis of the Maier–Saupe approach‡. His calculated value for the pitch of the helix agrees with experiment. The theory of Goossens will explain also the temperature variation of the pitch if the temperature dependence of the degree of order is taken into account[45].

Another explanation of the structural twistedness and the temperature dependence of the helical pitch is based on the anharmonicity of the forces of molecular interaction[46]. However, this will explain only the increase in pitch with fall in temperature, which occurs only in the vicinity (on the temperature scale) of smectic phases, a fact that can in principle be attributed to the formation of nuclei (clusters) of a smectic in the cholesteric phase.

Yet another explanation[47] of the appearance of a cholesteric phase attributes it to long-range van der Waals forces of interaction between molecules. On this model such a phase may even be formed by molecules having mirror-image symmetry (optically inactive). This extremely untrivial case has not yet found experimental confirmation.

The first attempts at extending the Maier–Saupe approach[40] to an $A$ smectic phase involved[48,49] introducing two parameters of order, orientational (as in nematic liquid crystals) and translational. A molecular-statistical theory of more complicated types of smectic ($C$, $B$, and $H$) has been developed quite recently[50]. Here molecules are regarded as rigid rods, interactions between permanent dipoles of individual segments of the molecules must be taken into account, and the repulsion potential of the molecules within a single smectic layer must be written in explicit form. Interaction between layers is neglected. The molecular field approximation predicts theoretically[50] phase transitions of the second kind between phases $A$ and $C$, as well as between $B$ and $H$, whereas transitions between any other pairs of mesophases are of the first kind. In conformity with theory[50] smectics $A$ and $B$ are characterised by free rotation of molecules about the long axes; free rotation is absent from smectics $C$ and $H$, in which molecules are tilted relative to the smectic axes, and the dipoles are oriented in definite fashion. The suggested pattern has been subjected to criticism[38,51]. Insufficient experimental data are yet available either to support or to disprove the theoretical view[50].

## III. ANISOTROPY OF PROPERTIES

### 1. Orientation of Molecules

A liquid crystal run into a test-tube is a macroscopically homogeneous "polycrystalline" specimen (a turbid liquid). A "single crystal" must be prepared in order that the anisotropy of properties of a liquid crystal can be studied. This can be accomplished by orienting the whole molecular ensemble either by means of an external field or by the boundary conditions at the walls of the microcuvette. In the latter case planar orientation is distinguished from homotropic orientation (Section II, 1). As soon as the orientation of the molecules at the boundary has been

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‡It must be noted that the optical activity of individual molecules is due to intramolecular interactions of the "electric dipole–magnetic dipole" type, so that it is different in nature.

firmly established, alignment of the remaining molecules parallel to the former is energetically most favourable (departure from the specified orientation increases the elastic energy).

The microrelief of a glass surface (or of electrodes) having a characteristic dimension[52] of the order of 10 Å is usually employed for the planar orientation of liquid crystals. The walls are rubbed with a cloth or polished in a definite direction (Chatelain's method[53]) or else layers of metals or dielectrics sputtered askew are used[54]. Homotropic orientation is usually effected by means of monolayers of surface-active agents such as lecithin, alkoxybenzoic acids, polyamide resins, or organosilicon compounds[55]. Fig. 5 illustrates diagrammatically the two chief modes of orientation of liquid crystals—(*a*) planar orientation due to the microrelief of a metal film sputtered askew and (*b*) homotropic orientation due to a film of a surface-active agent—where it can be demonstrated rigorously that both configurations correspond to minimum elastic energy of the liquid crystal[52].

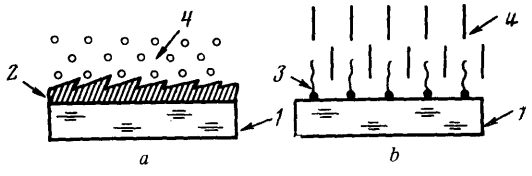



**Figure 5.** Orientation of a liquid crystal by a surface: *a*) planar; *b*) homotropic: 1) support; 2) obliquely sputtered metal film; 3) surface-active molecules; 4) rodlike liquid-crystal molecules.

If the liquid is a single crystal, almost all its properties are anisotropic, with the anisotropy more marked the greater the degree of ordering $S$. This quantity $S$ has meaning only for a single crystal, and is a thermodynamic function depending on the properties of the substance and the temperature, but independent to a first approximation of the orienting agent[11]. Thus, if a single crystal having a certain value of $S$ could be obtained by means of a magnetic field of 1 kG, increasing the field to 20 kG will not lead to an increase in $S$.[56] Incomplete orientation of a specimen (in the absence of a single crystal) can in principle be described by a different parameter—the degree of orientation—but this is not a fundamental characteristic of the substance. We cre compelled to consider this aspect in some detail, for until recently many studies were published in which the physical characteristics of the substance had been determined on unoriented specimens. This involves loss of information to the same extent as in the replacement of a solid single crystal by a polycrystalline powder.

## 2. Electrical and Magnetic Properties

Fig. 6*a* illustrates a typical temperature dependence of the degree of ordering of a nematic liquid crystal. The temperature variation of the anisotropy of the diamagnetic susceptibility $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ §, and also that of the electronic portion of the dielectric susceptibility $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, are completely determined by the temperature dependence of $S$ and can be calculated from the anisotropy of these parameters in the solid phase:

$$\Delta\chi_{nlc} = S\,\Delta\chi_s; \quad \Delta\alpha_{nlc} = S\,\Delta\alpha_s \qquad (2)$$

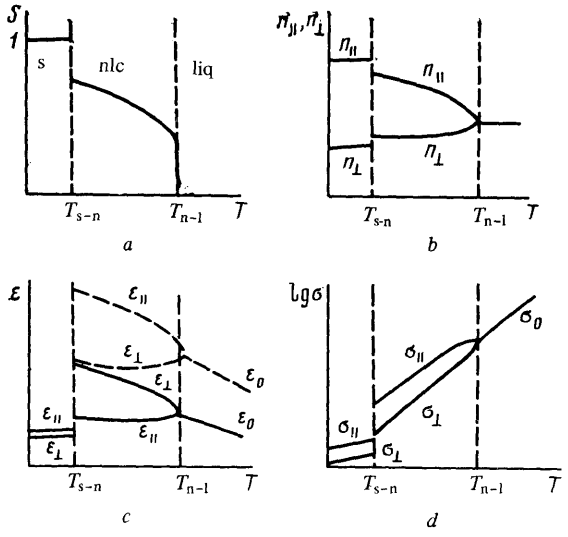



**Figure 6.** Typical temperature dependence for nematic liquid crystals (nlc) of: *a*) degree of ordering; *b*) refractive indices; *c*) dielectric constant; *d*) electrical conductivity. Here $T_{s-n}$ and $T_{n-l}$ are the solid-nematic and nematic–isotropic liquid phase transition temeratures.

The mean values $\bar{\chi}$ and $\bar{\alpha}$ in the liquid-crystalline phase are equal to the values $\chi_i$ and $\alpha_i$ for the isotropic phase (apart from the temperature variation of $\chi$ and $\alpha$). In view of the cylindrical symmetry of distribution of molecules in a nematic liquid crystal, these average values are given by the formulae

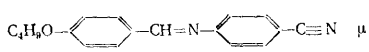
$$\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) \approx \chi_i; \quad \bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \approx \alpha_i \qquad (3)$$

More complicated equations hold for the anisotropy of the refractive indices $\Delta n = n_{\parallel} - n_{\perp}$, connected with $\alpha_{\parallel}$ and $\alpha_{\perp}$ by the Lorentz–Lorenz relations[57], for the total dielectric susceptibility $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, including the orientational component[58], and for the anisotropy of electrical conductivity $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. However, the general rule of a monotonic fall is maintained for all these quantities: $\Delta n$, $\Delta\epsilon$, $\Delta\sigma \to 0$ as $S \to 0$. Typical temperature variations of longitudinal and transverse components of refractive indices, dielectric constants, and electrical conductivities of a nematic liquid crystal are illustrated in Fig. 6*b–d*.

§The subscripts denote directions parallel and perpendicular to the long molecular axes (to the "director" of the nematic liquid crystal).

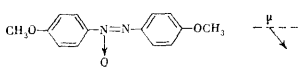
It is noteworthy that $\Delta\chi$, $\Delta n > 0$ in all known nematic and smectic liquid crystals, in conformity with the anisotropy of the magnetic and electronic components of the electric polarisability of oblong molecules. Nevertheless, the sign of $\Delta\sigma$ is different in the two types of mesophases: in the nematic type $\Delta\sigma > 0$ (except for the temperature range in the vicinity of the smectic phase, when nuclei of smectic order are present), since the charge carriers (ions) move more readily in the direction of the long axes of the molecules; in smectic liquid crystals the mobility of the ions is greater along the smectic layers, i.e. normal to the molecular axes, so that $\Delta\sigma < 0$.

The dielectric anisotropy of a nematic liquid crystal may be either positive (Fig. 6*c*, full curves) or negative (broken curves in Fig. 6). This is determined by the components of the orientational polarisability and depends on the relation between the anisotropy of the electronic polarisability of a molecule and the permanent dipole moment $\mu$, as well as the angle $\beta$ between the dipole moment and the long axis of the molecule[58]. The quantity $\Delta\epsilon > 0$ is characteristic of molecules having a longitudinal dipole moment (i.e. with $\beta \to 0$), e.g.




(XI)

When the angle $\beta$ is sufficiently large, the case $\Delta\epsilon < 0$ is realised, e.g. in *pp'*-dimethoxyazoxybenzene




(XII)

where $\beta \simeq 60°$. As the frequency of the electric field is raised, the quantities $\epsilon_\parallel$ and $\epsilon_\perp$ exhibit dispersion in different frequency ranges[59]. Dispersion is developed by $\epsilon_\perp$ at frequencies comparable with the frequency of rotation of molecules about the long axis ($f_D^\perp \simeq 10^8$ Hz); that of $\epsilon_\parallel$ occurs at significantly lower frequencies. With long molecules[60] such as




(XIII)

the frequency $f_D^\parallel \simeq 10^4$ Hz, and is determined by hindered rotation of molecules about the short axis. Owing to the dispersion of $\epsilon_\parallel$ and $\epsilon_\perp$ the sign of $\Delta\epsilon$ may change from positive to negative in different frequency ranges[12]. This property can be used in electro-optical devices based on field effects in order to diminish the disconnection time. The dielectric anisotropy of smectic liquid crystals may change sign depending on the temperature, which is explained by pair correlations of neighbouring dipoles[61].

The local anisotropy of electrical properties of cholesteric liquid crystals (within a layer thickness, much smaller than the pitch of the helix) is characterised by the same rules as for the nematic type (e.g. there may be substances having $\epsilon_\parallel - \epsilon_\perp < 0$ and $\epsilon_\parallel - \epsilon_\perp > 0$). Sometimes, of course, anisotropy parameters are introduced to describe a macroscopic specimen having a helical structure. The components of $\epsilon_h$ and $\sigma_h$ parallel and perpendicular to the axis of the helix are then related with the components $\epsilon_\parallel$, $\epsilon_\perp$ and $\sigma_\parallel$, $\sigma_\perp$ by the self-evident formulae

$$\varepsilon_{\parallel h} = \varepsilon_\perp;\ \varepsilon_{\perp h} = \frac{1}{2}(\varepsilon_\parallel + \varepsilon_\perp);\ \sigma_{\parallel h} = \sigma_\perp;\ \sigma_{\perp h} = \frac{1}{2}(\sigma_\parallel + \sigma_\perp)\ . \quad (4)$$

## 3. Elastic Properties

The elastic properties of an ordinary liquid can be characterised by a single parameter, its compressibility. The elastic energy of a "liquid rod" is unaffected by bending, shearing, or twisting. The situation is different with an anisotropic liquid. For example, three quite different deformations—bending, splaying, and torsion, denoted for brevity *B*, *S*, and *T* deformations—can be imagined for a nematic liquid crystal[12]. Fig. 7 illustrates these three types of deformation, characterised by the respective moduli of elasticity $K_{33}$, $K_{11}$, and $K_{22}$, whose order of magnitude is $10^{-7}$–$10^{-6}$ dyn. The elastic force required for a deformation is proportional to that deformation, i.e. to the gradient of the angle of rotation of some molecules relative to others:

$$F_{\text{elast}} = K_{ii}\frac{\partial\varphi}{\partial z}, \quad (5)$$

The elastic energy is expressed in quadratic form:

$$g_{\text{elast}} = \frac{1}{2}K_{ii}\left(\frac{\partial\varphi}{\partial z}\right)^2 \quad (6)$$

A rigorous expression can be obtained for the elastic energy of combined deformation[62]. Elastic coefficients are usually determined from an electro-optical experiment[63]. Attempts have also been made to deduce the temperature dependence of moduli of elasticity from the molecular-statistical theory[64]. The same moduli of elasticity are introduced for cholesteric as for nematic liquid crystals.

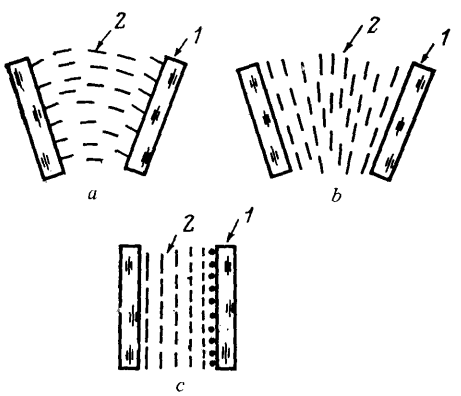



**Figure 7.** Types of deformation of nematic liquid crystals: *a*) bending; *b*) splaying; *c*) twisting: 1) oriented support; 2) liquid-crystal molecules.

A different situation is found with smectic liquid crystals[65]. In the simplest type—an *A* smectic—the moduli of elasticity for bending and torsional deformations tend to infinity, with only $K_{11}$ remaining finite. The explanation is that an *A* smectic "resists" any deformation in which the distance between the smectic layers changes. Comparing splaying and bending (Fig. 8), for example, we note that in the former case the smectic layers are curved, but the molecules remain normal to them as before, and the distance *d* between the layers is unchanged.

The deformation is described by a finite modulus $K_{11}$. In the second case the distance between the layers must change for the deformation to occur. The impossibility of such change is expressed by the condition $K_{33} \to \infty$. Torsional deformation is also difficult, as can easily be realised on trying to screw in imagination a pile of thin plates. On the other hand, in contrast to a nematic liquid crystal, it makes sense for an $A$ smectic to introduce a compressibility coefficient $\bar{B}$ representing the increase or decrease in the interlayer distances. This type of deformation does not involve the position of a "director", and the elastic energy is given by a term

$$g_{\text{elast}} = \frac{1}{2}\bar{B}\left(\frac{\partial U}{\partial z}\right)^2, \qquad (7)$$

where $U$ is the displacement of the smectic layer along the coordinate $z$ normal to the layer. The parameter $\bar{B}$ has the same dimensions and order of magnitude as the compressibility coefficients of ordinary liquids. It is interesting that in nematic phases adjacent on the temperature scale to an $A$ smectic a fall in temperature is accompanied by divergence between the moduli of bending and torsional deformations ($K_{33}$, $K_{22} \to \infty$) as these phases approach the point of transition into the $A$ smectic, a phenomenon explained by a mechanism of formation of nuclei of smectic order in the nematic phase. The modulus $K_{22}$ in a cholesteric liquid crystal also tends to infinity as a neighbouring smectic phase is approached (with change in temperature)[66].

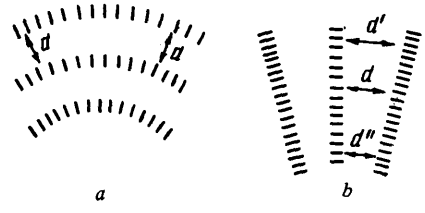



Figure 8. Deformation of an $A$ smectic: *a*) splaying; *b*) hypothetical bending.

Elasticity theory for other types of smectic is very complicated. For example, the simplest description of a $C$ smectic requires the introduction of ten elasticity coefficients (the coefficient $\bar{B}$ and nine moduli[10] are related to the orientation of the "director" and of order of magnitude $10^{-6}$ dyn).

## 4. Viscosity Characteristics

The viscosity of a liquid crystal depends on how the "director" is situated relative to the gradient of the rate of flow. This was known long ago[67], but only recently it has been shown by Leslie and by Ericksen[68] that the viscous properties of a nematic liquid crystal can be described completely by five independent coefficients $\alpha_i$ ($i = 1-5$), the Leslie coefficients. Sets of coefficients $\alpha_i$ have been determined for *pp'*-dimethoxyazoxybenzene[69] (XII) and for *p*-butyl-*p'*-methoxybenzylidenaniline (I)[70] from experiments on the Rayleigh scattering of light and on the discharge of a nematic liquid crystal from a capillary. Especially clear experiments were made by Gähwiller, who examined the rate of discharge of a nematic liquid crystal from a capillary of rectangular cross-section (50 × 40 × 0.4 mm) placed in a magnetic field (up to 4 kG) governing the orientation of the liquid-crystal molecules (this applies only at very low rates of flow, when the orienting effect of the flow is insignificant in comparison with the action of the field). Fig. 9 shows the geometry of the experiment. The corresponding viscosity coefficients $\eta_1$, $\eta_2$, and $\eta_3$ were respectively 103, 23.8, and 41.6 cP. These coefficients, together with results of an additional experiment to measure the angle of orientation of the molecules by the flow ($\tan^2\theta = \alpha_3/\alpha_2$), were used to determine all the Leslie coefficients. The great anisotropy of the viscosity of a nematic liquid crystal (e.g. $\eta_1/\eta_2 \simeq 4$) leads to appreciable anisotropy of the mobility of impurity ions, and hence to anisotropy of the electrical conductivity[71] ($\sigma_{\parallel}/\sigma_{\perp} \simeq 1-2$).

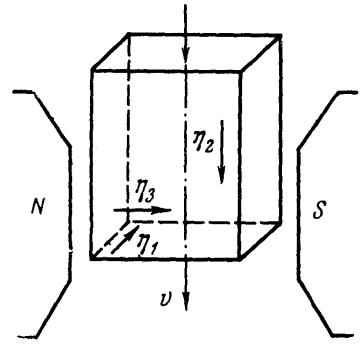



Figure 9. Geometry of Gähwiller's experiment. The "director" direction corresponding to the measured viscosity coefficients $\eta_1$ and $\eta_3$ is determined by the magnetic field; that corresponding to the measured coefficient $\eta_2$ by the material flux v with the field switched off and with an increased rate of discharge; directions of orientation of molecules are denoted by arrows.

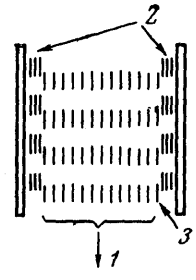



Figure 10. Outflow of $A$ smectic from a capillary: 1) outflowing liquid column; 2) layer fixed adjacent to wall; 3) site of rupture of smectic layers.

Cholesteric and smectic liquid crystals exhibit abnormally large viscosity coefficients (from measurements in capillaries), although their Leslie coefficients are of the same order as those for nematic liquid crystals (from the scattering of light). This increase in the observed

(apparent) viscosity coefficients was attributed by Helfrich[72] to a "penetration" effect (the flowing liquid crystal penetrates through the helical or layer "construction" specified by the boundary conditions at the walls of the capillary). This can be illustrated vividly for a cholesteric liquid crystal by imagining that we are trying to remove a well lubricated screw of large pitch from a threaded orifice, which may be effected by turning the screw. The force of the pressure is consumed in rotating the screw, whose rate of translational motion is small. Thus the "director" of a cholesteric liquid crystal, for which the boundary conditions determine the helical orientation of molecules on the wall of a circular capillary, is also compelled to rotate as material is discharged from the capillary. Here friction may increase the effective viscosity coefficient by factors of $10^5$. In the case of smectic liquid crystals discharge should involve the "extrusion" of smectic layers (Fig. 10), whose position is fixed on the wall of the capillary. This is an example of non-Poiseuille and non-Newtonian liquid flow. With indefinite orientation of cholesteric and smectic liquid crystals relative to the capillary (as in most experiments) the apparent viscosity coefficients are almost arbitrary (over a range of $10^5$).

## IV. INFLUENCE OF EXTERNAL FACTORS

### 1. General Considerations

Molecules of substances that form liquid crystals themselves exhibit no abnormal properties. At temperatures appreciably above the clear point of nematic liquid crystals, for example, we are dealing with ordinary liquids, whose Kerr constants are no larger than for nitrobenzene (except in the temperature range of the isotropic phase near the transition point, where the Kerr constant may either increase, decrease, or even change sign owing to the short-range order in the arrangement of the molecules[73]). Similarly, esters of cholesterol in the isotropic phase have the same specific optical rotation as have optically active liquids (alcohols, sugar, etc.), but do not form liquid-crystalline phases. The dipole moments and the components of the electrical and magnetic susceptibilities of the molecules also have the same order of magnitude for mesogenic and non-mesogenic substances.

The uniqueness of the properties of liquid crystals—their high sensitivity to external factors—is due to the extremely delicate intermolecular interactions governing the long-range orientational order in the arrangement of molecules. Which specific molecular characteristics are responsible for the tendency of molecules to form an ordered state is the main problem of a molecular-statistical theory of liquid crystals, which is still far from solution. But as soon as long-range order has been established, with the degree of order depending on external factors, the latter influence the anisotropy of almost all the parameters of the liquid crystals. Examples are the dependence of the pitch of the helix of a cholesteric liquid crystal on the temperature or the field and the pressure dependence of the optical anisotropy of a nematic liquid crystal.

Furthermore, many electro- and magneto-optical phenomena are based on reorientation of the "director" (without change in the degree of order). This process of change in optical properties can be divided into three stages. (*a*) Owing to the large anisotropy (as in solid crystals) of the electrical parameters ($\Delta\epsilon$, $\Delta\sigma$, and $\Delta\chi$) the "director" of a liquid crystal "interlocks" with an external field: an orienting moment acts on the molecules of the liquid crystal. In a magnetic field, for example, the axes of the molecules tend to arrange themselves parallel to the field. (*b*) Since a liquid crystal is liquid, the molecules actually undergo reorientation under conditions of competition with elastic forces (in some cases this reorientation is accompanied by mass transfer of liquid—by a flow). (*c*) Change of orientation is easily recorded optically owing to the great anisotropy of optical properties (refractive indices and absorption).

### 2. Examples of Electro-optical and Magneto-optical Effects

In order to simplify discussion of the three most characteristic effects—the Fréedericksz transition in nematic liquid crystals, uncoiling of the helix in cholesteric liquid crystals, and wavelike instability in smectic liquid crystals—we shall regard a liquid crystal as a pure dielectric, through which an electric current does not flow. In reality this is impossible of achievement, since even with the most careful purifications some quantity of ionic impurities will remain in the liquid crystal, and given appreciable *ionic conductivity* $\sigma \simeq 10^{-12}$–$10^{-14}$ ohm$^{-1}$ cm$^{-1}$). With perfect purification ions may still be generated by the injection of electrons from the electrode followed by their "capture" by neutral molecules of the substance. In some publications current–voltage characteristics on liquid crystals have been interpreted in terms of an electronic mechanism of conduction. Such views are incorrect, since the electronic conductance of a liquid crystal is extremely small; it should be comparable in order of magnitude with the intrinsic conductivity of impurity-free organic dielectrics such as anthracene and naphthalene. At the present time it is impossible even to state definitely what these values are; calculations give $\sigma < 10^{-19}$ ohm$^{-1}$ cm$^{-1}$. Electron currents can be observed experimentally in liquid dielectrics only under the abnormal conditions of pulse photoconduction on substances of very low electron affinity[74]. Under normal conditions we are always dealing with an ionic current, although the current carriers (ions) may not be intrinsic, but generated near the electrodes by the injection or exclusion of electrons. In this case an electrochemical process takes place on the electrode.

(*a*) Fréedericksz transition in a nematic liquid crystal

Considering now the simplest example of the reorientation of a nematic liquid crystal in an electric or magnetic field—the Fréedericksz transition[75]—we suppose that the microcuvette illustrated in Fig. 11*a* is filled with a liquid crystal of *p*-*p'*-butoxybenzylidenaminobenzonitrile (XI) and maintained at a temperature corresponding to the nematic range of this compound (64–103°C). Because of the presence of the cyano-group the molecule of (XI) has a dipole moment $\mu \simeq 4.5$ D directed along its long axis[76], so that the longitudinal component (in the direction of the axis of orientation of the molecules) of the static dielectric constant exceeds significantly the transverse component: $\epsilon_{\parallel} \simeq 25$ and $\epsilon_{\perp} \simeq 7$. Let the glasses of the microcuvette be so treated that the molecules of the adjacent layer of the liquid crystal are rigidly fixed parallel to the glass (planar orientation) and do not change their orientation in any circumstances. When an electric

field is applied, a turning moment will act on the molecules of the liquid crystal, tending to reorient them with the direction of the maximum component of the dielectric constant coinciding with that of the field. The reason is that the polarisation induced in the dielectric (the dipole moment of unit volume) is proportional to the dielectric constant; hence the polarisation is greater for the direction of $\epsilon_{\parallel}$. As a consequence, interaction of the induced moment with the external field leads to rotation of the optical axis of the single crystal, with the exception of molecules adjacent to the wall. The proportion of oriented dipoles is $\sim\exp(-\mu E/kT) \simeq 10^{-4}$–$10^{-2}$ for typical field strengths. The "director" of the ensemble of interacting molecules, i.e. the longitudinal axis of their cylindrical distribution, is oriented parallel to the field. Rotation of the molecular ensemble is opposed by the elastic energy of interaction of the molecules (Eqn.6).

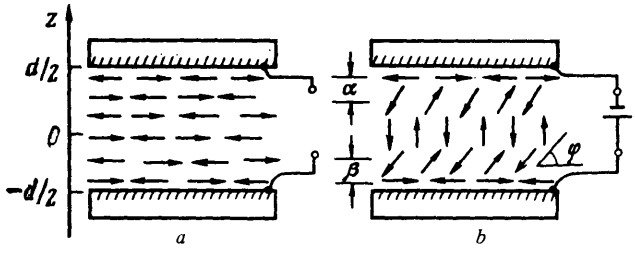



Figure 11. Illustration of the Fréedericksz effect in nematic liquid crystals: *a*) initial orientation of molecules: *b*) orientation of molecules at voltages exceeding the threshold value.

Fig. 11*b* shows regions $\alpha$ and $\beta$, in which the molecules are forced to detach themselves from their neighbours, although they "would have preferred" to remain parallel to the latter. As a result of competition between dielectric and elastic moments ($\Delta\epsilon E^2/4\pi$ and $K_{11}\partial^2\varphi/\partial z^2$), deformation has a threshold character. The threshold voltage is

$$v_0 = \pi\sqrt{4\pi K_{11}/\Delta\varepsilon} \quad . \tag{8}$$

Deformation begins from the middle of the layer ($z = 0$), and extends to the electrode with increase in the field strength, embracing more and more new layers of molecules. With the maximum field almost all molecules other than those adjacent to an electrode are reoriented perpendicular to the electrodes, which can easily be observed optically from the disappearance of double refraction by the liquid-crystal layer. Expressions for the reaction and relaxation times can be obtained[12] from the kinetics of this process taking into account the moment of viscous friction for the "director" (in addition to dielectric and elastic components).

Roughly the same pattern is observed for the twisted structure of a nematic liquid crystal (with mutually perpendicular directions of the "director" on the opposite electrodes), as well as for nematic crystals with $\epsilon_{\parallel} < \epsilon_{\perp}$, if the initial orientation was homotropic.

(*b*) Cholesteric–nematic phase transition

Fig. 12*a* represents the planar texture of a cholesteric liquid crystal when the molecules are oriented parallel to the glasses of the cuvette (in the absence of electodes), while the axis of the cholesteric helix is correspondingly perpendicular to them. Such a texture reflects circularly polarised light selectively[77] if the polarisation corresponds in sign to the twist of the helix, while the wavelength (in a vacuum) satisfies the relation $\lambda = \frac{1}{2}P\bar{n}$ (where $P$ is the pitch of the helix and $\bar{n}$ the mean refractive index of the liquid crystal). The selective reflection is caused by the diffraction of light on the cholesteric planes (analogous to the Wulf–Bragg diffraction of X-rays on ordinary crystals). Measurements of the wavelength of the selective reflection provides a method for determining the pitch $P$ of the helix.

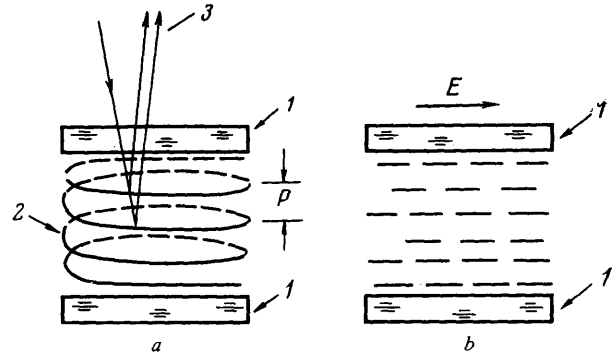



Figure 12. Cholesteric → nematic phase transition, with electric field applied along the surface of the glasses: *a*) planar cholesteric texture in absence of field; *b*) nematic phase with $E > E_0$: 1) glasses (in absence of electrodes); 2) cholesteric helix of pitch $P$; 3) diffracting light rays.

We now imagine that the dielectric anisotropy of the cholesteric liquid crystal is positive, i.e. that $\epsilon_{\parallel} > \epsilon_{\perp}$ with respect to the "director"), and that the substance is located in a field $E$ perpendicular to the axis of the helix. It is clear that all molecules will tend to orient themselves parallel to the field, which is incompatible with a helical structure and requires an increase in the elastic energy of the liquid crystal. With a sufficiently strong field the helix begins to uncoil (as is evident from the shift to longer wavelengths in the selective reflection maximum), and ultimately a phase transition takes place from cholesteric to nematic liquid crystals (Fig. 12*b*). The threshold field strength for the transition is inversely proportional to the pitch of the helix[78]:

$$E_0 = \frac{\pi^2}{P_0}\sqrt{4\pi K_{22}/\Delta\varepsilon} \quad . \tag{9}$$

(*c*) Instability of smectic liquid crystals

Formally a Fréedericksz transition occurs also with an *A* smectic, as with a nematic mesophase, and the same formula gives the threshold voltage (Eqn.8). However,

the deformation itself is too small to be recorded ("illusory" transition[79]). As already discussed in Section III, 3, the weakness of the deformation is due to the tendency of an *A* smectic to maintain unchanged the distance between the layers (whereas reorientation requires such change). Since the reorientation of molecules forms the basis of several other, more complicated electro-optical phenomena, e.g. electrohydrodynamic, the properties of smectic liquid crystals are on the whole far less subject to the influence of fields than are those of nematic and cholesteric mesophases¶.

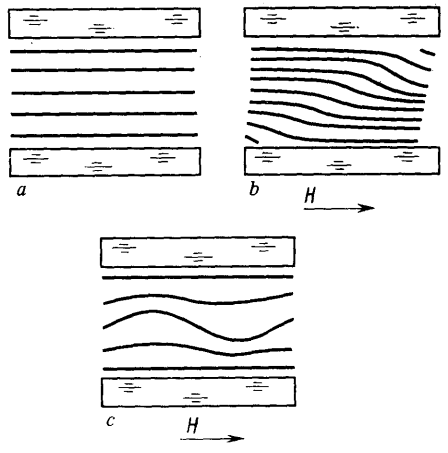



Figure 13. Instability of smectic liquid crystals in a magnetic field with $\Delta\chi > 0$: *a*) initial orientation (the lines represent smectic layers); *b*) hypothetical Fréedericksz transition leading to deformation of smectic structure with change in interplanar spacing; *c*) wavelike deformation with interplanar spacing almost unchanged.

Perhaps the most characteristic instability of a smectic liquid crystal in an external field is its wavelike deformation, which requires almost no change in the interlayer distance[10]. If $\Delta\chi > 0$ and the magnetic field is parallel to the layers, i.e. perpendicular to the axes of the molecules (Fig. 13*a*), the molecules will tend to reorient parallel to the field, which would have led to crumpling of the layers near the glasses, which is energetically disadvantageous (Fig. 13*b*). A compromise is provided by wavelike deformation, with which a minimum is reached in the total (electrical and elastic) energy (Fig. 13*c*). The period *b* of such deformation is the geometric mean of the layer thickness *d* and the "depth of penetration" $\lambda = (K_{11}/B)^{\frac{1}{2}} \simeq 20$ Å: i.e. $b = 2(\pi\lambda d)^{\frac{1}{2}}$ (~5μm for $d = 0.1$ cm), and the critical field is

$$H_c^2 = 2\pi K_{11}/\lambda\, d\,\Delta\chi \quad (\approx 60 \text{ kG}) \,. \tag{10}$$

¶This makes it difficult to measure the anisotropy of the electrical and other parameters of smectic liquid crystals.

(*d*) Electrohydrodynamic instability of nematic liquid crystals

The notion of a liquid crystal as an ideal dielectric must be rejected in considering this problem: electrohydrodynamic processes in a liquid crystal involve currents. A physical description of electrohydrodynamic instabilities is fairly complicated. The main cause of periodic liquid flows is the spatial separation of ions and consequent nonuniform distribution of ionic current in the specimen owing to the anisotropy of electrical conductivity. Because of friction the fluxes of matter break down the "monocrystallinity" of the specimen and the initial uniform distribution of the "director", causing three-dimensionally periodic deformation of this distribution. As the field becomes stronger, the periodic motion of the liquid is replaced by turbulence, which is accompanied by local changes in optical anisotropy and hence by intense scattering of light[80,81] (dynamic scattering). This effect usually develops in nematic liquid crystals having negative dielectric anisotropy (with $\Delta\sigma > 0$), but may occur even when $\Delta\epsilon > 0$, in particular when $\Delta\sigma < 0$,[82] as well as with $\Delta\epsilon = 0$.[83]

3. Effects of Temperature and Other Factors

Such factors as pressure, temperature, and optically inactive additives exert a relatively weak influence on the ordered character of nematic liquid crystals, and hence on the anisotropy of their properties. A different situation obtains with cholesteric mesophases, the helical pitch of which is extremely sensitive to the above factors. The explanation is that the energy of intermolecular interaction responsible for the helical structure is only $10^5$ of that determining the nematic order[45]. A sharp change in pitch is accompanied by marked changes in optical properties, precisely at the spectral positions of maximum selective reflection[15] and the point of inversion of the sign of optical activity[84]. For example, the temperature of a layer of a cholesteric liquid crystal can be recorded optically to better than 0.02 deg.[84]

In most cases (for an exception see e.g. Ref. 85) the pitch of the helix *P* increases with fall in temperature, the relative change $P^{-1}|\,dP/dT|$ reaching 100 $\text{deg}^{-1}$ (cholesteryl nonanoate at 75°C). The reason for the variation in pitch with temperature has not been finally elucidated[44-46]. With cholesteric liquid crystals formed by optically active molecules not derived from cholesterol, such as compound (IV),[21] the temperature dependence of the pitch is very slight, and such substances are of the greatest interest for electro-optical applications. With increase in pressure from 1 to 2000 bars a considerable change has been observed[86] in the wavelength of maximum selective reflection (from the violet to the red part of the spectrum) by a cholesteric liquid crystal. The pitch of the helix can be changed also by adding optically inactive impurities to cholesteric mesophases[87].

Optically active additions to nematic liquid crystals lead to the formation of a cholesteric structure[88]. At low concentrations *c* of the additives the pitch of the helix is inversely proportional to the concentration:

$$P = (2\beta c)^{-1}, \tag{11}$$

where $\beta$ is the twisting power of a specific additive. The same effect is obtained on addition of an optically active impurity to a compensated mixture (with $P = \infty$) of cholesteric liquid crystals.

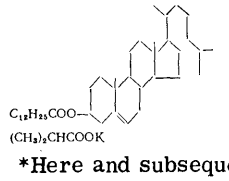
The property of twisting a nematic into a cholesteric structure is in general inherent in any chiral macroscopic species (possessing no plane of mirror-image symmetry), and the pitch of the helix is inversely proportional to the concentration $c$ of these species in the mesophase [10]. At higher concentrations $c$ the relation (11) breaks down. The twisting power $\beta$ cannot be regarded as exclusively a property of the additive [89], but depends also on the solvent. Anomalous results—such as (*a*) the production of nematic–cholesteric mixtures with the same sign of rotation (dextrorotatory) on the addition to a nematic liquid crystal of cholesteric components with a different sign of rotation [90] and (*b*) the production of a laevorotatory mixture from two dextrorotatory components [91]—can be explained by taking into account not only $\beta$ but also the twisting power of the solvent induced by the solute [92].

## V. CHEMICAL STRUCTURE AND PROPERTIES

### 1. Chemical Classes

The >5000 liquid-crystalline compounds known at the present time include representatives of various classes—acyclic, isocyclic, aromatic, heterocyclic, organometallic compounds, steroids, and salts of organic acids (Table 1)[2].

Table 1.

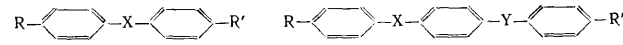
| Formula | Transition temperatures* | | | | |
|---|---|---|---|---|---|
| | $T_{s\text{-}sm}$ | $T_{s\text{-}n}$ | $T_{sm\text{-}n}$ | $T_{sm\text{-}c}$ | $T_{cl}$ |
| $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ | 11.7 | — | — | — | 15.5 |
| $C_5H_{11}$–C$_6$H$_4$–COOH | — | 54 | — | — | 105 |
| $CH_3O$–C$_6$H$_4$–CH=N–C$_6$H$_4$–$C_4H_9$ | — | 22 | — | — | 47 |
| $C_2H_5OCO$–(C$_6$H$_4$)$_4$–$COOC_2H_5$ | 284 | — | — | — | 367 |
| $C_9H_{19}$–C$_6$H$_4$–(N=N)$_2$–C$_6$H$_4$–$C_9H_{19}$ | 140 | — | 146 | — | 151.5 |
| $(CH_3O$–C$_6$H$_4$–CH=N–C$_6$H$_4$–$)_2Hg$ | — | 209 | — | — | 285 |
|  | 63.5 | — | — | 78.8 | 84.8 |
| $C_{15}H_{23}COO$–C$_6$H$_4$–$(CH_2)_2CHCOOK$ | 240 | — | — | — | 335 |

*Here and subsequently the following subscripts are used to denote phases in the symbols for phase transition temperatures: c = cholesteric; i = isotropic; n = nematic; s = solid; and sm = smectic. As an example $T_{s\text{-}sm}$ is the temperature of transition from the solid to the smectic state. All transitions from solid to mesomorphic and from mesomorphic to the isotropic state are also denoted as melting points $T_m$ and clear points $T_{cl}$ respectively.

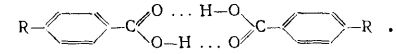
A small group comprises acyclic liquid crystals, mainly unsaturated aliphatic acids and their derivatives. In it may be included a few esters of carbonylbisamino-acids of general formula ROCOCHR'NHCONHCHR'COOR. These compounds are obtained from optically active esters of valine and leucine, and form a smectic phase [93].

A more representative group consists of isocyclic liquid crystals (~200 compounds [2]). Among them only 4,4″-dialkyltercyclohexanes and *trans*-4-alkylcyclohexanecarboxylic acids do not contain benzene rings. They are characterised by formation of a plastic mesophase. The remaining liquid crystals of this group contain aromatic rings together with the isocyclic residue. These are mainly 2,6-di-*p*-R-benzylidenecyclohexanones, where R = Alk, AlkO, or AcylO. Analogous derivatives of cyclopentanone and cycloheptanone have also been obtained.

More than 50% of known liquid crystals are benzene derivatives, a considerable proportion of which can be represented by the formulae



where R, R′ = Alk, AlkO, AcylO, AlkOCOO, AlkOCO, Hal, $NO_2$, or CN, while X and Y represent single bonds or the groups N:N, N:NO, CH:CH, CH:N, CH:NO, COO, C≡C, etc. *para*-Substituted benzoic and cinnamic acids are also mesomorphic, forming in the liquid-crystalline state dimers, e.g.



Certain derivatives of naphthalene [2,94], 2,7-disubstituted derivatives of fluorene and fluorenone, and also 4,4‴-disubstituted *p*-quaterphenyls possess the properties of liquid crystals. This applies also to unsubstituted *p*-quinque-, *p*-sexi-, and *p*-septi-phenyls.

Most known heterocyclic liquid crystals (~700) have an analogous structure to the benzene derivatives, but with one of the benzene rings replaced by pyridine, pyrimidine, pyrazine, pyridazine, or 1,2,4,5-tetrazine. Liquid-crystalline compounds are known also in other classes of heterocycles, e.g. quinolines [95] and benzazoles [96].

Cholesteric liquid crystals are formed by cholesterols, thiocholesterols, stigmasterols, ergosterols, and certain other sterols substituted in the hydroxy-group. Chloro-, bromo-, and iodo-cholesterols are also mesomorphic.

Around 200 liquid-crystalline compounds are salts of aliphatic or aromatic acids with alkali or alkaline-earth metals, or hydrohalides of substituted pyridines and quinolines.

### 2. Structure and Transition Temperatures

The demand by technology for liquid-crystalline materials has been the main stimulus to the establishment of rules between structure and mesogenicity and to the prediction of transition temperatures. The first requirement to be met by such materials is the occurrence of a mesophase over a wide temperature range including room temperature. Mixtures of liquid-crystalline compounds provide the best means of achieving this aim, since individual substances rarely have melting points below 40°C. However, individual liquid crystals are required to have melting points as low as possible and a wide temperature range of existence of the mesophase.

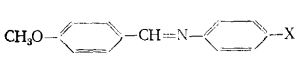
Examination of experimental data on transition temperatures and especially study of these temperatures in various homologous series have yielded several empirical conclusions on the relation between structure and mesogenicity. These rules apply to temperatures of transitions from one mesophase to another and from a mesophase to an an isotropic state, whereas temperatures of transition from the crystalline state to mesophase vary irregularly.

Only observations of a general character have been made on the latter, applicable also to melting points of non-mesomorphic compounds and consisting in a rise in such temperatures with increase in molecular weight, polarisability, polarity, and molecular symmetry, as well as on formation of intermolecular hydrogen bonds.

The occurrence of regularities in the transition points between one mesophase and another or the isotropic liquid is due primarily to the fact that the structure of a given mesophase and the relative arrangement of molecules in it are common to compounds having different structures. Yet such compounds may form solid crystals differing in structure and with different relative arrangements of the molecules in the crystal lattice. Small variations in molecular structure may lead to packing in a different three-dimensional lattice with markedly different intermolecular distances and a different arrangement of the molecules, which will produce significantly different intermolecular interactions and hence melting points. Furthermore, transition from the crystalline to the mesomorphic state will be accompanied by a greater change in energy of intermolecular interaction than in transitions between mesophases or from a mesophase to an isotropic liquid. This rule is apparent in the heats of transition: thus for *pp'*-dialkoxyazoxybenzenes the heats of transition crystal–mesophase, smectic–nematic, nematic–isotropic, and smectic–isotropic liquid are respectively 11.7–28.0, 0.02–2.30, 0.27–2.30, and 6.97–7.90 kJ mole$^{-1}$.[97] A detailed account has been given[98] of the thermodynamic properties of liquid crystals.

In investigations of the correlation between molecular structure and mesogenicity the greatest attention has hitherto been paid to transition points between mesophases and especially to the temerature $T_{cl}$ of transition from a mesophase to an isotropic liquid. At the clear point the energy of thermal motion of the molecules becomes equal to the energy of intermolecular interaction ensuring long-range orientational order. The clearing temperature is thus a measure of the mesogenicity of a compound or of the thermal stability of the mesophase (if a compound A exists as a mesophase from 70 ot 200°C, and a compound B over the range 200–201°C, the mesophase of B has the greater thermal stability). In comparisons of this kind it is unimportant whether the clear point lies above or below the melting point of the solid crystal (enantiotropic or monotropic liquid crystals respectively).

Two conclusions concerning transition temperatures follow from the Maier–Saupe theory of nematic liquid crystals (Section II, 2), which is based on dispersion forces of attraction between molecules: firstly, molecules possessing anisotropy of polarisability are necessary for establishment of the liquid-crystalline state, and the transition temperature rises with increase in such anisotropy; secondly, permanent dipoles can exert only a weak influence on transition temperatures. A comparison has been made of the variation in the anisotropy of polarisability of the substituent X and the clearing temperatures of azomethines (XIV) and esters (XV) [99]


(XIV)


(XV)

X = F, Cl, Br, $CH_3$, $CH_3O$, $C_2H_5O$, $NO_2$, CN.

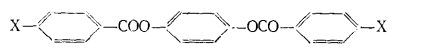
According to the Maier–Saupe theory the clear point is given by

$$T_{cl} = A/4.54\,kV^2, \qquad (12)$$

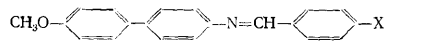
where $k$ is Boltzmann's constant, $V$ is the molar volume at $T_{cl}$, and $A$ is proportional to the square of the anisotropy of polarisability of the molecule[40]. Expressing the anisotropy in terms of the sum of the polarisabilities $\Delta\alpha_M$ of the main part of the molecule and $\Delta\alpha_X$ of the substituent, we obtain

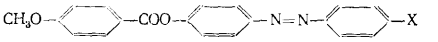
$$T_{cl} \propto (\Delta\alpha_M)^2 + 2\,\Delta\alpha_M \cdot \Delta\alpha_X + (\Delta\alpha_X)^2 \ . \qquad (13)$$

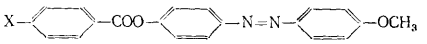
Neglecting the last term (since $\Delta\alpha_M \gg \Delta\alpha_X$), we obtain a linear relation between $T_{cl}$ and $\Delta\alpha_X$. Experimental data on esters (XV) are well represented by a straight line, and those on azomethines (XIV) also reveal a well defined tendency for $T_{cl}$ to rise with increase in $\Delta\alpha_X$. Examples for several other series


(XVI)


(XVII)


(XVIII)


(XIX)


(XX)

(Table 2) confirm this tendency, although the methoxy-derivatives may exhibit regular deviations.

Table 2. Effect of terminal substituents X on clear points.

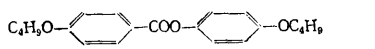
| X | $(\Delta\alpha_X)$, Å$^3$ | Clearing temperature $T_{cl}$, °C | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | (XIV)[99] | (XV)[100] | (XVI)[101] | (XVII)[101] | (XVIII)[5] | (XIX)[2] | (XX)[2] |
| F | 0.5 | 26 | 180 | 199 | — | 265 | 198 | — |
| $CH_3$ | 1.2 | 38 | 199 | 236 | 265 | 279 | 271 | 281 |
| Cl | 2.5 | 47 | 212 | 246 | 275 | 295 | 250 | 293 |
| $CH_3O$ | 3.1 | 102 | 223 | 300 | 300 | 318 | 316 | 316 |
| Br | 3.9 | — | 213 | 252 | 277 | 294 | 275 | 292 |
| $NO_2$ | 4.0 | 82.5 | — | 281 | — | 308 | 317 | 310 |
| $C_2H_5O$ | 4.2 | 122 | — | 287 | 295 | 304 | 300 | — |
| CN | 4.4 | 119 | 249 | 353 | — | — | 322 | 327 |

Extension of the above equations to other classes is restricted both by the scarcity of data on the quantity $A$ and molar volume $V$ and by the discrepancies found sometimes between calculated and experimental values, probably resulting from the postulates made in the theory. It must be borne in mind also that a substituent introduced into a molecule not only changes the polarisability but may produce several other effects, e.g. by changing the molecular geometry, which will have a significant influence on the clearing temperature. As a consequence it is difficult to make an unambiguous interpretation of many experimental results on transition points in liquid-crystalline compounds. Clearly, however, increase in the anisotropy of polarisability should lead to a rise in the clear point. The quantity $V$ should be regarded probably as a factor representing the effect of steric forces of repulsion between molecules in the mesophase. The increase in intermolecular distance caused by these forces leads to a weakening of intermolecular forces of attraction and hence to a fall in the clearing temperature.

The anisotropy of electronic polarisability is determined to a first approximation by the geometrical anisotropy. As a consequence, mesomorphic properties are present in the *trans*-forms of *pp'*-disubstituted stilbenes

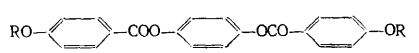
and *p*-substituted cinnamic acids, but absent from the *cis*-analogues. Among alkoxybenzoic acids only the *para*-isomers are mesomorphic, whereas the *ortho*- and *meta*-isomers are not. These facts can be used in determining molecular structure when it is necessary to choose between linear and branched configurations of isomers.

The introduction of additional benzene rings has a greater effect on the clearing temperature than have terminal substituents. In a series of esters, for example, the transition points vary as follows with increase in the number of benzene rings [102,103]:



(XXI)

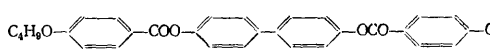
$T_{s-n} = 86°$, $T_{n-i} = 91°$



(XXII)

*a*) R = Me: $T_{s-n} = 213°$, $T_{n-i} = 297°$;

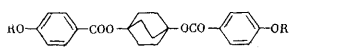
*b*) R = Bu: $T_{s-n} = 153°$, $T_{n-i} = 241°$



(XXIII)

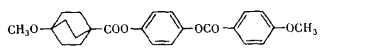
$T_{s-sm} = 171°$, $T_{sm-n} = 184°$, $T_{n-i} = 358°$.

Replacing the *p*-phenylene rings in (XXII) by the rigid but less polarisable bicyclo[2,2,2]octane rings leads to fall in the nematic–isotropic transition point [104]:



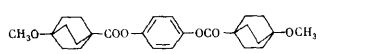
(XXIV)

a) R = $CH_3$; $T_{s-n}$ = 185°, $T_{n-i}$ = 269°;
b) R = $C_4H_9$; $T_{s-n}$ = 152°, $T_{n-i}$ = 221°



(XXV)

$T_{s-n}$ = 189°, $T_{n-i}$ = 221°



(XXVI)

$T_m$ = 209°, $T_n$ = 130°

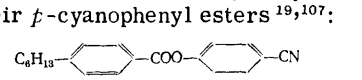


(XXVII)

$T_m$ = 197°, $T_n$ = 195°.

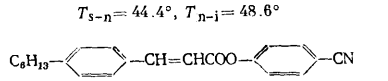
The width of the bicyclo-octane ring is comparable with that of the benzene ring (5.0 and 4.9 Å), but the latter is more planar (2.7 instead of 4.5 Å thick). In view of the possibility of rotation of molecules in liquid crystals about the long axis, the effect of the latter factor is neglected. The probable reason for the considerable fall in thermal stability of the mesophase (by 100 deg) on passing from (XXIV) to (XXVII) is that the cyclohexane fragment is less rigid than the bicyclo-octane ring. The diminished molecular rigidity results in disruption of linearity and thereby diminished anisotropy of polarisability of the molecule. A fall in the clear point is observed also on passing from esters of biphenyl-4,4′-diol to those of bicyclohexyl-4,4′-diol. [105]

The role of an additional double bond in a molecule of a liquid crystal has been examined in *p*-alkylbenzenzoic acids [106] and their *p*-cyanophenyl esters [19,107]:



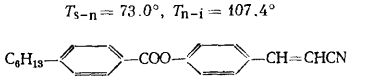
(XXVIII)

$T_{s-n} = 44.4°$, $T_{n-i} = 48.6°$



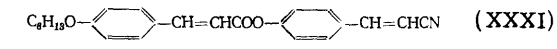
(XXIX)

$T_{s-n} = 73.0°$, $T_{n-i} = 107.4°$



(XXX)

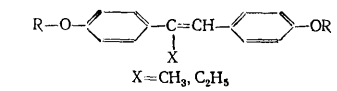
$T_{s-n} = 97.5°$, $T_{n-i} = 147.7°$



(XXXI)

$T_{s-n} = 93.8°$, $T_{n-i} = 226.5°$

The rise in the clearing temperature in this case can also be treated as a consequence of increased anisotropy of polarisability of the molecule. The higher values for (XXX) than for (XXIX) can be explained by the longer conjugated chain containing the double bond in the former. This reflects the fact that the anisotropy of polarisability is influenced not only by the overall linear configuration of the molecule and the presence of readily polarisable structural units but also by the possibility of conjugation between various parts of the molecule (terminal and central groups, benzene rings, double bonds). Introduction of the α-alkyl group in the stilbene derivatives



(XXXII)

disrupts conjugation in the molecule, with a consequent fall in the clear point for the methyl homologue from 176 to 95°C and for the ethyl homologue [108] from 189 to 121°C. Data on the variation of the clearing temperature due to the substitution of azomethines [109] and of biphenyl derivatives [5] can be interpreted similarly.

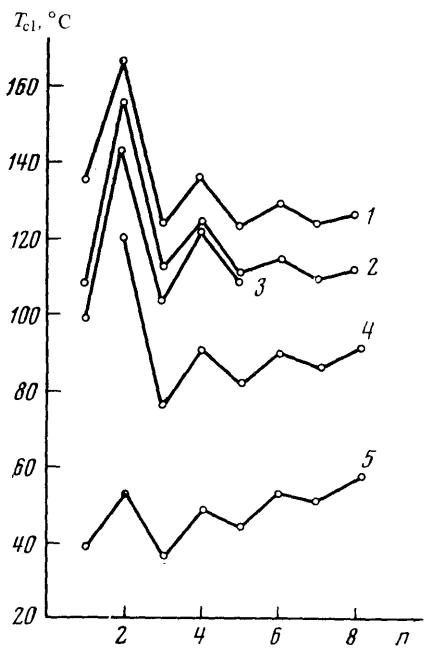
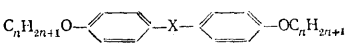
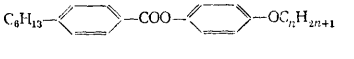


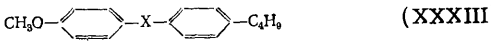

Figure 14. Clear points of the compounds [2]



where X represents: 1) N:NO; 2) N:N; 3) CH:N; 4) COO; 5) and of



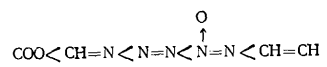
A closely related problem is the influence of the central group on the thermal stability of the nematic phase (Fig.14). Data are available also for alkylalkoxy-derivatives with one pair of substituents [110]:



(XXXIII)

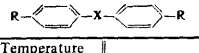
| X = | CH=CH | N=N | N=N | N=CH | CH=N | N=N | N=CH | CH=N | C≡C | COO | OCO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_{cl}$, °C | 121 | 77 | 74 | 70 | 53 | 49 | 49 | 46 | 37 | 24 | 22 |

With an unsymmetrical central group the isomers in the series (XXXIII) (excluding nitrones) have closely similar clear points. As appears from the above data, the central groups X can be arranged in the sequence



of increasing thermal stability of the mesophase. On passing from non-conjugated esters to partly conjugated azomethines and to planar and conjugated azo-compounds and stilbenes the anisotropy of polarisability tends to increase in the same sequence.

Table 3. Calculated parameters of central groups for determining clear points of [111]



| X | Temperature parameter, deg | X | Temperature parameter, deg |
|---|---|---|---|
| N=N | 0 | CH=N | −9 |
| CH=CH | +51 | COO | −35 |
| N=N ↓ O | +21 | C=C | −33* |
| | | CH=CCl | −32 |
| CH=N ↓ O | +8 | | |

*Taken from Ref. 112.

Statistical treatment of a large quantity of experimental data [111] on the clearing temperatures of nematic liquid crystals led to suggested parameters defining the influence of central and terminal groups (Tables 3 and 4). An unknown clear point is determined as the sum of the parameters of central and terminal groups. Thus for *p*-butyl-*p'*-methoxystilbene [110]

$$T_{cl} = 55° (OCH_3) + 15° (C_4H_9) + 51° (CH=CH) = 121°;$$

$$T_{cl}^{exp} = 121° .$$

However, considerable discrepancies between calculated and experimental values are found for the same substituents in an azomethine (61 and 47°C), an azo-compound (70 and 47°C), and an azoxy-compound (91 and 71°C). The additive approach is evidently of limited application to the determination of clear points.

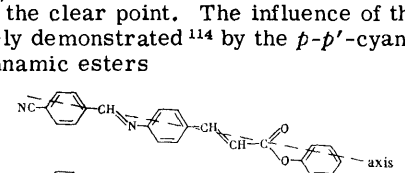
The variation of the clearing temperature with growth of the alkyl chain also exhibits several peculiarities—(i) alternation, i.e. a rise in the clear point on passing from a liquid crystal having an even number of atoms (including oxygen) in the chain to a liquid crystal with an odd number of atoms, followed by a fall on subsequently passing from an odd to an even number of atoms, (ii) a fall in the case compounds whose clear points lie above 80°C, and (iii) a rise in compounds having clear points below 80°C—which can be explained by the Maier–Saupe theory [112]. For an odd atom the increment of polarisability along the long axis of the molecule is about double the increment transverse to the axis, but for an even atom in the chain the contributions to the polarisability parallel and transverse to the axis are roughly equal, which leads to the alternation in clearing temperature. The overall anisotropy of polarisability increases with growth of the alkyl chain, which causes a rise in the clear point for compounds having low clear points (increase in $A$ in Eqn.12). In compounds having high clearing temperatures the increase in mobility of the alkyl chain begins to have an effect, which increases as the chain becomes longer, with growth in the steric forces of repulsion (increase in $V$ in Eqn.12) and fall in the clear point.

Table 4. Calculated increments of terminal groups for determining clear points of [111]

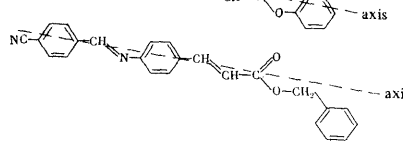


| R | Temperature parameters, deg | | | | | |
|---|---|---|---|---|---|---|
| | $n=1$ | $n=2$ | $n=3$ | $n=4$ | $n=5$ | $n=6$ |
| $C_nH_{2n+1}$ | −2 | 5 | 12 | 15 | 14 | 2 |
| $C_nH_{2n+1}O$ | 55 | 75 | 56 | 61 | 55 | 58 |
| $C_nH_{2n+1}COO$ | 65 | 67 | 63 | 54 | 50 | 45 |
| $C_nH_{2n+1}OCOO$ | 68 | 61 | 42 | 41 | 43 | 35 |

The above examples of the relation between clearing temperature and structure were concerned with the variation of the anisotropy of the molecular polarisability, i.e. with the quantity $A$ in Eqn.(12). No reliable data are available on the dependence on the molar volume $V$. However, it is known that increasing the width of the molecule (defined as the diameter of the smallest cylinder into which the molecule can be placed), e.g. by introducing a side-chain, leads to a fall in the clear point [5,113]. Broadening the molecule increases the interaxial distances in the mesophase, which weakens intermolecular interactions and lowers the clear point. The influence of this factor is effectively demonstrated [114] by the *p-p'*-cyanobenzylidenaminocinnamic esters



(XXXIV)



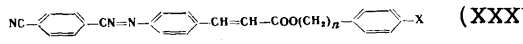
(XXXV)

The explanation of this effect is that, when $n$ is even (e.g. in compound XXXIV), the benzene ring of the ester group fits along the long axis of the molecule, but when $n$ is odd (as in XXXV) it fits across this axis, thereby increasing the width of the molecule. A similar observation has been made on phenylalkanoates of sterols [115].

The clear points of substituted derivatives (XXXVI) vary with $n$ and the location of the substituent (Table 5). When $n$ is even, substitution at position 4″ increases the anisotropy of the molecule and hence raises the clearing temperature, but 3″-substitution widens the molecule and

lowers this temperature. When $n$ is odd, 4″-substitution also has the latter effects. With 3″-substitution conformers may apear in which the substituent widens the molecule and lowers the clear point, but the substituted benzene ring may occupy a position in which the substituent has no broadening effect ($n = 1$, X = Cl). The change in clearing temperature with the parity of $n$ in unsubstituted compounds (XXXVI) reaches 240 deg, and in 4″-substituted derivatives >360 deg (Table 5).

Table 5. Clear points for the compounds



(XXXVI)

| X | Clear points, °C | | | |
|---|---|---|---|---|
| | $n = 0$ | $n = 1$ | $n = 2$ | $n = 3$ |
| H | 280.2 | 38.5 | 187.7 | 36.4 |
| 4″-Cl | 338 | —30* | 217.8 | 13 |
| 4″-$CH_3$ | 290—331 | —30* | 226.5 | 7 |
| 3″-Cl | 231.5 | 47.5 | 150.6 | 32.8 |
| 4″-$CH_3$ | 219.4 | 26 | 154.5 | 9 |

*Mesophase not observed on cooling to −30°C.

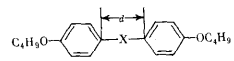
Introduction of a side-chain into the molecule of a liquid crystal lowers not only the clear point but often also the melting point, which provides a method for obtaining low-temperature liquid crystals [100]. However, melting-point depression is not observed in all cases [5,116].

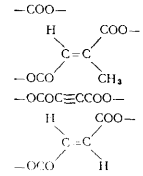
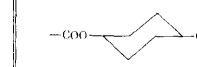
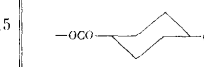
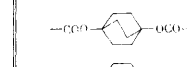
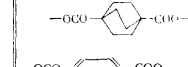
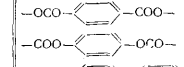
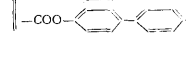
Thus the Maier–Saupe theory is useful in a qualitative discussion of the relation between structure and clear point. However, there are also other approaches to the theory of nematic liquid crystals. As a generalisation of the Maier–Saupe approach the molecular-statistical theory of such mesophases [41,117] takes into account not only dispersion forces but also interactions between permanent dipoles, induced dipole–dipole and dipole–quadrupole interactions, and also steric forces of repulsion. It has been suggested [118] that the agreement between experimental and theoretical values [41,117] is a consequence of the introduction of correcting parameters into the theory, and a general form of interaction potential between rodlike molecules is proposed.

The geometrical anisotropy of molecules is a decisive factor in the formation of nematic phases in solutions of macromolecules and viruses [119], but its role is not so obvious for thermotropic liquid crystals. Unambiguous conclusions cannot be reached from a direct comparison of the clearing temperatures with the length of the latter (Table 6). There is undoubtedly a tendency for the thermal stability of the mesophase to improve as the molecule becomes longer, but it is further influenced by the considerable differences in electronic structure and geometry of the central groups. Increase in the geometrical anisotropy of the molecule can be regarded as a factor favouring formation of a mesomorphic state, regardless of the presence of anisotropy of the $\pi$-electron polarisability.

The cholesteric liquid crystals known at the present time contain one or more asymmetric carbon atoms, although a cholesteric mesophase can probably be formed by molecules containing other chiral units. These liquid crystals are formed not only by steroids but also by compounds containing an asymmetric carbon atom in an alkyl chain, e.g. (IV). As racemates such compounds form nematic liquid crystals, but in optically active form give a cholesteric mesophase. The thermodynamic properties of the nematic (racemic) phase are identical with those of the cholesteric phase. Ideas developed for nematic liquid crystals can be applied to the relation between structure and cholesteric mesogenicity.

Table 6. Clear points of esters of *p*-n-butyoxyphenol [120]



| X | $d$, Å | $T_{cl}$, °C | X | $d$, Å | $T_{cl}$, °C |
|---|---|---|---|---|---|
|  | 3.5 | 92 |  | 10.0 | 157 |
| | 7.8 | 94 | | | |
|  | 8.15 | 99.5 |  | 10.0 | 220 |
| | 7.8 | 144 |  | 9.6 | 221 |
| | | |  | 9.75 | 226 |
| | | |  | 9.6 | 235 |
| | | |  | 9.75 | 241 |
| | | |  | 13.95 | 358 |

The general demands on structure of potentially smectic substances are the same as for nematic compounds. A specific aspect is that smectic liquid crystals consist of molecules having a longer terminal substituent. Thus in homologous series [2] the lower members are nematic, intermediate members possess smectic and nematic properties, and the higher members form smectic liquid crystals. Another feature of smectic mesophases is the significant role of permanent dipole moments in ensuring smectic ordering, as is evident both from theory (Section II, 2) and from dielectric data (Section III, 2). Specific comparisons of chemical structure and properties (in particular transition temperatures) require accurate knowledge of the structure of the smectic mesophase. Although smectic liquid crystals have been found in many classes of compounds, precise identification of the mesophase ($S_A$, $S_B$, $S_C$, etc.) has been accomplished only in rare cases, and conclusions on the relation between structure and properties cannot be correct at the present time.

## 3. Dielectric Properties of Liquid Crystals

Dielectric properties are an important characteristic of liquid crystals, determining in the case of nematics the possibility of their use in electro-optical devices. Thus those having a small negative dielectric anisotropy $\Delta\epsilon$ are used in instruments based on the dynamic scattering effect, whereas liquid crystals having a large positive or negative anisotropy $\Delta\epsilon$ are employed in devices based on field orientational effects. Threshold voltages (Eqn.8)

and connection times of field orientational effects depend on this anisotropy[12]:

$$\tau_{conn} = \frac{4\pi\gamma_1 d^2}{\Delta\varepsilon U^2 - 4\pi^3 K_i}, \quad (14)$$

where $K_i$ is the coefficient of elasticity, $\gamma_1$ the coefficient of viscosity, and $d$ the thickness of the layer of liquid crystals.

The dielectric constants of liquid crystals are determined in flat cells on specimens oriented by the walls or by an external magnetic field. Owing to the difficulties of obtaining uniformly oriented specimens of smectic liquid crystals, their dielectric properties have been studied less fully.

Application of an external electric field to an isotropic liquid causes a static polarisation $P$ equal to the sum of the orientational, electronic, and atomic polarisations and depending on the strength $E$ of the applied field and the dielectric constant $\epsilon$ of the liquid[121]:

$$P = P_o + P_e + P_a = \frac{\varepsilon - 1}{4\pi} \cdot E \quad (15)$$

The orientational polarisation $P_o$ is determined by the magnitude and direction of the permanent dipole moment, and for non-polar molecules $P_o = 0$. The electronic polarisation $P_e$ depends on the ease of displacement of the electron orbitals relative to the nuclei under the influence of the electric field, i.e. on the electronic polarisability $\alpha$:

$$P_e = \frac{4}{3}\pi N\alpha . \quad (16)$$

For organic molecules the atomic polarisation is usually taken to be $P_a = 0.1 P_e$.[121]

The dielectric constants of liquid crystals are related to the degree of ordering $S$, the mean polarisability $\bar{\alpha}$, the anisotropy of polarisability of the molecule $\Delta\alpha$, the dipole moment $\mu$, and its angle $\beta$ relative to the long axis of the molecule[58]:

$$\frac{\varepsilon_\parallel - 1}{4\pi} = NhF\left[\bar{\alpha} + \frac{2}{3}\Delta\alpha S + F\frac{\mu^2}{3kT}\{1 - (1 - 3\cos^2\beta)S\}\right] \quad (17)$$

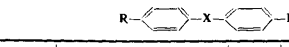
$$\frac{\varepsilon_\perp - 1}{4\pi} = NhF\left[\bar{\alpha} - \frac{1}{3}\Delta\alpha S + F\frac{\mu^2}{3kT}\left\{1 + \frac{1}{2}(1 - 3\cos^2\beta)S\right\}\right] \quad (18)$$

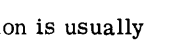
$$\frac{\Delta\varepsilon}{4\pi} = NhF\left\{\Delta\alpha - F\frac{\mu^2}{2kT}(1 - 3\cos^2\beta)S\right\} \quad (19)$$

where $N$ is the number of molecules in unit volume, $T$ K is the temperature, $k$ is Boltzmann's constant, and $h$ and $F$ are factors representing the field in space and the Onsager reaction field. It follows from Eqns.(17)–(19), deduced from Onsager's theory of dielectrics, that the dielectric properties of liquid crystals are determined by the molecular parameters, the parameter $S$ characterising the liquid-crystalline state, and the temperature, where $S$ is strongly dependent on temperature, but the other parameters vary little. Equation (19) indicates that, for molecules having $\mu = 0$ and for those having $\mu \neq 0$ with $3\cos^2\beta = 1$ (i.e. with $\beta = 55°$), the anisotropy $\Delta\epsilon$ is determined by the value of $\Delta\alpha$.

Equations (17)–(19) have been tested quantitatively on *pp'*-dimethoxyazoxybenzene[122]. Comparison of the angles $\beta$ determined by three different methods gave values of 65°, 62°, and 75° obtained from dielectric measurements, the Kerr constant, and group dipole moments respectively. The first two methods yield similar values, but the high value obtained by the third method is attributed[122] to the absence of accurate data on the angle of the dipole moment of the azoxy-group. Use of these formulae to determine dielectric constants is restricted by the lack of accurate data on molecular polarisabilities, dipole moments, and the angles $\beta$. Nevertheless, Eqns.(17)–(19) can be used for a qualitative and semi-quantitative interpretation of experimental results.

Table 7. Dielectric constants of nematic liquid crystals of



| No. | R | R' | X | $\varepsilon_\parallel$ | $\varepsilon_\perp$ | $\Delta\varepsilon$ | Reduced* temp. $T/T_{cl}$, K | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | $C_5H_{11}$ | $C_5H_{11}$ | N=N | 2.82 | 2.38 | +0.44 | 0.97 | 124 |
| 2 | $C_7H_{15}$ | $C_7H_{15}$ | N=N<br>↑<br>O | 2.71 | 2.31 | +0.4 | 0.97 | 124 |
| 3 | $C_5H_{11}$ | $C_5H_{11}$ | N=N | 3.74 | 3.50 | +0.24 | 0.97 | 124 |
| 4 | $C_6H_{13}O$ | $OC_6H_{13}$ | N=N | 3.26 | 3.22 | +0.04 | 0.97 | 122 |
| 5 | $C_6H_{13}O$ | CN | N=N | 22.3 | 11.2 | +11.1 | 0.97 | 122 |
| 6 | $C_8H_7$ | $C_8H_{11}$ | COO | 4.56 | 4.28 | +0.28 | 0.98 | 123 |
| 7 | $C_5H_{11}O$ | $C_4H_9O$ | COO | 5.12 | 5.32 | −0.20 | 0.98 | 123 |
| 8 | $C_5H_{11}O$ | CN | COO | 27.80 | 11.66 | +16.14 | 0.98 | 123 |
| 9 | CN | $OC_5H_{11}$ | COO | 11.60 | 6.04 | +4.56 | 0.98 | 123 |
| 10 | $CH_3O$ | $OCOCH_3$ | CH=N | 5.68 | 6.60 | −0.92 | 0.98 | 123 |
| 11 | $C_3H_7O$ | $OCOCH_3$ | CH=N | 5.54 | 5.94 | −0.40 | 0.98 | 123 |
| 12 | $C_7H_{15}O$ | $OCOCH_3$ | CH=N | 5.08 | 5.33 | −0.25 | 0.98 | 123 |
| 13 | $C_5H_{11}O$ | CN | CH=N | 22.63 | 9.82 | +12.81 | 0.98 | 123 |
| 14 | CN | $OC_5H_{11}$ | CH=N | 17.23 | 7.87 | +9.36 | 0.98 | 123 |
| 15 | $C_7H_{15}$ | CN | COO–  –COO | 37.7 | 7.8 | +29.9 | 125° C | 122 |
| 16 | $C_2H_5O$ | $OC_6H_{13}$ | C(CN)=CH | 6.4 | 11.3 | −5.3 | 60° C | 125 |

*Reduced temperatures are used to eliminate the implicit dependence of $\epsilon$ on $T$ involved in the parameter $S$ in Eqns.(17)–(19).

The measured dielectric constants of liquid crystals (Table 7) clearly indicate the significant part played by permanent dipole moments in determining the dielectric properties. Non-polar molecules (No.1 and 2) have small values of $\epsilon$ and $\Delta\epsilon$, which increase somewhat on introduction into the molecule of weakly polar substituents (alkoxy-groups) or a polar central bond (azoxy, azomethine, or ester groups). The greatest effect is exerted by the nitrile group ($\mu = 4.18$), which, depending on the position at which it is introduced, may produce either a large positive anisotropy $\Delta\epsilon$ (No. 4, 8, 13, and 15) or a large negative value (No. 16).

A quantitative assessment of the role of group dipole moments in determining dielectric constants was obtained by comparing calculated molecular dipole moments with the effective values determined from dielectric measurements[123]. Calculation, which took into account the degree of order $S$, was based on projections of the dipole moment of each group on the long and short axes of the molecules ($\mu_{i\parallel}$ and $\mu_{i\perp}$):

$$\mu_\parallel^{theor} = \left[\sum \mu_{i\perp}^2 \cdot (1 - S) + (1 + 2S) \cdot \left(\sum \mu_{i\parallel}\right)^2\right]^{1/2} \quad (20)$$

$$\mu_\perp^{theor} = \left[\sum \mu_{i\perp}^2 \cdot \left(1 + \frac{S}{2}\right) + (1 - S) \cdot \left(\sum \mu_{i\parallel}\right)^2\right]^{1/2} . \quad (21)$$

The $\mu_i$ values used in the calculations are given in Table 8. Dipole moments were determined from dielectric measurements by means of formulae analogous to those proposed by Onsager for isotropic dielectrics [123]:

$$\mu_{\parallel}^{exp} = \frac{9kT}{4\pi N} \frac{(\varepsilon_{\parallel} - \bar{n}^2) \cdot (2\varepsilon_{\parallel} + \bar{n}^2)}{\varepsilon_{\parallel} (\bar{n}^2 + 2)^2} \quad (22)$$

$$\mu_{\perp}^{exp} = \frac{9kT}{4\pi N} \frac{(\varepsilon_{\perp} - \bar{n}^2)(2\varepsilon_{\parallel} + \bar{n}^2)}{\varepsilon_{\parallel} (\bar{n}^2 + 2)^2}, \quad (23)$$

where $\bar{n}$ is the mean refractive index of the liquid crystal. Measurements of the dielectric constant were made at a temperature of 0.98 $T_{cl}$ K, with the degree of order taken to be $S = 0.4$. In all the examples cited [123] $\mu^{theor}$ exceeds $\mu^{exp}$ usually by at most 30%. Thus data on group dipole moments can be used to determine the sign of $\Delta\epsilon$ and to estimate dielectric constants.

Table 8. Group dipole moments $\mu_i$. [123]

| Group | $\mu_i$ | $\mu_i$ | $\mu_{i\parallel}$ | $\mu_{i\perp}$ |
|---|---|---|---|---|
| Ph–C(=O)–O–Ph | ↗ | 1.90 | 0.89 | 0.68 |
| Ph–C(=H)–N–Ph | ↘ | 1.57 | 0.40 | 1.51 |
| Ph–$CH_3$ | ← | 0.37 | −0.37 | 0 |
| Ph–CN | → | 4.18 | 4.18 | 0 |
| Ph–O–$CH_3$ | ↙ | 1.28 | −0.40 | 1.22 |
| Ph–O–C(=O)–$CH_3$ | ↖ | 1.69 | −0.69 | 1.54 |

Introduction into the molecule of a nitrile group with a dipole moment directed along the long axis leads to increases not only in $\epsilon_{\parallel}$ but also in $\epsilon_{\perp}$ (Table 7). This is a consequence of the imperfect orientation of molecules in the liquid-crystalline phase ($S \neq 1$).

Changing the sites of substituents has different effects on $\epsilon_{\parallel}$ in azomethines (Table 7, No. 13 and 14, $\epsilon_{\parallel} = 22.6$ and 17.2) and in esters (No. 8 and 9, 27.8 and 10.6). In both cases $\epsilon_{\parallel}$ is determined mainly by the group dipole moment of the nitrile group, to which is added (No. 8 and 13), or from which is subtracted (No. 9 and 14), the parallel component of the ester ($\mu_{\parallel} = 0.89$) or azomethine ($\mu_{\parallel} = 0.40$) the central group. Since the component $\mu_{\parallel}$ of an ester group is more than double that of an azomethine group, the observed effects are also more pronounced in the esters. In the case of liquid crystals having slight anisotropy $\Delta\epsilon$ transposition of substituents may lead to change not only in the dielectric constant but also in the sign of $\Delta\epsilon$. This has been observed in isomeric phenyl benzoates [126] and 4(4′)-butyl-4′(4)-methoxyazoxybenzene [127] (incidentally, our results indicate that the characteristics measured in Ref. 126 do not apply to the same isomer).

The dielectric constants of liquid crystals depend not only on molecular structure, degree of order, and temperature but also on the frequency of the applied electric field (Section III, 2).

## VI. LIQUID-CRYSTALLINE MATERIALS

### 1. General Requirements

The practical utilisation of thermotropic liquid crystals requires a set of properties that individual liquid-crystalline componds do not usually possess. For example, the working substance in indicator devices operating on the dynamic scattering effect should be in a liquid-crystalline state throughout the temperature range in which the device functions (laboratory and domestic instruments require liquid crystals melting at or below 0°C and clearing at or above 50°C). The electrical conductivity should be sufficient for an effect to appear ($\geq 10^{-10}$ ohm$^{-1}$ cm$^{-1}$) but at the same time not too high ($< 10^{-7}$ ohm$^{-1}$ cm$^{-1}$), so that electrolytic processes that would lower the operating resources of the instrument are slowed down and the consumption of energy is diminished. The working substance should have a slight negative dielectric anisotropy ($\Delta\epsilon$ from −0.2 to −0.6), with definite viscosity characteristics to ensure acceptable durability (until the appearance of scattering) and relaxation times (around 100 ms), it should be photochemically stable, and it should be oriented in the cell in a specified manner. Several less fundamental requirements (stability in moisture, atmospheric oxygen, etc.) may be satisfied by the technique of filling and hermetically sealing the indicator cell.

For indicators operating on orientational effects the working substance should usually have positive dielectric anisotropy, but the conductivity requirement is significant only in the sense that diminishing the conductivity (to $< 10^{-12}$ ohm$^{-1}$ cm$^{-1}$) may considerably increase the operating resources and decrease the consumption of current.

Cholesteric liquid crystals for thermographic purposes should operate in a specified temperature range (sometimes very narrow, $< 1$ deg), have high thermal sensitivity, and be resistant to light and chemical attack by the atmosphere.

As a consequence of the above and several other requirements, individual compounds are not used for practical application, but more or less complicated compositions or liquid-crystalline materials.

### 2. Liquid-crystalline Mixtures

Mixtures of two or more liquid crystals are used to achieve the required temperature range for a nematic mesophase. Attempts are made to find a eutectic composition, at which the melting point passes through a well defined minimum for a given combination of individual components, whereas the variation of the clear point is approximately linear. Fig. 15 shows the phase diagram for a binary mixture of *p*-cyanophenyl *p*-hexylbenzoate (A) and *p*-heptylbenzoate (B). [128] The maximum temperature range of existence of the mesophase (~30 deg) evidently corresponds to the eutectic mixture, containing ~50% of component B. The problem of finding the eutectic of binary and ternary mixtures can be solved by simple trial and error, although this is quite laborious in the latter case. With four or more components trial and error is unsuitable, and the thermodynamic constants of the components and mathematical methods must be employed to find the optimum composition.

On the assumption that mixtures of structurally similar components are nearly ideal solutions the composition and

the melting point of the eutectic of an $i$-component mixture can be calculated from a set of $i$ le Châtelier-Schröder-van Laar equations [129,130] containing $i$ unknowns

$$\begin{cases} \ln X_1 = \frac{\Delta H_1}{R} \cdot \left(\frac{1}{T_m} - \frac{1}{T_{m1}}\right) \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \ln X_i = \ln(1 - X_1 - \ldots - X_{i-1}) = \frac{\Delta H_i}{R} \cdot \left(\frac{1}{T_m} - \frac{1}{T_{mi}}\right), \end{cases} \quad (24)$$

where $X_i$, $T_{m,i}$, and $\Delta H_i$ are respectively the mole fraction, the melting point, and the heat of fusion of the $i$th component, and $R = 8.314$ J mole$^{-1}$ deg$^{-1}$. The clear point of such systems can be calculated with sufficient accuracy by means of the equation [131]

$$T_{cl} = \sum X_i T_{cl\,i}, \quad (25)$$

in which $T_{cl,i}$ is the clear point of the $i$th component.

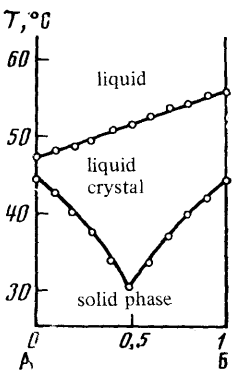



Figure 15. Diagram of phase transitions of $p$-cyanophenyl: A) $p$-hexylbenzoate; B) $p$-heptylbenzoate.

In several cases (biphenyls, azoxy-compounds) the calculated values agree well with experiment, but this method is not universally applicable. Thus clearing temperatures calculated for liquid-crystalline $p$-cyanophenyl $p$-alkylbenzoates differ considerably (by up to 20 deg) from the experimental values [132]. In these cases the problem of finding the eutectic composition can be solved by a simplex method of experiment design [133] consisting in an initially arbitrary (approximate) choice of composition and "step" for its variation, experimental determination of the melting points of $i + 1$ mixtures (where $i$ is the number of components), and mathematical treatment of the results [133], followed by choice of a new initial composition and interval of variation until a eutectic with specified properties is attained.

Even the first experiments on the use of this method have shown [128] that good results can be obtained with a comparatively small number of experiments. Thus it was necessary to measure the melting points of only eight mixtures in order to find the eutectic composition of the ternary system of mixed carbonates $p$-$C_4H_9C_6H_4COO$-$p'$-$C_6H_4OCOOR$ (R = $C_6H_{13}$, $C_7H_{15}$, $C_8H_{17}$), and the calculated melting point (68.5°C) coincided with the value determined from the thermogram. Calculation based on Eqn.(24) gave too low a melting point (63°C) for the eutectic mixture [128].

Even more complicated problems than lowering the temperature of formation of the mesophase and extending the temperature range of its existence are solved by trial-and-error selection of the component composition of liquid-crystalline mixtures. For example, materials with a relatively small positive dielectric anisotropy $\Delta\epsilon$ and a wide temperature range of the mesophase can be used in indicator devices operating on the field effect. Yet the large majority of liquid-crystalline compounds of this type are benzonitrile derivatives [134] having a large dielectric anisotropy [19] and high melting points. By mixing liquid crystals having a large positive dielectric anisotropy with low-temperature liquid crystals having a small negative dielectric anisotropy we can select a composition satisfying the above requirements. Thus mixing in different ratios $p$-$p'$-butoxybenzylidenaminobenzonitrile (BBABN) ($\Delta\epsilon = +19$ at 63°C, [135] m.p. 64°C, $T_{cl}$ = 105°C) with a 2 : 1 mixture of $p$-butyl-$N$-$p'$-methoxybenzylidenaniline (BMBA) and $p$-butyl-$N$-$p'$-ethoxybenzylidenaniline (BEBA) ($\Delta\epsilon = -0.46$ at 25°C, m.p. −12°C, $T_{cl}$ = 48°C) we can obtain the mixtures listed in Table 9 [136,137].

Table 9. Effect of additions of BBABN on phase transition temperatures and sign of dielectric anisotropy of mixtures of BMBA and BEBA.

| Mixture, mass % | | $T_m$, °C | $T_{cl}$, °C | $\Delta\epsilon$ at 24°C |
|---|---|---|---|---|
| ⅓BEBA + ⅔BMBA | BBABN | | | |
| 100 | 0 | −12 | +48 | −0.5 |
| 99.1 | 0.9 | −13 | +49 | −0.3 |
| 98.2 | 1.8 | −13 | +50 | −0.1 |
| 95.5 | 4.5 | −10 | +52 | +0.7 |
| 92.0 | 8.0 | −2 | +55 | +1.5 |
| 85 | 15.0 | +2 | +60 | +3.2 |
| 69 | 31.0 | +22 | +74 | +6.5 |
| 0 | 100 | +64 | +105 | +18.0 (64° C) |

Admixture of non-mesophasic compounds having a large dipole moment and compatible with the liquid crystal can be used to control the sign and the magnitude of the dielectric anisotropy. Thus additions of 2% and 7% of $p$-dimethylaminobenzonitrile [138] to a mixture of azoxy-compounds (Merck, m.p. = −5°C, $T_{cl}$ = +75°C, $\Delta\epsilon = -0.2$) yields respectively $\Delta\epsilon = +1.1$ and +3.8 with a fall in the clear point (67 and 48°C).

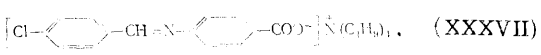
### 3. Additions for a Specified Conductivity

As already remarked above, liquid-crystalline materials in devices using dynamic scattering should have a definite electrical conductivity. Well purified liquid crystals are considerably less conducting than is required, and do not exhibit dynamic scattering of light. Unpurified substances, although scattering light on application of an electric field, cannot be used technically, since the nature and the content of their impurities are practically uncontrollable, depend on the quality and the "previous history" of the raw material, are sensitive to slight changes in the conditions of production and purification, etc.

In practice materials of specified conductivity and threshold voltage are obtained by the use of ionic additives or electron donors and acceptors [139], which probably form charge-transfer complexes with the components of the liquid-crystalline material. In the latter case the increase

in conductivity is caused by dissociation of the charge-transfer complexes into ions[71]. Acceptor additives[139] (tetracyanoquinodimethane, tetracyanoethylene, dichlorodicyanobenzoquinone), when introduced into mixtures of liquid-crystalline azoxy-compounds, effectively increase the conductivity with slight anisotropy (i.e. the ratio $\sigma_{\parallel}/\sigma_{\perp}$) and raise the threshold of dynamic scattering in an alternating current[83]. The conductivity of *p*-butyl-*N*-*p*′-methoxybenzylidenaniline was greatly increased by introduction of the charge-transfer complex of benzoquinone and quinol[142].

Tetra-alkylammonium halides can be used as ionic additives for nematic liquid crystals[140], with the anisotropy of the conductivity increasing with decrease in the ionic radius of the halogen. Choice of ions that are "compatible" with the structure of a given liquid crystal enables us to diminish such undesirable side-effects as fall in the temperature of transition to an isotropic liquid and decrease in the degree of ordering of the liquid crystals. Thus the use has recently been proposed[141] of additions of tetrabutylammonium salts of substituted benzoic acids $p$-$RC_6H_4COON(C_4H_9)_4$ (where R = $NO_2$, Cl, $NH_2$, $CH_3$, etc.) or threadlike compounds, e.g.



(XXXVII)

4. Orienting additions

As already noted above, liquid crystals in electro-optical cells should be oriented parallel or perpendicular (homotropically) to the walls. Such orientation can be attained by chemical or mechanical treatment of the surfaces, as well as by introducing into the liquid crystals orienting additives that are adsorbed on the surface[143], the orienting effect being determined in the latter case by the chemical nature of the additive, the surface, and the liquid crystal, as well as by the topology of the surface.

An example of an orienting addition is 0.5% of polyamide resin introduced into *p*-butyl-*N*-*p*′-methoxybenzylidenaniline and Schiff bases of similar structure to ensure their homotropic orientation[144,145]. Lecithin[146] and silicone oil[146,147] applied to glass have a similar effect. Addition of 0.25–2.5% of hexadecylammonium bromide to nematic liquid crystals[148] also leads to their homotropic orientation, whereas smaller quantities of the additive produce planar orientation[149], since the additive molecules are then able to "lie" on the electrode surface.

Orienting additives of various classes—amines, carboxylic acids, etc.—are known, most of which change chemically during operation of the cell, so that their orienting influence becomes weaker. At the present time, therefore, silane surface-bonding agents have found application[150]; they react chemically with the glass or quartz, which improves considerably their reliability. Various types of orientation can be obtained depending on the geometry chosen for the additive. Thus homotropic orientation of liquid crystals is ensured by $C_{18}H_{37}N^{+}(CH_3)_2 \cdot [CH_2]_3Si(OCH_3)_3Cl^{-}$ hydrolysed on glass, with vertical octadecyl groups, and planar orientation by $CH_3NH[CH_2]_3 \cdot Si(OCH_3)_3$ molecules.

It is clear from the above that the production of liquid-crystalline materials is a quite complicated scientific and technical problem. No materials have yet apeared that satisfy all the technical requirements[151]. Improvement of the chemical and electrochemical stability of liquid crystals, extension of the temperature range of existence of the mesophase (especially to lower temperatures), decrease in the threshold and working voltages, improvement of the temporal characteristics, and other aspects are still urgent problems.

## VII. FIELDS OF APPLICATION

The main peculiarity of liquid crystals is their ability to change their optical properties under the influence of almost any external factor. Therefore the number of applications suggested by various workers is immense. However, restricting consideration to those liquid crystals whose characteristics enable them to compete with traditional materials, we can distinguish the most important uses as electro-optical devices, thermography, spectroscopy, and certain others. Below we shall briefly examine several examples, with literature references only to the most typical papers, without any claim to completeness.

1. Electro-optical Devices

Because of the extremely low power consumption by the exciting source ($10^{-4}$–$10^{-6}$ W cm$^{-2}$ layer surface) nematic liquid crystals have already found wide application in indicators of numerical and graphic information for such electronic devices as wrist-watches and pocket calculators[152]. These instruments are autonomic (i.e. not connected to the mains), and in effect only liquid-crystalline "dials" are able to ensure that their batteries will function for a long time. Here it is important that not only the power input but also the supply voltage should be small (the latter a few volts), which makes it possible to use integral circuits as radio units. Indicators usually operate either on the dynamic scattering effect or on the twist effect, the latter similar to the Fréedericksz effect. The required numerals are displayed e.g. by feeding a voltage to a definite combination of segments of transparent electrodes formed into a typesetting "eight" (similar to that indicated by the postmark on envelopes). The range of possible application of indicators is, clearly, not restricted to watches and calculators. They can be used whenever information is to be displayed to human beings, e.g. in calculating machines, advertising panels, measuring instruments[153], control devices[154], etc. In all these cases the rapidity of response of the liquid crystals need not be better than 0.1 s (since the inertia of the human eye is almost the same), and liquid crystals can provide this with a symbol of high contrast range. Next is the production of coloured information indicators either by the use of dye molecules incorporated into liquid-crystalline matrices[155] or on the interference principle.

Another important trend in the electro-optics of liquid crystals is the attempt to produce a flat television screen for the reproduction of moving images[156]. Here the demands on the time characteristics of liquid crystals are far more severe, and success depends both on the development of liquid-crystalline materials with more rapid response and a more sharply defined threshold dependence of contrast on voltage and on the level of semiconductor technology necessary for the production of complicated mosaic devices for controlling the liquid-crystalline units. The preparation of new liquid crystals having diminished viscosity coefficients and increased elastic coefficients (to improve rapidity of response), is now the most important but hardly the most easily solved problem in the chemistry of nematic liquid crystals.

A third line of advance is the application of liquid crystals to optics[157], quantum electronics, holography, and equipment for the optical processing of information[158]. Here they are used to control the degree of coherence of a laser beam, for the phase modulation and deflection of beams with response in the millisecond range, for transforming an image from a cathode-ray tube (incoherent) to an image in coherent beams with subsequent registration on holograms, etc. Equipment has also been suggested for pictorial logic on liquid crystals[159].

Finally, electro-optical liquid-crystalline materials have been used to make X:ray, ultraviolet, and infrared images visible[160]. A film of the liquid crystals is placed in contact with a film of a photoconductor sensitive to the given spectral range. Variation of the electrical resistance of the photoconductor leads to variation in the voltage on the liquid-crystalline film with a corresponding change in its optical properties. The received (invisible) image can be made visible by means of an external liquid-crystalline intensifer. Procedures have also been proposed for visualisation of the emission of lasers without the use of photoconductors—by thermal effects in nematic[161], cholesteric[162], or smectic[163] liquid crystals. Defects in integral circuits can be visualised[164] by means of liquid crystals. A very complete survey of the most recent fields of application of liquid crystals has appeared[165].

## 2. Thermography

In virtue of the ability to reflect light selectively cholesteric liquid crystals find wide application in laboratories and in industry for the convenient visualisation of thermal fields and the measurement of temperature. Thermography by means of such mesophasss can be widely used also for detecting external factors leading to change in temperature, such as optical, X-ray, microwave, and radioactive emissions, currents of air, etc.

Portions of the human skin lying over malignant tumours and certain other seats of inflammatory processes have a rather higher temperature, and the use of cholesteric liquid crystals in polymer films (or applied directly to the skin) provides an effective method for locating foci of disease[4,166-168].

The high resolving power of cholesteric liquid crystals (of the order of the thickness of a layer, i.e. 20–90 $\mu$m) permits their use in microelectronics to reveal technical defects in microcircuits[171,172], the thermography of the thermal fields of transistors[173], which will reveal the "hottest" sites, so that cooling can be provided for in advance, in order to improve the reliability of the circuit.

The possible use of cholesteric liquid crystals in aerodynamic experiments[174] can be based on differences in the rate of cooling of the preheated mesophase depending on the rate of flow around the model.

Devices enabling the distribution of light flux across the diameter of a laser beam have been based on cholesteric liquid crystals[175]. The latter can be used also to determine internal stresses and defects in metals and alloys[176].

Further details of the thermographic applications of cholesteric liquid crystals can be found in Ref. 14. A detailed bibliography has been published[177] on the application of liquid crystals.

## 3. Spectroscopy

Use in spectral investigations may provide information either on the properties of the liquid crystal itself or on those of molecules dissolved in it. When liquid crystals are used as solvents, the spectra of oriented molecules can be obtained, since the long axes of dissolved molecules are oriented on the average parallel to the "director" of a nematic liquid crystal. The dissolving power of liquid crystals is almost equivalent to that of ordinary isotropic solvents, and an appropriate liquid-crystalline solvent can be selected for any substance. Such investigations are restricted by the absorption of light by the liquid crystal itself. For example, the use in ultraviolet spectroscopy of nematic mesophases containing aromatic or heteroaromatic rings is limited by the intrinsic absorption at wavelengths shorter than 350 nm. This limit can be shifted to 250 nm by using a compensated cholesteric phase as solvent[178,179] or a nematic liquid crystal based on cyclohexane. The ultraviolet or infrared spectra of oriented liquid crystals can be used to determine the polarisation of the moments of electronic or vibrational transitions in the molecules forming the liquid crystals[40,180,181], by the application of polarised radiation (parallel or perpendicular to the "director").

Examination of the dichroism of the electronic absorption by impurity molecules of dyes (or related compounds) in oriented liquid crystals and matrices[182] permits determination of the direction of the electron oscillators in these molecules, leading in several cases to conclusions on the geometrical configuration of the molecule. For example, determination of the directions of the oscillators of two long-wavelength bands due to symmetrical biscyanine dyes shows that these oscillators are mutually perpendicular[183]. The directions of oscillators in molecules of aromatic hydrocarbons have been determined by the same method[184]. Analysis of the dichroism of liquid crystals of solutions of autocomplexes of 1,4-naphthaquinone and 1,3,5-trinitrobenzene provides indications on the molecular geometry of the complexes and in several cases refinement of the specific mechanism of intramolecular charge transfer in these compounds[185]. By measuring the dichroism of rod-shaped impurity molecules, we can also investigate the structure of the liquid-crystalline matrices themselves[57].

Even at concentrations of 1–2% the dissolution of chiral compounds in a nematic liquid crystal converts the latter into a cholesteric phases (induced cholesteric liquid crystals[186,187]). Since the specific rotation of a cholesteric phase is a thousandfold that of any isotropic solution, it has been proposed to use this effect as a method of proving the chirality of molecules possessing very small specific rotations or present in small quantities. The helical pitch of an induced cholesteric liquid is in most cases so large that the selective reflection lies in the infrared[188]. The pitch and the direction of the helix have been determined from the dispersion curves of optical rotation in the infrared[189].

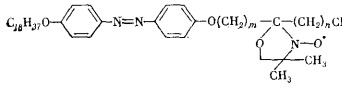
The addition of chiral molecules to a *C* smectic also produces a twist in its structure, the pitch in this case being about the same as for nematic–cholesteric mixtures[190].

Optically inactive molecules dissolved in a cholesteric liquid crystal exhibit in an absorption band circular dichroism induced by the liquid crystal[191,192]. This dichroism is caused not simply by the helical ordering of the dissolved molecule in the cholesteric matrix but by electronic or magnetic interactions of the chromophore of the solute molecule with the solvent[193]. The molar amplitude of the induced dichroism ($\sim 10^7$ deg cm$^2$) is tenfold that of the circular dichroism in chiral hexahelicene ($8.62 \times 10^5$ deg cm$^2$).[194] The directions of polarisation

of the moments of optical transitions have been determined for the dissolved molecule from the sign of the induced dichroism [191-193].

The largest number of spectroscopic investigations using liquid crystals have been made in the nuclear magnetic resonance range. Several reviews have been published on this aspect [14,195,199,210]. The n.m.r. spectra of a liquid-crystalline phase contain considerably more lines than do the spectra of an isotropic liquid. This is due to the presence of direct interactions between protons, which vanish in the isotropic state because of the high rotational mobility of the molecules. The degree of ordering of a liquid crystal can be determined from the n.m.r. spectra, and measurement of relaxation times will give information on the dynamics of orientational fluctuations in these systems. The fine structure of n.m.r. spectra may disappear with liquid crystals whose molecules contain many interacting protons. Such liquid crystals can be used as solvents; the resonance lines of a dissolved molecule are then observed on a smooth background. The n.m.r. spectra of simple molecules in anisotropic matrices are used to determine bond angles and lengths in the molecules.

Quite a large number of studies have been made on the use of liquid crystals in electron spin resonance spectroscopy [14,197,198]. Nematic, smectic, and compensated cholesteric liquid crystals are used as solvent. Employment of a liquid-crystalline solvent will give more complete information on the e.s.r. spectra of polyradicals. An interesting example of the use of e.s.r. spectroscopy to investigate the structures of liquid crystals is an examination of the mobility of the alkyl chains in *pp'*-dioctadecyloxyazoxybenzene [199]. Compounds of the type



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well miscible with the liquid crystal, were added (0.3%) as spin label. Transition from the solid phase of the azoxybenzene derivative to the smectic *B* phase was shown to be accompanied by increase in the mobility of the alkyl chains, and on passing from smectic *B* to smectic *C* the angle between the long axes of the molecules and the smectic plane increased.

Mössbauer spectroscopy has been used to determine the structural parameters of smectic phases [200]. The possibility has been demonstrated [201] of determining the ordering tensor of the Mössbauer label from its $\gamma$-resonance spectra in nematic and cholesteric mesophases.

## 4. Other Examples

Here we shall mention only those new trends in the application of liquid crystals on which information has appeared quite recently and which appear to be especially interesting. It has been proposed to use liquid crystals for the visualisation of ultrasonic fields and to record acoustic holograms [202], for visualisation of the distribution of mechanical stresses in various rigid objects, and to analyse gases and vapours [15].

Owing to the ordered character of a mesophase, rodlike impurity molecules dissolve in it better than do branched molecules. Ths forms the basis for the use of liquid crystals as stationary phase for the separation of isomers in gas–liquid chromatography [203,204]. Their use as anisotropic solvents in chemical reactions also is extremely promising. Both the mechanism and the kinetics of the reaction may be changed. Examples are molecular rearrangements [205,206] and polymerisations in the liquid-crystalline state [207,208].

Among important practical results may be cited the discovery of ferroelectricity in a chiral *C* smectic [26,209]. Liquid ferroelectrics may be extremely useful in nonlinear optics (e.g. for regenerators of the second harmonic of light with high resistance to laser emission); they can be used in new forms of piezo- and pyro-transducers, memory devices, etc.

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# Reactions of Organic Compounds with Higher Fluorides of *f*- and *d*-Elements in Groups V and VI

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The interaction of higher fluorides of *f*- and *d*-elements in Groups V and VI of the Periodic System with alkanes, alkenes, aromatic compounds, and also hetero-organic derivatives containing silicon, nitrogen, phosphorus, oxygen, and sulphur is surveyed. The relative oxidising powers of the inorganic fluorides are assessed. Organic donors possessing lone pairs of electrons form with penta- and hexa-fluorides of low oxidising power relatively stable adducts, least stable with the hexafluorides. Highly active inorganic fluorides undergo with organic compounds redox and substitution reactions, yielding complicated mixtures of metal-containing and fluorinated organic substances. A list of 169 references is included.

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## I. INTRODUCTION

Reaction between various classes of organic compounds and inorganic fluorides such as silver(II), cerium(IV), lead(IV), bismuth(III), manganese(III), and cobalt(III) fluorides, which are selective fluorinating agents, has formed the subject of reviews[1,2] and books[3-5], and use of several of these agents has been shown to be highly effective. Hitherto, however, no summary has appeared of results on the reaction of organic compounds with higher fluorides of actinides and *d*-elements in Groups V and VI of the Periodic System, which exhibit not so much fluorinating as strongly complexing properties. Inadequate study has been made of the chemistry of complex compounds of *d*- and *f*-elements having a high formal degree of oxidation of the central atom and with coordination numbers $\geqslant 6$. The present Review represents an attempt to make certain generalisation on the basis of material published up to 1975 inclusive.

The terminology and the classification of Mulliken and Pearson[6] have been adopted in characterising donor–acceptor interactions and those of Ingold[7] and Tobe[8] for the reactions. The term "adduct" for compounds isolated individually and for those in solution is used in Cotton and Wilkinson's concept[9] as definition of a compound formed by two neutral molecules, one of which is a donor of electrons and the other an acceptor.

Towards most organic compounds not containing strongly electronegative substituents the higher fluorides of transition elements exhibit the properties of Lewis acids of various strengths (electrophilic reagents), defined by Mulliken[6] as $v$-type acceptors, having vacant orbitals on the central atom, which are able to accept the electrons of donors or abstract an electron from the reagent in the case of a redox step.

The present review discusses donors of various types[6]—$\sigma$-donors supplying electrons from a bonding orbital of a $\sigma$-bond, $\pi$-donors interacting with the acceptor by means of $\pi$-electrons of double bonds, and $n$-donors possessing lone pairs of electrons.

In order to analyse the laws governing the interaction of various classes of organic compounds with fluorides of *d*- and *f*-elements, the relative oxidising powers of the latter are assessed in Section II.

## II. RELATIVE OXIDISING POWERS OF HIGHER FLUORIDES

After formation of bonds with fluorine in a higher state of oxidation Group V pentafluorides and Group VI hexafluorides have the respective structures $M^{5+}(d^0)F_5^-$ and $M^{6+}(d^0)F_6^-$:[10,11] i.e. no unpaired *d*-electrons remain in their outer orbitals. McDiarmid has found very good agreement between experimental ultraviolet absorption bands of molybdenum and tungsten hexafluorides and the bands to be expected from ligand field theory[11]. He estimates the splitting of the *d*-orbitals of molybdenum(VI) fluoride due to the ligand field as 40 000 $cm^{-1}$, which indicates a high stabilisation energy of the bonding $t_{2g}$ orbitals. All six electronic transitions in the two hexafluorides are from $\sigma$- and $\pi$-orbitals of metal–fluorine bonds to $n(d)t_{2g}$ atomic orbitals of the metal. Pentafluorides of Group VI metals have one unpaired *d*-electron; the electronic structure of the outer shell of uranium(V), neptunium(V), and plutonium(V) fluorides is respectively $5f^0$, $5f^1$, and $5f^2$.

Molecules of the pentafluorides have a trigonal bipyramid structure[12,13] with $D_{3h}$ point group symmetry, whereas molecules of the hexafluorides form a regular octahedron[10,13,14] with symmetry $O_h$. Distortion of the structure of fluoride molecules having unpaired electrons in *d*- and *f*-orbitals of the central atom (molybdenum(V), neptunium(VI), and plutonium(VI) fluorides)—the Jahn–Teller effect—is not observed, since for transition-metal complexes it is significant only when the antibonding $e_g$ orbitals have different populations of electrons[15]. In most of the above fluorides only the $t_{2g}$ orbitals are filled, for which this effect is considerably weaker and produces no appreciable distortion of the geometry of the complex[16].

In the solid state pentafluorides exist as partly ionised tetramers of various types[12]. In the gas phase the pentafluoride of vanadium is monomeric, but those of niobium, tantalum, and molybdenum are polymers with various proportions of tri-, di-, and mono-mers, among which an equilibrium determined by the temperature is established[12,17-19]. All the hexafluorides are highly volatile monomers in the gas phase[10], which can be explained by their greater coordination saturation than that of the pentafluorides.

The hexafluorides of actinides have been arranged[20] in the sequence—plutonium(VI) > neptunium(VI) > uranium(VI)—of diminishing oxidising power. The plutonium compound is a considerably stronger fluorinating agent than is the uranium derivative, and oxidises bromine trifluoride to the pentafluoride, whereas the trifluoride converts various uranium compounds, as well as metallic uranium, into uranium hexafluoride. Sulphur tetrafluoride does not react with uranium hexafluoride, but is converted into sulphur hexafluoride by plutonium hexafluoride. Finally, plutonium hexafluoride fluorinates uranium tetrafluoride and diuranium nonafluoride to the hexafluoride[21,22]. Plutonium(VI) fluoride reacts vigorously with several organic compounds[23,24] that are stable towards uranium hexafluoride.

Few data are available on the oxidising power of neptunium hexafluoride, merely[20] that it partly oxidises bromine trifluoride to the pentafluoride. In the gas phase uranium(VI) fluoride does not react with molecular bromine, whereas the neptunium compound is reduced to the tetrafluoride[25]. A method has been patented[26] for separating a mixture of uranium and neptunium hexafluorides by reducing the latter on cobalt(II) fluoride granules at 105–220°C to the tetrafluoride. These results indicate that neptunium occupies an intermediate position between plutonium and uranium with respect to the oxidising power of its hexafluoride.

A review[2] stated that vanadium pentafluoride was unable to substitute fluorine for hydrogen atoms in organic compounds, and only in certain cases able to add fluorine to double bonds. Such a description of the oxidising capabilities of the pentafluoride does not correspond to information from other sources. Clark and Emeléus showed[27] that vanadium(V) fluoride was a stronger fluorinating agent than bromine(III) and iodine(V) fluorides, and reacted quantitatively with tetrachloromethane at room temperature to form Freons of the methane series, including tetrafluoromethane. More severe conditions—in an autoclave at 220°C—are required for the reaction between tetrachloromethane and uranium hexafluoride[28-30]. O'Donnell et al., who studied[31-35] the reactivity of fluorides of *d*-elements in Groups V and VI, as well as uranium, in redox and exchange reactions, and later Reynes et al.[36] have shown that the reaction $UF_4 + 2VF_5 \rightarrow UF_6 + 2VF_4$ already occurs at 60°C. Thermodynamic calculation of the change in Gibbs free energy $\Delta G^\circ_{298}$ of this reaction from the standard Gibbs free energies of formation $G^\circ_{f298}$ [37,38] shows that $\Delta G^\circ_{298} = -9$ kcal mole$^{-1}$: i.e. the reaction is thermodynamically possible. The results indicate that the oxidising power of vanadium pentafluoride is greater than that of uranium hexafluoride.

Uranium(VI) fluoride in turn converts tungsten(IV) and molybdenum(V) fluorides into the corresponding hexafluorides[32], and molybdenum hexafluoride oxidises[31] tungsten tetrafluoride to the hexafluoride. Furthermore, uranium hexafluoride is reduced vigorously by tetrachloroethylene[39], whereas molybdenum and tungsten hexafluorides do not react under these conditions[40]. Moreover, molybdenum hexafluoride reacts with tetrachloromethane and tetrachlorosilane, but tungsten hexafluoride does not react with these compounds right up to 220°C.[28,41] These results are consistent with conclusions reached by O'Donnell et al.[32], who arranged the hexafluorides in the reactivity sequence uranium > molybdenum > tungsten.

The oxidising power of molybdenum pentafluoride has not been studied, but the same type of structure as for niobium and tantalum pentafluorides[12] and the similar action of such reagents as ammonia[42], pyridine and its derivatives, and acetonitrile[43,44] indicate only a slight difference in chemical activity. Nevertheless, the molecule contains[5] an unpaired *d*-electron in the outer shell of the molybdenum ion, and is potentially more active. Fairbrother[45] mentions that niobium and tantalum pentafluorides, in contrast to the pentachlorides, exhibit no tendency to reduction and the elimination of halogen. Qualitative observations suggest[33,46] that niobium pentafluoride is rather more strongly oxidising than is tantalum pentafluoride. Brown[47] states that for the pentafluorides the strength of the Lewis acids decreases in the sequence tantalum > niobium > vanadium, i.e. in the reverse order to the decrease in oxidising power.

Thus on the basis of the above results the higher fluorides can be arranged in the sequence

$$PuF_6 > NpF_6 > VF_5 > UF_6 > MoF_6 > WF_6 > MoF_5 \geqslant NbF_5 \geqslant TaF_5$$

of diminishing oxidising power. This sequence is consistent with conclusions reached by Galkin and Tumanov[48] from a thermodynamic investigation of the dissociation of hexafluorides to tetrafluorides, who arranged the hexafluorides in the sequence

$$PuF_6 < NpF_6 < UF_6 < MoF_6 < WF_6,$$

of increasing thermodynamic stability. It is consistent also with an investigation[49] of the action of elementary iodine on uranium(VI) fluoride. The sequence suggests that the oxidising power of fluorides of *d*-elements in the same group becomes weaker with increase in the nuclear charge of the central ion, whereas for *f*-elements the oxidising power increases with the nuclear charge and the number of unpaired *f*-electrons in the outer orbitals.

Table 1. Force constants[50] of metal–fluoride bonds $f_d$, energies of rupture of bonds[51] $E_{M-F}$, and standard enthalpies of formation of fluorides $-\Delta H^\circ_{f,298}$.

| Fluoride | $PuF_6$ | $NpF_6$ | $VF_5$ | $UF_6$ | $MoF_6$ | $WF_6$ | $MoF_5$ | $NbF_5$ | $TaF_5$ |
|---|---|---|---|---|---|---|---|---|---|
| $f_d$, mdyn Å$^{-1}$ | 3.59 | 3.71 | — | 3.78 | 4.73 | 5.13 | — | — | — |
| $E_{M-F}$, kcal mole$^{-1}$ | — | — | 114 | 108 | 105 | 121 | — | 142 | — |
| $-\Delta H^\circ_{f,298}$, kcal mole$^{-1}$ | 407[52] | 459[53] | 341[38] | 510[37] | 372[54] | 411[55] | 347[56] | 414[57] | 435[58] |

It is not without interest to compare the sequence of higher fluorides according to their oxidising power with certain molecular constants and thermodynamic functions of the compounds. Comparison of the data in Table 1 with the suggested reactivity sequence shows that increase in oxidising power is accompanied by a decrease in the metal–fluoride stretching force constants, in the energy of rupture of the bond, and by increase in the standard enthalpies of formation for the penta- and hexa-fluorides of *d*- and *f*-elements.

The higher chlorides of most of the elements considered are regarded by Hammond[59] as stronger acceptors than are the corresponding fluorides, owing to the great electronegativity of fluorine.

In actinide hexafluorides *f*-electrons are included in the bond with the fluorine atom. Bagnall[60] notes that the different spatial configuration of *f*-orbitals from *d*-orbitals may lead to different stereochemical consequences for the octahedral

symmetry inherent in hexafluorides. This would apparently have a definite influence on the chemical properties of the actinide hexafluorides.

The reaction of fluorides of *d*- and *f*-elements with members of various classes of organic compounds will be discussed in the following Sections.

## III. ORGANIC σ-DONORS

### 1. Alkanes, Cycloalkanes, and Halogenated Alkanes

Research on the reaction between alkanes and higher fluorides of *d*- and *f*-elements was connected chronologically with the development of atomic technology, in particular with the manufacture of uranium hexafluoride, when it appeared necessary to produce organic compounds, used as greases and packing, that were resistant to the action of uranium hexafluoride, fluorine, and hydrogen fluoride[61-64].

Straight-chain alkanes right up to n-hexadecane react vigorously with uranium hexafluoride, with charring and the liberation of hydrogen fluoride, uranium tetrafluoride, and intermediate fluorides of uranium[63,64]. Reaction may or may not be accompanied by degradation of the carbon skeleton of the alkane depending on the conditions. A process has been patented[65] for fluorinating alkanes and chloroalkanes containing 1–12 carbon atoms with uranium hexafluoride at 70–600°C.

Colourless molybdenum and tungsten hexafluorides form yellow to orange solutions with n-hexane and cyclohexane. The rate of decomposition in the system formed by molybdenum hexafluoride with n-hexane is 1% $h^{-1}$.[66] Ultraviolet spectral measurements reveal the presence of weak equimolecular complexes ($K_{ass}$ = 0.3–0.6 M).

Addition of vanadium pentafluoride and uranium hexafluoride to n-heptane and cyclohexane produces brown precipitates[67], indicating reduction of the fluorides, apparently to vanadium tetrafluoride and intermediate fluorides of uranium.

In connection with the use[68] of tetrachloromethane for the preparation of uranium tetrafluoride from the hexafluoride a study was made of the reaction of this hexafluoride and several related fluorides, e.g. molybdenum and tungsten hexafluorides, with chlorinated derivatives of methane, ethane, and propane[29,30,63,64,69,70]. It was found that at 25°C uranium hexafluoride was soluble in chloroform, tetrachloromethane, dichloroethylene, pentachloroethane, and perchloroethane[63,64]. A simple eutectic containing 6.5 mole % and melting at −28.9°C occurs in the uranium(VI) fluoride–tetrachloromethane system[71]. At room temperature a solution of the hexafluoride is stable for several weeks. Heating in an autoclave to 150°C leads to an exothermic reaction[63,68], the composition of the reaction products depending on the ratio of the reactants and the temperature. With an equimolecular mixture the products are $UF_5$, $U_2F_9$, $U_4F_{17}$, chlorine, and predominantly Freon 13. A threefold excess of tetrachloromethane yields uranium tetrafluoride, chlorine, and Freon 11. No detailed study of the reaction mechanism has been made; it is suggested that the reaction is catalysed by uranium tetrafluoride[68]. Under normal pressure this reaction occurs over the range 400–500°C.

Even at room temperature plutonium hexafluoride reacts vigorously with tetrachloromethane to form the tetrafluoride with Freons 12 and 13.[22] On reaction with tetrachloromethane at 20°C vanadium pentafluoride, which also possesses strong fluorinating properties, yields[27] a series of chlorofluoro-derivatives of methane up to tetrafluoromethane, with vanadium tetrachloride and trichloride. Molybdenum hexafluoride reacts with tetrachloromethane at 150–220°C to give $Mo(Cl, F)_5$, $CCl_3F$, $CCl_2F_2$, and traces of $CClF_3$. Tungsten(VI) fluoride is inert under these conditions.

Chloro-fluorinated alkanes are considerably more inert than the hydrocarbons and their chloro-derivatives. Thus difluorodichloromethane, chlorotrifluoromethane, and dichlorotetrafluoroethane do not react with plutonium hexafluoride at room temperature[72,73], although such reaction is thermodynamically possible for the first two compounds even with uranium hexafluoride[24]. However, while inert to pure uranium hexafluoride at 150°C, dichlorodifluoromethane partly reacts at this temperature even with uranium during the reduction of plutonium from a mixture of plutonium and uranium hexafluorides[72,73]. This indicates either that reduction by this reactant has a radical mechanism or that the process is catalysed by plutonium fluorides. Study of the binary liquid–liquid systems has shown[74,75] that uranium and molybdenum hexafluorides do not react with dichlorotetrafluoroethane.

Perfluoroalkanes are stable towards all the above fluorides, the most active of which—plutonium hexafluoride—gives a stable solution in n-perfluoroheptane[22]. Vanadium(V), molybdenum(VI), tungsten(VI), and uranium(VI) fluorides are stable in solution in perfluoroalkanes of various chain lengths[61,63,64] and in perfluorinated cyclohexane[64,66], methylcyclohexane[67], and dimethylcyclohexane[76,77]. In the systems formed by tungsten hexafluoride with perfluoro-n-pentane and perfluorocyclopentane the components are miscible in all proportions to form non-ideal solutions[78,79], which indicates the presence of intermolecular interactions. Niobium and tantalum pentafluorides are almost insoluble[67] in perfluoromethylcyclohexane, apparently because of their polymeric structure in the solid state.

According to Mulliken[6] the above alkanes, cycloalkanes, and their chlorinated derivatives are weak Lewis bases or σ-type donors with almost the same basicity (judging by the ionisation potentials) for alkanes and cycloalkanes having the same number of carbon atoms. On interaction of σ-donors and *v*-acceptors such as the higher fluorides of *d*- and *f*-elements, formation of stable complexes should not be observed[6], as is fully confirmed by the above examples. During irreversible oxidative fluorination the alkanes, chloroalkanes, and their cyclic derivatives will gradually become inert to all inorganic fluorides right up to plutonium hexafluoride as the hydrogen and chlorine atoms are successively replaced by fluorine.

### 2. Organosilicon Compounds

Vacant *d*-orbitals of the silicon atom, in contrast to carbon, are closely similar in energy characteristics to the outer *s*- and *p*-orbitals, which has a corresponding effect on the behaviour of silicon.

Tetrachlorosilane reacts[80] with vanadium pentafluoride at room temperature to form vanadium monochloride trifluoride, tetrafluorosilane, and chlorine; with uranium hexafluoride[32] it forms the tetrafluoride, tetrafluorosilane, and chlorine on being heated to 100°C; and with molybdenum hexafluoride it reacts only slightly[31] even above 100°C, giving the mixed compound $Mo_2Cl_3F_6$ and tetrafluorosilane in low yield. No reaction has been detected

in the binary systems formed by tetrachlorosilane with tungsten hexafluoride[31], and with niobium and tantalum pentafluorides[33].

In tetramethylsilane molybdenum and tungsten hexafluorides form red solutions that lose their colour on being frozen, which indicates that stable adducts are absent. Niobium pentafluoride is almost insoluble in this reagent[41].

The reaction of tungsten hexafluoride with methoxytrimethylsilane yields a series of derivatives $(CH_3O)_nWF_{6-n}$ ($n = 1-6$): i.e. it results in complete replacement of fluoride ions by methoxy-groups[81]. The reaction products included tungsten oxide tetrafluoride $WOF_4$ and unidentified compounds. With phenoxytrimethylsilane the products are phenoxytungsten pentafluoride and *cis*- and *trans*-diphenoxytungsten tetrafluoride[82]. The considerable bulk of phenyl in comparison with methyl groups apparently prevents the coordination of more than two around the tungsten atom. Reaction of molybdenum hexafluoride with dimethyldimethoxy-, methyltrimethoxy-, and tetramethoxy-silane yields[83] dimethylsilicon difluoride, methylsilicon trifluoride, and tetrafluorosilane respectively, as well as tetramethoxymolybdenum difluoride and pentamethoxymolybdenum fluoride. Noble and Winfield[84] described the preparation of a series of methoxy- and phenoxy-tungsten(VI) fluorides of general formula $(RO)_nWF_{6-n}$ (where $n = 1-4$ for the methoxy-group, and 1 or 2 for the phenoxy-group) by mixing tungsten hexafluoride with methyltrimethoxy-, dimethyldimethoxy-, and dimethyldiphenoxy-silane. At 80°C *cis*-dimethoxytungsten tetrafluoride decomposes with the formation of $WOF_4.(CH_3)_2O$. The action of various proportions of tetramethoxysilane on tungsten hexafluoride at 20°C yields[85] tetrafluorosilane, methoxytungsten pentafluoride, and *cis*-tetramethoxytungsten difluoride.

When a mixture of tungsten hexafluoride and trimethylsilyldiethylamine[82] is left at 20°C for 24 h, it is converted into bisdiethylaminetungsten tetrafluoride and then into tetrakisdiethylaminetungsten difluoride, the first of these compounds being a monomer and the second a polymer having fluoride bridges. A complex having the ligands in the proportions 3 : 3 was not observed.

Table 2. Products of the reactions of higher fluorides of *d*- and *f*-elements with organosilicon compounds.

| Compound | Colour | M.p. (decomp.), °C | Ref. | Compound | Colour | M.p. (decomp.), °C | Ref. |
|---|---|---|---|---|---|---|---|
| $MoF(OMe)_5$ | — | — | 83 | $WF_4(NEt_2)_2$ | brown | — | 82 |
| $MoF_2(OMe)_4$ | — | — | 83 | $WF_2(NEt_2)_4$ | brown | — | 82 |
| $WF_5(OMe)$ | white | (135), 80—85 | 81, 84, 85, 123, 144 | $TaF_3(NEt_2)_2$ | yellow | 203 | 86 |
| | | | | $NbF_4(NEt)$ | orange | 150 | 86 |
| *cis*-$WF_3(OMe)_3$ | white | 17—19 | 81 | $NbF_3(NEt_2)_2$ | pink | 82 | 86 |
| $WF_3(OMe)_3$ | white | 57—59 | 81 | $NbF_4(NEt_2)_2 \cdot Py$ | brown | 56 | 86 |
| *cis*-$WF_2(OMe)_4$ | — | 82 | 81, 85 | $TaF_4(NEt_2)$ | yellow | 123 | 86 |
| $WF(OMe)_5$ | — | — | 81 | $TaF_4(NEt_2) \cdot Py$ | yellow | 115 | 86 |
| $W(OMe)_6$ | — | — | 81 | $TaF_3(NEt_2)_2 \cdot Py$ | brown | 51 | 86 |
| $WF_5(OPh)$ | red | 80 | 82, 84, 123, 144 | $TaF_4(NEt_2) \cdot 4MePy$ | yellow | 122 | 86 |
| $WF_4(OPh)_2$ | red | — | 82, 84 | $TaF_3(NEt_2)_2 \cdot 4MePy$ | brown | 20 | 86 |

The action of trimethylsilyldiethylamine on niobium and tantalum pentafluorides yields fluorotrimethylsilane and a series of compounds (Table 2) in which one or two fluoride ions have been replaced by a diethylamino-group[86]. On treatment with pyridine or 4-methylpyridine these compounds form adducts in which the coordination number has increased to 6. Replacement of >2 fluoride ions in the pentafluorides was considered to be disadvantageous for steric and electronic reasons, since dialkylamino-ligands, being good donors for *d*-elements, in this case form considerably weaker Lewis acids than the pentafluorides—the diethylamino-tetrafluoride and the bisdiethylamino-trifluoride—which are already incapable of reaction with a base (tetrakisdiethylaminotungsten difluoride can be obtained from tungsten hexafluoride).

It follows from the above account that tetrachlorosilane reacts only with fairly strongly oxidising fluorides such as those of vanadium(V), uranium(VI), and molybdenum(VI). Higher fluorides of niobium, tantalum, molybdenum, and tungsten readily undergo substitution with organosilicon compounds containing alkoxy-, phenoxy-, and dialkylamino-groups:

$$MF_6 + R_nSi(OR)_{4-n} \rightarrow MF_{2+n}(OR)_{4-n} + R_nSiF_{4-n},$$

or

$$MF_6 + nRO^- \rightarrow MF_{6-n}(OR)_n + nF^-,$$

i.e. the substrate molecule is attacked by the nucleophilic group $RO^-$, which is a stronger nucleophile than the fluoride ion, and for this reason displaces the latter from the coordination sphere of the central ion. Thus nucleophilic substitution of the $S_N$ type occurs formally with penta- and hexa-fluorides of *d*-elements. Partial or complete substitution of fluoride ions in the electrophilic substrate molecule is observed depending on the conditions and on the steric characteristics of the entering group. Available data support rather an associative mechanism of nucleophilic substitution of the fluoride ion in pentafluorides and in tungsten and molybdenum hexafluorides. Thus exchange of fluorine is slowed down for *cis*-tetramethoxytungsten and tetrakisdialkylaminotungsten difluorides, which may indicate the formation of intermediate seven-coordinated compounds. Octahedral complexes having the electron confirguration $d^0$, $d^1$, $d^2$ and a partly covalent bond can be regarded[88] as coordinatively unsaturated compounds, capable under certain conditions of giving complexes of coordination number >6 by an $S_N2$ type of associative mechanism; on the other hand, an $S_N1$ dissociative mechanism of substitution is more typical of octahedral complexes having a large number of unpaired *d*-electrons. The definite effect of the nature of the entering group on the rate of substitution in the above reactions of pentafluorides and of tungsten and molybdenum hexafluorides with nucleophilic reagents can apparently be regarded as some confirmation of an associative mechanism.

It is of interest to examine the above reactions in terms of bond strengths and the electronic character of the reagents. The silicon–oxygen bond is thermodynamically more stable than the silicon–carbon bond (108 and 76 kcal $mole^{-1}$ respectively)[89], but the former is relatively easily cleaved by electrophilic reagents (such as the higher fluorides of *d*-elements in the present case), whereas the silicon–carbon bond is relatively inert in these reactions. Under electrophilic attack the silicon–chlorine bond (91 kcal $mole^{-1}$) is also more reactive than the less stable silicon–carbon and carbon–chlorine bonds (81 kcal $mole^{-1}$), judged by the action of tetrachlorosilane and tetrachloromethane on molybdenum(VI) fluoride[31,41]. It must be supposed that rupture of silicon–carbon bonds will be observed on attack by less electrophilic reagents than the higher fluorides of *d*-elements. Silicon–nitrogen and silicon–oxygen bonds show the same behaviour in the above reactions.

The organosilicon compounds studied are σ-donors in relation to the higher inorganic fluorides, and theoretically[6] are unable to form any stable complexes in a σ-donor–$v$-acceptor system, as is illustrated by the above results. With increase in donor strength towards the above fluorides of $d$-elements the organosilicon compounds can be arranged in the sequence

$$SiR_4 \leqslant SiCl_4 < R_3Si(OPh) < R_3Si(OR) < R_2Si(OR)_2 < RSi(OR)_3 < Si(OR)_4 < R_3Si(NEt_2),$$

which corresponds to increase in nucleophilicity of groups replacing the fluoride ion, in the sequence

$$R^- \leqslant Cl^- < PhO^- < RO^- < R_2N^-.$$

## IV. π-DONORS

### 1. Alkenes and their Halogenated Derivatives

Ethylene and trichloroethylene were tried[64,68] as reductants for uranium(VI) fluoride, and expectedly proved more active than alkanes. The hexafluoride is reduced to uranium tetrafluoride even at −50°C by liquid trichloroethylene, which adds two fluorine atoms at the double bond. In the gas phase at 75–480°C this reaction also yielded the tetrafluoride, with hexachlorobenzene as one of the organic products[28]. In both cases the precipitated tetrafluoride was contaminated with organic compounds of unknown composition[28,90].

Reduction by tetrachloroethylene at 260–315°C yields[39] uranium tetrafluoride uncontaminated by any organic impurities. Analysis of the material balance in the patent[39] shows that the organic reaction product has the empirical formula $C_2ClF_5$. However, the appearance of Freons 114 and 116 is thermodynamically most probable[24] under these conditions; perhaps the reaction products comprise an equimolecular mixture thereof. Reddish-brown and yellow solutions respectively (stable in the absence of moisture) are formed in the binary liquid–vapour systems comprising tetrachloroethylene with molybdenum and tungsten hexafluorides. Calculation of excess free energies from published data[40] indicates the presence of approximately equimolecular adducts in the liquid phase. These compounds are unstable, since the hexafluorides can be removed from the solution when dry nitrogen is blown through.

The solubility of molybdenum pentafluoride and hexafluoride in hexachlorobuta-1,3-diene has been studied[91] between −25 and +120°C, red–violet solutions being obtained in all cases. Complete miscibility between the hexafluoride and the chlorocarbon is observed at 5–30°C. The liquid pentafluoride gives with this solvent a system comprising two liquids of limited miscibility with a consolute point at 105.3°C representing 0.635 mole fraction of molybdenum(V) fluoride. Neither the pentafluoride nor the hexafluoride was reduced under the experimental conditions.

As hydrogen and chlorine atoms in alkanes are replaced by fluorine, the sensitivity to electrophilic attack diminishes, while that to nucleophilic attack increases[92–94]. For this reason the above relatively weakly oxidising inorganic fluorides—at least those to the right of uranium hexafluoride—will apparently not react with fluoroalkenes.

Alkenes and chloroalkenes act as weak π-donors towards electrophilic reagents[6]. Unstable π-complexes are formed in these systems by means of π-electrons of the double bonds supplied to the acceptor.

Equimolecular π–$v$ adducts, formed[40] by tetrachloroethylene with tungsten and molybdenum hexafluorides respectively, can apparently be regarded as intermediates in the reduction of the hexafluorides followed by addition of halogens at the double bond. The reduction of uranium hexafluoride to the tetrafluoride by chlorinated ethylenes[28,39,90] apparently takes place in two stages: addition of thorime atoms to the chloroethylenes is followed by substitution of chlorine by fluorine atoms in the chlorofluoroalkanes.

### 2. Aromatic Compounds

Benzene, toluene, and xylenes react with uranium hexafluoride at room temperature to form the tetrafluoride, hydrogen fluoride, and carbonaceous substances of unknown composition[64,95]. Nitrobenzene yields a turbid red solution[64]. Molybdenum hexafluoride is rapidly reduced in benzene and xylene to give a dark blue precipitate[95]. Binary systems of tungsten hexafluoride with benzene, toluene, and $p$- and $m$-xylenes have a red colour[41,95–97] and give equimolecular adducts. It was originally stated[98] that, in a bomb at 110°C, the hexafluoride is reduced by benzene to tungsten tetrafluoride. However, these results have not been confirmed[41], since heat-treatment of mixtures of the hexafluoride with benzene and toluene at 110°C or exposure to ultraviolet radiation has given a non-volatile, viscous dark brown liquid in which the ratio of fluorine to tungsten is ~4.7 and ~4.5 for the mixtures with benzene and with toluene respectively.

Addition of perfluorotoluene to a stable colourless solution of vanadium pentafluoride in perfluoromethylcyclohexane produces a red coloration, which then disappears. Similar changes have been observed in the absence of a diluent, as well as with hexafluorobenzene and perfluoro-$p$-xylene[67]. This indicates that the pentafluoride is reduced with preliminary formation of an unstable intermediate compound. Solutions of uranium hexafluoride in hexafluorobenzene, perfluorotoluene, and perfluoro-$p$-xylene have an orange colour[67,95,97], with those in the second solvent the most stable. A similar effect has been observed[95] with vanadium(V) and iodine(VII) fluorides. Molybdenum hexafluoride forms with hexafluorobenzene and octafluorotoluene orange-brown solutions, containing equimolecular adducts and stable for at least 24 h. The system with perfluoro-$p$-xylene is the least stable[95]. The pale yellow solutions of tungsten hexafluoride in perfluorinated benzene, toluene, and xylenes do not decompose[41,95,97] for a long time. Since niobium and tantalum pentafluorides are sparingly soluble in perfluoroarenes[67], no information is available on their behaviour in these solvents.

A recent paper[99] reports that the hydrogenation of benzene in the presence of an equimolecular mixture of hydrogen and tantalum(V) fluorides at 200°C gives high yields of toluene and ethylbenzene. Alkyl radicals are assumed[99] to be generated during the saturation of aromatic to alicyclic systems, after which ring cleavage occurs to give alkanes that interact with the radical-ions of benzene. It is noteworthy that the use of niobium and tantalum pentafluorides as Friedel–Crafts catalysts had been reported earlier[45].

Richardson and Bartlett have obtained[100] salts of the cation $C_6F_6^+$ by condensing hexafluorobenzene and tungsten hexafluoride on powdered $AsO_2F_6$, $SbO_2F_6$, and $Sb_2O_2F_{11}$ at −196°C, which are then allowed to warm up slowly to 0°C. The resulting salts have the composition $C_6F_6^+AsF_6^-$,

$C_6F_6^+SbF_6^-$, and $C_6F_6^+Sb_2F_{11}^-$, and gradually decompose at room temperature. The action of nitric oxide on the arsenic salt leads to quantitative formation of benzene and $AsNOF_6$.

The system comprising tungsten hexafluoride and a solution of naphthalene in tetrachloromethane has an orange–brown colour and equimolecular adducts[95]. In contrast, octafluoronaphthalene loses its colour when the supply of the hexafluoride ceases[82]. This is indirect evidence of the brief existence of adducts in this system. A product of the fluorination of dimethylnaphthalene, perfluoro-2-methylbicyclo[4,4,0]decane, forms stable colourless solutions with molybdenum, tungsten, and uranium hexafluorides[101].

The above results indicate that both aromatic hydrocarbons and their halogenated derivatives behave as weak $\pi$-donors towards the higher fluorides of the *d*- and *f*-elements considered, as also towards other halides, e.g. chlorides[6,102]. Interactions of such $\pi$–*v* type are characteristically weak[6]. Hammond et al.[59,103], who undertook a systematic study based on spectrophotometric measurements of equilibrium constants, enthalpies, and thermochromism of systems formed by aromatic compounds and their halogenated derivatives with various halides of *f*- and *d*-elements in Groups IV–VI of the Periodic System, described all such interactions as "extraordinarily weak or almost contact". They attribute this[59] to unfavourable steric factors involved in contact between planar aromatic systems and the sperically symmetrical hexafluoride molecules, and to the slight overlap between the orbitals of the aromatic ligands and those of the halide molecules. Plane–plane interactions would have been sterically more favourable than the plane–sphere interactions.

Stronger interactions occur in the Menshutkin complexes (of antimony trichloride with arenes)[102], apparently owing to change in the geometry of the acceptor molecule and greater availability of its orbitals for displacing the electrons of the donors. Usanovich et al.[104] have investigated Menshutkin complexes by $\gamma$-resonance spectroscopy, and shown that complex formation is due to the transfer of $\pi$-electrons of the aromatic ring to *p*-orbitals of the antimony atom. In the fluorides under consideration here such a mechanism of electron transfer, it appears, will be weakened by the greater electronegativity of fluoride ions.

## V. *n*-DONORS

### 1. Nitrogen-containing Compounds

It seens useful to begin with ammonia our consideration of the interaction of higher fluorides of *d*- and *f*-elements with nitrogen-containing organic compounds, since many of these are its derivatives. The reaction products are listed in Table 3.

Vanadium pentafluoride reacts with ammonia, ethylenediamine, tetramethylethylenediamine, and pyridine with reduction and the formation of $VF_4.L$, adducts of polymeric structure[12,105,106]. In ammoniacal uranium hexafluoride the pentafluoride is formed between −50 and −30°C, a mixture with $NH_4UF_5$ as the temperature rises to 0°C, and the latter compound at 100°C. 2-Fluoropyridine reacts[107] with uranium hexafluoride to give an adduct $UF_6.2NC_5H_4F$; in solution in dichloromethane the adduct is $UF_6.NC_5H_4F$.

A process has been patented[108] for separating a mixture of hydrogen and uranium(VI) fluorides by means of fluoroaliphatic and fluoroheterocyclic amines and diamines. The separation is based on the formation by these compounds of a stable adduct with hydrogen fluoride, while the hexafluoride is inert towards them.

At −130°C molybdenum hexafluoride is reduced by ammonia to the pentafluoride[109], which forms several ammines depending on the conditions. Keeping the

Table 3. Products of the reactions of higher fluorides of *d*- and *f*-elements with nitrogen-containing organic compounds.

| Compound | Colour | M.p.(decomp.), °C | Ref. | Compound | Colour | M.p.(decomp.), °C | Ref. |
|---|---|---|---|---|---|---|---|
| $VF_4 \cdot NH_3$ | orange | (250) | 12,105 | $WF_6 \cdot TMEn$ | — | (95) | 107 |
| $VF_4 \cdot 3En$ * | — | — | 105 | $3WF_6 \cdot 2TMEn$ | — | (155) | 107 |
| $VF_4 \cdot TMEn$ ** | — | — | 106 | $WF_6 \cdot Me_2NCOH$ | — | — | 107 |
| $VF_4 \cdot Py$ | pinkish grey | (150) | 12,105 | $2WF_6 \cdot 3Py$ | white | (115) | 107,112 |
| $UF_4NH_4F$ | yellow-green | (400) | 30 | $WF_6 \cdot 2Py$ | white | (146) | 113 |
| $UF_6 \cdot 2NC_5H_4F$-β | — | — | 107 | $WF_6 \cdot Py$ | white | 104 | 113 |
| $UF_6 \cdot NC_5H_4F$-β | — | — | 107 | $Nb(Ta)F_5 \cdot 2NH_3$ | — | — | 42,105,114 |
| $MoF_6 \cdot 2Py$ | yellow | — | 107 | $Nb(Ta)F_5 \cdot Me_3N$ | — | — | 13,117 |
| $MoF_6 \cdot 2CH_3CN$ | — | — | 111 | $Nb(Ta)F_5 \cdot Et_3N$ | red-brown | — | 118,119 |
| $MoF_5 \cdot NH_3$ | red-brown | — | 42,43,110 | $Nb(Ta)F_5 \cdot 2EtNH_2$ | green | — | 118 |
| $MoF_5 \cdot CH_3CN$ | white | — | 44 | $Nb(Ta)F_5 \cdot Et_2NH$ | red-brown | — | 118 |
| $MoF_5 \cdot 2CH_3CN$ | white | — | 43,111 | $Nb(Ta)F_5 \cdot CH_3CN$ | — | — | 44,107 |
| $MoF_5 \cdot CH_2ClCN$ | white | — | 44 | $Nb(Ta)F_5 \cdot CH_2ClCN$ | — | — | 44,116 |
| $MoF_5 \cdot Py$ | — | — | 40,43 | $Nb(Ta)F_5 \cdot EtCN$ | — | — | 44,116 |
| $MoF_5 \cdot 2Py$ | pink | — | 43 | $NbF_5 \cdot 2Me_2NCOH$ | — | — | 120 |
| $WF_6 \cdot 4NH_3$ | brown | — | 13,112 | $NbF_5 \cdot 1,6En$ | — | — | 115 |
| $WF_6 \cdot N_2H_4$ | — | — | 111 | $Nb(Ta)F_5 \cdot 2Py$ | — | — | 44,114,115,120 |
| $WF_6 \cdot 2N_2H_4$ | — | — | 107 | $TaF_5 \cdot 2$-Me—Py | — | — | 44 |
| $WF_6 \cdot 3MeNH_2$ | white | — | 112 | $TaF_5 \cdot 4$-Me—Py | — | — | 44 |
| $WF_6 \cdot Me_3N$ | — | (150) | 107,113 | | | | |
| $2WF_6 \cdot 3Me_3N$ | — | (120) | 107 | | | | |

* En = tetraethylenediamine.

** TMEn = tetramethylethylenediamine.

pentafluoride in an atmosphere of ammonia for a long time yields a monoammine[42,43,110]. With pyridine[107] and acetonitrile[111] the hexafluoride gives adducts of composition $MoF_6.2L$.

Tungsten hexafluoride reacts with liquid ammonia[13,112] to give the tetrammine $WF_6.4NH_3$, and with hydrazine in acetonitrile[107,111] to yield 1 : 1 and 1 : 2 compounds, whereas molybdenum hexafluoride is reduced[111] by hydrazine with separation of the tetrafluoride, the complex $MoF_4.2NH_4F$, nitrogen, and ammonia. The reaction of tungsten hexafluoride with methylamine[112] gives $WF_6.3CH_3NH_2$, and with trimethylamine[107,113] $WF_6.(CH_3)_3N$ and $2WF_6.3(CH_3)_3N$ are formed; tetramethylethylenediamine[107] gives the complexes $WF_6.C_2H_4N_2(CH_3)_4$ and $3WF_6.2C_2H_4N_2(CH_3)_4$, dimethylformamide[107] $WF_6.DMF$, and pyridine $2WF_6.3C_5H_5N$,[107,112] $WF_6.2C_5H_5N$, and $WF_6C_5H_5N$.[113] The fluorine-19 nuclear magnetic resonance spectra of the first of these pyridine complexes show that one of the fluorine atoms is not equivalent to the other five, while the octahedral symmetry of the compound is preserved[107,112]. Conductivity measurements suggest[107] the structure $2[WF_5.C_5H_5N]^+F^-.C_5H_5N$.

Fluorides of quinquevalent niobium, tantalum, and molybdenum, in contrast to other pentahalides, e.g. the chlorides, do not undergo reduction on reaction with nitrogen based[114,115]. With ammonia they form adducts[42,105,114] of the types $Nb(Ta)F_5.2NH_3$ and $MoF_5.NH_3$; with acetonitrile, chloroacetonitrile, and propionitrile[44,116] equimolecular complexes are formed, but molybdenum pentafluoride forms also[43,111] $MoF_5.2CH_3CN$. With trimethylamine niobium and tantalum pentafluorides give[13,117] equimolecular complexes. Cryoscopic measurements enabled Buslaev et al.[118] to demonstrate the establishment of the equilibrium

$$2\{NbF_5 \cdot NEt_3\} \rightleftharpoons [NbF_6]^- + [NbF_4 \cdot 2NEt_3]^+$$

results which have since been confirmed by ebullioscopic and conductometric investigations on the system[119]. Treatment of molybdenum pentafluoride with pyridine yields[43] 1 : 1 and 1 : 2 adducts, whereas those of niobium and tantalum give 1 : 2 adducts[44,114,115]; the last two compounds are stable in air, but decompose when heated. Tantalum(V) fluoride forms equimolecular adducts with 2- and 4-methylpyridines, and perhaps also a 1 : 2 adduct with the latter. Investigation of the infrared spectra suggests that $MF_5.L$ adducts are monomeric, with symmetry lower than would correspond to the $C_{4v}$ point group, whereas adducts of type $MF_5.2L$ may be ionised[44,114] $[MF_4L_4]^+[MF_6]^-$.

According to the first ionisation potentials[6] and the above experimental results the donor strength of nitrogen-containing organic compounds increases in the sequence

$$MeCN < EtCN < Py < NH_3 < MeNH_2 < EtNH_2 < Me_2NH < Et_2NH < Me_3N < Et_3N.$$

All these compounds have a lone pair of electrons on the nitrogen atom and are $n$-donors, strong Lewis bases. With the above fluorides of $d$- and $f$-elements nitrogenous compounds are able to form quite stable $n$-donor–$v$-acceptor adducts. The above sequence shows that the donor power increases on passing from heteroaromatic amines to primary, secondary, and tertiary aliphatic amines having small groups. It becomes weaker as hydrogen atoms in the alkyl groups are replaced by fluorine atoms, and in perfluoroalkylamines is almost completely absent[5]. Fluorine as a substituent has a similar effect on arylamines and heteroaromatic amines. This is supported by a patent[108] indicating that perfluorinated alkylamines, dialkylamines, peperidine, and pyrrolidine do not exhibit donor properties towards uranium hexafluoride.

Relatively strongly oxidising fluorides, such as those of vanadium(V), uranium(VI), and molybdenum(VI), are reduced by ammonia and, apparently, other organic compounds of greater basicity, and in the lower state of oxidation form quite stable adducts with excess of the organic reagent. In these complicated reactions not only does the state of oxidation of the central ion change but also the coordination number, with simultaneous substitution of ligands.

In reactions in which the inorganic fluorides do not undergo redox processes with nitrogen-containing organic compounds the coordination number increases by the addition of fresh organic ligands to the central atom. All these reactions can be included among nucleophilic additions of the $Ad_N$ type. The most characteristic coordination numbers of the metals in these adducts are $V^{IV}$ 5 and 6, $M^V$ (M = Nb, Ta, Mo) 6 and 7, $Mo^{VI}$ 8, $W^{VI}$ 7–9, $U^{IV}$ 5, and $U^{VI}$ 7 and 8. The maximum coordination numbers are observed with ligands of small bulk—ammonia, primary alkylamines—whereas ligands having less favourable steric characteristics, e.g. tertiary amines, form complexes having lower coordination numbers. Pentafluorides of $d$-elements exhibit a clear tendency to acquire a six-coordinated structure. This indicates that the adducts have an octahedral structure, which is probably the most advantageous under these conditions.

Table 4. Products of the reaction of organophosphorus compounds with fluoride of $d$- and $f$-elements.

| Compound | Colour | M.p. (decomp.), °C | Ref. | Compound | Colour | M.p. (decomp.) °C | Ref. |
|---|---|---|---|---|---|---|---|
| $WF_6 \cdot PPh_3$ | — | (85) | 107 | $WF_6 \cdot \{OP(OPh)_3\}_n$ | red | — | 124 |
| $WF_6 \cdot PMe_3$ | orange | (80) | 113 | $WOF_4 \cdot OP(OMe)_3$ | — | — | 124 |
| $[(MeO)_3PMe]^+[WOF_5]^-$ | orange | (90) | 123 | $WOF_4 \cdot OP(Me)(MeO)_2$ | — | — | 124 |
| $(MeO)_2MePO \cdot WOF_4$ | — | — | 123 | $[W_2O_2F_9]^-[(MeO)_3PMe]^+$ | — | — | 124 |
| $MeOWF_5 \cdot 1,3\,Py$ | brown | — | 123 | $Nb(Ta)F_5 \cdot L$; L = $(PhO)_3PO$, $(BuO)_3PO$, $Bu_3PO$ | — | — | 135 |
| $PhOWF_5 \cdot Me_3N$ | red | — | 123 | $Ph_3PO$, $\{(CH_3)_2N\}_3PO$ | | | |

## 2. Phosphorus-containing Compounds

Tervalent phosphorus and nitrogen exhibit definite similarity in their chemistry, which is lost in states of higher oxidation. Table 4 lists products formed by several phosphorus-containing compounds with fluorides of $d$- and $f$-elements. Vanadium(V) fluoride is reduced by phosphorus trichloride[80] to vanadium chloride trifluoride, and by phosphorus trifluoride[35] to vanadium(IV) fluoride; in both cases phosphorus is oxidised to its pentafluoride. Phosphorus trichloride and trifluoride both convert uranium hexafluoride into the tetrafluoride[32,121], with temperatures of 150–300 °C regarded as optimum. Phosphorus trifluoride is used to convert molybdenum hexafluoride into the pentafluoride[31,122], and tungsten hexafluoride into the tetrafluoride[31]. Niobium and tantalum pentafluorides do not react with phosphorus trifluoride, but undergo exchange with the trichloride and tribromide, being converted ultimately into the corresponding pentabromides or pentachlorides and phosphorus trifluoride[33].

The $^{19}F$-n.m.r. spectra of the adduct $WF_6.(CH_3)_3P$ in acetonitrile show that the tungsten is surrounded by six equivalent fluorine atoms[107,113]. It is suggested[113] that, as in the corresponding adduct with trimethylamine, a loose seven-coordinated structure is present in this compound.

At temperatures above 0°C tungsten hexafluoride reacts vigorously with trimethyl phosphite to give a dark orange liquid, whose composition depends on the reaction conditions[123], in particular on the ratio of the reactants. The reaction can in general be represented by the equations

$$(MeO)_3P + WF_6 \rightarrow (MeO)_2PF + MeOWF_5$$

$$(MeO)_3P + MeOWF_5 \rightarrow [(MeO)_3PMe]^+ \cdot [WOF_5]^-.$$

The formation of methyltrimethoxyphosphonium oxopentafluorotungstate shows that, in the presence of a suitable substrate, methoxytungsten pentafluoride develops a tendency to lose the methyl group as a methyl cation, which coordinates with the nucleophilic phosphorus atom or a fluoride ion:

$$MeOWF_5 \rightarrow [Me^+ + WOF_5^-] \rightarrow MeF + WOF_4.$$

This compound reacts with benzene to give toluene[123]:

$$MeOWF_5 + C_6H_6 \rightarrow C_6H_5Me + HF + WOF_4.$$

It is assumed that such reactions do not take place with phenoxytungsten pentafluoride. At 90°C the complex phosphonium salt decomposes:

$$[(MeO)_3PMe]^+ \cdot [WOF_5^-] \rightarrow WOF_4 \cdot OP(Me)(OMe)_2 + MeF.$$

Dimethyl methylphosphonate is formed from trimethyl phosphite by a Michaelis–Arbuzov rearrangement in the presence of the electrophilic catalyst tungsten hexafluoride, and gives the tungsten oxide fluoride an adduct in which the ligand occupies a *trans*-position with respect to the oxygen atom. Methoxytungsten and phenoxytungsten pentafluorides, like tungsten hexafluoride, are Lewis acids; the phenoxy-complex is converted on treatment with trimethylamine into a non-volatile red 1 : 1 adduct; methoxytungsten pentafluoride reacts with pyridine to give $CH_3OWF_5.1.3C_5H_5N$. The above results show that the reactions of tungsten hexafluoride with alkylphosphines, which contain only carbon–phosphorus bonds, are essentially additions similar to the reactions with amines. Attack by electrophilic reagents such as the hexafluoride on alkyl and aryl phosphites leads to rupture of a phosphorus–oxygen bond and replacement of an alkoxy-group by a fluorine atom.

Walker and Winfield[124] have investigated the reaction between tungsten hexafluoride and compounds containing a four-coordinated phosphorus atom. Even in benzene at 20°C triphenyl phosphate is converted into a red precipitate of undetermined composition. At 20°C trimethyl phosphate in proportions of 3–1 relative to tungsten hexafluoride gives after 2 h a mixture of phosphoryl and methyl fluorides, methoxytungsten pentafluoride, hexafluorophosphate and $W_2O_2F_9^-$ ions, and the equimolecular adduct of tungsten oxide tetrafluoride and trimethyl phosphate. It is assumed[124] that the hexafluorophosphate ion and methyl fluoride are formed from methoxytungsten pentafluoride and trimethyl phosphate. In the authors' opinion the presence of the hexafluorophosphate ion is due to the formation of trifluorodimethoxyphosphorane, present as tetramethoxyphosphonium hexafluorophosphate. At 20°C a mixture of tungsten hexafluoride, with dimethyl methylphosphonate passes into a mixture of methyldifluorophosphine oxide, methyl fluoride, the adduct $WOF_4.CH_3PO.(OCH_3)_2$, and the salt $[(CH_3O)_3PCH_3]^+[W_2O_2F_9]^-$. With dimethyl hydrogen phosphite at −80°C the hexafluoride gives phosphorus trifluoride and a non-volatile colourless deposit, which at 20°C rapidly becomes dark blue[124,125].

The above results indicate that alkyl phosphites and phosphates with tungsten hexafluoride undergo substitution at the site of rupture of a phosphorus–oxygen bond with subsequent exchange of alkoxy-groups and a fluoride ion. In view of the considerable difference in energy between bonds formed by phosphorus with carbon and with oxygen respectively (63 and 95 kcal mole$^{-1}$) it must be supposed that in organic derivatives of phosphorus the latter are considerably more subject than the former to the action of electrophilic reagents, and readily undergo exchange.

Table 5. Products of the reactions of higher fluorides of *d*- and *f*-elements with oxygen- and sulphur-containing compounds.

| Compound | Colour | M.p.(decomp.), °C | Ref. | Compound | Colour | M.p. (decomp.), °C | Ref. |
|---|---|---|---|---|---|---|---|
| $MoF_6 \cdot Me_2O$ | — | — | 43 | $WF_6 \cdot Me_2SO$ | — | — | 141 |
| $MoF_6 \cdot Me_2S$ | — | — | 43 | $WOF_4 \cdot (RO)_2SO$ | — | — | 123 |
| $MoOF_4 \cdot (MeO)_2SO$ | — | — | 83 | $[WOF_5]^-[(RO)_3S]^+$, R=Me; Et; Ph | — | — | 123 |
| $MoF_5 \cdot Me_2O$ | white | (60) | 43 | $NbF_5 \cdot Me_2O$ | red | 31.5 | 117,120,136—138 |
| $MoF_5 \cdot Me_2S$ | yellow | (20) | 43 | $NbF_5 \cdot Me_2S$ | white | 76.2 | 44,136,137 |
| $WF_6 \cdot Et_2O$ | — | — | 96,129,135 | $NbF_5 \cdot Et_2O$ | — | −7.8 | 13,123,136—138 |
| $WF_5(OEt)$ | — | — | 123,144 | $NbF_5 \cdot Et_2S$ | — | 85 | 13,123,136—138 |
| *cis*-$WF_4(OEt)_2$ | — | — | 129 | $NbF(OEt)_4$ | yellow | 35 | 133 |
| $WOF_4 \cdot Et_2O$ | — | (25) | 129,135 | $NbF_{5-n}(OEt)_n$, $n=1-3$ | — | −20 ÷ −60 | 133 |
| $WF_6 \cdot Et_2S$ | yellow | (20) | 115,135 | $NbF_5 \cdot Me_2SO$ | — | — | 44,116,117 |
| $WF_6 \cdot 2Et_2Se$ | orange | (20) | 115,135 | $NbF_5 \cdot 2Me_2SO$ | — | 44 | 123,139,142,143 |
| $WOF_4 \cdot EtOH$ | — | — | 129 | $TaF_5 \cdot Me_2O$ | red | 80 | 117,123,136—138 |
| $WSF_4 \cdot EtSH$ | — | — | 131 | $TaF_5 \cdot 2Me_2O$ | — | — | 117 |
| $WF_5(SEt)$ | — | — | 131 | $TaF_5 \cdot Me_2S$ | white | 66,5 | 44,136,137 |
| *trans*-$WF_4(SEt)_2$ | — | — | 131 | $TaF_5 \cdot Et_2O$ | — | −17.8 | 13,111,136,137 |
| $WF_5S(SEt) \cdot EtSH$ | — | — | 131 | $TaF_5 \cdot Et_2S$ | — | — | 13,111,136,137 |
| $WF_5(OMe)$ | white | 85 (135) | 123,144 | $TaF(OEt)_4$ | yellow | 30 | 133 |
| *cis*-$WF_4(OMe)_2$ | white | 18 (80) | 81,84 | $TaF_{5-n}(OEt)_n$, $n=1\div3$ | — | −20 ÷ −60 | 133 |
| *trans*-$WOF_4 \cdot Me_2O$ | white | 10 (20) | 84,135 | $TaF_5 \cdot Me_2SO$ | — | — | 44,116,117,139 |
| $WF_5(OPh)$ | red | 80 (180) | 82,84,123,144 | $TaF_5 \cdot 2Me_2SO$ | — | 63,5 | 116,139 |
| $WF_4(SPh)_2$ | — | — | 131 | | | | |
| $WSF_3(SPh) \cdot CH_3CN$ | — | — | 131 | | | | |

In the case of triphenyl phosphate, however, cleavage of a phosphorus–oxygen bond is not observed, which may be attributable to a change in the character of the bond or in its accessibility to electrophilic attack resulting from the presence of an aromatic ring instead of an alkyl group.

The reaction of a trialkyl phosphate with tungsten hexafluoride can presumably be written

$$(RO)_3PO + 3WF_6 \rightarrow 3ROWF_5 + POF_3.$$

In the case of dialkyl alkylphosphonates the alkylphosphonic difluorides are formed, but not phosphoryl trifluoride, since the carbon–phosphorus bond is not involved in the reaction (at least at 20°C).

From theoretical considerations[126] and the above results it may be concluded that the donor power of tervalent phosphorus compounds towards the compounds surveyed here increases in the sequence

$$PF_3 < PCl_3 < PBr_3 < P(Ph)_3 < P(OMe)_3 < P(Me)_3.$$

The corresponding sequence for organic compounds of four-coordinated phosphorus is

$$(PhO)_3PO < (MeO)_3PO < (MeO)_2MePO.$$

Despite the absence of data for alkyl dialkylphosphinates and trialkylphosphine oxides in relation to tungsten hexafluoride, it may be supposed that the variation in their donor strength will be similar to that established[127] for uranyl and plutonium(VI) nitrates:

$$(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO.$$

A study[128] of the reaction of niobium and tantalum pentafluorides with tributylphosphine and triphenylphosphine oxides, tributyl phosphate, and hexamethylphosphoramide revealed in all cases the formation of adducts $MF_5.L$. Tributylphosphine oxide replaces fluorine in the $MF_5$ molecule to give *cis*- and *trans*-$[MF_4((CH_4H_9)_3PO)_2]^+ . [MF_6]^-$. The donor power of the organophosphorus ligands increases in the sequence

$$(PhO)_3PO < (BuO)_3PO < Ph_3PO < [(CH_3)_2N]_3PO < Bu_3PO.$$

### 3. Oxygen- and Sulphur-containing Compounds

#### (*a*) Alcohols and thiols

Treatment of tungsten hexafluoride with ethanol produces a colourless solution[96], in which Buslaev et al.[129] established the presence of the anion $WOF_5^-$, indicating the considerable tendency of tungsten to form a multiple bond with oxygen. Other reaction products present are *cis*-diethoxytungsten tetrafluoride and $WOF_4.C_2H_5OH$ with a *trans*-arrangement of the oxygen atom and the alcohol molecule. Examination by the same workers of the stereospecificity of substitution in octahedral $d^0$ complexes[130] with ligands capable of forming multiple bonds with the central atom has established a *cis*-effect for a multiply bonded ligand, i.e. substitution primarily of a ligand in a *cis*-position relative to the multiply bonded ligand.

Treatment of a solution of ethanethiol in acetonitrile with tungsten hexafluoride yielded products analogous to those obtained with ethanol[131] (Table 5). A small excess of the thiol gives the unstable ethylthiotungsten pentafluoride, when then passes into the more stable *trans*-diethylthiotungsten tetrafluoride (with ethanol *cis*-diethoxytungsten tetrafluoride is obtained). With increase in the excess of ethanethiol adducts—$WSF_4.HSC_2H_5$ and $C_2H_5SWSF_3.HSC_2H_5$—are formed with the multiply bonded sulphur atom *trans* to the ligand molecule. Compounds of similar structure solvated by acetonitrile are present as intermediates. With benzenethiol the hexafluoride gives[131] the stable *trans*-diphenylthiotungsten tetrafluoride, which after a long time passes into the adduct $C_6H_5SWSF_3.CH_3CN$; no product having the composition $C_6H_5SWF_5$ has been observed.

In absolute ethanol niobium pentafluoride forms an electrically conducting dark red solution. The Nb-n.m.r. spectra[93] indicate the presence of the hexafluoroniobate anion, but no cation is detected[132]. Buslaev et al.[133] suggested that the complex anion is probably accompanied in this system by a cation that dissociates according to the scheme

$$[NbF_4(EtOH)_2]^+ \rightarrow NbF_4(OEt) \cdot EtOH + H^+ \rightarrow [NbF_4(OEt_2)]^- + 2H^+.$$

The latter workers studied the reaction of niobium[133] and tantalum[134] pentafluorides with the corresponding pentaethoxides $M(OC_2H_5)_5$, and obtained products $MF_{5-n}.(OC_2H_5)_n$ with $n = 1$–4 (Table 5). These compounds are oligomers containing on the average $m \simeq 2$ and 3.8 monomers for $n = 4$ and 1 respectively: i.e. the degree of polymerisation decreases with increase in the covalent character of the compound as metal–fluorine are replaced by metal–ethoxy bonds (in the solid state the pentafluorides exist as tetramers[12]).

The above results indicate that alcohols and thiols react with electrophilic fluorides—tungsten(VI), niobium(V), and tantalum(V)—by rupture of alkoxy–hydrogen (alkylthio–hydrogen) bonds with replacement of fluorine in the acceptor by an alkoxy-group under mild conditions (below 0°C). The scheme

$$WF_6 + RO{-}H \rightarrow ROWF_5 + HF$$

may be suggested. This stage apparently occurs, similarly to the reactions of organosilicon compounds[87], via formation of seven-coordinated compounds with the hexafluoride (six-coordinated for the pentafluorides) by an $S_N2$ mechanism with subsequent cleavage of a metal–fluorine bond and elimination of hydrogen fluoride. The relatively unstable[131] ethoxytungsten (or ethylthiotungsten) pentafluoride decomposes further according to the equation

$$EtOWF_5 \xrightarrow{t} WOF_4 + EtF,$$

or adds a second alkoxy-group

$$EtOWF_5 + EtO{-}H \rightarrow (EtO)_2WF_4 + HF.$$

The diethoxytungsten tetrafluoride is in turn converted into oxotungsten tetrafluoride:

$$(EtO)_2WF_4 \xrightarrow{t} WOF_4 + Et_2O$$

similarly to the dimethoxy-derivative (Ref. 85 and Table 2). The reaction mechanism with ethanethiol is apparently the same as that with ethanol[131], but the former exhibits greater donor strength, since, despite the larger bulk, three fluorine atoms in the tungsten hexafluoride molecule are replaced by an alkylthio-group, but only two by ethanol.

#### (*b*) Ethers and sulphides

Ethers, like alcohols, possess weakly basic properties: with Lewis acids, e.g. boron trifluoride, they form stable adducts by virtue of the presence of lone pairs of electrons on the oxygen. In contrast, uranium hexafluoride reacts vigorously with diethyl ether, to give uranyl and

hydrogen fluorides with a carbonaceous substance of unknown composition[64]. Hexa- and penta-fluorides of *d*-elements in Groups V and VI form with ethers the series of compounds shown in Table 5. When a 1 : 5 mixture of tungsten hexafluoride and dimethyl ether is kept in a steel bomb at 100–110°C for 5 h, the products are methyl fluoride, the adduct $WOF_4.(CH_3)_2O$, and a mixture of lower tungsten oxide fluorides and organic compounds[84,135]. Study of the volatility, infrared spectra, and $^{19}F$-n.m.r. spectra suggests[84] that the adduct is a monomer of octahedral structure with the oxygen atom *trans* to the organic ligand. From an investigation of the reaction between tungsten hexafluoride and diethyl ether Buslaev et al. concluded[129] that the complex $WOF_4.(C_2H_5)_2O$ is obtained via an unstable intermediate compound $C_2H_5OWF_5$, owing to the tendency to form the more stable multiple bond W=O. It is pertinent to mention the observation by Noble et al.[123] that $CH_3OWF_5$ is able to lose the alkyl as the methyl cation.

Below room temperature the reaction of the hexafluorides with ethers and with dialkyl sulphides and selenides yields the adducts $MoF_6.(CH_3)_2O$, $MoF_6.(CH_3)_2S$,[43] $WF_6.(C_2H_5)_2O$,[96,129,135] $WF_6.(C_2H_5)_2S$, and $WF_6.2(C_2H_5)_2Se$.[115,135] The donor power towards the hexafluorides increases in the sequence $R_2O < R_2S < R_2Se$. It is assumed that tungsten hexafluoride is partly ionised in the adducts with sulphur and selenium derivatives[115,135]. Molybdenum pentafluoride forms equimolecular adducts with dimethyl ether and dimethyl sulphide, which readily eliminate the ligand molecules in a vacuum at 60 and 20°C respectively[43].

Niobium and tantalum pentafluorides form relatively stable compounds with dimethyl ether[117,120,136–138] and with dimethyl sulphide[44,136,137] (Table 5), which in a vacuum at the melting point distil without decomposition. Equimolecular adducts of these pentafluorides with diethyl ether and sulphide have not been isolated in the crystalline state, but information on them has been obtained from a study of their solutions[43,44,97,115]. It has been concluded from the $^{19}F$-n.m.r. spectra that $NbF_5.(C_2H_5)_2O$, $NbF_5.(C_2H_5)_2S$,[116] and $TaF_5.(CH_3)_2O$ [117] are monomers with octahedral coordination. Conductivity measurements indicate a greater degree of association of adducts with sulphides than of those with ethers[139].

The above results show that under mild conditions ethers, dialkyl sulphides, and dialkyl selenides as *n*-donors[6] form with pentafluorides and hexafluorides of *d*-elements adducts that, like amines, act as nucleophilic reagents. These complexes have the structure of oxonium or sulphonium salts, as is confirmed by their conductivity. The most stable complexes are obtained with niobium, tantalum, and molybdenum pentafluorides, which are stronger Lewis acids than are the hexafluorides. Under more severe conditions (at elevated temperatures and pressures) ethers and apparently their sulphur and selenium analogues undergo cleavage by hexafluorides at the carbon–oxygen bond analogous to the cleavage of ethers by hydrohalic acids[140].

Muetterties noted[107] that the fluorine atoms are not entirely equivalent in the adducts, especially in $WF_6.R_2O$, and suggested an oxonium salt type of structure $[WF_5.R_2O]^+F^-$. If this hypothesis is correct, the course of the reaction is analogous to the cleavage of ethers:

$$1)\quad R\ddot{O}R + WF_6 \rightarrow [R{-}\underset{\underset{WF_6}{|}}{\ddot{O}}{-}R]^+ \cdot F^- \xrightarrow{t} ROWF_5 + RF.$$

Since $(RO)_2WF_4$ has been detected among the reaction products[129], an additional fluorine atom in $ROWF_5$ may be replaced:

$$2)\quad ROWF_5 + ROR \xrightarrow{t} (RO)_2WF_4 + RF.$$

The possible presence of hydrogen fluoride as an impurity in tungsten hexafluoride does not exclude the probability of another well known[140] reaction path, giving an alcohol, which then reacts more readily with the hexafluoride:

$$R_2O + HF \rightarrow [R\overset{H}{\ddot{O}}R]^+ \cdot F^- \rightarrow ROH + RF$$

$$ROH + WF_6 \rightarrow ROWF_5 + HF \text{ etc}$$

Hydrogen fluoride may thus act as a catalytic additive. On the basis of available data it is not possible to give preference to either mechanism.

Under the conditions investigated niobium, tantalum, and molybdenum pentafluorides do not undergo substitution with ethers, but form adducts usually of coordination number 6, sometimes 7. They are compounds of *n*–*v* type[6], in most cases relatively stable. Below room temperature molybdenum and tungsten hexafluorides give with ethers and sulphides less stable adducts of coordination number 7.

### (*c*) Dimethyl sulphoxide, dialkyl sulphites, and diphenyl sulphite

As regards acetone all that is known[96] is that tungsten hexafluoride forms red solutions. Dimethyl sulphoxide differs from its oxygen analogue in having a non-planar molecule and in the presence of a $p_\pi$–$d_\pi$ component of the S=O double bond. Hydrogen atoms in an $\alpha$-position with respect to the sulphur or carbon atom in a sulphoxide or a ketone are capable of substitution by halogen[89].

A study of the interaction of tungsten hexafluoride and dimethyl sulphoxide based on infrared and $^{19}F$-n.m.r. spectroscopy has established[141] that the main product, a viscous yellow oil, consists largely of two compounds—$WF_6.(CH_3)_2SO$ and $WOF_4$—accompanied by bisfluoromethyl ether, hydrogen fluoride, and $W_2O_2F_9^-$. This indicates a complicated reaction mechanism involving cleavage of S=O and C–S bonds with replacement of hydrogen by fluorine in the alkyl group.

Niobium and tantalum pentafluorides form 1 : 1 and 1 : 2 adducts with dimethyl sulphoxide[44,116,120,139,142]. On the basis of conductivity measurements and of infrared and $^{19}F$-n.m.r. spectral data it has been suggested[139,142,143] that $NbF_5.2(CH_3)_2SO$ is ionised as $[NbF_4.L_4]^+[NbF_6]^-$. This is confirmed by the known ability of dimethyl sulphoxide to solvate primarily electrophilic species, cations[89,126]. The corresponding equimolecular compound does not contain the hexafluoroniobate anion[143]. The adduct $TaF_5.2(CH_3)_2SO$ has different $^{19}F$-n.m.r. spectra from the analogous niobium compound, and is considerably more soluble in excess of the ligand. Establishment of the equilibria

$$2TaF_5 + 4L \rightleftharpoons TaF_6^- + TaF_4 \cdot L_4^+$$

$$2TaF_4 \cdot L_4^+ \rightleftharpoons TaF_6^- + TaF_2 \cdot L_n^{2+} + (8-n)\,L$$

was suggested[118].

The above results indicate that pentafluorides undergo addition reactions with dialkyl sulphoxides to form ionised complexes of coordination number 6 and 7, whereas tungsten hexafluoride, the least strongly oxidising among

hexafluorides, undergoes complicated substitution reactions, elucidation of whose mechanism requires further research.

Dimethyl sulphite converts molybdenum hexafluoride into $MoOF_4$, the organic reaction products being methyl fluoride and $CH_3O.SO.F$.[83] Apparently the mechanism is

$$MoF_6 + (RO)_2SO \rightarrow ROMoF_5 + ROS(O)F$$
$$ROMoF_5 \xrightarrow{t} MoOF_4 + RF .$$

Between −40 and +20°C dimethyl, diethyl, and diphenyl sulphites react similarly with tungsten hexafluoride[123,144]:

$$(RO)_2SO + WF_6 \rightarrow ROWF_5 + ROS(O)F .$$

Fluorosulphite esters give sulphur dioxide and the alkyl fluoride on thermal decomposition, and sulphur dioxide and hydrogen fluoride on hydrolysis. At moderate temperatures the compounds $CH_3OWF_5$ and $C_6H_5OWF_5$ are relatively stable monomers, which sublime readily in a vacuum and are soluble in benzene. At 135°C the former decomposes into $WOF_4$ and fluoromethane. The $^{19}F$- and $^1H$-n.m.r. spectra indicate[123] the presence of the adducts $WOF_4.(RO)_2SO$ and $[(RO)_3S]^+[WOF_5]^-$.

Thus dialkyl sulphites react with hexafluorides of *d*-elements with substitution of fluorine in the acceptor molecule by an alkoxy-group at the site of rupture of the sulphur–oxygen bond, by a mechanism presumably analogous to the cleavage of ethers.

### 4. Carboxylic Acids

The most characteristic reaction of carboxylic acids with halides, e.g. of phosphorus (Lewis acids), is the formation of acid halides. Molybdenum, tungsten, and uranium hexafluorides behave similarly towards acetic acid at 40–60°C,[145] giving acetyl fluoride and the corresponding oxide fluoride. The scheme

$$UF_6 + 2CH_3COOH \rightarrow UO_2F_2 + 2CH_3COF + 2HF$$
$$WF_6 + 2CH_3COOH \rightarrow WO_2F_2 + 2CH_3COF + 2HF$$
$$MoF_6 + CH_3COOH \rightarrow MoOF_4 + CH_3COF + HF$$

was suggested.

A study of the reaction of tungsten hexafluoride with acetic and thioacetic acids by $^{19}F$-n.m.r. spectroscopy has shown[131] that sulphur and oxygen atoms are detached from the latter to give tungsten oxide and sulphide tetrafluorides:

$$2WF_6 + 2CH_3COSH \rightarrow WSF_4 + WOF_4 + 2CH_3COF + 2HF .$$

With increase in the ratio of thioacetic acid to the hexafluoride the tetrafluorides pass into the dimeric anions $W_2O_2F_9^-$ and $W_2S_2F_9^-$, and obviously into $WSF_5^-$ (since $WOF_5^-$ is present in the acetic acid system). It had been shown earlier[139] that the fluorine atom *trans* to the oxygen in $WOF_5^-$, and the bridging fluorine atom in the dimer $W_2O_2F_9^-$, carry a considerable proportion of the negative charge. It is significant[131,137] that both the carbonyl C=O and the C–O or C–S bonds are ruptured in the reaction in thioacetic acid—and it must be assumed in acetic acid (more correctly in their anions)—and also that the systems contain anions of the types $WOF_5^-$, as well as the compounds $WOF_4$ and hydrogen fluoride.

On the basis of experimental results[131] the interaction of tungsten hexafluoride with thioacetic acid can be written

$$1)\quad WF_6 + R{-}C\begin{matrix}O\\ \diagdown\\ S^-\end{matrix} \rightarrow WSF_5^- + R{-}\overset{O}{\overset{\diagup}{C}}{-}F$$
$$2)\quad WSF_5^- + H^+ \rightarrow WSF_4 + HF \rightleftharpoons W_2S_2F_9^- + H^+ .$$

In the second reaction the proton apparently coordinates with the fluorine atom of the substrate on which the negative charge is concentrated[139,146]. The appearance of $WOF_4$ together with $WSF_4$ as reaction product can be attributed to the existence of resonance structures of the acid anion[89], which leads to cleavage of the bonds attaching carbon to sulphur and to oxygen.

Trifluoroacetic acid, of similar strength to hydrochloric acid, reacts with uranium hexafluoride according to the equation[145,147]

$$2UF_6 + 2CF_3COOH \rightarrow 2HUF_6 + CF_3COF + CO_2 + COF_2$$

Hexafluorouranic acid is unstable, and decomposes[145] at 60°C into uranium(V) and hydrogen fluorides. In excess of the solvent the complex acid is converted into $2UF_5.CF_3COOH$. The diminished stability of trifluoroacetic acid (which undergoes degradation, whereas acetic acid is merely dehydrated) is attributed[145] to the proximity of fluorine atoms to the carbonyl group. Indeed, the presence of uranium(V) and carbon dioxide among the reaction products indicates decarboxylation, which is known to occur readily if a strongly electron-accepting group, in the present case trifluoromethyl, is attached to an $\alpha$-carbon atom:

$$CF_3{-}C\begin{matrix}O\\ \diagdown\\ O^-\end{matrix} + UF_6 \rightarrow CF_4 + UF_5 + CO_2 .$$

On the other hand, the presence of trifluoroacetyl fluoride indicates the progress in parallel of a reaction analogous to that occurring with acetic acid[131,145]. It is evident that the reaction is actually more complicated, and further research is necessary in order to refine the mechanism.

## VI. COMPLEX FORMATION WITH ORGANIC LIGANDS

Although various compounds of *d*- and *f*-elements exhibit a strong tendency to form complexes[148], the fluorides are less strongly complex-forming than other compounds having ligands located to the left of fluorine in the spectrochemical series (e.g. chlorides, bromides). This is probably due to the greater electronegativity and the small size of fluoride ions, which form a compact screening shell diminishing the accessibility of vacant orbitals of the central atom in the fluorides for overlapping with the orbitals of organic ligands. This may explain why chlorides of *d*-elements are stronger Lewis acids than are the corresponding fluorides.

Fluorides of *d*-elements in the lower formal degrees of oxidation such as 3–5 have strong intermolecular coordinate bonds and, as Walton[149] has shown, form in the solid state lattices in which the metal is situated in an octahedral environment of six halide ions. The fall in the boiling point with increase in the number of ligands in the sequence of fluorides

$$MF_3 > MF_4 > MF_5 > MF_6$$

both for the same element and on moving from left to right along a series in the Periodic System, indicates an increase in coordination saturation and a decrease in the strength of intermolecular bonds. On the whole, hexafluorides possess a more covalent character than do tetra- and penta-fluorides. We shall examine the opportunities for inorganic fluorides in various states of oxidation to coordinate ligands containing lone pairs of electrons.

Trifluorides of *p*-elements—aluminium, gallium, indium—form[150] equimolecular adducts with diethylamine and tributylamine, and $MF_3.3NH_3$ with ammonia. Aluminium tribromide behaves similarly[151] towards dialkyl sulphides and selenides. Muetterties reported[107] that antimony and arsenic trifluorides give equimolecular adducts with dioxan and dimethylformamide, $2SbF_3.L$ is formed with pyridine and trimethylamine, and $SbF_3.2(CH_3)_2SO$ has been obtained with dimethyl sulphoxide. It may be supposed that interaction of trifluorides of *d*-elements with organic ligands will yield compounds of tetrahedral structure, since the considerable bulk of the ligands will prevent the appearance of adducts having higher coordination numbers.

Numerous examples of the preferential formation of $MF_4.2L$ adducts in reactions with amines, pyridine and its derivatives, dimethyl sulphoxide, and several other ligands have been demonstrated by Muetterties[107,152] for tetrafluorides of *d*-elements (titanium, zirconium, molybdenum) and *p*-elements (silicon, germanium, tin) and by Ennan[153] for silicon tetrafluoride. It was concluded[152] that octahedral coordination of the adducts with the metal tetrafluorides was preferred stoichiometrically. Smaller coordination numbers were observed probably because of steric hindrance in the case of bulky compounds having a metal–nitrogen bond, but this was almost completely absent from the metal–oxygen bond.

It follows from the above account that pentafluorides of *d*-elements form equimolecular adducts, considerably more rarely 1 : 2 compounds, with almost all organic ligands having lone pairs of electrons: i.e. a clear tendency to form complexes with octahedral coordination is evident in this case too.

Cotton and Wilkinson[148] point out that, in the ligand-field approximation for *d*-electrons, octahedral coordination contributes about double the energy separation of bonding $t_{2g}$ and antibonding $e_g$ orbitals in comparison with a tetrahedral field. This will obviously make octahedral coordination advantageous for complexes, including fluorides having a small number of unpaired *d*-electrons. The fluorides of *d*-elements discussed here are compounds of this type. Hence, under otherwise similar conditions, the energy of stabilisation of the ligand in an octahedral field should be the dominant factor. It is probably for this reason that tri-, tetra-, and penta-fluorides of *d*-elements undergo addition with *n*-donors possessing lone pairs of electrons, thereby acquiring a tetrahedral configuration with trifluorides (in the case of large ligands preventing a higher coordination number) and an octahedral configuration with tetra- and penta-fluorides.

Basolo and Johnson noted[154] that four-coordinated systems of *d*-elements react predominantly with the formation of new metal–ligand bonds, to which a high charge on the central ion makes a considerable contribution. Evidently there is every reason to apply this to pentafluorides. They add ligands more easily than do tri- and tetra-fluorides, in order to complete the octahedral coordination. This requires the formation of only one new metal–ligand bond, whereas in tri- and tetra-fluorides greater energy is necessary to break the considerable intermolecular forces in the condensed state and to create more than one new metal–ligand bond.

The situation is different with hexafluorides of *d*-elements, since they are structures having the energetically advantageous octahedral coordination. These hexafluorides differ greatly in oxidising and complexing properties. As shown above, the hexafluorides of *f*-elements surpass appreciably those of *d*-elements in oxidising power. This difference may be due to differences in the number of spatial configuration of *d*- and *f*-orbitals, which in turn presupposes different configurations and energies of formation of bonds. To the approximation of crystal field theory Bagnall[60] supposes that for *f*-orbitals an eight-coordinated structure is preferable, corresponding to a point group of symmetry $D_{6h}$ (a regular hexagonal bipyramid) or the octahedral $O_h$ (bonds directed from the centre towards the corners of a cube). Six-coordinated geometry of type $O_h$ or $D_{4h}$ is more favourable[148] for complexes of *d*-elements.

Matters are more complicated in the actual molecules of hexafluorides of *f*-elements, for *d*-electrons are also involved in bond formation (electronic structures—uranium $5f^36d7s^2$, neptunium $5f^46d7s^2$ or $5f^57s^2$, and plutonium $5f^67s^2$).[60] Nevertheless, available data indicate that in a six-coordinated structure hexafluorides of *f*-elements are less stable than are those of *d*-elements, and the stability of the compounds diminishes with increase in the number of *f*-electrons, an example being the decrease in stability in the sequence $UF_6 > NpF_6 > PuF_6$. For the reasons discussed above the hexafluorides of *d*- and *f*-elements will obviously differ also in complexing power, although no data are at present available providing unambiguous support for this hypothesis. It can be concluded from the work of Weinstock[10,155] that in general the stability of the hexafluorides diminishes with increase in the number of unpaired electrons—for the transition series

$$4d\text{—}MoF_6\,(d^0) > TcF_6\,(d^1) > RuF_6\,(d^2) > RhF_6\,(d^3)$$

$$5d\text{—}WF_6\,(d^0) > ReF_6\,(d^1) > OsF_6\,(d^2) > IrF_6\,(d^3) > PtF_6\,(d^4)$$

and for the actinides

$$5f\text{—}UF_6\,(5f^0) > NpF_6\,(5f^1) > PuF_6\,(5f^2).$$

The most intensive investigation has been made on the interaction of organic ligands with tungsten hexafluoride, which exhibits extremely weak oxidising properties and is more convenient for investigation than are other hexafluorides. In complexing power it is very close to the pentafluorides of *d*-elements. Jorgensen assumed[156] that the tungsten atom in the hexafluoride bore a formal charge of +5, whereas in molybdenum and rhenium hexafluorides the corresponding charge was +6. If this is in fact the case, the difference in oxidising power between molybdenum and tungsten hexafluorides is explicable: the latter is very similar to pentafluorides both in its comparatively weak oxidising power and in its tendency to form complexes, whereas molybdenum hexafluoride is a quite strong oxidant, and frequently undergoes complex formation only after reduction to the quinquevalent state.

Hexafluorides form the most stable complexes with *n*-donors having a relatively simple structure: e.g. nitric oxide gives $NO^+MoF_6^-$ and $NO^+UF_6^-$. The enthalpy of formation of the latter compound is −52 kcal mole$^{-1}$.[159] The formal state of oxidation of the metal in these compounds is +5. Tungsten hexafluoride does not react with nitric oxide.

Donors having a non-linear structure, such as nitrosyl and nitryl fluorides, give with uranium hexafluoride the compounds $NOUF_7$, $NO_2UF_7$, and $(NO_2)_2UF_8$,[160,161] with molybdenum hexafluoride $NOMoF_7$ and $NO_2MoF_7$,[161] and with tungsten hexafluoride $NOWF_7$ and $NO_2WF_7$.[162] The enthalpies of decomposition of $NOUF_7$ and $NO_2UF_7$ are respectively[161] 16.6 and 13.8 kcal mole$^{-1}$.

Uranium hexafluoride forms with alkali-metal fluorides a series of complexes varying in composition; with sodium fluoride, in particular, $NaUF_7$ [163] and $Na_2UF_8$ [164]

are obtained (having enthalpies of decomposition of 15.9 and 19.1 kcal mole$^{-1}$ respectively—given by other workers[165] as 9.4 and 23.5 kcal mole$^{-1}$). The complexes $Na_3UF_9$ and $Na_3U_2F_{15}$ are also known[166]. Molybdenum and tungsten hexafluorides also form with sodium fluoride 1 : 1 and 1 : 2 complexes[163,167]. Neptunium and plutonium hexafluorides on treatment with sodium fluoride are reduced to the quinquevalent and quadrivalent states respectively, with liberation of elementary fluorine and formation of $Na_3NpF_8$ and $Na_3PuF_7$.[166]

The enthalpies of decomposition show that the complexes of hexafluorides with the above ligands are quite stable, except in the last two cases. The alkali-metal fluorides are ionic in character, their anions acting as donors with one lone electron in their ability to form stable bonds with $\upsilon$-acceptors, in the present case halides of $d$- and $f$-elements. The nitric oxide, nitrosyl fluoride, and nitryl fluoride molecules possess a lone pair of electrons (they are $n$-donors) and a considerable capacity for polarisation, which also ensures relatively stable bonding with hexafluorides. The coordination numbers of the metals in these complexes are 7–9.

Among the classes of organic compounds considered, the following $n$-donors—amines, ethers, dialkyl sulphides, sulphoxides, and selenides, and pyridine and its derivatives—are able to form such bonds. The majority of published studies are concerned with the interactions of these donors with tungsten hexafluoride, in which it develops a coordination number 8, more rarely 7 or 9. In the case of the other hexafluorides only the adducts with pyridine and 2-fluoropyridine—$MoF_6.2C_5H_5N$, $UF_6.C_5H_4FN$, and $UF_6.2C_5H_4FN$—are known[107]. No investigations have yet been published on the structure of these compounds, their stability, or the effect of the nature and the geometrical dimensions of the ligand molecules on the properties of the adducts formed with hexafluorides.

It has been suggested in a recent publication[169] that compounds of $d$- and $f$-elements develop greater chemical differences in aqueous solution than as anhydrous halides and oxides. One might agree with this, since fluorine is located somewhat to the right of such anions as nitrate, chloride, etc. in the spectrochemical series, and theoretically have a greater levelling effect on the chemical individuality of the central ion in the adduct; on the other hand, water is situated to the right of fluorine in this series. It must also be borne in mind that the properties of halides of $d$- and $f$-elements have been studied considerably less fully in non-aqueous than in aqueous systems, so that there are as yet inadequate grounds for such a statement.

Investigation of the reactions of hexafluorides with organic $n$-donors necessitates a relatively complicated experimental technique, but the results may well make a definite contribution to the theory of complex formation by $d$- and $f$-elements and permit the use of organic donors as selective chemical reagents in fluorination, exchange, and addition reactions involving metal fluorides.

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# Effect of Radioactive Emission on the Catalytic Properties of Solid Materials

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The general state of the problem of the radiation modification of the action of solid catalysts is discussed, in relation to various types of heterogeneous catalytic reactions, on the basis of 190 references.

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## I. INTRODUCTION

Many research workers have turned their attention to the problem of radiation heterogeneous catalysis, for solid catalysts often undergo considerable activation on irradiation. On the other hand, attempts have been made to improve the chemical efficiency of the irradiation of a reaction system by the introduction of solids, since radiolytic reactions (other than chain processes) usually give low yields of the required product. Furthermore, study of the adsorption and catalytic properties of irradiated specimens will contribute to a better understanding of general aspects of heterogeneous catalysis, in particular the relation between the activity of a solid catalyst and defects in its crystal structure.

Because of the abundance of information on this aspect, the Review will not contain any detailed discussion of the mechanisms of the radiation-catalytic processes occurring in each individual case. We have tried to report the general state of the problem, with detailed consideration only of the clearest examples with the aim where possible of revealing general features inherent in various groups of phenomena.

It is necessary to distinguish cases in which preliminary exposure of the catalyst (in the absence of reactants), by producing radiation damage in the solid specimen, confers on it new catalytic properties from cases in which a considerable proportion of the radiant energy absorbed by the catalyst during the reaction is utilised in activating gas molecules adsorbed on its surface. In the latter case thermodynamically forbidden processes may occur[1]. The radiation modifcation of solid catalysts is in some way connected with the appearance of various kinds of interior and surface defects.

## II. PRINCIPAL MECHANISMS OF RADIATION DAMAGE

The interaction of high-energy radiation with a solid result in various types of disturbance[2-5]: (1) vacancies are unoccupied lattice points; (2) interstitial atoms have been displaced from their usual position in the lattice and are located between lattice points (vacancies and interstitial atoms may be formed simultaneously by the Frenkel mechanism, i.e. by escape of an atom from a lattice point into an interstice; vacancies may arise also by a Schottky mechanism, when an atom that has vaporised from the crystal surface is replaced by an atom from a deeper layer; and vacancies may combine to form spherical pores or flat circular voids); (3) displacement peaks are regions containing up to $10^4$ displaced atoms, such defects usually arising at the end of the path of the moving particles; (4) impurity atoms are chemically foreign atoms formed as a result of nuclear reactions occurring in the solid under the influence of the radiation; (5) the non-equilibrium electrons and holes produced by the ionisation of atoms and the excitation of electrons (ionisation effects) may be localised on biographic defects to form $F$- and $V$-centres respectively, and the ionisation effects may lead to coloration, luminescence, and the formation of free radicals; and (6) thermal peaks are high-temperature regions containing a few thousand atoms and reaching 1000 K, such defects being formed along the path of a fission fragment or a dislodged charged atom.

The various types of electromagnetic and corpuscular radiation are able in general to induce any type of disturbance in a solid, but the efficiency of formation varies. Furthermore, the mechanisms of the action of radiation on metals and on semiconductors are not identical[6]. Ionisation effects, which occur with almost all types of radiation, are very short-lived in metals, since they are rapidly reduced by radiationless transitions. Relatively stable changes occur only on the direct transfer of energy to the atomic framework of the lattice, with the generation of Frenkel pairs (interstitial atom + vacancy). Therefore the most intense effect is produced by bombarding metals with neutrons or heavy charged particles. Semiconductors and dielectrics, in contrast, are distinguished by the ease of formation of diverse stable defects.

The first of three possibilities when non-metals are irradiated[7] involves only direct ionisation, i.e. the production of non-equilibrium charge carriers. Such an effect is observed when X-rays, $\gamma$-rays, fast electrons, or positrons are used. The excess concentration of free current carriers of the same sign is given by the formula $\Delta n = g\tau$, where $g$ is the rate of generation of carriers (which is proportional to the intensity of the $\gamma$-irradiation) and $\tau$ is their average lifetime[8,9]. Since $\tau$ is usually extremely short, specimens possess no radiation "memory". Under these conditions stable defects can appear only when electrons or holes are localised on biographic surface defects.

In the second case[7] irradiation (mainly neutron) initiates a nuclear reaction, which enriches the semiconductor with a donor or an acceptor impurity. This irreversible process, which is accompanied by a shift in the electron equilibrium, can become significant only when atoms having a sufficiently large capture cross-section for neutrons are present in the substance.

The third possibility is that the specimen possesses a brief "memory" owing to the appearance of interior structural defects of the Frenkel type. Atoms that have penetrated into interstices contribute new donor levels to the energy spectrum of the semiconductor, and vacancies contribute acceptor levels, which are responsible for the shift in the electron equilibrium [10]. It was suggested [11] that, as along as the energy parameter of the bombarding particle $\epsilon = mE/M$ is large in comparison with the forbidden gap $E_e$ of the crystal ($m$ is the mass of the electron, $M$ the mass of the particle, and $E$ the kinetic energy of the latter), it dissipates most of its energy on ionisation processes. When $\epsilon < E_e/8$, elastic collisions begin to predominate, leading to the displacement of lattice atoms. The number of atoms displaced in unit volume in unit time is [12] $N_d = \varphi n \sigma_d \overline{\nu}$, where $\varphi$ is the density of incident particles, $n$ the density of atoms, $\sigma_d$ the cross-section of collisions leading to displacements, and $\overline{\nu}$ the mean number of atoms displaced by a primary atom, given by [13] $\overline{\nu} = 0.5[1 + \ln(E_m/2E_d)]$, in which $E_m = 4MM'E/(M + M')^2$, while $E_d$ is the threshold energy of displacement of an atom and $M'$ its mass. The displacement of atoms in dielectrics, in contrast to semiconductors, may be caused also by ionisation phenomena, which sometimes play a leading role. Various mechanisms of formation of these defects were suggested by Varley [14] and by Seitz [12].

Diffusion of the resulting vacancies and interstitial atoms produces an annealing effect as a consequence of their mutual annihilation. Thus after a certain time specimens of $n$-germanium that had been exposed to $\alpha$-particles [15] acquired their original properties, but the annealing of specimens initially having $p$-conductance was only partial: the conductivity and the Hall coefficient did not return to the values characteristic of unexposed semiconductors. A series of theoretical studies have been made on the kinetics of the annealing of Frenkel pairs [16-19]. The saturation of radiation effects during prolonged exposure at high temperatures may be due to annealing.

## III. EFFECT OF IONISING RADIATION ON THE ADSORPTIVE POWER AND THE CATALYTIC ACTIVITY OF SOLIDS

The influence of ionising radiation on the catalytic properties of solids should be interpreted in terms of one of the current theories of heterogeneous catalysis, which involve different concepts of the primary mechanisms of the interaction of the reactants with the catalytic surface. According to Balandin's theory [20] the activity of a catalyst depends on the presence in its lattice of atomic groupings (multiplets) arranged in definite fashion, on which reactant molecules are adsorbed and thus activated. If the changes in the lattice parameters produced by the ionising radiation contribute to the establishment of such a structure, the radiation will have a promoting effect on the solid catalyst; when exposure results in the degradation of active multiplets, poisoning of the catalyst is observed.

The electronic theory of catalysis [21] is based on the hypothesis that the free electrons and holes localised on surface defects play an active part in the primary acts of adsorption and activation of reactant molecules on a semiconductor catalyst surface. Since their equilibrium concentration depends unambiguously on the position of the Fermi level in the band structure of the semiconductor, any factor (including radiation) that displaces this level will cause a change in the catalytic properties of the specimen. These concepts form the basis of theoretical studies [22,23] on the influence of radiation on the adsorptive power and the catalytic activity of semiconductors. Experimental techniques have been described in detail [24] for the oxidation of carbon monoxide on nickel(II) oxide exposed to $\gamma$-rays. Some idea of the present state of the problem of the action of radiation on the adsorption and catalytic characteristics of solids can be obtained from reviews [25,26].

### 1. Adsorption

Investigation of the adsorption properties of irradiated specimens will give a clearer idea of the disturbances, produced than will examination of catalytic reactions, which usually have a complicated mechanism.

The chemisorption of hydrogen on zinc oxide (an $n$-type semiconductor) at 20°C hardly affects the electrical conductivity of the adsorbent, whereas chemisorption under the influence of $\gamma$-rays is accompanied by a considerable increase in conductivity [27]. The explanation given was that hydrogen is adsorbed in an uncharged form in the absence of radiation, whereas in a radiation field the free holes produced are captured by hydrogen molecules. This excludes recombination with the latter of the free electrons, which are involved in conduction. In contrast, the chemisorption of oxygen in the absence of radiation leads to a sharp fall in conductance, and, when it is switched on, additional chemisorption takes place with simultaneous increase in conductivity. The probable reason is that exposure converts oxygen into a form with a smaller negative charge, and also that the concentration of excess current carriers increases in the bulk of the zinc oxide. In the absence of irradiation neither hydrogen nor oxygen was chemisorbed on aluminium oxide (in contrast to zinc oxide) at 20°C, but in the presence of $\gamma$-rays the chemisorption of oxygen was more rapid than that of hydrogen [28]. This was attributed to the presence in aluminium oxide of a considerable number of efficienct centres, which captured some of the free holes necessary for the chemisorption of hydrogen.

The quantity of hydrogen chemisorbed on a $\gamma$-alumina surface was used [29] to determine the maximum density of adsorption centres ($\sim 5.5 \times 10^{12}$ cm$^{-2}$) produced by continuous cobalt-60 $\gamma$-rays at a dosage rate of 350 rad s$^{-1}$. On preliminary irradiation this quantity was $\sim 3 \times 10^{11}$ cm$^{-2}$. Electron spin resonance established the approximate equality of the concentration of radiation defects responsible for the adsorption of hydrogen and of paramagnetic centres produced by the irradiation of aluminium oxide. A study was made [30] of the effect of such radiation on specimens of $\gamma$-alumina differing in specific surface. The intrinsic volume of one adsorption centre was found for each case from the specific surface and the number of active centres (determined kinetically). The chemisorption rate constant for hydrogen increased on passing from small to large such volumes. The rate of chemisorption is given [31] by the equation

$$-\frac{dp}{d\tau} = \alpha K p^{\frac{1}{2}} I S (1 - \theta),$$

where $p$ is the pressure of hydrogen, $\tau$ the time, $\alpha$ the surface density of adsorption centres, $I$ the dosage rate, $S$ the total area of the catalyst, and $\theta$ the proportion of adsorption centres occupied.

Despite the variation in the phase constitution and the specific surface of the adsorbents used, the initial rates of chemisorption of oxygen on the $\gamma$-irradiated aluminium

oxide were approximately the same [32], and the radiation efficiency of chemisorption of molecules was closely similar to the yield of pairs of excess current carriers. Termination of exposure led to cessation of radiation chemisorption, which indicated the short lifetime of the adsorption centres. The initial rate of chemisorption was directly proportional to the quantity of catalyst and the power of the $\gamma$-rays, but independent of the oxygen pressure [33]. The chemisorption was irreversible, the maximum number of chemisorbed molecules being $2.5 \times 10^{12}$ cm$^{-2}$.

In the Reviewers' opinion the above publications leave no doubt that free current carriers generated by the radiation are involved in the adsorption of hydrogen and oxygen on semiconducting adsorbents, with the chemisorption of hydrogen involving free holes, and that of oxygen free electrons of the semiconductor. In both cases the initial rate of chemisorption is directly proportional to the power of the radiation. The fact that the initial rate of adsorption of oxygen, in contrast to that of hydrogen, is independent of the pressure is probably due to the more efficient adsorption of oxygen by the irradiated aluminium oxide [28].

Exposure of $\gamma$-alumina in equilibrium with carbon monoxide to cobalt-60 $\gamma$-rays at 300 K results in almost complete adsorption of the gas [34]. If irradiation was terminated before adsorption was complete, a post-radiation effect was observed: with rise in temperature from 300 to 375 K the initial rate of adsorption remained unchanged, but then began to fall, owing to thermal annealing of the active centres produced by the radiation. Adsorption of carbon monoxide, nitrous oxide, and oxygen at 77 K on $\gamma$-alumina exposed to $\gamma$-rays either previously or during adsorption (dosage rate 1000 rad s$^{-1}$) produced no change in form or intensity of the electron spin resonance spectrum [35]. Thus adsorbed gases do not interact with paramagnetic centres formed on irradiation, but heating $\gamma$-alumina with carbon monoxide or oxygen to 300 K was accompanied by a change in the e.s.r. signal. In contrast to carbon monoxide, the extra quantity of carbon dioxide adsorbed in the field of the $\gamma$-rays (300 rad s$^{-1}$) was $<10\%$ of the quantity adsorbed by aluminium oxide in the thermal process [36]. The activation energy of desorption of carbon dioxide from the surface was the same (4.5 kcal mole$^{-1}$) whether or not the adsorbents had been irradiated and whatever the dosage. When specimens on which carbon dioxide had been adsorbed by means of radiation were kept for 30 days or were heated, the bonding became stronger (the activation energy increased to 11 kcal mole$^{-1}$).

Several other cases have been noted of enhanced adsorptive power resulting from the irradiation of solids. Thus silica gel exposed to cobalt-60 $\gamma$-rays was a considerably more active adsorbent for nitrogen, hydrogen, carbon monoxide and dioxide, ammonia, and ethylene than before exposure [37], which was attributed to detachment of hydroxy-groups from the surface or direct interaction of the ionising radiation with gas molecules. Exposure of $\gamma$-alumina to cobalt-60 $\gamma$-rays (300 rad s$^{-1}$) had a favourable influence on the quantity of ethylene adsorbed and strengthened its bonding with the surface [38].

The system comprising benzene and silica gel exposed to $\gamma$-rays (640 rad s$^{-1}$) at the temperature of liquid nitrogen was studied in detail [39,40]. The radiation leads to the reaction

$$\equiv Si{-}O{-}H \rightarrow \equiv Si{-}O^{\cdot} + H$$

in the silica gel; the liberated hydrogen atoms either combine to form molecules or interact with benzene molecules to form $C_6H_7^{\cdot}$ radicals. The silica-gel radicals $-Si-O^{\cdot}$ are also able to react with benzene molecules and $C_6H_7^{\cdot}$ radicals:

$$\equiv Si{-}O^{\cdot} + C_6H_6 \rightarrow \equiv Si{-}O{-}C_6H_6^{\cdot}$$

$$\equiv Si{-}O^{\cdot} + C_6H_7^{\cdot} \rightarrow \equiv Si{-}O{-}C_6H_7 \ .$$

If hexane molecules had been present on the silica-gel surface their interaction with hydrogen atoms would have yielded $C_6H_{13}^{\cdot}$ radicals [41].

Preliminary irradiation also affects the adsorption properties of solids, though usually to a less extent. Silica gel after treatment with $\gamma$-rays, for example, acquires an appreciable ability to adsorb hydrogen [42]. This is accompanied by the appearance of colour centres, which were identified [42] with holes associated with excess of oxygen in the silica. The adsorption of hydrogen involved interaction of these holes with electrons of the gas molecules, with consequent decolorisation of the colour centres. Reactor radiation, hard X-rays, $\gamma$-rays, and exposure to slow electrons from a high-frequency discharge promoted the adsorption of gases by silica gel [43] in the sequence—carbon dioxide < oxygen < hydrogen—but with proton beams and $\alpha$-rays the adsorption capacity increased from hydrogen to carbon dioxide and oxygen. No stimulation of the adsorption of argon by radiation was detected. The absorptive capacity of irradiated silica gel for hydrogen increased with its contamination by aluminium [44]. That of beryllium oxide for hydrogen was only slightly enhanced by exposure to $\gamma$-rays [45]. Exposure of $\gamma$-alumina to fast neutrons impared its adsorptive properties for krypton [46], and to n,$\gamma$-rays those for benzene and water vapour [47]. Treatment of nickel oxide in a nuclear reactor increased the subsequent sorption of hydrogen and oxygen [48].

It may be concluded from the above results that the enhancement of the adsorptive power of oxides produced by radiation is in many cases due to the appearance of non-equilibrium current carriers in their interior and on the surface. However, whereas free electrons or holes are the main agents in the continuous exposure of adsorbents, the centres of adsorption after preliminary irradiation are charge carriers produced by the radiation and trapped by biographic or radiation surface defects. Thus analysis of numerous e.s.r. spectra of irradiated sorbents before and after the adsorption of oxygen, carbon monoxide, and other electron acceptors indicates [49] that paramagnetic centres formed in a solid by the trapping in structural defects of electrons generated by the radiation are transformed into molecular ions—$O_2^-$, $CO^-$, $CO_2^-$, etc.

## 2. Isotopic Exchange and Ortho–Para Conversion of Hydrogen and the Isotopic Exchange of Oxygen

Isotope exchange is one of the simplest reactions, with a comparatively simple experimental technique. Together with the ortho–para conversion of hydrogen such exchange has therefore been used quite often as a model reaction.

Electron diffraction revealed structural disturbances in the metal lattices after the pretreatment of platinum and nickel catalysts with accelerated argon ions, which affected the rate of exchange between hydrogen and deuterium [50]. Preliminary bombardment of magnesium oxide with neutrons increased the rate of this exchange and of the ortho–para conversion of hydrogen [51,52], which e.s.r. data showed to be due to the appearance of electrons localised on surface radiation defects. On the other hand, these reactions were slower on specimens of alumina that

had first been irradiated with neutrons. If, however, the aluminium oxide contained small additions of salts of transition metals, $n,\gamma$-radiation had a considerable activating influence for the ortho–para conversion of hydrogen[54]. Enhanced catalytic activity towards deuterium–hydrogen exchange was observed[55] in irradiated powdered oxides—ZnO, MgO, $V_2O_5$, $BaTiO_3$, $CaSiO_3$, $KAlSi_3O_8$, etc.—whose treatment with neutrons in a nuclear reactor resulted in a considerable change in the rate of the process, whereas $\gamma$-irradiation was far weaker in increasing the rate, and sometimes had hardly any effect.

The rate of exchange on titanium dioxide at the temperature of liquid nitrogen increased by a factor of $10^4$ after $\gamma$-irradiation (dosage rate 120 rad $s^{-1}$, integral dose $1.7 \times 10^7$ rad).[56] When the temperature of the irradiated catalyst rose to 0°C, its activity dropped sharply and the e.s.r. signal became weaker.

Parallel variation of the e.s.r. spectrum and of the catalytic activity towards deuterium–hydrogen exchange was established also for the pretreatment of silica gel with $\gamma$-rays (integral dose from $2 \times 10^5$ to $2 \times 10^7$ rad).[57] The activity of the catalyst increased with the radiation dose, the duration and temperature of the heat-treatment preceding irradiation, and also the contamination of the specimens with aluminium. The considerably more rapid annealing of catalytic activity in hydrogen than in a vacuum was attributed to irreversible adsorption of hydrogen on active centres of the catalyst, which, according to optical and e.s.r. spectroscopy, were holes stabilised on oxygen atoms adjacent to aluminium atoms. After $\gamma$-irradiation (dosage rate $1.2 \times 10^{17}$ eV $g^{-1}$ $min^{-1}$) the activation energy of deuterium–hydrogen exchange had fallen from 9 to 2 kcal $mole^{-1}$, which was regarded[58] as due to a change in the reaction mechanism. The increase in the rate of exchange between hydrogen and deuterium observed in ethylene was attributed[59] to the appearance of unpaired electrons in the $\gamma$-irradiated aluminosilicate catalyst (dosage rate 100 rad $s^{-1}$, integral dose $1.5 \times 10^6$ rad). Their concentration was determined by e.s.r. as $4 \times 10^{18}$ spins $g^{-1}$. The enhancement of the catalytic activity of aluminosilicate cracking catalysts towards this reaction after their $\gamma$-irradiation was accompanied by an increase in optical absorption by the specimens, both parameters increasing with the radiation dose. However, no direct relation was detected between the numbers of active centres and colour centres during annealing.

$\gamma$-Irradiation ($2 \times 10^7$ eV $g^{-1}$ $min^{-1}$ for 0.5 h) had a promoting effect on the subsequent catalysis for $\gamma$-alumina of deuterium–hydrogen exchange at −78°C.[61] It is significant that radiation treatment of specimens already subjected to thermal activation at 400°C and of unactivated specimens increased their activity by factors of 7 and 1000 respectively, although in the latter case the radiation effect underwent more rapid annealing. The active centres were identified[61] with electrons or holes localised on structural defects, which was supported by results[62,63] recording the appearance of signals due to paramagnetic resonance absorption in $\gamma$-alumina after its treatment with $\gamma$-rays. The conclusion that short-lived radiation defects are not involved in deuterium–hydrogen exchange is inconsistent with data[64] indicating a sharp fall in catalytic activity of the $\gamma$-alumina after the $\gamma$-rays had been switched off. The initial reaction velocity in a system comprising 10% of hydrogen, 10% of deuterium, and 80% of helium over aluminium oxide was increased by irradiation by a factor of 1000 at 50°C, but only by factors of 4–5 at 150°C, owing to thermal annealing of the radiation active centres in the catalyst[64]. Investigation of the influence of $\beta$- and $\gamma$-rays, and also of ultraviolet radiation, on isotope exchange between benzene and heavy water on the surface of platinum dioxide[65] showed that the reaction was accelerated only by the action of radiation on the reaction mixture.

The effect of the temperature of preliminary conditioning of a catalyst on the magnitude of the radiation effect[61] has been observed by many other workers. Thus the rate of the ortho–para conversion of hydrogen on the surface of magnesium oxide that had been thermally activated at 675°C remained unchanged after irradiation of the catalyst by cobalt-60 $\gamma$-rays[66], but if the specimen had been activated at 500°C, its subsequent irradiation trebled the activity. When the system was irradiated during the reaction, the rate of the latter increased tenfold. It was concluded[66] that the action of the radiation involves neither an increase in the adsorption of hydrogen nor its radiolysis.

A detailed investigation on $\alpha$-alumina that had been exposed to cobalt-60 $\gamma$-rays ($10^{18}$ eV $g^{-1}$ $h^{-1}$) at 77 K showed[67] that specimens that had been activated at 560°C exhibited no e.s.r. signal and their catalytic activity remained unchanged after irradiation, which caused a signal to appear. Hence unpaired electrons produced during irradiation are unable to influence the course of the reaction, which supports the view[67] that the action of coupled electrons is necessary for the dissociation of hydrogen molecules. However, the activity of a specimen that had been preheated at 200°C—insufficient for its activation—and then irradiated reached that of a specimen that had been activated at 550°C.

It can thus be accepted as fully proved that the radiation sensitivity of catalysts for deuterium–hydrogen exchange diminishes with rise in the temperature of their thermal activation. A study of the effect of neutron irradiation or bombardment with $\alpha$-particles on the catalytic properties of strongly activated $\gamma$-alumina specimens even revealed a negative radiation effect[68]. This work also showed that poisoned catalysts—water, hydrogen, and acetylene were used as poisons—were more sensitive to radiation. A mechanism is therefore quite likely in which irradiation, like high-temperature evacuation, removes from the catalyst surface foreign gases blocking the active centres.

Several papers have recently appeared[1] on the action of radiation on homomolecular oxygen isotope exchange. Although this reaction does not take place on silica gel, it occurs at an appreciable rate on specimens exposed to integral doses $\geqslant 7 \times 10^6$ rad of cobalt-60 $\gamma$-rays[69,70]. The degree of conversion increases with the total catalytic surface area and the radiation dose. This effect was attributed to the formation of active centres of the type $\geq Si^{\cdot}$ or $\geq SiO^{\cdot}$ in the silica. After the action of $\gamma$-rays on lanthanum, samarium, and gadolinium oxides the rate of the process increased hundredfold[71]. More detailed study of the reaction on gadolinium oxide exposed to cobalt-60 $\gamma$-rays (integral dose $4 \times 10^5$ to $1.8 \times 10^7$ rad) at −85°C revealed an interesting relationship[72]: with increase in the integral dose the catalytic activity increased, and then somewhat diminished; after repeated growth in activity, the latter became independent of the radiation dose. The decrease in catalytic activity on exposure to doses exceeding 1.2 Mrad was explained by the association of primary defects. The secondary increase in activity was probably due to an increase in the number of association complexes.

Under a pressure of 20 mmHg at temperatures of 300° to 400°C the rate of exchange of oxygen on neodymium

oxide was approximately the same in a field of cobalt-60 $\gamma$-emission (200 rad $s^{-1}$) as in the absence of irradiation. Below 300°C there was hardly any change on the unexposed sesquioxide, but under irradiation the rate increased as the temperature fell from 300 to 20°C. This is because at low temperatures the reaction velocity on biographic active centres became incomparably smaller than the rate on radiation defects. At high temperatures the exposure of various oxides to cobalt-60 $\gamma$-rays did not lead to their activation, but at low temperatures their activity increased initially in proportion to the radiation dose, and then ceased to depend on it [74]. The radiation susceptibility diminished on passing from dielectrics to intrinsic semiconductors, and disappeared completely in substances having a forbidden gap $<2$ eV. [74] Similar results were obtained with preliminary radiation modification of the oxides. The activity of specimens that had been irradiated in an atmosphere of oxygen exceeded the activity of those that had been exposed in a vacuum.

In spite of the many experimental results on isotope exchange, it is still difficult to reach any conclusions on general aspects of the process or on its mechanism. Only the dependence of the radiation susceptibility of catalysts on the width of the forbidden gap [74] is of universal character, as we shall see later.

### 3. Decomposition of Hydrogen Peroxide and Certain Other Compounds

Study of the effect of radiation on the rate of decomposition of hydrogen peroxide was initiated [75] by recording the decrease in the catalytic activity of platinum during the reaction occurring in an X-ray field. Radiation poisoning of platinum is produced also by pretreatment with $\gamma$-rays [76]. Other workers also found [77,78] that exposure of platinum catalysts deposited on semiconductor carriers to a mercury–quartz lamp has an adverse influence on their catalytic properties in a subsequent reaction. Especially strong deactivation was observed when the dielectric silicon dioxide was used as carrier. However, direct $\gamma$-radiation of the hydrogen peroxide–platinum reaction system resulted in an appreciable increase in the rate of decomposition of the peroxide [79].

Another study [80] demonstrated the role of the carrier in the activation of a silver–silver oxalate catalyst by $\gamma$-rays (integral doses $2 \times 10^3$, $1.2 \times 10^5$, and $2.4 \times 10^5$ rad). The activity of the catalyst had changed little after irradiation, but was increased by subsequent heating. The explanation offered was that radiolytic silver, formed in the carrier on exposure, accelerated thermal decomposition of the salt with the separation of active silver. Introduction of a $\beta$-ray source (the sulphur-35 isotope) into the carrier of an iron phthalocyanine–barium sulphate catalyst improved the stability of the catalyst: the number of moles of hydrogen peroxide decomposed per mole of iron phthalocyanine decomposed increased in direct proportion to the specific radioactivity of the specimen [81]. Thus with catalysts of specific radioactivity 10.2 and 238.0 mc $g^{-1}$ the stability increased by 9% and 45% respectively.

The decomposition of hydrogen peroxide on neodymium oxide was accelerated after pretreatment of the latter in a nuclear reactor [82]. The active centres thus formed were so stable that annealing the catalyst at 110°C for 24 h, though lowering the activity, did not bring it down to that of the unirradiated specimen. The rate of decomposition of hydrogen peroxide on nickel oxide and the quantity of excess oxygen adsorbed both increased in parallel with the energy absorbed from cobalt-60 $\gamma$-rays (integral dosage $10^7$–$8 \times 10^9$ rad). [83] With a dose of $10^8$ rad the catalytic activity of the nickel oxide was double that of unirradiated specimens. The electrical conductivity of the oxide simultaneously diminished.

Many workers choose the decomposition of formic acid as model reaction. Thus the catalytic activity of copper and silica gel is somewhat improved after bombardment with fast neutrons [84]. An interesting study was made of this reaction [85,86] occurring at a high temperature on a single crystal of silver pre-irradiated with accelerated argon ions. Electron diffraction showed that the radiation treatment led to the formation of point defects and dislocations in the crystal lattice. Two competing processes—increase in the activation energy of decomposition and enhancement of the reproducibility coefficient† —were involved. Depending on which face of the single crystal was subjected to ion bombardment, one of these processes predominated, and thereby determined the sign of the radiation effect.

Preliminary irradiation of a catalyst comprising a mixture of aluminium and silicon oxides in a nuclear reactor somewhat lowered the rate of cracking of cumene at 300–450°C. [87] However, if the specimen had been "alloyed" with zinc and vanadium additions before exposure, the rate of the process was more than doubled, which indicated that impurity centres played an active part. A possible mechanism of interaction between corpuscular radiation and impurity atoms was illustrated [88] by the decomposition of nitric oxide on catalysts consisting of alumina (a dielectric), nickel monoxide (a *p*-type semiconductor), and tin dioxide (an *n*-type semiconductor) with additions of boron and lithium oxides. After exposure to neutrons (dosage rate $10^{11}$ n $cm^{-2}$ $s^{-1}$) for 3 h and standing for 1 month, the tin dioxide showed an increase, and the nickel monoxide a decrease, in catalytic activity. The reaction velocity had diminished on the catalyst comprising 90% $Al_2O_3$ + 10% $Li_2O$, but had increased on 90% $Al_2O_3$ + 10% $B_2O_3$. This was attributed to a change in the electronic properties of the oxides, both directly under the influence of the neutron irradiation and as a result of interaction with $\alpha$-particles generated in the course of the nuclear reaction of lithium-6 and boron-10 atoms with neutrons.

Pretreatment of a copper catalyst with neutrons (integral flux $3 \times 10^{18}$ n $cm^{-2}$) lowered the activation energy of the dehydrogenation of cyclohexane from 41 to 17.5 kcal $mole^{-1}$ and accelerated the process fivefold [89]. This was attributed to the appearance of foreign (probably nickel) atoms in the specimen as a consequence of a nuclear reaction. No change in activity was observed when a copper catalyst was exposed to $\gamma$-rays. The emission from a nuclear reactor changed the catalytic activity of oxides of certain amphoteric elements in the thermal decomposition of light and heavy water [90]. This phenomenon was regarded as due to change in both electronic and structural characteristics of the specimens.

The decomposition of *n*-hexane was investigated on a potassium–chromium–alumina catalyst ($Al_2O_3 : Cr_2O_3 : K_2O$ = 90.7 : 5.6 : 3.7 mole %) irradiated in a nuclear reactor with slow neutrons [flux(0.8 and 1.2) $\times 10^{13}$ n $cm^{-2}$ $s^{-1}$] and with $\gamma$-rays [91]. After the radiation treatment the yield of hydrogen diminished, while that of gaseous hydrocarbons somewhat increased, indicating more intense cracking.

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† A reproducibility coefficient is not actually mentioned in Refs. 85 and 86 (Ed. of Translation).

Roasting the exposed catalysts did not destroy the radiation effect, but the latter disappeared completely when the experiment was repeated. The parallelism between the rate of cracking and the concentration of the radioactive chromium-51 isotope produced suggested that the latter had a promoting effect. This is confirmed by results[92] for the reaction occurring on $\gamma$-alumina to which chromium or chromium-51 (a source of $\gamma$-rays) had been added: the rate of cracking increased on introduction of the latter.

The favourable effect of induced radiation was clearly shown by a study[93] of the decomposition of n-butane (dehydrogenation, cracking, isomerisation) on alumina catalysts containing 10% of vanadium(V), molybdenum(VI), and tungsten(VI) oxides respectively, after irradiation with slow neutrons (flux $10^{13}$ n $cm^{-2}$ $s^{-1}$) in a nuclear reactor. Before irradiation the activity of these catalysts decreased in the above sequence. The catalytic activity of the first of them was unaffected by the neutron treatment (whether for 3 days or for 1 month). Prolonged irradiation of the aluminium–molybdenum oxide catalyst resulted in the appearance of the molybdenum-99 isotope, a source of $\beta$- and $\gamma$-rays, which led to a slight increase in the degree of conversion of the butane. Interaction of the aluminium–tungsten oxide catalyst with neutrons was accompanied by formation of the tungsten-185 and -187 isotopes, whose induced radioactivity far exceeds that of molybdenum-99. This was regarded as the reason why the activity of the specimens had more than doubled.

Preliminary $\gamma$-irradiation of catalysts also changed the rate of decomposition. Thus an appreciable increase in the rate for isopropylbenzene on aluminosilicate catalysts was accompanied[94] by the appearance of colour centres, formed by aluminium atoms on each of which a hole was localised. These centres were probably responsible for accelerating the reaction. An increased rate of dealkylation of isopropylbenzene was observed also after $\gamma$-irradiation of pure silica gel[95]. Here biographical defects in the catalyst surface, which trapped free holes formed under the influence of the radiation, were regarded as the active centres. The radiation treatment of silica on which a gas had been adsorbed showed that dealkylation resulted from the direct capture of free holes by the semiconductor. This yet again indicates an electronic mechanism for the radiation promotion of silicon dioxide.

Preliminary irradiation of magnesium oxide with $\gamma$-rays from a caesium-137 source (integral dose $2.5 \times 10^7$ rad) led to a decrease in the rate of decomposition of potassium perchlorate accompanied by a fall in the threshold temperature at which this reaction becomes possible[96]. Radiation was shown to produce a contraction in the crystal lattice of the oxide with the generation of free electrons. Recombination of the latter with free holes involved in the process had an adverse effect on the activity of the oxide.

Studies of decomposition occurring on solid catalysts under the influence of continuous irradiation usually attempt to elucidate how the rate of homogeneous radiolysis changes on the introduction of catalysts possessing various properties. It will be shown that such an approach enables the maximum amount of information to be extracted on the primary steps of interaction on the catalyst surface.

The rate and the degree of decomposition of potassium oxalate in aqueous solution under the influence of $\gamma$-rays increased considerably in the presence of a suspension of zinc oxide[97]. The dependence of the rate of $\gamma$-radiolysis of pentane in the presence of silica gel, magnesium oxide, or aluminium oxide on their surface coverage by the initial gas suggested[98–101] the active transfer of the emission energy absorbed by the solid to the adsorbed molecules. It was assumed that use was made of the energy evolved on the annihilation of electron–hole pairs generated in the oxides by the radiation, this process involving holes localised on adsorbed pentane molecules and free electrons.

The importance of short-lived radiation defects was confirmed[102] by the hundredfold increase in the yield of hydrogen from the $\gamma$-radiolysis of water when the process occurred on a silica-gel surface. Electron spin resonance showed that the emission was unable to create permanent defects in the catalyst but only excited states, whose energy was consumed in the decomposition of adsorbed molecules. A strong dependence of radiation-chemical yields on the surface coverage of solids by the starting material was observed also in the $\gamma$-radiolysis of heptane on aluminosilicate, aluminium–tungsten, and aluminium–molybdenum catalysts[103–105] and in the decomposition of isopropylbenzene on aluminium silicate[106,107]. The equality of the rates of homogeneous and heterogeneous processes when surface coverage by the initial molecules exceeds a monolayer indicates that the emission energy is transferred only to the first adsorbed layer. The ability of solids to transmit emission energy to adsorbed molecules is strongly dependent on their chemical nature. Thus the rate of the $\gamma$-radiolysis of ammonia on a zeolite in the sodium form exceeded considerably the rate of the homogeneous process[108–110], but when the calcium form was used the yield of hydrazine was the same in the two cases.

The view that a catalyst is an energy converter, transforming one type of motion (e.g. the kinetic energy of substrate molecules) into a different form important for the activation of molecules (e.g. into the vibrational energy of molecules), was expressed as early as the 1920s.[111] This concept formed the basis of the first theoretical interpretation of the phenomena involved in the effect of radiation on the catalytic properties of solid materials[112]. The hypothesis[113] that the radiation-catalytic activity of solids is determined by their heat capacity, increase in which should be accompanied by a decrease in activity, has not found experimental confirmation.

The rate of decomposition of carbon dioxide exposed to cobalt-60 $\gamma$-rays, X-rays, and strontium-90 $\beta$-rays is sharply increased by the introduction of silica gel, alumina, and magnesium oxide into the system[114,115]. Radiation-chemical yields are extremely slightly dependent on temperature and on the nature of the emission. Investigation of this reaction occurring under the influence of $\gamma$-rays (2.8 Mrad $h^{-1}$) on oxides having different electronic characteristics led to the conclusion[116] that the intensity of heterogeneous radiolysis diminishes from intrinsic to $n$-type and then to $p$-type semiconductors. The high-temperature $\gamma$-radiolysis of water vapour accelerated considerably in the presence of zinc oxide, with a forbidden gap of 3 eV; the effect of vanadium pentoxide, with a gap of 0.5 eV, was hardly noticeable[117].

The deduction that energy is transmitted to the adsorbed substance more efficiently in the case of dielectrics and semiconductors is supported by many investigations. Thus the degree of decomposition of azoethane fell on passing to catalysts having a narrow energy gap, to magnesium(II), silicon(IV), titanium(IV) oxides, (8.7, 8.0, and 3.0 eV respectively), etc.[118,119] This problem was examined in detail in studies[120,121] of the dehydrogenation of cyclohexane on dielectric oxides (silica, alumina, aluminium silicate), $n$- and $p$-semiconductors (zinc and nickel monoxides), and metals (nickel, 7% platinum/

/silica). In the thermal process the specific activities of the catalysts formed the sequence

$$Pt/SiO_2,\ Ni > NiO > ZnO,\ Al_2O_3 \cdot SiO_2 > MgO,\ ZrO_2,\ Al_2O_3,\ SiO_2.$$

Under the influence of continuous $\gamma$-irradiation ($3.4 \times 10^{16}$ eV $g^{-1}$ $s^{-1}$) the relation between the activities was inverted: materials having a wide forbidden gap were the most active. It is significant that, in contrast to semiconductors and metals, radiation-active dielectrics showed the presence of paramagnetic centres and $C_6H_7^{\bullet}$ radicals when cyclohexane was adsorbed during irradiation. The dependence was interpreted[120,121] on the hypothesis that the cyclohexane molecule is activated by the energy evolved on recombination of a free electron with a hole previously trapped by the molecule. This energy is equal to the difference between the width of the forbidden gap and the heat of adsorption of the gas molecule, so that substances having a wide energy gap should possess the maximum activity. The conclusion that free current carriers—not stable defects—play the main part in the decomposition of cyclohexane is supported by the fact[122] that the degree of decomposition of the initial gas on an aluminosilicate catalyst (10% $Al_2O_3$) under direct $\gamma$-irradiation exceeds considerably the extent of decomposition on a previously irradiated specimen.

While completely accepting the viewpoint of the authors[120,121], the Reviewers would like to stress that it would have been wrong to base prediction of the radiation-catalytic activity of solids solely on the width of the forbidden gap, without regard to the heat of adsorption of the molecules. Furthermore, the recombination of electron–hole pairs on adsorbed molecules may meet serious competition from their recombination on other local centres (impurities, defects), which are present in abundance on solid surfaces.

## 4. Decomposition of Alcohols and Isomerisation of Hydrocarbons

Although the catalytic decomposition of alcohols usually takes place by a fairly complicated mechanism, study of this particular class of reactions has revealed several interesting laws governing the interaction of reactants with the surface of irradiated catalysts. The dehydration of n-decanol and isomerisation of the resulting dec-1-ene were studied[123,124] on samples of alumina that had been subjected to preliminary irradiation. X-Rays had a favourable effect on the degree of conversion, treatment with cobalt-60 $\gamma$-rays and reactor $n,\gamma$-radiation lowered the catalytic activity of the oxide, and exposure to fast neutrons produced no observable change. Interesting results were reported[125] for this reaction occurring on alumina that had been exposed to neutrons ($8 \times 10^{12}$ n $cm^{-2}$ $s^{-1}$) for 1–10 days. Catalysts that had been irradiated for a few days exhibited a negative radiation effect. The yield of unsaturated hydrocarbons increased as the duration of neutron bombardment was lengthened. This was attributed to the occurrence of two competing processes—the negative influence of the direct interaction of neutrons with active centres in the alumina and the promoting effect of the high-energy radiation emitted from the short-lived aluminium-28 and oxygen-19 isotopes formed in the specimens as a result of a nuclear reaction.

The catalytic activity of silica in the isomerisation of butene and the conversion of cyclopropane into propene was increased by preliminary irradiation with X-ray bremsstrahlung[126]. The rate of the second process diminished when the catalyst was heated to 100°C, and fell sharply at 200°C, whereas the activity of the silica towards the first reaction became appreciably lower only at 400°C. This was explained by the generation of two types of active centres on the surface. The great thermal stability of the radiation active centres involved in the isomerisation of butene was noted also in the neutron pretreatment of silica gel, aluminium silicate[127], and also potassium aluminate catalysts[91], which exhibited a fifty-fold radiation activation.

Study of the thermal dissociation of ethanol on neutron-treated zinc oxide—(2.3 and 3.9) $\times 10^{13}$ n $cm^{-2}$ $s^{-1}$—showed[128] that increasing the duration of the radiation intensified dehydrogenation and tended to suppress dehydration. This effect was attributed[129] to the appearance of gallium as donor impurity in the zinc oxide, which raised the Fermi level and should thus[21] lead to a similar change in selectivity of the catalyst. The shift in the decomposition of propan-2-ol towards dehydrogenation after the irradiation of yttrium[130] and neodymium[131] oxides with thermal neutrons ($1.2 \times 10^{13}$ n $cm^{-2}$ $s^{-1}$) was explained by production of the radioisotopes—yttrium-90, terbium-166 and neodymium-147, neodymium-149.

Many studies have confirmed the decisive role of the electronic properties of irradiated catalysts in the decomposition of alcohols. For example, the rate of dehydrogenation of ethanol on copper(II) oxide increases after its $\gamma$-irradiation, with an increase in the electrical resistance, but on copper(I) oxide it falls in parallel with the latter[132]. Continuous exposure of zinc oxide (an $n$-semiconductor) to $\gamma$-rays ($4.5 \times 10^5$ r $h^{-1}$) activated it for the dehydrogenation of methanol, whereas chromic oxide (a $p$-semiconductor) was poisoned under the same conditions[133] (the increase in the rate of this reaction on zinc oxide when $\gamma$-irradiation was begun has been confirmed[134,135]). Exposure of two preparations of tungsten disulphide differing in stoichiometric composition[136]—$WS_{1.99}$ (an $n$-semiconductor) and $WS_{2.3}$ (a $p$-semiconductor)—to a flux of slow neutrons ($1.2 \times 10^{13}$ n $cm^{-2}$ $s^{-1}$) and to $\gamma$-rays ($10^4$ r $s^{-1}$) in a reactor led to the formation in the bulk of the specimens of the tungsten-187, tungsten-185, and sulphur-35 isotopes ($\beta$- and $\gamma$-sources), which activated the disulphides for the dehydration of n-decanol; the electrical conductivity of the first preparation fell, whereas that of the second preparation increased.

Among investigations on the decomposition of alcohols on solids into which radioactive isotopes had been introduced during preparation, note must be taken of a series of papers by Balandin, Spitsyn, and their coworkers. The increases in the degree of dehydration at 350°C of alcohols on magnesium sulphate catalysts containing the radioactive sulphur-35 isotope, in comparison with specimens to which non-radioactive sulphur had been added, were respectively 200%, 121%, 42%, and 26% for n-pentanol, n-hexanol, n-decanol, and n-dodecanol[136,137].

The effect of internal $\beta$-emission on the catalytic properties of solid materials was thoroughly studied[138–141] with as example the dehydration of cyclohexanol on magnesium sulphate to which had been added sodium sulphate and calcium chloride containing either non-radioactive sulphur and calcium or their radioactive isotopes sulphur-35 and calcium-45. The non-radioactive additives diminished significantly the catalytic activity of the magnesium sulphate, whereas the radioactive additions, while themselves not catalysing the reaction, increased considerably the degree of dehydration. Activation energies for the reaction on the radioactive specimens were somewhat

lower. A linear relation was observed between the activity and the dosage rate of self-irradiation of the catalysts: the degree of conversion of the alcohol increased in parallel with the specific activity of the specimens.

The mechanism of the influence of internal radioactive emission on the catalytic properties of solids evidently differs from that of external radiation. For example, the degree of dehydration of n-dodecanol on alumina diminished on continuous irradiation of the system with electrons, but introduction of a source of electrons (calcium-45) into the catalyst increased sharply the activity of the specimen [123]. The same conclusion can be reached by comparing the above results [138-141] with data [142] indicating that exposure of the cyclohexanol–magnesium sulphate system to external X-rays does not increase the degree of dehydration of the alcohol, although it produces high-energy electrons within the catalyst. Electron-microscopic investigation [143] of non-radioactive specimens of potassium, magnesium, and barium sulphates and of molybdenum trioxide, as well as specimens containing various quantities of radioactive sulphur and molybdenum isotopes, showed that the radioactive substances had considerably more developed surfaces. However, this alone is insufficient to explain the enhanced catalytic activity of radioactive specimens. The catalytic activity of specimens of magnesium sulphate containing sodium sulphate labelled with radioactive sulphur, calculated per unit surface for the dehydration of cyclohexanol, increased with the $\beta$-radioactivity [144].

Among the investigations on the decomposition of alcohols under the influence of continuous external $\gamma$-irradiation we would like to note a series of papers by Vladimirova, Zhabrova, and their coworkers. The view that dielectrics are the most active in transmitting the energy of the radiation was again confirmed [145-147]: the rate of decomposition of methanol on silica and alumina exceeded the rate of the homogeneous process by a factor of 10; the rates on the semiconducting zirconium(IV), zinc(II), magnesium(II), and nickel(II) oxides by factors of 2–3; and on metals the intensification of the reaction was hardly appreciable; but the presence of activated carbon slowed down the reaction. The radiation-catalytic activities of diamond and graphite—the same chemical substance in different electronic modifications—were compared [148]. Diamond (natural and synthetic), having a forbidden gas of 7 eV, contributed to reaction velocities exceeding the rate of the homogeneous radiolysis of methanol by a factor of 100. Graphite, whose conductance is almost metallic, was not a radiation catalyst.

With the smallest (0.7%) surface coverage of silica gel the yield of decomposition products from methanol was the highest, exceeding hundredfold the yield of homogeneous radiolysis, but with a monolayer the increase was only tenfold [149]. A more detailed investigation [150,151] revealed the interesting fact that, with the same quantity of methanol on silica and alumina surfaces, their catalytic activity was independent of the specific surface and the size of the globules. This indicates yet again that free current carriers, generated by radiation inside the solid, are involved in the decomposition of adsorbed molecules, and that their diffusion from the interior to the surface is more rapid than the primary steps in the radiation-catalytic reaction. The increase in the rate of the process observed with decrease in the quantity of substance adsorbed shows that catalytic activity is determined solely by the relation between the quantity of the compound adsorbed and the excess quantity of current carriers.

Analysis of numerous experimental data suggests that the mechanism of the decomposition of methanol is [28]

$$\text{Тв solid} \xrightarrow{\text{rad.}} K^+ + A^-$$

$$CH_3OH + K^+ \rightarrow \underset{\substack{\text{physical}\\ \text{adsorption}}}{CH_3OH^+}$$

$$\underset{\text{chemical}}{CH_3OH^+} + \ominus \rightarrow \dot{C}H_2OH + H$$

$$\dot{C}H_2OH + \dot{C}H_2OH \rightarrow (CH_2OH)_2$$

$$\dot{C}H_2OH \rightarrow CH_2O + H$$

$$H + H \rightarrow H_2 \ .$$

The energy evolved on the annihilation of an electron and a hole is consumed in the formation of a hydroxymethyl radical. These radicals recombine to form a molecule of ethylene glycol, and decompose to give a formaldehyde molecule.

## 5. Catalytic Hydrogenation

The hydrogenation of ethylene is most often chosen as model reaction, since in many cases this process does not require a high temperature. As early as 1932 a 5% increase in rate was recorded for this reaction taking place on a copper catalyst exposed to X-rays at room temperature [152].

Preliminary $\gamma$-irradiation of copper produced slight deactivation, whereas the catalytic activity of zinc oxide decreased by 80%. [153] This was attributed to a change in the charge structure of the semiconductor surface. The rate of hydrogenation of ethylene falls after zinc oxide has been exposed to $\gamma$-rays [55]. The decrease in catalytic activity of the oxide is not accompanied by change in the activation energy of the reaction, and heating the specimens restores their original properties. The active centres were assumed [154] to be interstitial $Zn^+$ cations, which are converted by ionising collisions with secondary electrons into inactive $Zn^{2+}$ cations; heat-treatment promotes the reverse process. In contrast to zinc oxide, silica gel, which is not a catalyst for this reaction, was appreciably activated after $\gamma$-irradiation for 20 h. [155]

Considerable increase in catalytic activity of copper, nickel, and platinum catalysts in the hydrogenation of ethylene was observed after their bombardment with accelerated positive argon ions [156-158]. Electron diffraction recorded significant structural disturbances in the crystal lattices. Heating the metals at 550°C annealed the defects and lowered the reaction velocity to values characteristic of unirradiated catalysts. On the other hand, structural defects generated in copper by $\alpha$-particles from a polonium-210 source caused a decrease in catalytic activity independently of the environment (hydrogen, vacuum) in which irradiation had occurred [159].

Examination of the effect of fast neutrons on the catalytic properties of zinc oxide showed [160] that the sign and the magnitude of the radiation effect depend on the chemical and thermal treatment of the catalysts preceding irradiation. The activity in the hydrogenation of cyclohexene of platinum catalysts deposited on aluminium silicate was unaffected by preliminary exposure to $\gamma$-rays [161]. However, the rate of this reaction was increased by the exposure of platinum–silica catalysts to a quartz–mercury lamp [162], the maximum increase in activity (double) being observed on illumination for 3–4 h. After exposure for 6 h the rate of the process returned to its initial value.

Passage of the catalytic activity through a maximum was recorded in the hydrogenation of nitrobenzene when a nickel catalyst was subjected to X-rays and $\beta$-particles [163]. This work also showed that the treatment of palladium with accelerated electrons increases the rate of hydrogenation of *p*-nitrotoluene in glacial acetic acid. The same result was obtained when platinum was exposed to $\beta$-rays of energy 3 MeV, whereas those of energy 2 MeV and X-rays produced no appreciable change. The radiation effect was attributed [163] to the appearance of defects in the structure of the catalysts.

The view that preliminary electromagnetic irradiation and exposure to a flux of light charged particles are unable to affect rates of hydrogenation appreciably is supported also by the hydrogenation of petroleum [164] and unsaturated hydrocarbons [165] on metals. Most investigators therefore relate the change in the rate of hydrogenation to the appearance of structural defects in the specimens. Thus work in which the rate of hydrogenation of acetone was trebled on neutron-irradiated specimens of nickel showed [166] that on thermal annealing the radiation activity of the catalysts disappears over a temperature range in which the number of point defects decreases sharply. Variation in the concentration of free current carriers probably also plays an important part in semiconductors subjected to $\gamma$-rays during the reaction. The positive radiation effect in the hydrogenation of carbon monoxide was found [167] to depend on the excess quantity of zinc in its oxide, which determined the electronic properties of the catalyst. The rate of this reaction trebled on zinc oxide at 160°C. [168] With rise in temperature the radiation effect diminished, and at 230°C disappeared altogether, probably owing to an increased rate of annealing of electron–hole pairs.

The influence of reactor radiation on the rate of the liquid-phase hydrogenation of dimethylprop-2-ynol and butynediol was studied by Sokol'skii et al. A comparison was made of the activities of platinum and osmium–platinum blacks obtained from the oxides with and without preliminary irradiation [169]. The considerably higher activity of the former was attributed to the increased degree of dispersion of the metals detected by X-ray diffraction. A similar pattern was observed in the hydrogenation of butynediol in ethanol on platinum and palladium catalysts [170]. This effect is due also to the appearance of impurity rhodium, silver, and cadmium atoms inside the platinum [171]. In the hydrogenation of the dimethylpropynol in dioxan on palladium catalysts obtained from the oxides exposed to neutrons and to $\alpha$-particles the reaction velocity increased by 100% and 60% respectively; the rate of the process in ethanol was independent of irradiation of the oxide [172].

Pretreatment in a nuclear reactor had a beneficial effect on the catalytic activity of 5% and 0.5% of platinum, palladium, and rhodium on $\gamma$-alumina in the hydrogenation of the dimethylpropynol in caustic soda [173,174]. The largest increase in activity was observed with the 0.5% platinum catalyst, when preliminary irradiation of the metal together with the carrier increased the activity of the catalyst by a factor of 5.2, but radiation treatment of the carrier separately before deposition of the active metal led to a fiftyfold increase in the rate of the process. A similar phenomenon, though less well defined, was observed also with the palladium and rhodium catalysts. Raising the temperature of the reaction diminished the radiation effect. The change in the electronic and structural properties of the carrier under the influence of radiation probably also played a part here.

Continuous $\beta$-irradiation of a platinum plate (of thickness equal to the range of a $\beta$-particle) doubled the rate of hydrogenation of benzene, which took place on platinum black deposited on the opposite side of the plate [175]. This was due to migration to the surface of defects generated inside metal by the radiation.

## 6. Catalytic Oxidation

Pretreatment of platinum black with X-rays in a moist atmosphere for 2 h increased by 16% the rate of conversion of sulphur dioxide into the trioxide at 260°C; [176] if the reaction temperature was raised to 400°C, only 1.3% activation of the catalyst was observed. Radiation treatment in dry air did not affect the catalytic activity. A similar result was obtained by workers [177] who observed an increased content of oxygen, formed by the radiolysis of air, in platinum that had been exposed to X-rays in a moist medium.

Preliminary bombardment of vanadium pentoxide with thermal neutrons ($10^{18}$ n cm$^{-2}$ s$^{-1}$) diminished its activity in the oxidation of sulphur dioxide [178]. Since this reaction took place above 500°C, the radiation effect was due to the production of stable defects, probably with the appearance of silver-110 atoms—$\gamma$- and $\beta$-sources—inside the catalyst. The rate of this process decreased on the pure pentoxide also when the latter was exposed to $\gamma$-rays during the reaction [179]. The magnitude of the radiation effect is a function of the initial properties of the catalyst. Under the influence of continuous exposure to X-rays the catalytic activity of pure titanium dioxide, which has little effect on the oxidation of sulphur dioxide, increased by 18.4%; irradiation of the more effective catalyst $TiO_2$ + $NH_4VO_3$ accelerated the reaction by only 12%, but the most active catalyst $TiO_2$ + $V_2O_5$ was poisoned [180]. Similar results were obtained for the conversion of ethanol into formaldehyde on vanadium pentoxide [181].

An electromagnetic radiation field usually has a marked effect on the ability of semiconductors to catalyse oxidation. Examples are the oxidation of propane on zinc oxide under the influence of X-rays [182] and also the oxidation of various hydrocarbons on dielectrics (silica gel, alumina, aluminium silicate) subjected to $\gamma$-rays [183]. Both effects were explained by the excitation of free current carriers in the solid. This is indicated also by the invariability of the rate of oxidation of hydrogen on platinum when the system is introduced into an X-ray field [184], since the electronic properties of a metal show little response to the influence of X-rays.

Many workers have dealt at length with the conversion of carbon monoxide into the dioxide. The effect of neutron bombardment (fluxes of thermal and fast neutrons respectively $2 \times 10^{11}$ and $7 \times 10^{9}$ n cm$^{-2}$ s$^{-1}$) of nickel oxide with 2.5 mole % of lithium oxide on the rate of this reaction has been studied [185,186]. The further intensification of the process when conducted directly in a nuclear reactor instead of on previously irradiated specimens indicates the definite roles both of short-lived defects and of stable disturbances resulting from the nuclear reaction $^{6}Li(n,\alpha)^{3}H$. A definite correlation was detected between the catalytic activity and the hole conductance of nickel oxide. Pretreatment of nickel and zinc monoxides with $\gamma$-rays had no appreciable influence on their activity [187]. However, other workers showed [188] that the $\gamma$-irradiation of nickel

monoxide in a vacuum had an adverse effect on its catalytic properties, but in an atmosphere of oxygen a beneficial effect. This was explained by the radiation-stimulated migration of activated oxygen deep into the lattice of the catalyst.

The electron bombardment—$(3-12) \times 10^{12}$ el $cm^{-2}$ $s^{-1}$—of cuprous oxide led to its deactivation, in spite of an increase in the specific surface[189]. This phenomenon is connected with decrease in the concentration in the mobility of free holes in the bulk of the catalyst. Over the temperature range 80–300°C the activation energy of the oxidation of carbon monoxide on alumina under the influence of X-rays was zero, but with further rise in temperature it reached 18 kcal $mole^{-1}$, coinciding with the activation energy of the thermal process[190].

As we have been able to see, ionising radiation is a powerful factor influencing the adsorption and catalytic properties of solids. In spite of a vast quantity of experimental results accumulated by the present time, however, scientists are still far from a generally accepted interpretation of this phenomenon, and still farther from being able to use radiation to control the activity and the selectivity of catalysts. An increasing number of authors interpret radiation effects on the basis of an electronic theory of catalysis. Such an approach permits the most productive utilisation of existing theoretical ideas on the interaction of electromagnetic and corpuscular radiation with solids.

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# Methods of Synthesis of Peptides

**Yu.V.Mitin and N.P.Zapevalova**

Chemical methods for the activation of the carboxy-groups of the aminoacid used to synthesise peptides are examined, and the possible reaction mechanisms are described. Examples of the synthesis of certain peptides are presented. The bibliography includes 151 references.

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## I. INTRODUCTION

This review deals with the methods for the activation of the carboxy-groups of the *N*-acylaminoacids which may be used to form the peptide linkage. It includes data published up to 1964. The methods of synthesis of peptides published up to 1965 have been examined in detail in familiar monographs devoted to the chemistry of peptides[1,2]. The review is not concerned with the methods for the detection of the functional groups of aminoacids, the problems of the isolation and purification of peptides, and the methods for the determination of the purity of synthetic peptides.

## II. ACTIVATED *N*-ACYLAMINOACID ESTERS

The activated esters of *N*-substituted aminoacids are extremely convenient for the synthesis of peptides. The possibility of the isolation, purification, and storage of the activated esters greatly facilitates peptide synthesis. Furthermore, there are wide possibilities for varying the properties of activated esters, in particular aryl esters, by selecting suitable substituents in the benzene ring.

One may state without exaggeration that *N*-hydroxysuccinimide esters have enjoyed the greatest popularity in recent years[3,4]. They have been used more frequently than *p*-nitrophenyl[5] and 2,4,5-trichlorophenyl esters[6]. The synthesis of *N*-hydroxysuccinimide esters presents no difficulties; they can be readily obtained with the aid of dicyclohexylcarbodiimide or mixed anhydrides[7], or from the *N*-hydroxysuccinimide esters of dichloroacetic[8] or trifluoroacetic[9] acids.

After the *N*-hydroxysuccinimide esters had been proposed for the synthesis of peptides, esters based on hydroxylamine derivatives began to attract attention because of their high reactivity, the ready availability of the reagents required, and the low degree of racemisation or its absence.

Esters derived from *NN*-dialkylhydroxylamines, in particular those derived from 1-hydroxypiperidine[10,11], which have been synthesised with the aid of carbodiimide or mixed anhydrides, have been proposed as acylating agents. The esters derived from *NN*-dialkylhydroxylamines exhibit a comparatively weak acylating capacity, but, in the presence of acetic acid as the catalyst, acylation proceeds at an appreciable rate at room temperature. The enhancement of reactivity can be explained by the protonation of the nitrogen atom of the hydroxylamine:

$$R{-}COONR'R'' \xrightarrow{H^+} R{-}C\overset{+}{O}ONHR'R'' \quad .$$

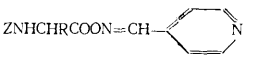
Certain small peptides have been synthesised with the aid of 1-piperidinyl esters[12-14], but their inadequate reactivities precluded their wide employment in peptide chemistry. Some studies have been devoted to esters derived from aldoximes and ketoximes[15-18]:

$$RCOON{=}C\begin{matrix}R'\\R''\end{matrix} \quad ,$$

where R′ = alkyl or aryl and R″ = alkyl or hydrogen. The esters of ketoximes are stable crystalline substances with a fairly high reactivity in relation to amines. When they react with aminoacid esters or free aminoacids at room temperature, peptides are obtained in 50-90% yield. The degree of racemisation in the synthesis of Anderson's tripeptide was 20%,[15,16] but this hardly reflects the properties of the activated esters, since the ester derived from 3-nitroacetophenoxime, used to study the racemisation reaction, has been synthesised with the aid of carbodiimide from Z-Gly-L-Phe-OH. There is no doubt that the racemisation occurred mainly in the synthesis of the ester itself, which, incidentally, does not rule out the formation of a racemic product also when the activated ester combines with ethyl glycinate.

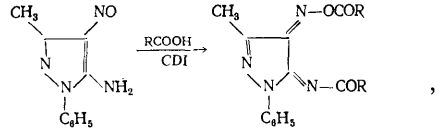
The synthesis of peptides with the aid of esters derived from ketoximes in the presence of acetic acid is more effective[17]. The addition of 1-1.5 moles of acetic acid increases the yield of peptides on average by 20-30%. Esters of ketoximes made it possible to synthesise serine and threonine peptides without protecting the hydroxy-group and also ω-nitroarginine peptides in 83-98% yield. The solubility of simple ketoximes in water facilitates the isolation and purification of peptides after the reaction. The method has been recommended for the stepwise synthesis of various peptides.

Interesting results have been obtained with esters derived from pyridine-4-aldoxime[18]:



In terms of their reactivity in the presence of acetic acid, esters derived from pyridine-4-aldoxime approach 2,4,6-trichlorophenyl esters and surpass *p*-nitrophenyl esters.

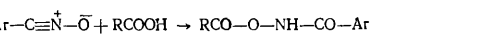
Using esters obtained from pyridine-4-aldoxime, certain peptides constituting fragments of angiotensin have been synthesised. An advantage of esters of pyridine-4-aldoxime is the ease of elimination of the reaction products and of the excess ester, since pyridine-4-aldoxime and the esters obtained from it readily dissolve in an acid medium. Esters derived from 5-amino-3-methyl-4-nitroso-1-phenylpyrazole can also be included among esters obtainable from oximes[19]:



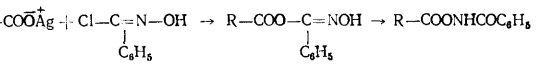
where CDI is carbodiimide.

They exhibit a high acylating activity and make it possible to synthesise peptides in high yields (90–95%) over a period not exceeding 1 h. Certain di-, tri-, and tetrapeptides have been synthesised with the aid of esters of this type. The Weygand[20] and Izumiya[21] tests showed that there is no racemisation at all in this reaction. The esters have yet another interesting feature: they are coloured red, while the reaction product (substituted 5-amino-4-nitrosopyrazole) is green, which makes it easier to follow the condensation reaction.

Hydroxamic acid esters have also attracted attention. A study on the synthesis of benzohydroxamic acid esters and the corresponding nitriles[22] via the mechanism



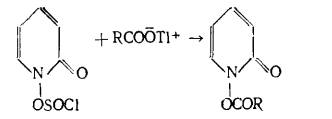
is of interest. The yield of esters in this reaction varies from 65 to 100%. Benzohydroxamic acid esters are fairly reactive and react with aminoacid esters at room temperature, giving peptides in yields not exceeding 75%. The low yields are caused by the Lossen rearrangement. Activated esters of the same type can be obtained also by the condensation of *N*-protected aminoacids with hydroxamic acids in the presence of carbodiimide[22] or by the reaction of the silver salts of *N*-protected aminoacids with the chloride of benzohydroxamic acid[23,24]; smaller yields are obtained from triethylammonium salts:



Although the majority of the esters are crystalline substances, they need not be isolated for peptide synthesis. The presence of acetic acid in the reaction of benzohydroxamic acid esters with amines appreciably accelerates the process. The authors believe[24] that the degree of racemisation does not exceed 0.1% for many peptides.

Esters based on *N*-hydroxyurethanes (for example, $HONHCOOC_2H_5$, which is both a hydroxamic acid and a carbamic acid ester) are likewise of interest. These esters have been synthesised with the aid of carbodiimide and mixed anhydrides in yields exceeding 90%.[25] A characteristic feature of these compounds is their appreciable resistance to the Lossen rearrangement. Esters based on *N*-hydroxyurethanes react readily both with aminoacid esters in an organic medium and with aminoacid salts in an aqueous medium. The yields of peptides are more than 90 and approximately 80% respectively. The use of *N*-hydroxyurethane as an additive in the carbodiimide synthesis of peptides lowers the degree of racemisation to 0–2% (Anderson's test). In contrast to *N*-hydroxysuccinimide[26], no side reactions were observed under these conditions, even if the mixture of *N*-hydroxyurethane with carbodiimide was kept at room temperature for many days[25].

Related but somewhat unusual esters are those derived from 1-hydroxy-2-pyridone[27,28]. They can be synthesised from acylaminoacid chlorides and 1-hydroxy-2-pyridone or from 2-oxo-1-pyridyl chlorosulphite and thallium salts of acylaminoacids[28]:

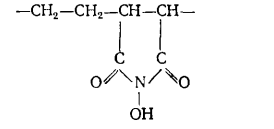


2-Oxo-1-pyridyl esters exhibit a high acylating activity, but, owing to their low stability and the difficulty of their synthesis, they have not so far found applications in the synthesis of peptides.

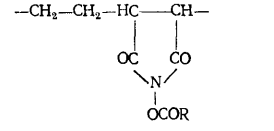
Despite the wide use of esters derived from *N*-hydroxysuccinamide in the synthesis of peptides, the search for new *N*-hydroxyimides of dibasic acids is being continued. Thus, the esters derived from *N*-hydroxyglutarimide have been synthesised and tested[29]. These esters, obtained with the aid of dicyclohexylcarbodiimide, are highly reactive, but do not have an appreciable advantage over esters derived from *N*-hydroxysuccinamide.

This can probably be also said of esters obtained from *N*-hydroxyphthalimide, first proposed in 1961[30] and recently used in the synthesis of certain peptides corresponding to the oxytocin sequence[31].

Activated esters obtained from polymers containing *N*-hydroxyimide groups are of particular interest. The copolymerisation of ethylene with maleic anhydride followed by treatment with hydroxylamine yielded a polymer containing units resembling *N*-hydroxysuccinimide:



Polymers of this type, which can be both soluble in organic solvents[32] and insoluble and cross-linked[33,34], can be obtained. An *N*-protected aminoacid RCOOH can be added with the aid of carbodiimide to the polymer, which gives rise to an activated polymeric ester:

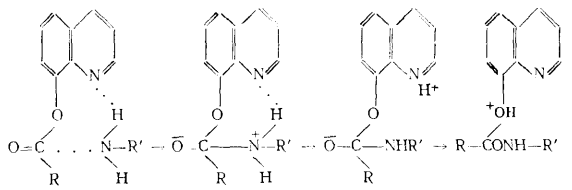


The latter can react with a solution of an amino-component in dimethylformamide. The yield of peptides in this reaction exceeds 90% as a rule if the activated ester is taken in a threefold excess. In the presence of equimolecular amounts of the reactants, the yield of peptide varies within wide limits (from 40 to 100%), depending on the nature of the aminoacid.

Polymeric activated esters are convenient because they obviate the need for the procedure involving the elimination of the excess of the activated ester and the ester component. At the same time they exhibit a high acylating activity, comparable to that of the usual esters obtained from *N*-hydroxysuccinimide. A heptapeptide corresponding to the 159–165 sequence of carboxypeptidase A (H–Ser–Pro–Cys–Ser–Glu–Thr–Tyr–OH) has been synthesised with the aid of polymeric activated esters in an overall yield of 59.5% before the elimination of protecting groups and 47.6% after their elimination[33]. The synthesis

of the octapeptide Boc–Met–Asp(OBzl)–Ser(Bzl)–Ser(Bzl)–Thr–Ser(Bzl)–Ala–Ala–OBzl has been achieved with an overall yield of 27%, the yields in the individual stages lying in the range 57–100%.[32]

Much attention has been devoted to activated esters whose reactivity can be accounted for by intramolecular base catalysis, in the first place esters derived from 8-hydroxyquinoline[35-39]. Kinetic studies on the aminolysis of these esters suggested the following reaction mechanism[36]:



This type of influence of nucleophiles adjoining the ester carbonyl group has also been noted in other examples, which will be discussed below.

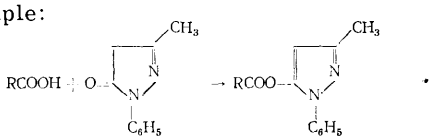
Esters are synthesised from 8-hydroxyquinolines either with the aid of carbodiimides or using mixed anhydrides, the yield being 70–90%. The esters formed by 8-hydroxyquinoline with the majority of benzyloxycarbonylamino-acids are stable crystalline substances, readily soluble in the usual organic solvents. The reaction with the amino-components proceeds at room temperature over a period of 4–20 h, the yields of peptides amounting to 75–97%. It is of interest that neither acetic acid nor heavy metal salts have any influence on the kinetics of the aminolysis reaction, which is consistent with the mechanism involving intramolecular catalysis[36]. Racemisation was not observed in the synthesis of Z–Leu–Phe–Val–OBu-t.[37] The reactivity of the esters derived from 5-chloro-8-hydroxyquinoline and 5,7-dichloro-8-hydroxyquinoline exceeds somewhat that of esters obtained from 8-hydroxyquinoline itself and they may be synthesised by the same methods[38]. Their suitability for the synthesis of peptides has been demonstrated in relation to a number of di-, tri-, tetra-, and penta-peptides, obtained in 65–97% yield. However, one should note that only comparatively simple aminoacids were used in all cases: glycine, alanine, valine, leucine, phenylalanine, and *S*-benzylcysteine.

In contrast to the esters obtained from 8-hydroxyquinoline, those of 3-hydroxy- and 6-hydroxyquinolines are appreciably less reactive, particularly the esters obtained from 6-hydroxyquinoline[39]. Apart from 8-hydroxyquinoline, 8-hydroxyquinaldine has been used to synthesise activated esters[40]. Furthermore, the copolymerisation of 8-benzyloxy-5-vinylquinaldine with divinylbenzene gave a polymer containing 8-hydroxyquinaldine groups. After the removal of the benzyl group, the copolymer was used to synthesise polymeric activated benzyloxycarbonylalanine esters[40]. Aminolysis by ethyl glycinate gave the dipeptide Z–Ala–Gly–$OC_2H_5$ in 87% yield.

The effect of the intramolecular base catalysis was manifested to a greater extent for esters based on 2-hydroxypyridine[41] and 2-mercaptopyridine[42]. Esters have been synthesised from 2-hydroxypyridine with the aid of carbodiimide in pyridine. In other solvents, 2-pyridyl esters could not be synthesised. The majority of 2-pyridyl esters of t-butoxycarbonylaminoacids are crystalline, readily soluble substances with a very high reactivity. According to kinetic measurements, the time of 50% reaction with amines is between 8 and 86 min. Under these conditions, *p*-nitrophenyl esters have a half-reaction time ranging from 540 to 1900 min. However, such a high reactivity has been observed only in non-polar solvents (chloroform, methylene chloride, etc.). In polar solvents, for example, in dimethylformamide, the activity of 2-pyridyl esters is sharply reduced, which has been explained by the inactivating influence of polar solvents on the intramolecular base catalysis[41].

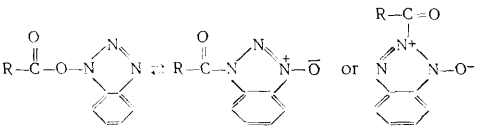
Pyridyl esters react readily with amino-components, forming peptides in 80–96% yield. They can be used to synthesise peptides on a polymeric carrier; thus oxytocin has been obtained in 70% yield using a fivefold excess of 2-pyridyl esters at each stage. Pyridyl esters react fairly readily with alcohols and hydroxyacids, so that they can be used to synthesise depsipeptides. 2-Pyridyl thio-esters, which can be readily obtained with the aid of carbodiimide, mixed anhydrides, or acid chlorides, have similar properties. They also readily react with amines and alcohols in non-polar solvents; on the other hand, in polar solvents (dimethylformamide, dimethyl sulphoxide) their reactivity falls. In contrast to 2-pyridyl esters, 3-pyridyl and 4-pyridyl esters of acylaminoacids are less reactive, which can be explained by the absence of intramolecular base catalysis. However, their reactivity is nevertheless fairly high, in particular, that of 3-pyridyl esters, which exceeds even the reactivity of *p*-nitrophenyl esters[43]. In contrast to 2-pyridyl esters, 3-pyridyl esters are very stable. Their reaction with amino-components gives rise to peptides in yields ranging from 50 to 97%.

All pyridyl esters have the advantage that the hydroxypyridines formed in the synthesis of peptides can be readily washed out of the reaction products. In a certain sense, the esters derived from the enolic form of substituted pyrazolone resemble 2-pyridyl esters[16]. They are readily obtained with the aid of carbodiimide or mixed anhydrides, for example:



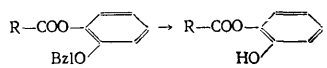
The esters obtained from the enolic form of pyrazolones have a high reactivity, similar to that of *p*-nitrophenyl esters, and readily react with amino-components, forming peptides in 70–80% yield. The esters synthesised from the pyrazolone enol can be used to synthesise peptides in an aqueous organic medium, using in the reaction aminoacid salts as the amino-component. The yields of peptides are in this case 60–73%. The degree of racemisation determined by Anderson's method proved to be 8.4%; admittedly, one must bear in mind that the activated ester Z–Gly–Phe–OPyr has been synthesised from the dipeptide Z–Gly–Phe–OH with the aid of dicyclohexylcarbodiimide, which might have involved some racemisation already in the stage involving the synthesis of the activated ester itself.

1-Benzotriazolyl esters obtained with the aid of carbodiimide are exceptionally reactive[44]. For example, the reaction of the activated ester of benzyloxycarbonylphenylalanine with the ethyl ester of valine at 0°C leads to the formation of more than 90% of the peptide after only 5 min. It is of interest that 1-benzotriazolyl esters undergo a rearrangement on crystallisation from solution. They exist in solution in the form of *O*-esters and in the crystalline state in the form of *N*-acylbenzotriazole oxide:

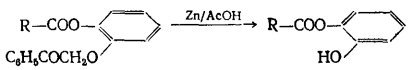


However only three 1-benzotriazolyl esters (BT) have been described hitherto: Z–Phe–OBT, Z–Gly–OBT, and Z–Thr–OBT. The high reactivity of 1-benzotriazolyl esters is apparently the reason why they are difficult to handle. 1-Hydroxybenzotriazole can probably be usefully employed as an additive in the carbodiimide synthesis, which will be discussed below.

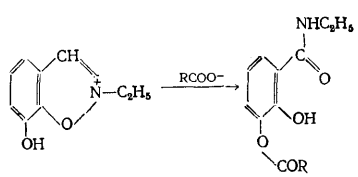
Activated esters of another type, whose enhanced reactivity can be explained by intramolecular catalysis, are those derived from catechol (*o*-hydroxyphenyl esters). They can be synthesised either from *o*-phenylene sulphite or, in a much higher yield, from *o*-benzyloxyphenol, by condensation with the aid of carbodiimide followed by the elimination of the benzyl group by hydrogenolysis or by treatment with hydrogen bromide in acetic acid[45]:



One can also begin with *o*-phenacyloxyphenol, since the phenacyl group is eliminated under milder conditions than the benzyl group[46]:



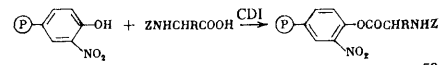
*o*-Hydroxyphenyl esters of acylaminoacids are fairly reactive. Thus the *o*-hydroxyphenyl ester of phthaloylglycine gives 91% of the peptide on reacting with ethyl glycinate at room temperature for 1 h.[45] For comparison, one may point out that phenyl phthaloylglycinate forms less than 1% of the peptide under the same conditions; the most important feature is that there is no racemisation at all when *o*-hydroxyphenyl esters are used. Because of this, *o*-hydroxyphenyl esters have been employed to synthesise polypeptides by the condensation of *o*-hydroxyphenyl esters of various tripeptides, for example, Lys–Ala–Ala[46,50]. 4,5-Dichloro-2-hydroxyphenyl esters are approximately three times as reactive as *o*-hydroxyphenyl esters, but they have not been used for the synthesis of peptides owing to the difficulty of obtaining them[45]. Esters containing the hydroxy-group in the *o*-position relative to the ester group are obtained ultimately by the reaction of the 2-ethyl-7-hydroxybenzoisoxazolium cation with acylaminoacids[51,52]:



(A number of intermediates are not indicated).

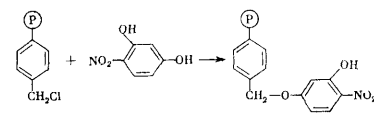
The activated esters formed are highly reactive. Thus the corresponding ester of benzyloxycarbonylglycine reacts with phenylalanine in aqueous sodium bicarbonate solution and forms 91% of benzyloxycarbonylglycylphenylalanine after 15 min. Peptide esters, in particular benzyloxycarbonylglycylphenylalanine, obtained from the 2-ethyl-7-hydroxybenzoisoxazolium cation, are very resistant to racemisation even under fairly severe conditions (12 h in 0.4 M solution of triethylamine in dimethylformamide). 2-Ethyl-7-hydroxybenzoisoxazolium fluoroborate is apparently one of the most interesting reagents for the synthesis of peptides[51]. Esters based on *o*-nitrophenol, which have been investigated in detail recently by Bodanszky and coworkers[53–56], are very promising. In contrast to *p*-nitrophenyl esters, *o*-nitrophenylesters are very reactive; the rate of their aminolysis depends less on the nature of the solvent, which can be accounted for by the intramolecular influence of the *o*-nitro-group. The high reactivity of these esters permitted their successful employment for the synthesis of protected oxytocin, the yield at each stage amounting to 80–95%.

Among other types of activated esters, much attention has been devoted to esters with a polymeric base. Their advantage is that the procedure involving the isolation of the peptide synthesised is greatly facilitated. This is particularly important for activated esters based on nitrophenols, as the latter are difficult to remove from peptides by hydrolysis. Polymeric phenols are obtained either by the copolymerisation of substituted styrenes with divinylbenzene[57–59], or by a reaction involving the polymer chain[60,61], or the phenol-formaldehyde condensation is used[62]. Activated polymeric esters of acylaminoacids are synthesised with the aid of carbodiimide[59,60]:

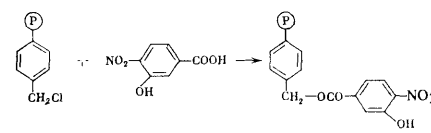


Using such esters, certain di- and tri-peptides[59] as well as bradykynin were synthesised in an overall yield of 39%. Naturally, the method can be used only in those cases where all the protected intermediate peptides are soluble in organic solvents.

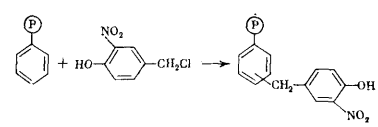
It was also found that the polymeric carrier obtained by the polymerisation of substituted styrene is not very strong mechanically, which leads to the fragmentation of polymer grains[60]. This necessitated the search for other methods whereby a polymeric carrier containing nitrophenol groups can be prepared. Chloromethylated cross-linked polystyrene was used for this purpose and nitroresocinol was attached to it in the presence of a base[61]:



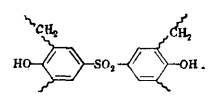
This polymeric carrier was mechanically strong and was used to synthesise various peptides. In another instance, 3-hydroxy-4-nitrobenzoic acid was attached to chloromethylated polystyrene[60]:



or 4-hydroxy-3-nitrobenzyl chloride was used, reacting with the styrene–divinylbenzene copolymer in the presence of aluminium chloride[63]:

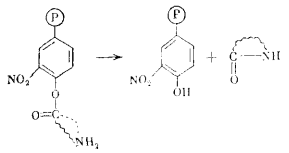


In all cases, activated esters were synthesised with the aid of carbodiimide and then, using 1.5 times the amount of the required polymeric activated ester, certain peptides were obtained, but, despite the excess of the activated ester, the yield was lower than in those cases where the synthesis was carried out in solution[60]. The polymeric activated ester, obtained on the basis of the condensation resin



had similar properties; the yield of peptides synthesised from it did not exceed 70%.[62]

Thus despite a number of useful properties, polymeric activated esters having the above structure are not appreciably advantageous compared with the analogous low-molecular-weight compounds. Their only advantage is perhaps in the case where they are used to cyclise peptides[64]. The peptide attached to polymeric nitrophenol can undergo only intermolecular cyclisation after the removal of the protecting group from the amino-group at the end of the chain; intermolecular condensation is then virtually ruled out:

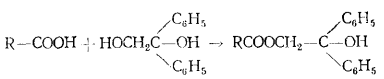


The yield of cyclopeptides was greater than in the analogous cases where a soluble activated ester is used.

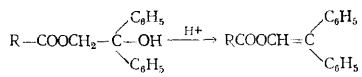
Esters of acylaminoacids and peptides based on 4-methylthiophenol have interesting properties[65-68]. Methylthiophenyl esters exhibit a very weak acylating activity and the methylthiophenyl group can be regarded as a protecting group. However, when the sulphide is oxidised to sulphone by hydrogen peroxide or peracids, the reactivity of the ester increases sharply and it can be used for the effective synthesis of peptides. The applicability of esters derived from methylthiophenol (MTP) has been demonstrated in relation to the synthesis of the heptapeptide Z–Lys(Z)–Leu–Lys(Z)–Ile–Ala–Lys(Z)–Val–OMTP, which was obtained in 73% yield by the condensation of the 4-methanesulphonylphenyl ester ($MSO_2P$) of the tripeptide with the methylthiophenyl ester of the tetrapeptide[66]:

$$Z\text{—Lys(Z)—Leu—Lys(Z)—OMSO}_2\text{P} + \text{H—Ile—Ala—Lys(Z)—Val—OMTP} \rightarrow$$
$$\rightarrow Z\text{—Lys(Z)—Leu—Lys(Z)—Ile—Ala—Lys(Z)—Val—OMTP.}$$

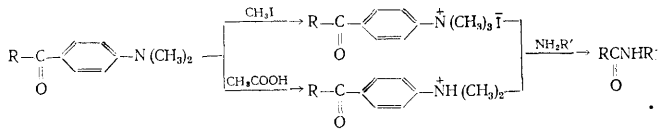
Unfortunately this entailed a partial loss of optical activity (approximately 5%). Furthermore, this method of activation, involving the use of strong oxidants (30% $H_2O_2$ or 85% *m*-chloroperbenzoic acid), is contraindicated for peptides containing methionine, cysteine, or cystine[68]. Other aminoacids are quite stable under the activation conditions, and their methylthiophenyl and methanesulphonylphenyl esters are stable crystalline substances. After the removal of the protecting groups, the salts of the aminoacid esters may be obtained. Methylthiophenyl esters constitute an example of esters with variable reactivity. Another example of esters of this kind is provided by those derived from 1,1-diphenylethylene glycol, the primary hydroxy-group of which can be readily esterified with the aid of thionyl chloride in pyridine:[69]



This ester is inactive, but, when it has been treated with trifluoroacetic acid, it readily splits off water and is converted into the activated 2,2-diphenylvinyl ester:



This ester reacts readily with the amino-component at room temperature, forming the peptide in 80% yield after 1.5 h. The malonic ester is introduced to bind the diphenylacetaldehyde produced. Using the 2,2-diphenylvinyl ester in the last stage of the synthesis of antamanide, it was possible to achieve cyclisation in 20% yield, which is a fair result compared with other methods[69]. Esters based on *p*-dimethylaminophenol, which may be obtained with the aid of dicyclohexylcarbodiimide or by the mixed anhydride method, have similar properties[70]. Dimethylaminophenyl esters are inert with respect to amines, but, on being protonated or treated with methyl iodide, they react readily with the amino-group, forming peptides:



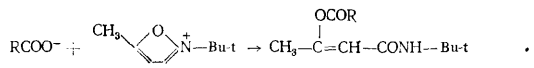
A number of di-, tri-, and tetra-peptides have been synthesised using dimethylaminophenyl esters in 50–98% yield[71].

Among activated esters of this type, the pentafluorophenyl esters, which can be synthesised either with the aid of carbodiimide or mixed anhydrides, or a complex of pentafluorophenol with dicyclohexylcarbodiimide, are of considerable interest[72]. The pentafluorophenyl esters exhibit an exceptional reactivity and permit the synthesis of peptides in yields exceeding as a rule 90%. Many peptides, including oxytocin, corticotropin, and antamanide, have been synthesised with the aid of pentafluorophenyl esters[73,74]. Presumably such esters will find extensive applications in peptide chemistry. Activated esters based on a phenol containing the sulphonamide group have been proposed[75]:

$$ZNHCHRCOO\text{—}C_6H_4SO_2NHCOCH_3$$

These esters have been synthesised with the aid of phosphoryl chloride in pyridine. Measurements of the rate of aminolysis have shown that their reactivity is equal to that of *p*-nitrophenyl esters. The yields of peptides were 65–90%; the *p*-acetylsulphamidophenol formed in the reaction can be readily removed by hydrolysis with an aqueous sodium bicarbonate solution. The addition of acetic acid to the reaction mixture has some catalytic effect.

The products of the interaction of Woodward's K-reagent with acylaminoacids can also be classified as activated esters[76]:



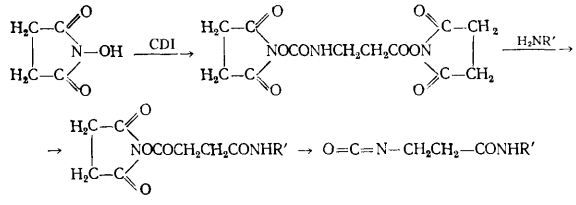
The substituted vinyl esters of *N*-protected aminoacids obtained in this way are stable crystalline substances and exhibit an appreciable acylating activity. For example, when the activated ester of benzyloxycarbonylglycine was allowed to react with benzylamine, the amide was obtained in 98% yield[76].

## III. ACTIVATION OF THE CARBOXY-GROUP IN *N*-ACYLAMINOACIDS IN THE PRESENCE OF THE AMINO-COMPONENT

The methods for the activation of the carboxy-group in the presence of the amino-component have an undoubted advantage, since in this case the entire process is simplified and the probability of other processes (side reactions) is reduced. Although there are considerable difficulties in the selection of the reactants which interact selectively with the carboxy-group, efforts in this direction have not

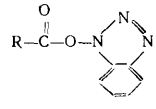
been unsuccessful. The most striking example in this field, which has played a decisive role in the development of the chemistry of peptides, is provided by various carbodiimides, in the first place by cyclohexylcarbodiimide. Studies on these lines are being successfully continued at the present time and very interesting results have been obtained in many instances. During the last five years, particular attention has been devoted to the modification of the carbodiimide synthesis by employing various additives which would tend to decrease the degree of racemisation and would eliminate side reactions. Interest in this type of modification of carbodiimide synthesis was aroused by reports concerning the favourable influence of the addition of *N*-hydroxysuccinimide in the synthesis of peptides with the aid of dicyclohexylcarbodiimide[77,78]. It was shown that the addition of one equivalent and more of *N*-hydroxysuccinimide not only prevents the formation of *N*-acylurea, but also suppresses racemisation almost completely. Some time later it was observed that, together with the favourable effect, the addition of *N*-hydroxysuccinimide can also give rise to an undesirable side process[26,79].

When *N*-hydroxysuccinimide reacts with carbodiimide, the product is the ester formed from *N*-hydroxysuccinimide and succinimido-oxycarbonyl-β-alanine, which can readily react with the amino-component and can undergo other changes:



This side process is particularly dangerous when the carboxy-component is only weakly reactive owing to steric hindrance (for example, valine and isoleucine)[80] and in some cases the addition of *N*-hydroxysuccinimide does not prevent racemisation (for example, up to 46% for Z-Pro-Val-Pro-OBu-t)[81].

All these findings stimulated the search for more effective additives to carbodiimide in order to reduce the degree of racemisation and suppress side reactions. A large number of hydroxy-compounds were tested and it was established that many of them react similarly to *N*-hydroxysuccinimide[82]. Hydroxytriazoles and hydroxytriazines proved to be particularly valuable, although the effect of the additive depends also on the structure of the peptide and the nature of the solvent. 1-Hydroxybenzotriazole is the most convenient substance. Since the effect depends only slightly on the structure of the substituted hydroxybenzotriazoles, it is useful to employ unsubstituted 1-hydroxybenzotriazole[44]. It is suggested that 1-acyloxybenzotriazole

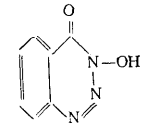


is a reaction intermediate which reacts subsequently with the amino-component forming the peptide. Certain 1-acyloxybenzotriazoles have been isolated and characterised.

Unfortunately, 1-hydroxybenzotriazole does not always rule out racemisation either. Thus, in the synthesis of Z-Pro-Val-Pro-OBu-t, it was found that the amount of racemic product is 9%.[83] However, in most cases racemisation was not observed, and, what is also important, the yields of peptides in the presence of added 1-hydroxybenzotriazole were higher than in the presence of *N*-hydroxysuccinimide.

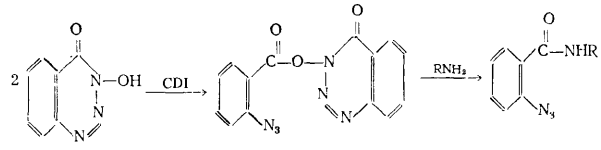
The addition of 1-hydroxybenzotriazole to carbodiimide makes it possible to add Boc-His(Bzl)-OH without racemisation[84]. Condensation with the aid of carbodiimide alone is accompanied in this instance by appreciable racemisation.

Further research led to an even more effective compound—3-hydroxy-4-oxo-3,4-dihydro-1,2,3-benzotriazine[82]:



Its addition to carbodiimide made it possible to obtain optically pure peptides even in those cases where neither 1-hydroxybenzotriazole nor *N*-hydroxysuccinimide (this is even less effective) were able to suppress racemisation completely. Thus, the degree of racemisation was 38% in the synthesis of Tfa-Pro-Val-Pro-OBu-t without any additive in the carbodiimide, in the presence of one mole of *N*-hydroxysuccinimide the degree of racemisation was 17%, the addition of one mole of 1-hydroxybenzotriazole resulted in a degree of racemisation of 3.4%, while the addition of one mole of 3-hydroxy-4-oxo-3,4-dihydro-1,2,3-benzotriazine reduced the degree of racemisation to less than 1%.[82]

However, the yield of peptides in the presence of 3-hydroxy-4-oxo-3,4-dihydro-1,2,3-benzotriazine is less than in the presence of 1-hydroxybenzotriazole, although it is higher than in the presence of *N*-hydroxysuccinide. The reduction of the yield is the result of a side reaction involving carbodiimide[84]:

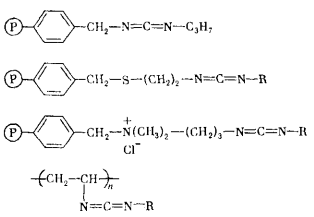


It is of interest that this type of side reaction occurs when the reaction mixture contains all the components at once. On the other hand, if the synthesis is carried out initially without the amino-component (pre-activation) and the latter is added only after a certain time, the side reaction is not observed and the peptides are obtained in very high yields. Unfortunately such pre-activation does not always guarantee the absence of racemisation[82].

The introduction of additives into carbodiimide has been very popular recently. Carbodiimide synthesis with added *N*-hydroxysuccinimide and 1-hydroxybenzotriazole competes successfully with azide coupling; its use permitted a number of complex peptide syntheses (glucagon[85], thyrocalcitonin[86], and secretin[87]).

As regards the carbodiimide synthesis itself, polymeric modifications of carbodiimide are of interest. In particular, the polymeric carbodiimide $-[-(CH_2)_6-N=C=N-]_n-$ has been obtained[88,89] and the use of an excess of this compound led to the synthesis of certain simple dipeptides in high yields: Z-Gly-Gly-$OC_2H_5$ (92%), Pht-Gly-Glu$(OBzl)_2$ (89%), and Z-Cys(SZ)-Gly-OBzl (93%). However, the

syntheses of more complex peptides have not been reported. Other polymeric carbodiimides have also been synthesised[90]:



However, only a few simple peptides have been synthesised with their aid.

In 1961 Wolman and coworkers proposed a method for the synthesis of peptides involving the oxidation of acylaminoacid hydrazides[91,92]:

$$R{-}CONHNH_2 + NH_2R' \xrightarrow{O} RCONHR' + N_2 \quad .$$

Later it was found in 1968 that acylaminoacids phenylhydrazides can be oxidised to phenylazoacylaminoacids, which are fairly stable crystalline compounds[93]:

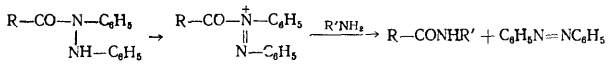
$$R{-}CONHNHC_6H_5 \xrightarrow{O} RCON{=}NC_6H_5 \quad .$$

Acylaminoacid phenylhydrazides have been synthesised from acylaminoacids and phenylhydrazines under the influence of papain:

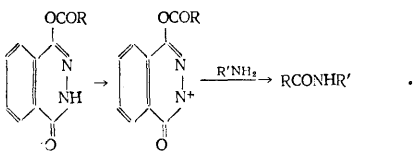
$$RCOOH + NH_2NHC_6H_5 \xrightarrow{\text{papain}} RCONHNHC_6H_5 \quad .$$

This novel procedure for the preparation of hydrazides gives fairly high yield of the product and is fairly general. The hydrazides have been oxidised by *N*-bromosuccinimide and lead tetra-acetate in 70–83% yield. Phenylazoacylaminoacids and peptides react very readily with the amino-group. Thus, in the reaction of Z–Gly–Phe–N=NC$_6$H$_5$ with H–Gly–Phe–NHNHC$_6$H$_5$, the degree of conversion was 90% after 8 min. The degree of racemisation in the synthesis of the tripeptide Z–Gly–Phe–Gly–OC$_2$H$_5$ varied from 0 to 4.5%, depending on the conditions of synthesis. The best result was obtained when redistilled ethyl glycinate was used as the amino-component.

In this type of peptide synthesis, it is possible to use acylaminoacid 1,2-diphenylhydrazides, which can be oxidised by *N*-bromosuccinimide or 1-chlorobenzotriazole to azonium salts, and these readily react with the amino-component, forming peptides[69]:



The yields of peptides amount to 70–80%. A similar result has been achieved with the aid of 4-acyloxyphthalazone[69]:



In both instances, the yield of peptides proved to be inadequate. The attempts to use these compounds for cyclisation in solution and on a polymeric carrier were unsuccessful.

A series of studies devoted to the use of phosphorus(III) compounds (phosphines and phosphites) in peptide synthesis is of particular interest. When these substances are used, unusual oxidation-reduction reactions take place during which the carboxy-group of the acylaminoacid is activated.

The reaction of a carboxylic acid, arenesulphenamide, and triphenylphosphine results in the formation of a carboxamide[94,95]. Heavy metal ions ($Cu^{2+}$, $Hg^{2+}$, etc.) are used to bind the thiophenol liberated:

$$(RCOO)_2Cu + ArSNHR' + (C_6H_5)_3P \rightarrow RCONHR' + (ArS)_2Cu + (C_6H_5)_3P{=}O \quad .$$

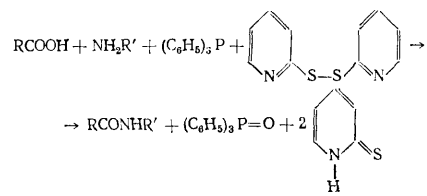
The arenesulphenamide can be replaced by a diaryl sulphide and an amine[96]:

$$RCOOH + (ArS)_2 + (C_6H_5)_3P + R'NH_2 \xrightarrow{Hg^{2+}} RCONHR' + (C_6H_5)_3P{=}O + (ArS)_2Hg \quad .$$

For example, Z–Phe–Gly–OC$_2$H$_5$ has been synthesised by this method in 96% yield[94].

Unfortunately, in the synthesis of a number of other peptides difficulties were encountered in their isolation from the reaction mixture. It was found that it was difficult to separate peptides from triphenylphosphine oxide and it was therefore necessary to employ in all cases chromatographic separation on silica gel, which greatly complicated the procedure[97]. The study of racemisation in the synthesis of Bz–Leu–Gly–OC$_2$H$_5$ showed that a racemic peptide is formed in appreciable amounts (3–8%).[79,80] Certain unsaturated compounds, for example, 2,3-dihydropyran and butyl vinyl ether, have been used instead of heavy metal ions to bind thiophenol[98]. The yield of peptides was then 90–97%. In order to facilitate the purification procedure and to increase the yield of peptides, the water-soluble reagents $[(CH_3)_2NC_6H_4]_3P$ and $[\overset{+}{I}(CH_3)_3NC_6H_4S]_2$ have been proposed[99]. In the synthesis of peptides, this made it possible to employ an excess of reagents, which were then readily removed by washing the peptides with water. Various dipeptides containing virtually all the natural aminoacids have been synthesised using the water-soluble reagents. The yield of peptides was 70–98%.[99]

Di-2-pyridyl disulphide proved to be a convenient compound for the oxidation-reduction condensation[98,100]. The 2-mercaptopyridine formed in the reaction with triphenylphosphine isomerises to the stable thiono-form and does not give rise to undesirable reactions:



Various dipeptides have been synthesised in 82–93% yield using di-2-pyridyl disulphide. One must note that aminoacids containing hydroxy-groups (serine, threonine, and tyrosine) do not require the protection of the hydroxy-group and the yields of peptides are high (84% for Z–Ser–Gly–OC$_2$H$_5$, 83% for 2-Thr–Gly–OC$_2$H$_5$ and 93% for Z–Tyr–Gly–OC$_2$H$_5$). In the synthesis of peptides from Z–Gln–OH and Z–Asn–OH, the dehydration of the amide groups was not observed and the yields of peptides proved to be 85–86%. The octapeptide Z–Ala–Gly–Leu–Gly–Gly–Gly–Leu–Gly–NHNHBoc was synthesised in 70% yield. The employment of di-2-pyridyl disulphide permitted the successful application of this method in solid-phase synthesis[98,101].

The influence of various additives on the degree of racemisation in the synthesis of Bz–Leu–Gly–OC$_2$H$_5$ by the oxidation-reduction condensation was investigated[102]:

$$(Bz{-}Leu{-}O)_2Cu + NPS{-}Gly{-}OC_2H_5 + (C_6H_5)_3P \rightarrow$$
$$\rightarrow Bz{-}Leu{-}Gly{-}OC_2H_5 + (NPS)_2Cu + (C_6H_5)_3P{=}O \quad .$$

Phenol, *p*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, *N*-hydroxysuccinimide, and trimethylacetic acid were also used as additives.

It was found that the content of the L-isomer increases from 57 to 80% as the p$K$ of the additive is reduced from 9.89 to 0.38. However, *N*-hydroxysuccinimide deviates from this relation, the content of the L-isomer amounting to 84% for p$K$ = 9.4. A study of the dependence of the degree of racemisation on the nature of the solvent and the structure of the mercury derivatives (added to bind thiophenol) showed that there is no clear-cut trend and the degree of racemisation remains considerable (5–63%).[103] Thus the oxidation-reduction condensation method can be used only for the stepwise growth of the peptide chain. An unusual version of the oxidation-reduction condensation is the method of synthesis of peptides using anodic oxidation for the regeneration of diaryl disulphides[104]. The thiophenol formed in the reaction is oxidised to diaryl disulphide, which is thus returned to the reaction:

$$RCO\bar{O} + NH_2R' + \overset{+}{P}R_3 + ArSSAr \rightarrow RCONHR' + O{=}PR_3 + 2ArSH$$

(anodic oxidation)

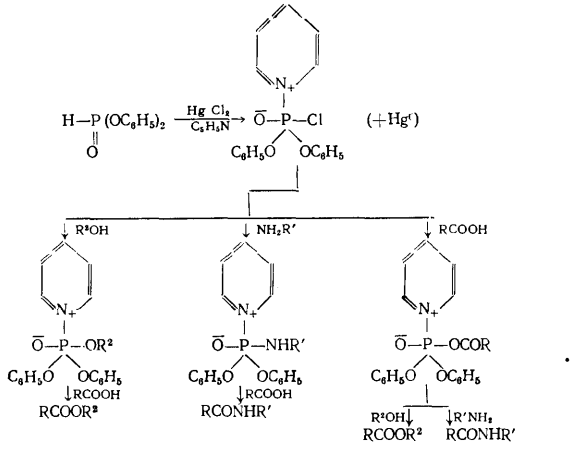
This process makes it possible to introduce the diaryl disulphide into the reaction in an amount which is much less than that corresponding to stoichiometry, and the probability of the formation of side products is thereby reduced.

The use of the oxidation-reduction reaction for the synthesis of various activated esters is of interest[105]:

$$RCOOH + HOR' + (C_6H_5)_3P + \text{(2-pyridyl disulphide)} \rightarrow RCOOR' + (C_6H_5)_3P{=}O + 2\ \text{(2-pyridinethiol)}$$

Pentachlorophenyl, succinimide, and 8-quinolinyl esters have been synthesised by this procedure in 60–86% yield. This method permits the easy synthesis of activated asparagine, glutamine, and nitroarginine esters.

Another example of the oxidation-reduction reaction leading to the activation of the carboxy-group is that of diphenyl phosphite with mercury(II) salts in pyridine[106]. Using this reaction, it is possible to synthesise both acid amides and esters. The reaction is carried out in all cases in pyridine either at 45°C or on boiling and proceeds via the following mechanism:




The reaction has been used to synthesise Z–Gly–Gly–$OC_2H_5$ and Z–Gly–Gly–OH, which were obtained in 94 and 50% yields respectively.

An interesting example of the use of phosphorus(III) compounds in the synthesis of peptides is the method based on the reaction of phosphines and phosphorous acid amides with carbon tetrachloride or tetrabromide[107,108]:

$$R_3P + CX_4 \rightarrow \underset{X^-}{R_3\overset{+}{P}{-}CX_3} \xrightarrow{R'COOH} \underset{X^-}{R_3\overset{+}{P}{-}OCOR'} \xrightarrow{R''NH_2} R'CONHR'' + R_3P{=}O\ ,$$

where

$$X{=}Cl,\ Br;\ R{=}CH_3{-}\text{(N-heterocycle)}{-}N,\ C_4H_9,\ (CH_3)_2N,\ (C_2H_5)_2N\ .$$

The reaction is carried out at a reduced temperature (between −20° and 0°C) and the yield of peptides is 60–85%. A study of racemisation in the synthesis of Bz–Leu–Gly–$OC_2H_5$ showed that the amount of racemic products obtained is usually 2–8% and that the degree of racemisation is much higher (88%) only in the case of triphenylphosphine. This shows that the carboxy-group is not activated via the stage involving the formation of acid chlorides, although it is known that the acid chloride is formed readily in the reaction of a carboxylic acid, carbon tetrachloride, and phosphines[109]. When the carboxy- and amino-components are present simultaneously, the activated species is apparently an acyloxyphosphonium ion[107,110]. It has been suggested that triphenyl phosphite be used for the synthesis of peptides in the presence of imidazole[111]. The reaction proceeds via the mechanism

$$RCOOH + NH_2R' + (C_6H_5O)_3P \xrightarrow{\text{imidazole}} RCONHR' + (C_6H_5O)_2PH(=O) + C_6H_5OH\ .$$

Various peptides have been synthesised in high yields with the aid of triphenyl phosphite; the method has been used successfully in the synthesis of biologically active peptides (fragments of gastrin, corticotropin, etc.)[112]. Diphenyl phosphite, which makes it possible to synthesise peptides in 65–90% yields in the presence of pyridine, proved to be just as effective[113,114]. A similar effect was achieved also when diaryl sulphites were used instead of phosphites[115].

The employment of *o*-nitrobenzenesulphenyl derivatives of aminoacids for the synthesis of peptides is of interest. It has been found that aryl thioesters of acylaminoacids and peptides can react with salts of *o*-nitrobenzenesulphenylaminoacids, to form peptides[116]:

$$ZNHCHRCOSC_6H_5 + NBSNHCHR'CO\bar{O}\overset{+}{N}a \rightarrow ZNHCHRCONHCHR'CO\bar{O}\overset{+}{N}a + NBSSC_6H_5\ .$$

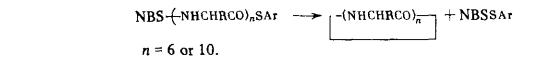
[where NBS is the *o*-nitrobenzenesulphenyl group]. The reaction requires fairly severe conditions: an aqueous methanol solution of the reactants was maintained for 6 h at 70°C and the yield of peptides was 56–76%. The attempts to use for this reaction the esters of *o*-nitrobenzenesulphenylaminoacids instead of the salts have not been successful. The method employing imidazole was more successful in this respect[117], which made it possible to reduce the reaction temperature to 45°C and to shorten the reaction time considerably (to 10–45 min):

$$ZNHCHRCOSAr + NBS(NHCHR'CO)_n OCH_3 \xrightarrow{4\ \text{equiv. of imidazole}} ZNHCHRCO(NHCHR'CO)_n OCH_3 + NBSSAr,$$

where Ar = $C_6H_5$, $C_6H_4NO_2$, or $C_6H_4CH_3$ and $n$ = 1–3.

The yield of peptides was about 90% and the degree of racemisation (Anderson's test) proved to be 4% for the *p*-nitrophenyl thioester. The method is convenient because it does not require the preliminary elimination of the protecting group from the amino-end of the peptide.

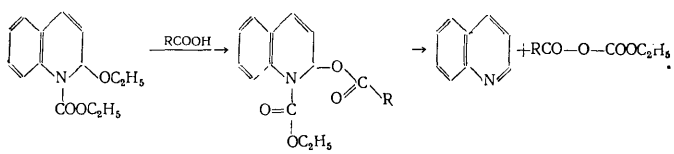
It was also tested in the cyclisation of certain hexa- and deca-peptides, and gave good results:



$n = 6$ or 10.

Antamanide was synthesised in this way in 30% yield[118]. It is noteworthy that this reaction occurs in pyridine or in tetrahydrofuran, while in dimethylformamide undesirable side reactions predominate. This limitation narrows the region where the reaction can be applied.

A very interesting development of the method of mixed anhydrides has been a series of studies on the application of 1,2-dihydroquinoline derivatives in the synthesis of peptides[119-122]. *N*-Ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline, which can be readily obtained from ethyl chloroformate and quinoline, is a fairly stable compound and does not react with amines; however, its reaction with carboxylic acids readily gives rise to mixed anhydrides:



Since the reaction is carried out in the presence of an amine, the mixed anhydride reacts with the latter immediately, forming an amide (peptide). Various peptides have been synthesised in yields exceeding 90% using *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline. The degree of racemisation was determined in the synthesis of ethyl benzoyl-leucylglycinate (Young test), which is a very sensitive peptide; however, the racemic product was not detected. In a study of the racemisation by a more accurate method[120], only a minimal degree of racemisation was detected (approximately 0.2%). Such unusual behaviour of the mixed anhydride can be accounted for by the fact that, as soon as it is produced, it immediately reacts with the amino-component, so that its lifetime is very short and side processes do not occur.

A polymeric modification of *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline has been described[121]. The polymer was obtained by the copolymerisation of 6-isopropenylquinoline with styrene, and was then converted into the active reactant by reaction with ethyl chloroformate and ethanol. The polymeric reactant makes it possible to synthesise peptides easily and rapidly in yields of 84-92%. After the reaction, the polymer can be again converted into the active reactant.

*N*-Isobutoxycarbonyl-2-isobutoxy-1,2-dihydroquinoline has been recommended for use in ordinary solid-phase synthesis of peptides (Merrifield's method)[122]. This reagent is just as effective as *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline. Certain peptides containing serine, threonine, and asparaginine have been obtained in yields of 80-95%. The octapeptide has been synthesised from Z(OCH$_3$)-Asp(OBzl)-Phe-Cys(Bzl)-Leu-Glu(OBzl)-Pro-OH and H-Gly-Ala-O-polymer (fourfold excess) as an example of the use of this reagent in the solid-phase synthesis. The latter was carried out over a period of 48 h and the yield was nearly quantitative. In order to determine the degree of racemisation, the dipeptide Ac-Ile-Gly-OCH$_3$ was used[123], the degree of racemisation found amounting to 4.1%. In the synthesis of the tripeptide Z-Gly-Ala-Leu-OBzl with the aid of *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline, the degree of racemisation was only 0.2%.[120]

The ynamines $R-C\equiv C-NR_2'$ have been suggested for the stepwise synthesis of peptides[124,125]:

$$RCOOH + NH_2R' + R''-C\equiv C-NR_2''' \rightarrow RCONHR' + R''CH_2CONR_2''' .$$

The reaction is carried out at 40°C in tetrahydrofuran, the yields of certain dipeptides amounting to 83-99%. However, the attempts to synthesise Z-Leu-Phe-Val-OCH$_3$ gave a poor yield of the tripeptide (25%) and the degree of racemisation was high, varying from 17 to 27% depending on the reaction temperature. It appears that ynamines must be used with caution in the synthesis of peptides. They proved to be much more effective in the preparation of symmetrical anhydrides used subsequently to synthesise peptides[124].

Diphenylphosphoryl azide[127], which can be readily obtained from diphenylphosphoryl chloride and sodium azide in acetone, proved to be a very interesting reagent for the synthesis of peptides. It is a stable non-explosive liquid, which can be distilled at a reduced pressure. When it is allowed to react with a solution containing carboxy- and amino-components, peptides are obtained at 0°C easily and in high yields:

$$RCOOH + NH_2R' + N_3PO(OC_6H_5)_2 \rightarrow RCONHR' .$$

It is suggested that the carboxylic acid azide RCON$_3$ is an intermediate. This is confirmed by the fact that, when a carboxylic acid, diphenylphosphoryl azide, and alcohols are heated, the corresponding urethanes are obtained:

$$RCON_3 \rightarrow RN=C=O \xrightarrow{R'OH} RNHCOOR' .$$

Diphenylphosphoryl azide is a universal reagent permitting the synthesis of peptides containing virtually any amino-acids in high yields. The following peptides have been synthesised with its aid (the yields are indicated in brackets):

Z—Asn—Phe—OCH$_3$ (80%); Z—Gln—Ser—OCH$_3$ (80%);
Z—Val—Tyr—OCH$_3$ (69%); Z—Thr—Phe—OCH$_3$ (72.5%);
Z—Met—Gly—OC$_2$H$_5$ (90%); Boc—Trp—Gly—OC$_2$H$_5$ (89.5%);
Z—Arg(NO$_2$)—Leu—OCH$_3$ (83%); Z—His—Leu—OCH$_3$ (95%).
Z—Leu—Leu—Val—Phe—OCH$_3$ (87%);

Racemisation was not observed in the synthesis of the tetrapeptide Z-Leu-Leu-Val-Phe-OCH$_3$, but Young's test showed that the degree of racemisation is about 5%.

## IV. OTHER METHODS FOR THE ACTIVATION OF THE CARBOXY-GROUP

Mixed anhydrides obtained from the esters of chlorocarbonic acids are very important in the synthesis of peptides. Despite the fact the method of mixed anhydrides was developed at the beginning of the 1950s, interest in this procedure has still not weakened; new studies in which new versions of the method are proposed are published fairly frequently.

A new method for the preparation of mixed anhydrides, based on the use of stable *N*-alkoxycarbonyl-*NNN*-trialkylammonium salts, is of interest[128]. Certain salts of this type are fairly stable and can be used to form mixed *N*-acylaminoacid anhydrides, for example:

$$BF_4^-R_3\overset{+}{N}-\underset{\underset{O}{\|}}{C}OC_4H_9 + ZNHCHR'COOH \rightarrow ZNHCHR'CO-O-CO-OC_4H_9 .$$

Certain di- and tri-peptides have been synthesised in this way in yields of 70-97%.

Another example of a new method of synthesis of mixed anhydrides involves the use of dihydroquinoline derivatives, which were considered in Section III.[119-122]

Among the methodological developments devoted to the use of mixed anhydrides, special attention should be given to the method based on the use of a large excess of the mixed anhydride[129]. This approach permits the synthesis of peptides in a nearly quantitative yield and makes it possible to carry out the process without the isolation and purification of the intermediate peptides. The method has been successfully applied in the synthesis of a fragment of the growth hormone[128], secretin[129], and other peptides.

Despite the fact that the mixed anhydrides with certain carboxylic and alkylcarbonic acids were introduced into peptide chemistry long ago and have gained general recognition by virtue of their high reactivity and the simplicity of their synthesis, the search for new types of mixed anhydrides is still being continued. The necessity for such search probably arises due to the instability of mixed anhydrides and the side reactions which occur in many instances. Admittedly the number of new types of mixed anhydrides is not all that large and they can hardly compete with the generally recognised mixed anhydrides.

One of such new mixed anhydrides proposed is the compound obtained by the reaction of toluene-*p*-sulphonic acid anhydride with hexamethylphosphoramide[131]:

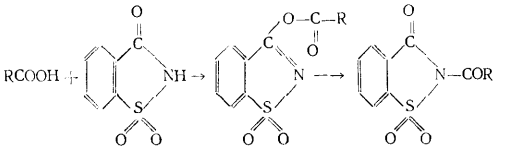
$$[(CH_3)_2N]_3PO + Tos_2O \rightarrow [(CH_3)_2N]_3\overset{+}{P}-O-\overset{+}{P}[N(CH_3)_2]_3 \cdot 2Tos\bar{O} \rightarrow$$
$$\xrightarrow{RCO\bar{O}} RCO-O-\overset{+}{P}[N(CH_3)_2]_3\,Tos\bar{O} \xrightarrow{R'NH_2} RCONHR' + [(CH_3)_2N]_3PO \quad .$$

The resulting acyloxytris(dimethylamino)phosphonium tosylate is fairly stable in solution and rapidly reacts with the amino-component, forming peptides in a high yield for the majority of aminoacids (81–96%). Aliphatic aminoacids containing hydroxy-groups (serine and threonine) cannot be used in this reaction without protecting the hydroxy-group. Histidine also gives unsatisfactory results. However, the absence of racemisation (less than 1%) is of interest; it can probably be accounted for by the impossibility of the formation of the oxazolone ring owing to the steric hindrance caused by the dimethylamino-groups. At the same time, the presence in solution of chloride or bromide ions may promote the appearance of the racemic product, which was noted previously[132].

The absence of racemisation permitted the use of this method for the coupling of large peptide fragments. The hexapeptide Z–Ile–Gly–Val– –Gly–Ala–Pro–$NH_2$ (the double dash indicates the junction of the fragments), the octapeptide Z–Gly–Leu–Leu–Gly–Gly– –Phe–Ala–Gly–$OCH_3$, and the octapeptide Z–Thr(t-But)–Ala– –Ile–Gly–Val–Gly–Ala–Pro–$NH_2$ have been obtained in yields of 84, 86, and 81% respectively. The reaction is carried out in hexamethylphosphoramide, which is an effective solvent for various peptides. Mixed anhydrides based on boric acid[133] have not been found to be quite so effective, for example:

$$RCO\bar{O} + ClB(OCH_3)_2 \rightarrow RCOOB(OCH_3)_2 \xrightarrow{R'NH_2} RCONHR' \quad .$$

By allowing the sodium salt of benzoylphenylalanine to remain in contact with chlorodimethoxyborane for 18 h at room temperature and then introducing freshly distilled ethyl glycinate into the mixture, the peptide Bz–L–Phe–Gly–$OC_2H_5$ was obtained in 31% yield. The analogous reaction at 55°C led to the formation of the racemate. The mixed anhydride acyloxydimethoxyborane undergoes a number of reactions, for example it gives rise to triacyloxyborane $(RCOO)_3B$, the symmetrical anhydride RCOOCOR, and other products. All these factors are responsible for the low yields of peptides[134]. A novel application of saccharin is its use in the synthesis of mixed anhydrides with acylaminoacids[135]:



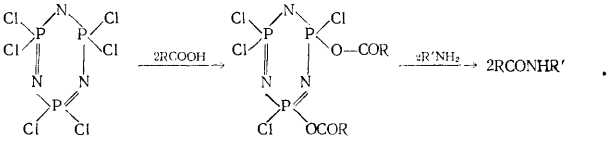
The mixed anhydrides are obtained with the aid of carbodiimide or thionyl chloride in 74–95% yield. They are readily crystallisable, highly fusible compounds with a considerable stability on storage. At the same time, they are very reactive, reacting readily with the amino-components at 0°C and forming peptides in 86–95% yield. They can be employed to synthesise peptides in an aqueous medium, using solutions of aminoacids and peptides in aqueous potassium bicarbonate. The yields of peptides are 63–95%, and the saccharin liberated in the reaction can be readily washed away with water.

The use of acylguanidine for the synthesis of peptides is of interest[136]. Acylguanidines are obtained in satisfactory yields by the reaction of methyl esters of acylaminoacids with free guanidine. Acylguanidines are crystalline compounds with fairly high melting points (150–190°C) and are soluble in polar solvents. They react fairly effectively with amines, forming amides (peptides); the protonation of guanidine is postulated in this process:

$$RCO-NH-\overset{\overset{\cdots}{NH}}{\overset{\|}{C}}-NH_2 \xrightarrow{H^+} R-CO-NH-\overset{\overset{+}{NH_2}}{\overset{\|}{C}}-NH_2 \xrightarrow{NH_2R'} RCONHR' + \overset{\overset{+}{NH_2}}{\overset{\|}{NH_2CNH_2}} \quad .$$

The reaction is carried out in an aqueous or aqueous organic medium at room temperature at pH 8. The yields of dipeptides are 68–90%.

The comparatively low yields of peptides and complete racemisation were noted when polyphosphoric acid esters $(C_2H_5O_3P)_n$ were used[137]. Peptides were synthesised by refluxing a solution in $CHCl_3$ or $CH_3CN$; their yield did not exceed 75% and the peptides of comparatively simple aminoacids were obtained: glycine, alanine, phenylalanine, and leucine. The method can be hardly used to synthesise even small peptides owing to the unduly severe condensation conditions. The application in the synthesis of peptides of hexachlorocyclotriphosphatriazine, which can react with two molecules of the acylaminoacid to form an unusual mixed anhydride, has been described[138]:



The symmetrical anhydrides of Boc-aminoacids, obtained with the aid of ynamines at 0°C[126]:

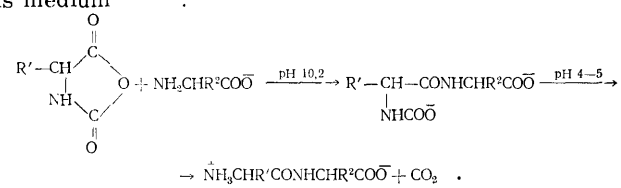
$$2R-COOH + CH_3C{\equiv}C-N(C_2H_5)_2 \rightarrow RCOOCOR + CH_3CH_2CON(C_2H_5)_2 \quad ,$$

or with the aid of phosgene at −40°C,[136,137] proved to be very effective. The reaction of the symmetrical anhydrides with the amino-component terminates after 10–30 min. All these factors make it possible to achieve a single peptide coupling after each 2–3 h in a yield exceeding 90% at each stage. The excess of the anhydride (an

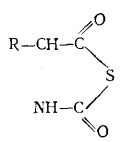
excess by a factor of 1.5 is used) and the Boc-aminoacid formed in the reaction can be readily regenerated after washing with a solution of sodium bicarbonate. Using symmetrical anhydrides, it has been possible to synthesise rapidly and in a satisfactory yield the nonapeptide Boc–Leu–Ile–Ile–Leu–Val–Pro–Pro–Phe–Phe–OBzl without isolating and identifying the intermediates[126].

The symmetrical anhydrides of t-butoxycarbonylaminoacids proved to be convenient reagents for the synthesis of peptides on a polymeric carrier[141]. The use of anhydrides ensures a high yield at each stage. An advantage of this synthesis is also that a comparatively simple regeneration of the excess anhydride is possible. A linear decapeptide, corresponding to antamanide, has been synthesised in 96% yield using symmetrical anhydrides.

The employment of internal anhydrides–*N*-carboxyanhydrides, which can be readily obtained from aminoacids by treatment with phosgene[142], proved to be very productive in the synthesis of peptides. Until recently, *N*-carboxyanhydrides were used mainly to obtain polypeptides and statistical copolypeptides. It was found that, under strictly controlled conditions, *N*-carboxyanhydrides can be used for the stepwise synthesis of peptides in an aqueous medium[142-145]:



For effective synthesis, it is necessary to maintain the pH within a narrow range, since at pH $< 10$ the carbamate of the dipeptide already loses $CO_2$, and the resulting dipeptide may react with the *N*-carboxyanhydride to form a side product. On the other hand, at pH $> 10.5$ the *N*-carboxyanhydride hydrolyses and other side reactions take place. When the pH is maintained rigorously in the range 10.2–10.5, peptides are synthesised at a very high rate. It is important that, among all the aminoacids, only lycine and cysteine require the protection of side groups. The C-terminal tetrapeptide gastrin H–Trp–Met–Asp–Phe–$NH_2$ has been synthesised in 1 h with the aid of *N*-carboxyanhydrides. For certain aminoacids (for example, histidine and glycine), it is useful to use thio-analogues of *N*-carboxyanhydrides (thiazolidine-2,5-diones)[146,147]:



In this case, the peptide synthesis can be carried out at lower pH values. The *N*-carboxyanhydride method can be conveniently used to synthesise peptide fragments consisting of 4–8 aminoacid residues. It has been applied successfully in the synthesis of ribonuclease fragments[148].

A disadvantage of this method is the low stability of the *N*-carboxyanhydrides, which cannot be synthesised before their immediate requirement and stored for a long time. Furthermore, serious difficulties are encountered in the synthesis of certain *N*-carboxyanhydrides and their thio-analogues. Efforts have been made recently to overcome these difficulties. It was found that *N*-carboxyanhydrides with a substituent at the nitrogen atom are much more stable than the unsubstituted *N*-carboxyanhydrides; they do not polymerise and at the same time react readily with the amino-components, forming *N*-protected peptides. The following protecting groups have been used: NBS[149,150], benzyl, 2,4-dimethoxybenzyl, 2,4,6-trimethoxybenzyl, diphenylmethyl, bis-(4-methoxyphenyl)methyl, and 9-xanthenyl[151]. Protected *N*-carboxyanhydrides have been synthesised either from unprotected *N*-carboxyanhydrides[149] or from protected aminoacids and phosgene[151]. Certain small peptides have been synthesised with the aid of protected *N*-carboxyanhydrides both in solution and on an insoluble polymeric carrier, the yield of peptides being very high in certain instances[150].

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# Vinyl Fluoride Polymers

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Results obtained on the polymerisation, copolymerisation, and graft copolymerisation of vinyl fluoride, various properties of the polymers thus produced, and also possible fields of application are discussed on the basis of 435 references published up to the beginning of 1976

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## I. INTRODUCTION

The polymerisation and copolymerisation of vinyl fluoride, as well as various properties of the resulting polymers, have been very intensively studied during recent years. Poly(vinyl fluoride) possesses good heat resistance, thermal stability, and chemical inertness, while being readily processed. Films of this polymer are distinguished by high mechanical strength, durability, flexibility, transparency, and enhanced resistance to the atmosphere and to light. Several copolymers and graft copolymers possess similar qualities. In virtue of these valuable properties polymers based on vinyl fluoride are currently among the principal types of fluorinated polymers widely employed in various branches of modern technology, building construction, agriculture, and everyday life.

A few review papers have been published on vinyl fluoride and its polymers [1-3], a subject that has been partly covered also in several books [4-6]. However, attention is paid in these publications mainly to the preparation and properties of vinyl fluoride itself, with little space devoted to the synthesis of its polymers and their properties. Moreover, they contain no results published during the past 4–5 years.

## II. POLYMERISATION OF VINYL FLUORIDE

Vinyl fluoride was prepared as early as 1901 by Swarts [7], but its polymerisation was accomplished only in 1934. [8] Quite detailed information both on the kinetics of the polymerisation of vinyl fluoride and on the properties of the polymer was published in 1946 by Newkirk [9].

Vinyl fluoride is more difficult to polymerise [8,10] than are e.g. vinyl chloride, vinylidene chloride, and vinylidene fluoride, owing to the appreciable inertness of the double bond and the great activity of vinyl fluoride radicals. The process is therefore very sensitive to the presence of impurities that may inhibit polymerisation [8,11-14]. The failures and difficulties met by the early investigators in their attempts to polymerise vinyl fluoride were due mainly to inadequate purity of the monomer, although the low reactivity of the double bond in vinyl fluoride was also quite important. The diminished activity of the double bond was due to a mesomeric effect weakening the inductive effect of the fluorine atom [15-18].

The successful development during recent years of methods for obtaining vinyl fluoride in a high state of purity has enabled its free-radical polymerisation to be achieved both by chemical initiation and under the influence of radiation.

### 1. Chemically Initiated Polymerisation of Vinyl Fluoride

Various organic peroxides have been most widely used to initiate the polymerisation of vinyl fluoride. Newkirk [9] obtained poly(vinyl fluoride) of density 1.39 g $cm^{-3}$, soluble in hot dimethylformamide, in dioxan, chlorobenzene, and several other solvents, by employing benzoyl peroxide as initiator. This polymerisation initiator was used also by other workers [12,19-23]. Other peroxides that have been widely used to polymerise vinyl fluoride are acetyl, diethyl, di-t-butyl [12], isobutyl [25], lauroyl [24,26], and polyperfluoropropylene, as well as t-butyl hydroperoxide [27].

The polymerisation of vinyl fluoride in the presence of peroxide initiators is strongly inhibited by oxygen [12]. Acetylene has a similar effect: the yield of poly(vinyl fluoride) in the presence of 2% of acetylene does not exceed 3%. [10,22] Polymerisation in the presence of 2.5% of 1,1-difluoroethane, initiated by benzoyl peroxide, gave a normal yield [12]. Traces of propene help to control the molecular mass, and the resulting polymer has a constant melt flow index [28].

The influence of benzene, methanol, propan-2-ol, and 1,3-dioxolan on the polymerisation of vinyl fluoride was studied [12]. All the organic solvents examined interacted with the monomer, and thus caused a sharp decrease in the molecular mass of the resulting polymer. This is shown especially clearly in the polymerisation of vinyl fluoride in tetrachloromethane in the presence of a peroxide [29]. The telomerisation of vinyl fluoride by chloroformates [30], iodotrifluoromethane [18], perfluorochloroalkenes [31], and perhalogenoethanes [32] has been studied in the presence of peroxides. The telomers obtained are used as plasticisers for poly(vinyl fluoride); they do not bleed and do not cause opacity in the polymer when bent [18].

Polymers of higher molecular mass are formed in the presence of water than in the presence of acetone [33,34].

Initiation of polymerisation by benzoyl or lauroyl peroxide in a fluorinated solvent—1,1,2-trichlorofluoroethane or iodotrifluoromethane—gave poly(vinyl fluoride) soluble in hot dimethylformamide[18]. A polymer of high molecular weight is formed also when the peroxide of a fluorinated acid[35] or trifluoromethyl peroxide[36] is used as initiator.

Two-stage polymerisation in aqueous suspension in the presence of benzoyl peroxide was suggested[37] for the preparation of light-resistant poly(vinyl fluoride). Processes were also developed for the continuous polymerisation of vinyl fluoride in aqueous suspension[38,39] and methods for separating the resulting polymer from water, which was subsequently recycled[28,37,39]. The polymerisation of vinyl fluoride was studied in the presence of various surface-active agents and stabilisers of suspensions—methylcellulose[40-42], glucose ethers and esters, water-soluble copolymers of ethylene, 2-ethylhexyl acrylate, and 2-ethylhexyl methacrylate[43], and also copolymers of vinyl acetate and allyl alcohol with maleic acid or anhydride[44].

Emulsion polymerisation had been most widely used for the preparation of poly(vinyl fluoride) used especially in coatings. Water alone or mixed with organic solvents was the dispersion medium[21,26,45-47]. The emulsifiers were magnesium dodecanesulphonate[40], sodium ditridecyl sulphosuccinate[27], sorbitol ethers or esters, or $C_{12-18}$ aliphatic acids[48].

As the polymerisation of vinyl fluoride in the presence of the usual peroxide initiators requires temperatures above 50°C and hence high pressures, the possibility of polymerisation at relatively low temperatures and pressures has been intensively examined during recent years. Use of various alkyl peroxodicarbonates as initiators has proved especially fruitful for this purpose. A most detailed study has been made of the polymerisation of vinyl fluoride in the presence of the di-isopropyl ester[21,49-53]. As the ester content increases from 0.28 to 0.98 wt.% on the weight of the monomer the rate of polymerisation in heptane solution increases in conformity with the equation $v = kc^{0.58}$, where $k$ is the overall polymerisation rate constant and $c$ the initiator concentration; the corresponding equation when the concentration of vinyl fluoride in heptane solution increases from 3.07 M to 9.20 M is $v = kc^{0.60}m^{1.10}$, in which $m$ is the monomer concentration.

The activation energy of polymerisation is ~17 kcal mole$^{-1}$. Methylcellulose[54], poly(vinyl alcohol)[55], and mixtures of water-soluble cellulose ethers and partly hydrolysed poly(vinyl acetate)[48] have been suggested as peptising agents for the suspension polymerisation of vinyl fluoride in the presence of di-isopropyl peroxodicarbonate. In order to improve the compatibility of poly(vinyl fluoride) with plasticisers the suspension polymerisation of vinyl fluoride is conducted in the presence of 0.05–2% (on the weight of the monomer) of carboxymethyl-, hydroxypropyl-, or hydroxyethyl-cellulose[56,57].

The emulsifiers used in the emulsion polymerisation of vinyl fluoride are dodecyl benzenesulphonate[54] and such non-ionogenic surface-active agents as alkyl or alkylphenyl ethers or esters of polyoxyethylene and polyoxypropylene[58], sorbitol and its ethers, and also esters of $C_{12-18}$ aliphatic acids[48]. Not only di-isopropyl peroxodicarbonate but also the dipropyl ester[59] and didecanoyl peroxide[26] have been used for the emulsion polymerisation of vinyl fluoride. An 85% yield of poly(vinyl fluoride) is obtained when polymerisation is initiated by 0.05–1.0 mole % of bis-2-t-butylcyclohexyl peroxodicarbonate[60].

The polymerisation of vinyl fluoride at ordinary temperatures and pressures can also be initiated by various redox systems, among which the most efficient are organoelementary compounds in the presence of oxygen, e.g. alkylboranes at 25–40°C.[23,26,61] The activation energy of polymerisation depends on the nature of the group in the alkyl borane: it is 6 and 15 kcal mole$^{-1}$ for triethylborane and tri-isobutylborane respectively. With increase in the ratio of molecular oxygen to the trialkylborane the rate of polymerisation passes through a maximum. Rise in temperature increases the probability of the formation of groups such as $CH_2.CHF.CHF.CH_2$.[18]

A kinetic study of the polymerisation of vinyl fluoride has been made in the presence of tri-n-butylborane[53,62]. The reaction velocities are given by the equations $v = kc^{0.61}$ and $v = kc^{0.65}m^{1.24}$ in the mass and in ethyl-acetate solution respectively. The activation energy of polymerisation is 10 kcal mole$^{-1}$. Polymer samples of crystallinity <30% are obtained by using as initiators organoboron compounds of the type $BR_3$ (where R represents a $C_{1-12}$ group) or RR'BX (where X = OR) with oxygen[63-66], and their coordination compounds with ammonia, hydrazine, hydroxylamine, and amines[67-71]. Trialkylboranes with hydrogen peroxide in the molar proportions 0.05–0.6 are also effective initiators[72,73].

Vinyl fluoride can be polymerised at ordinary temperatures by the use not only of alkylboranes but also of triethylaluminium, di-isopropylcadmium, diethylcadmium, di-isopropylzinc, diethylzinc, ethylzinc isobutoxide, or butylethylzinc in the presence of oxygen or a peroxide, e.g. benzoyl peroxide, 1-hydroxycyclohexyl peroxide, or cyclohexyl hydroperoxide[19,74]. The binary systems formed by diethylaluminium bromide or triethylaluminium with titanium tetrachloride[75,76] and by tri-isopropylaluminium with tetraisopropoxytitanium[77] have been tested. In the presence of tetraethyl-lead with sodium persulphate vinyl fluoride underwent polymerisation only at high temperatures and pressures (40–100°C above 150 atm)[78].

Heterogeneous catalysts comprising aluminium alkyls and titanium or vanadium halides proved ineffective for the polymerisation of vinyl fluoride[79,80]. However, soluble halogen compounds of vanadium combined with aluminium mono- or di-alkyls in the presence of polar solvents, e.g. vanadium acetylacetonate and an alkylalkoxyaluminium chloride in dimethylformamide, initiate the polymerisation of vinyl fluoride very vigorously at 20–50°C.[81] The activation energy of polymerisation fluctuates from 11 to 16 kcal mole$^{-1}$ depending on the nature of the radical R attached to the aluminium atom. Manganic acid and various of its salts are effective initiators of the polymerisation in aqueous suspension[82].

The systems formed by potassium peroxodisulphate with sodium sulphite and with sodium hydrogen sulphite have also proved effective[83]. In their presence vinyl fluoride undergoes emulsion polymerisation at relatively low temperatures (50–60°C), the resulting polymer does not settle on the walls, and it is readily removed from the reaction vessel.

With azo-compounds as initiators the polymerisation of vinyl fluoride is usually conducted at temperatures of 50–100°C and pressures exceeding 30 atm.[84] Thus in the presence of α-azoisobutyramidine[85,86] polymerisation takes place in aqueous medium at 70–90°C and 30 atm. A continuous process has been developed for polymerisation in aqueous suspension initiated by α-azoisobutyramidine hydrochloride[12,29,38,87-89]. 2,2'-Diguanyl-2,2'-azopropane dihydrochloride[28,37,39,90,91], 2,2'-diguanyl-2,2'-azobutane dihydrochloride, and azo-α-cyclopropylpropionamide hydrochloride[92] have also been used for this purpose. Polymerisation of vinyl fluoride has been initiated also by

$\alpha\gamma\gamma'$-trimethyl- and $\alpha\gamma$-dimethyl-$\alpha$-azovaleronitrile[93], 1-azocyclohexanecarbonitrile, $\gamma$-ethyl-$\gamma'$-hydroxyethyl-azobutyronitrile, and azo-disulphonates of alkali and alkaline-earth metals[45]. The most commonly used initiator for the polymerisation of vinyl fluoride has been azoisobutyronitrile[12,53,64,93,94], when the order of reaction with respect to the initiator is 0.55 in the mass.

### 2. Polymerisation of Vinyl Fluoride by Irradiation

When exposed to ultraviolet radiation in the absence of a sensitiser, vinyl fluoride does not polymerise but decomposes into acetylene and hydrogen fluoride[95], which is eliminated by a molecular mechanism. In the early work[9] polymerisation was effected by ultraviolet exposure in the presence of benzoyl, lauroyl, or acetyl peroxide in a quartz capillary. Several other publications appeared later[33,34,96]. Thus exposure of vinyl fluoride in acetone solution to ultraviolet radiation of wavelength 2537 Å at 27°C for 8 h gave 36% of the polymer[33,34].

The polymerisation of vinyl fluoride under the influence of cobalt-60 $\gamma$-rays has been studied in the greatest detail[97-109]. The first reports of the possibility of the radiation polymerisation of this monomer appeared as early as 1962–1963.[99-102] The laws governing such polymerisation in the mass, in the gas phase, and in the presence of various solvents have now been investigated in detail.

The polymerisation of vinyl fluoride in the mass has been conducted at dosage rates of 13–100 rad $s^{-1}$.[103] At and above 70 rad $s^{-1}$ the rate curves have a well developed sigmoid form, which is attributed to heterophase occurrence of the process. The rate of polymerisation passes through a maximum at a polymer yield of 45–65%. In the mass at 38°C the rate of polymerisation is proportional to the dosage rate to the power 0.42. The radiation-chemical yield lies in the range 8000–30 000 mol./100 eV, as a consequence of the chain character of the process.

Under the influence of $\gamma$-rays vinyl fluoride polymerises at less than half the rate for vinylidene fluoride and trifluoroethylene, but more rapidly than chloro-trifluoroethylene, hexafluoropropene, and perfluoroisobutene[110]. As with chemical initiation, the radiation polymerisation of vinyl fluoride is strongly inhibited by oxygen and by acetylene[99,111]; increasing the acetylene content of the monomer from 0.5% to 1% diminishes the rate of polymerisation almost to one-third.

In the first study of the gas-phase polymerisation of vinyl fluoride[112,113] irradiation with cobalt-60 $\gamma$-rays was employed at dosage rates of 10, 20, 70, and 100 rad $s^{-1}$. The increase from 10 to 100 rad $s^{-1}$ increases the rate of polymerisation from 1.29 to 22–23 g $litre^{-1}$ $h^{-1}$. Such a sharp increase is attributed to generation by the radiation of active centres in the product, polymerisation at which results in branched polymers. The radiation-chemical yield lies between 1670 and 15 670 mol./100 eV.

Detailed studies have been made also of the radiation polymerisation of vinyl fluoride dissolved in tetrachloromethane, benzene, dimethylformamide, dichloroethane[114,115], and a series of fluorinated hydrocarbons[116-118]. In the presence of tetrachloromethane the rate of polymerisation passes through a maximum at a monomer concentration of 0.80 M, exceeding by 50% the rate in the mass. With an initial monomer concentration of 0.26–0.35 M a colourless, viscous, oily product of molecular weight 320–540 is formed. Mole fractions of vinyl fluoride of 0.77 and above yield a solid polymer. The constant of chain transfer to tetrachloromethane is 0.0196. The infrared spectra[119] exhibit maxima in the regions of 790 and 712 $cm^{-1}$, indicating partial incorporation of the trichloromethyl group into the poly(vinyl fluoride) macromolecules.

The relative rate of polymerisation of vinyl fluoride is strongly dependent on the nature of the solvent[115]. Thus in benzene the rate drops sharply, and in dimethylformamide it is almost a linear function of the monomer concentration, but in dichloroethane the rate is higher than in the mass. Such variation in the rate of polymerisation of vinyl fluoride is due both to differences in the radiation-chemical yields of radicals from these solvents and to a redistribution between monomer and solvent of the energy absorbed from the radiation.

The dependence of the rate of the radiation polymerisation of vinyl fluoride on the dosage rate $I$ and the monomer concentration is described by different equations: in benzene $v = kI^{0.73}m^{2.7}$; in dimethylformamide $v = kI^{0.76}m^{2.2}$; in dichloroethane $v = kI^{0.86}m^{1.2}$; and in tetrachloromethane $v = kI^{0.80}m^{1.2}$. The activation energies of radiation polymerisation in the mass, in dimethylformamide, in dichloroethane, and in tetrachloromethane are respectively 5.7, 4.8–5.3, 5.5–6.1, and 5.0–5.5 kcal $mole^{-1}$ depending on the solute concentration. These values are 10–11 kcal $mole^{-1}$ smaller than the activation energy in the presence of material initiators, which is one of the advantages of radiation polymerisation.

Vinyl fluoride has been polymerised also in a plasma[120].

## III. STRUCTURE AND PROPERTIES OF POLY(VINYL FLUORIDE)

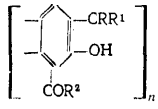
Poly(vinyl fluoride) gives relatively sharp X-ray diffraction patterns[121-124]. The crystallinity of specimens lies in the range 35–47% depending on the conditions of preparation. The unit cell possesses hexagonal symmetry. The macromolecules, like those of polyethylene or polyvinyl alcohol, have a planar zigzag conformation[65]. The interplanar spacing is 4.95 Å, and the repeat distance along the chain is 2.53 Å.[125,126].

One of the main factors determining many properties of poly(vinyl fluoride) is the sequence in which one unit is added to another in the macromolecule. "Head to tail" addition of monomer units was noted at an early stage by Newkirk[9]. Groupings of the CHF.CHF type, resulting from "tail to tail" addition, have been identified[127] in the nuclear magnetic resonance spectra. Bovey et al.[128] established by high-resolution n.m.r. spectroscopy the presence of a resonance line having a chemical shift of 8.33 ppm (on the $\tau$ scale), which may be due to "head to head" structures. The possibility of the presence of such units in the polymer chain is admitted by other workers who have studied the infrared and n.m.r. spectra of this polymer[129-135].

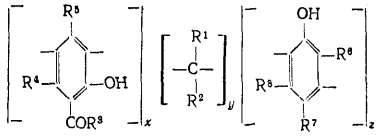
A distinguishing feature of poly(vinyl fluoride) is its great photostability[136], which is due to the complete transparency of its films in the ultraviolet and visible regions of the spectrum. Thus transparent films remained colourless and retained 50% of their original tensile strength after exposure to sunlight for 10 years[122]. Films 0.13 mm thick transmit $>90\%$ of radiation in the wavelength range 2350–1950 Å.[137]

Because of this great transparency, however, articles coated with such films are not always effectively protected from the action of ultraviolet radiation. Ultraviolet-absorbers must be introduced into the film, widely used

examples being triazoles [138,139], polymers of acrylic derivatives of acetophenones or benzophenone [140,141], polymers of general formula [142]



($R = R^1 = H$, $R^2 = C_6H_5$, and $n = 2$ or 3), and linear polymers having the structure [143]



($R^1$ and $R^2$ = H, $C_{1-6}$-Alk, chloroalkyl, furyl, vinyl, propenyl, or phenyl; $R^3 = C_{1-6}$-Alk or Ar; and $R^4$, $R^5$ = H, OH, Hal, Ar, aryloxyalkyl, or cyclohexyl). The same purpose can be achieved also by copolymerising [144] vinyl fluoride with a small quantity of the acrylic-acid derivative $CH_2:CR.COO.C_6H_4.CO.CH_2.CO.R'$ (R = H or $C_{1-3}$-Alk and $R' = C_{1-18}$-Alk or substituted phenyl). Other proposed ultraviolet-absorbers are benzophenone [146]†, various hydroxy-derivatives thereof [147-150], and the polyester obtained from adipoyl dichloride and 2,4,4'-trihydroxybenzophenone [151,152].

Poly(vinyl fluoride) films possess extremely good mechanical properties. Great strength is combined with elasticity and resistance to multiple bending even at low temperatures [122]. These properties are only slightly impaired by the prolonged action of water vapour [153]: thus at 99°C no appreciable deterioration in the elongation of films and their stability on multiple bending had occurred after 100 h. The films are characterised also by enhanced abrasion resistance [154-158], in which they are inferior only to polytetrafluoroethylene [159]. This property is fully consistent with the swellability, wettability, and surface free energy of poly(vinyl fluoride) [160].

Poly(vinyl fluoride) possesses great chemical resistance. The stability of the physical structure of films and their characteristic resistance to oxidation and hydrolysis were studied from the variation in properties on ageing in moist and dry atmospheres at high temperatures [122]. During ageing the tensile strength of a highly oriented film approaches that of films having less orientation of the molecules [161]. The polymer is stable towards caustic soda, hydrochloric and sulphuric acids, and primary and secondary amines [161,162]. It far surpasses in chemical stability poly(ethylene terephthalate), and is not inferior to a polyamide film. Treatment with nitrogen trifluoride or monofluoride at 80–100°C leads to the formation of cross-links in poly(vinyl fluoride) and improves the mechanical properties of the film [163,164]. The polymer can be chlorinated [165] and fluorinated [166] by the action of the gaseous halogens.

The product of the chemically initiated polymerisation of vinyl fluoride at temperatures above 100–110°C dissolves in such strongly polar solvents as *N*-substituted amides, dinitriles, thiolan dioxide, tetramethylurea, *N*-methylpyrrolidone, and γ-butyrolactone [12], the polymer separating out when the solution is cooled below 100°C. At room temperature poly(vinyl fluoride) dissolves well in hexamethylphosphoramide [167-169], perfluoropropane-2,2-diol, and 1,3-dichloro-1,1,3,3-tetrafluoropropane-2,2-diol [170]. The product of radiation polymerisation is considerably less soluble [171]. The conditions of preparation—dosage rate and radiation dose, temperature, presence of impurities and additives, and state of aggregation of the monomer during polymerisation—than have a marked effect on the solubility of the polymer. The solubility in boiling solvents of polymer samples obtained in the mass is respectively 30–35%, 22–27%, 10–15%, and 1–5% in dimethylformamide, hexamethylphosphoramide, cyclohexanone, and dioxan respectively [97]. Gas-phase polymerisation yields a product of enhanced solubility [113], and a polymer obtained in tetrachloromethane dissolves still better [172].

Because of the poor solubility of poly(vinyl fluoride) simple and reliable methods for determining its molecular mass were lacking until recently, so that only estimates were available [9,12,22]. In the first detailed study of the properties of solutions in dimethylformamide quantitative relations were deduced for determining the molecular mass and other characteristics of the polymer. The specimens used had been obtained in the presence of 0.003–0.2% of azoisobutyramidine at 67–97°C. The weight-average molecular mass of 9 samples studied varied from 143 000 to 654 000, and the number-average value from 76 400 to 218 000. The relation between the intrinsic viscosity and the molecular mass was given by $[\eta] = 6.42 \times 10^{-5} M_S^{0.80}$. More recently [50] molecular masses have been determined and the molecular-mass distribution has been studied for samples of the polymer obtained in the presence of α-azoisobutyronitrile, di-isopropyl peroxodicarbonate, and tributylboron monoperoxide as initiators, when the resulting polymer solutions had intrinsic viscosities of 1.58, 1.75, and 1.20 dl $g^{-1}$ respectively.

All the solvents for poly(vinyl fluoride) contain both groups that solvate the hydrocarbon portion and groups that interact with the polar part of the monomer units. Since interaction is probably of the nature of hydrogen bonding, the possibility of the latter must be taken into account in studying the interaction of various solvents with the polymer. It was established [174], for example, that replacing a hydrogen atom in polyethylene by a fluorine atom enhances its wettability by polar liquids capable of forming hydrogen bonds, whereas its wettability by non-polar liquids diminishes. A film of poly(vinyl fluoride) possesses relatively slight permeability to gases [175-177]. Its permeability to the vapours of organic solvents is also insignificant, except in the case of ketones, which probably cause the polymer to swell [178].

Sivadjian and his coworkers found [179] that at 25°C the water permeability of poly(vinyl fluoride) films is fourfold that of polyethylene, and sevenfold that of a Kel-F film. The probable reason is the possibility of free rotation of monomer units and larger segments in the crystal lattice of poly(vinyl fluoride) [137,162].

In its adhesive properties poly(vinyl fluoride) surpasses polytetrafluoroethylene by a factor of 4 and approaches polyvinyl alcohol [180]. Because of the vigorous growth in its application as a coating on various articles, however, various methods for improving its adhesive properties have recently been widely studied. In particular, this has been achieved by impregnating the surface

† Reference 145 appears to be missing and out of context: it is concerned with the heat-treatment of polymer films (Ed. of Translation).

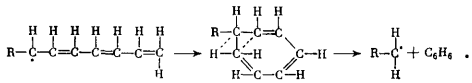
of a film of the polymer with a thermosetting resin[93] or by activating it by means of an electric discharge in the presence of such electrophilic substances as boron trifluoride, aluminium trichloride, chlorine, fluorine, etc.[168,181] The adhesion of a film of the polymer was improved also on bombardment with helium or hydrogen atoms[182]. The adhesion of a film was increased by factors > 100 when the surface was treated with substances capable of abstracting hydrogen and fluorine atoms, such as boron trifluoride, its hydrates, or etherates in the gas or liquid phase in the presence of oxygen at normal or elevated temperatures[161,162,183-185]. The adhesive properties of a poly(vinyl fluoride) film can be improved by treating its surface with a flame[186], nitrogen, an activated plasma[187], a diazo-compound[71,188-190], concentrated sulphuric acid, or hot alkali[191]. Polyurethanes[192] and polyamides[193] have been deposited on the film surface for the same purpose. In several cases adhesion is improved by modifying not the film itself but the metal surface to which the film adheres[186,194]. Thus treating an aluminium surface with a solution of trishydroxyethylamine increases the adhesion of a film of the polymer from zero to 1.1 kg.

Poly(vinyl fluoride) belongs to a class of polymers characterised by high melting points (197°C)[12,22] with relatively low heats of fusion, as follows from its thermodynamic parameters[93]—$\Delta H_M$ = 1800 cal mole$^{-1}$ and $\Delta S_M$ = 3.87 cal mole$^{-1}$ deg$^{-1}$.

This polymer is characterised also by great thermal stability, a consequence of the strength of the carbon–fluorine bond, the regularity of structure of the main chain, and the high energy of interchain interaction. The thermal stability depends on the method and conditions of preparation of the polymer. The product of free-radical initiation in the mass begins to decompose in a vacuum at 300°C, and in air at 170°C,[195] with respective activation energies of 44.0 and 21.0 kcal mole$^{-1}$. Thermal breakdown of the product of emulsion polymerisation begins in a vacuum at 290°C, with an activation energy of 51.0 kcal mole$^{-1}$.

The thermal stability of poly(vinyl fluoride) prepared by the radiation method has been studied in the greatest detail[195-198]. The polymer obtained in the mass begins to decompose in a vacuum above 300°C, and in air at 175°C, the activation energy being respectively 61.1 and 24.0 kcal mole$^{-1}$.[197] The product of gas-phase polymerisation begins to decompose at 300°C,[196] like that obtained in the mass. With further rise in temperature, however, the former polymer undergoes more intense breakdown than does the latter. The activation energy of degradation is also lower in the first case: 36.0 and 20.0 kcal mole$^{-1}$ in a vacuum and in air respectively. The enhanced thermal stability of the polymer obtained in the mass by the radiation method is explained both by its great purity and by the partial formation of three-dimensional structures during polymerisation.

The main product of the decomposition of poly(vinyl fluoride at 310–325°C is hydrogen fluoride[199-203]. Further rise in temperature changes the composition of the degradation products: at 332°C they comprise 10 components, and at 350°C about 13 components[198]. The infrared spectra of the polymeric residues show[198] that they consist of macromolecules cross-linked one to another and containing conjugated and isolated double bonds together with fused aromatic structures. It has been suggested that the elimination of hydrogen fluoride in the thermal degradation of poly(vinyl fluoride) takes place by a molecular mechanism. The presence of considerable quantities of benzene among the decomposition products is explained[198] as a result of secondary decomposition, probably following the formation and isomerisation of polyene radicals:



Toluene and xylene are formed similarly.

In spite of the enhanced stability of poly(vinyl fluoride) its successful processing and use of the resulting articles under various conditions require at present that it should be stabilised by means of various compounds[200]. These agents should meet various requirements[199]: (i) they should be good acceptors of hydrogen fluoride; (ii) they should be dienophilic, i.e. capable of Diels–Alder reactions; and (iii) they should possess antioxidant properties. Amines and amides containing mobile hydrogen atoms[203], glycerol monolaurate[204], and salicylate salts containing one or two substituents in the benzene ring[205] have been proposed as stabilisers for poly(vinyl fluoride). Substituted 1–8-octahydro-6-methylenenaphthalenes proved to be highly effective stabilisers[206]; they also lower the viscosity of the polymer melt, are fully compatible with it, and are insoluble in water. Terpenes, thiols, and disulphides are used as stabilisers when a film of the polymer is formed by extrusion[207]. Alkyl($C_{2-6}$) hydrogen fumarates and maleates raise to 250°C the temperature at which poly(vinyl fluoride) begins to decompose in air[208].

Other compounds that can be used as thermal stabilisers are urea and its derivatives[209], 1,1-diphenylcyclohexane-*pp'*-diol[210,211], thiobismethyl-t-butylphenol[212], terpenes and certain alkenoylamides and alkenoyloxyphenylbenzotriazole-containing polymers[207], polyvinylpyridine[213], polymers of *ortho*-hydroxylated and *para*-substituted phenol[214], 2,2'-thiobisalkylphenols, phenoxides, or salts of a carboxylic acid of a bivalent organometallic phosphite and tin 2-ethylhexanoate, dialkyl pentaerythritol phosphites or their mixtures, polyhydroxylated compounds either pure or combined with sulphur- or phosphorus-containing compounds[215], and compounds of type Zn(S.$PSR_2)_2$, where R is an aliphatic (normal or branched), cyclic, or aromatic radical containing 2–18 carbon atoms[216].

Copolymerisation of vinyl fluoride with bicyclo[2,2,1]-heptadiene[214] will raise by 20 deg the temperature at which poly(vinyl fluoride) begins to decompose. Alkali-metal formates are effective thermal stabilisers for the polymer. The potassium and sodium salts have proved the best[198]: addition of 0.5% of potassium formate raises to 270°C the start of decomposition; similar results are obtained with sodium formate. Certain cross-linking agents, such as amines, ammonia[217], and *cis*-dinitrogen difluoride, are suitable for improving the thermal stability of the polymer[164].

Poly(vinyl fluoride) differs from polytetrafluoroethylene and polychlorotrifluoroethylene in possessing high radiation resistance[218,219]. Whereas ionising radiation depolymerises the second polymer with cleavage of carbon–carbon bonds in the chain, poly(vinyl fluoride), as a polymer containing hydrogen, is cross-linked. Films of the latter remain unchanged at radiation doses up to 32 Mrad, whereas a polytetrafluoroethylene film becomes appreciably shorter even with a dose of 8 Mrad.[26] Irradiation with cobalt-60 $\gamma$-rays liberates various gaseous products, mainly hydrogen fluoride[220], the rate of evolution of which depends on the dosage rate in conformity with the equation $v = kI^{0.55}$. Exposure lowers the flow point of the polymer considerably[221], which is attributed to partial degradation

of chains, amorphisation of the polymer, the plasticising effect of simple substances formed by radiolysis, and the decrease in the energy of intermolecular interaction due to the decrease in polar groups.

Study of the relaxation properties of the polymer has begun only recently. Specimens obtained in different ways exhibit structural transition temperatures of −70.43 [−70 to −43 (?) (Ed.of Translation)], 125−150, and 195−235 °C.[49, 221] In order to interpret the mechanism of these transitions, a method of forced resonance vibrations was used to examine the dynamic mechanical properties of the polymer[221]. The temperature dependence of the dynamic Young's modulus $E$ and the mechanical loss factor $\tan\delta$ correlate well with the above values. The stress−strain curves are peculiar in character[49]: the polymer breaks without necking even at temperatures up to 80 °C. The curves do not exhibit a region of rubberlike elasticity.

Pure poly(vinylfluoride) melts in air with partial decomposition. The introduction of various plasticisers to lower the melting point is therefore of direct practical interest for its processing into films, sheets, and fibres. An investigation[222] of plasticisation within and between blocks used as plasticisers dimethyl, diethyl, dibutyl, and dioctyl phthalates, tritolyl phosphate, butyl stearate, castor oil, and fluorinated hydrocarbon oils. A specimen of the polymer containing 25−30% of dibutyl phthalate does not undergo degradation cross-linking and flows irreversibly at 165 °C. Similar results have been obtained for other plasticisers. Different methods of polymerisation result in different effects of plasticisation, which is more efficient for specimens obtained by the suspension method than by other processes. The tensile strength of the plasticised polymers[223] passes through a maximum when containing 5−6% of dioctyl phthalate, 2% of castor oil, or 1% of butyl stearate. In contrast, the elongation of the specimens at break passes through a minimum. X-Ray diffraction shows[223] that the crystallinity increases on the introduction of up to 2% of a plasticiser, owing to increased mobility of the chains, but begins to diminish with further increase in the plasticiser content.

The combination of good electrical properties with enhanced thermal stability, chemical inertness, photostability, and adhesive properties makes poly(vinyl fluoride) one of the first choices for use in electrical insulation[224]. In contrast to many polymers, the rate of charge accumulation is independent of the applied voltage and the ambient humidity[225], because of the low hygroscopicity of the polymer. Surface films are coated with bishydroxyalkylamides to prevent the accumulation of static charge[226,227]. The dielectric constant and the dielectric losses are tenfold those for the corresponding polymeric chloride and bromide[228-230]. The dielectric constant usually increases with rise in temperature, but diminishes with increase in frequency[231]. The reason is that, because of the comparatively small radius of the fluorine atom, the polymer chains, are able to perform rotational movements (of small amplitude) in which the monomer units rotate, which can be regarded as segmental motion[232-234].

## IV. COPOLYMERISATION OF VINYL FLUORIDE

Methods of preparation analogous to those used for poly(vinyl fluoride) have produced many diverse copolymers with novel properties of practical value.

The copolymerisation of vinyl fluoride with ethylene was first studied by Coffman[235,236], and later by Roedel[237], in the presence of carboxylated initiators over the range 50−150 °C. A more detailed investigation was made by Burkhart et al.[27,238] in the presence of various peroxides and by means of radiation at 160 °C and 100 atm. The copolymers were in all cases enriched with ethylene, independently of the ratio of the monomers in the initial mixture. A copolymer suitable for the production of films and fibres was obtained by conducting the process in solution and in suspension[239,240]. The initiators used were tri-isobutylboron, triethylboron monammine, sodium peroxodisulphate, iron(III) hydrogen sulphate, alkylalkoxyaluminium chlorides, benzoyl peroxide, and di-isopropyl peroxodicarbonate with molecular oxygen. The radiation copolymerisation of vinyl fluoride with ethylene was also studied[241].

Products of diverse properties are obtained by copolymerising vinyl fluoride[242-245] with propene, isobutene, bicycloheptane[246], and styrene[239,247]. A copolymer of vinyl fluoride with vinyl chloride was obtained by Thomas[11] as early as 1944, and was one of the first copolymers of vinyl fluoride. Copolymers with vinyl chloride suitable for the production of films, fibres, and coatings have been prepared by the use of benzoyl peroxide[11], organoboron initiators[247,248], di-isopropyl peroxodicarbonate[249,250], sodium persulphate, iron(II) salts[64,66,247,251-255], and catalysts of Ziegler−Natta type[247].

The radiation copolymerisation of vinyl fluoride with vinyl chloride has been studied in the greatest detail[256-263]. Under otherwise similar conditions the rate of copolymerisation is considerably lower than the rate of separate polymerisation of either component. Copolymers containing up to 50 mole % of vinyl fluoride are completely soluble in dimethylformamide, dioxan, cyclohexanone, 1,1-dichloroethane, and butan-2-one, but those having a higher content of the fluoride are only partly soluble at the boiling points of these solvents. They are transparent to ultraviolet radiation, but absorb strongly in the infrared[257]. The presence of vinyl fluoride units in the copolymers leads to the appearance of infrared absorption bands in the range 1035−1175 $cm^{-1}$. Ultraviolet exposure results in new infrared bands in the region of 1610, 1700, and 1720 $cm^{-1}$, which can be assigned to vibrations of the carbonyl group and of isolated and conjugated ethylenic bonds[258]. However, the bands at 690 and 1175 $cm^{-1}$, due to vibrations of carbon−chlorine and carbon−fluorine bonds respectively, become weaker.

Copolymers of vinyl fluoride and chloride are more wear-resistant than poly(vinyl chloride)[259]. Heat-treatment at 150 and 175 °C causes loss of fluidity owing to cross-linking of the macromolecules. The losses in weight in a vacuum at 200 °C are respectively 36%, 15%, and 9% for poly(vinyl chloride) and copolymers containing 12.1 and 21.6 mole % of vinyl fluoride[261]. The respective activation energies of thermal decomposition are 27.5, 30.2, and 37.5 kcal $mole^{-1}$: i.e. increase in the proportion of vinyl fluoride in the copolymer is accompanied by a parallel improvement of thermal stability. Copolymers obtained by the radiation method were thermally more stable than those resulting from chemical initiation. Thus for a copolymer containing 21.9 mole % of vinyl fluoride the loss in weight in a vacuum at 250 °C for 6 h was 35% and 46% for samples obtained by means of radiation and chemically.

The copolymerisation of vinyl fluoride with vinylidene chloride has been initiated by various peroxides[239,247] and organoboron compounds[239] in solution or in aqueous suspension in the presence of a dispersing agent. Kinetic study of the copolymerisation in the presence of di-iso-

propyl peroxodicarbonate[260] has revealed certain laws: initially the yield of copolymer is a linear function of time, and the rate of copolymerisation is proportional to the initiator concentration to the power 0.53; at high degrees of conversion the rate curves are sigmoid; and the copolymers are enriched with vinylidene chloride whatever the ratio of the monomers in the initial mixture.

The copolymerisation of vinyl fluoride with tetrafluoroethylene can be initiated by peroxides[240,246-266], organoboron catalysts[267], and di-isopropyl peroxodicarbonate dissolved in benzene, chloroform, or dimethylformamide[65]. The copolymer containing 85 mole % of vinyl fluoride has a glass point of 212–213°C; it is soluble in cyclohexanone and dimethylformamide[19].

Copolymerisation of vinyl fluoride with chlorotrifluoroethylene has been accomplished in the mass, in solution, and in suspension in the presence of benzoyl peroxide, di-isopropyl peroxodicarbonate, organoboron compounds, and also sodium persulphate and iron(II) sulphate[247,267-269]. The resulting copolymers dissolve in acetone, form transparent films, and have good electrical and thermal stability[270]. The presence of hydrogen and halogen atoms enables these copolymers to be cross-linked by ethyl cyanoacetate, hexanonitrile, acetonitrile, cyanoacetic acid, acrylonitrile, cyanoacetamide, etc.[271]

Vinyl fluoride copolymerises with trifluoroethylene in the presence of inorganic and organic peroxides, di-isopropyl peroxodicarbonate, and organoboron initiators in the mass, suspension, emulsion, and solution[66,240,267,272]. These copolymers are characterised by enhanced heat resistance and are suitable for the production of films[273].

The copolymerisation of vinyl fluoride with vinylidene fluoride has been studied in greater detail[29,65,239,272-274]. The reaction is initiated by benzoyl peroxide, sodium persulphate, di-isopropyl peroxodicarbonate, organoboron catalysts—triethylboron, tributylboron tri-isopropylboron, diethylboron ethoxide, diethylboron chloride, diborane—and oxygen. The resulting copolymers are soluble, and have been used to obtain thin films and coatings[275,276]. Exposure of a mixture of vinyl and vinylidene fluorides to $\gamma$-rays (dose 7.2 rad) yields a copolymer containing 52.7% of vinyl fluoride units[277].

Vinyl fluoride copolymerises readily with perfluoromethacryloyl fluoride—a monomer that does not polymerise alone—both in the presence of chemical initiators and on exposure to $\gamma$-rays[278]. The products are partly soluble in dimethylformamide. The thermal stability of the copolymer improves with increase in the content of the acid fluoride.

Products that are thermally more stable than poly(vinyl fluoride) are obtained by copolymerising vinyl fluoride with 1,1-difluoroisobutene[273], perfluoropropene[29,240,247], 1,1,2,4-tetrafluorobuta-1,3-diene[279], 1,1,2- and 1,1,3-trifluorobuta-1-diene [sic][280], fluorinated ketones[281,282], perfluoronitroisomethane [sic][283,284], halogenotrifluorocyclopropanes[283], and dichlorodifluoroethylene[285].

Vinyl fluoride copolymerises with vinyl acetate in bulk, solution, or aqueous dispersion in the presence of benzoyl peroxide[251,254,268,286,287] or on ultraviolet irradiation[288]. At 0–80°C copolymerisation takes place readily in the presence of di-isopropyl peroxodicarbonate and organoboron initiators[195,239,247]. The products possess great resilience and resistance to sunlight[289]. Aqueous solutions of partly hydrolysed copolymers of vinyl fluoride with vinyl acetate yield thermally reversible gels[286]. Detailed studies have been made of the radiation copolymerisation of vinyl fluoride and acetate in the mass and dissolved in 1,1-dichloroethane, acetone, dimethylformamide, and several other solvents[290,291]. The rates of copolymerisation in the mass and in 1,1-dichloroethane solution are proportional to the dosage rate to the power 0.78 and 0.55 respectively. Increase in the vinyl fluoride content of the copolymer is accompanied by an increase in its density, rises in the glass and flow points, and strengthening of the films formed from it. The activation energy of the thermal degradation of poly(vinyl acetate) and of copolymers containing 14% and 35% of vinyl fluoride is respectively 32.0, 40.7, and 43.5 kcal mole$^{-1}$.[209]

Under the influence of $\gamma$-rays vinyl fluoride copolymerises with vinyl propionate in the mass and in 1,1-difluoroethane solution[251,254]. The product is transparent and rubberlike, softens at 140°C, and decomposes at 285°C. Vinyl fluoride has been copolymerised also with 3,5-dichloromethylstyrene[255]. The suspension copolymerisation of vinyl fluoride has been accomplished also with vinyl butyrate, benzoate, and succinate, diethyl and dibutyl maleates, and dioctyl fumarate in the presence of lauroyl peroxide[43,44,251,254]. The resulting copolymers possess enhanced resistance to heat and light with good electrical insulation.

Investigation of the copolymerisation of vinyl fluoride with acrylic and methacrylic acids and esters in the presence of free-radical initiators has established[52,239,241,292-299] that the esters are less active than are the corresponding acids. A similar rule is observed in their radiation copolymerisation[297]. The rate of copolymerisation is proportional to the dosage rate to the power 0.55 to 0.80, and increases on passing from acrylates having large groups to the acid itself. The copolymers are enriched with the acrylic monomers in all the systems studied. Copolymers of vinyl fluoride with acrylic and with methacrylic acids, whether obtained chemically or by the radiation method, do not exhibit fluidity, though the glass point falls as the vinyl fluoride content increases. The copolymers with the esters develop rubberlike elasticity, and both glass and flow points rise with increase in the vinyl fluoride content, which is attributed to the strengthening of intermolecular interaction by the presence of the polar carbon–fluorine bond. The copolymers are intermediate in thermal stability between the corresponding homopolymers of the acrylic monomer and poly(vinyl fluoride)[209].

A copolymer of vinyl fluoride with *N*-vinylpyrrolidone has been prepared by a radiation method[300]. The latter component is more reactive than the former by a factor of 63, on interaction both with its own radical and with that of vinyl fluoride. The solubility of the copolymer depends on the dosage rate and on the integral dose. Chemically prepared copolymers are completely soluble in polar solvents[301].

The copolymerisation of vinyl fluoride with acrylonitrile has been widely studied in the mass, in solution, and in suspension in the presence of benzoyl and lauroyl peroxides, di-isopropyl peroxodicarbonate, perfluoroacyls, and organoboron compounds at 0–50°C.[44,248] Water-soluble copolymers of maleic anhydride with ethylene or vinyl acetate served as dispersing agent for the suspension copolymerisation[44]. A radiation method has also been used for the copolymerisation of vinyl fluoride with acrylonitrile in the mass and in solution in benzene and dimethylformamide[256,302]. Examination of the influence of rate of irradiation on rate of copolymerisation established the same rules as for the binary systems of vinyl fluoride with vinyl chloride, vinylidene chloride, and *N*-vinylpyrrolidone. Copolymers of irregular structure are formed, but with a high content of vinyl

fluoride in the initial monomer mixture short segments comprising vinyl fluoride and acrylonitrile units alternate. The copolymers are obtained in cross-linked forms, so that they are only partly soluble; the insoluble portions of the copolymers are enriched with acrylonitrile units.

Waxlike solid copolymers of vinyl fluoride with hydrogen cyanide [303] are obtained in the presence of free-radical initiators at 135°C and 1000 atm. Copolymers of vinyl fluoride can be obtained with methylenemalononitrile, $\alpha$-cyanoacrylamide, methylenemalonamide [304], and $\alpha$-acetamidoacrylamide [305,306].

Several studies have been made also on ternary copolymers of vinyl fluoride. Thus readily soluble, non-flammable products are obtained by copolymerising vinyl fluoride and tetrafluoroethylene with chlorotrifluoroethylene [307], vinyl chloride, and vinylidene fluoride respectively. The ternary copolymer comprising 60% of vinyl fluoride, 25% of tetrafluoroethylene, and 15% of vinyl chloride possesses good physicochemical and adhesive properties [308]. Copolymerisation of vinyl fluoride with chlorotrifluoroethylene and vinylidene fluoride under the influence of $\gamma$-rays has been described [254]. Polymers that melt with decomposition are obtained by copolymerising vinyl fluoride with bishydroxyalkyl maleates and vinylidene halides [267]. Heat-resistant copolymers of vinyl fluorides with bicyclo-[2,2,1]hept-2-ene and *N*-carboxylated bicyclo[2,2,1]hept-2-ene derivatives have been prepared [309]. Copolymers having good cross-linking properties are obtained from vinyl fluoride with acrylates and $\alpha\beta$-alkenes [310]. Vinyl fluoride can be copolymerised with a small quantity of vinyl acetate and itaconic acid or with maleic anhydride and isobutyl vinyl ether to improve the dyeing properties of poly(vinyl fluoride) fibres [309]. A copolymer of high adhesive power, soluble in cheap solvents, is obtained from vinyl fluoride with vinyl benzoate, bis-2-chloroethyl vinylphosphonate, itaconic acid, and tetrafluoroethylene [311]; the product melts at 182°C.

Radiation copolymerisation of equimolecular ternary mixtures of vinyl fluoride and vinyl acetate with vinyl chloride and with methyl methacrylate respectively has been studied in the greatest detail [312-316] with the use of cobalt-60 $\gamma$-rays at dosage rates of 16, 70, and 100 rad $s^{-1}$ for various lengths of time. The order of reaction with respect to the dosage rate is respectively 0.74 and 0.64 for the two ternary systems. Copolymers obtained in the initial stages are in all cases enriched with the more active monomers—vinyl acetate with vinyl chloride and methyl methacrylate respectively—but as they are consumed the content of vinyl fluoride in the monomer mixture increases, with a consequent increase in its content in the copolymer also. The infrared spectrum [315,316] of the ternary copolymer of vinyl fluoride with vinyl chloride and acetate shows a sharp drop in intensity of carbon–chlorine stretching vibrations in comparison with the spectrum of the binary copolymer of the latter components. Furthermore, bands in the range 1000 to 1200 $cm^{-1}$ are broadened by the presence of bands due to stretching vibrations of ester carbon–oxygen–carbon bonds and of carbon–fluorine bonds. The nuclear magnetic resonance spectrum [315,316] of this copolymer contains three groups of signals, in the ranges 1.7–2.5, 4.0–4.7, and 4.9–6.5 ppm: the sharp peak at 2.0–2.05 ppm corresponds to methoxy-groups in vinyl-acetate segments; and the signal in the range 4.0–5.5 ppm is due to the superposition of signals of tertiary protons in fluoromethylene, chloromethylene, and acetoxymethylene groups. The ternary copolymers of vinyl fluoride and acetate with vinyl chloride and with methyl methacrylate respectively have lower glass points than have the corresponding binary copolymers, and these fall with increase in the vinyl fluoride content of the copolymer [314].

## V. GRAFT POLYMERISATION OF VINYL FLUORIDE

At the end of the 1960s, when the valuable properties of poly(vinyl fluoride) had become clear, intensive study began both of the preparation and of the properties of graft copolymers based on vinyl fluoride [317,318]. The low boiling point, resistance to polymerisation in the presence of material initiators, and inertness towards most polymers hinder considerably the graft polymerisation of vinyl fluoride by chemical and mechanochemical methods. The most effective has proved to be the radiation method, by which has now been accomplished the graft polymerisation of vinyl fluoride to cellulose and its derivatives, natural silk, wool, kapron fibre, polyalkenes, and halogenated and several other polymers [98,113,319-340].

The radiation graft polymerisation of vinyl fluoride to cotton cellulose and cellulose hydrate has been conducted in the mass in the presence of dimethylformamide, ethanol, and water [325,326]. With increase in the time of irradiation both the overall conversion of vinyl fluoride and the yield of the graft copolymer increase.

Graft polymerisation of vinyl fluoride from the vapour phase goes best on mercerised and "inclusion" cellulose [326]. This is due to enhancement of the reactivity of cellulose by the loosening of its structure during mercerisation and inclusion. The increase in weight due to the grafted poly(vinyl fluoride) is larger in the presence of the vapours of such "including" substances as dimethylformamide or isopentanol than on an already "included" specimen. The larger gain in the first case is due to the grafting of vinyl fluoride at the instant at which the cellulose swells.

The grafting of poly(vinyl fluoride) to cotton cellulose weakens the infrared absorption band in the range 1325 to 1350 $cm^{-1}$, due to deformation vibrations of primary hydroxy-groups [330]. This indicates that active grafting centres are located at these groups. The band in the region of 900 $cm^{-1}$ also diminishes in intensity, which is attributed to loosening of the structure of compact segments of cellulose under the influence of the grafted poly(vinyl fluoride) chains.

The infrared spectra of cellulose hydrate [330] exhibit the same changes as in cotton cellulose, but the weakening of vibrations in the range 3200–3300 $cm^{-1}$ is most clearly evident. Absorption diminishes also in the range 1000 to 1020 $cm^{-1}$, which suggests that active centres may well be formed not only at primary but also at secondary hydroxy-groups. Modified cellulose hydrate containing 8% of poly(vinyl fluoride) resists the action of sulphuric acid for 1 month, whereas an unmodified specimen breaks down completely within a few minutes. Increase in the content of the grafted polymer diminishes the sorption of water vapour, which is attributed to the strongly hydrophobic character of the poly(vinyl fluoride) side-chains.

Study of the thermal stability of graft copolymers of cotton cellulose with poly(vinyl fluoride) in a vacuum and in air over the temperature range 270–370°C has established [333] that the initial rates of decomposition of the copolymers are considerably lower than those of the initial cellulose.

The graft polymerisation of vinyl fluoride on cellulose triacetate fibre is more rapid than on the diacetate [327], which is due to the greater radiation sensitivity of the

former. Graft copolymers of the diacetate and the triacetate containing >40% of poly(vinyl fluoride) dissolve neither in acetone nor in chloroform, and undergo partial swelling in dimethylformamide and cyclohexanone.

Graft polymerisation of vinyl fluoride to natural silk does not take place in the absence of solvents [331]. The presence of such liquids as water, methanol, and ethanol has a sensitising effect on grafting, and the increase in weight reaches 20% on the weight of the silk. The grafting of vinyl fluoride effects a marked improvement in the acid resistance of natural silk, which is attributed to shielding of the peptide links by the grafted polymer chains [332,333]. Furthermore, grafting improves the resistance of silk to heat and light, as well as its oil- and water-repellent properties. Electron microscopy has established that the grafting of vinyl fluoride to natural silk diminishes the fibrillarity characteristic of the original fibre [335,341]. Individual globular structures are also observed, whose presence is due to the grafted chains of lyophobic poly(vinyl fluoride).

Vinyl fluoride has been grafted from the vapour phase to kapron fibre at dosage rates of 12–100 rad $s^{-1}$, [113,317,323] when the resulting copolymers contain up to 31% of the grafted polymer. In the presence of water vapour the gain in weight increases to 60%. [336] This may be due to the great swelling of kapron fibre in water vapour and to the sensitising action of radicals formed in the radiolysis of water. The yield of graft copolymer is lower in the presence than in the absence of methanol and ethanol vapours. Grafting is influenced also by the fibre structure [336]: the gain in weight is larger on an unoriented than on an oriented fibre and a tyre cord. The grafting of vinyl fluoride enhances the light, heat, and chemical resistance of kapron [113].

Radiation vapour-phase grafting of vinyl fluoride has been accomplished also on natural wool [333]. Grafting is greatest in the presence of water vapour. At 90°C modified wool containing 10% of a poly(vinyl fluoride) graft dissolves more slowly than unmodified wool in caustic soda by a factor of almost 400.

Detailed studies have been made on the radiation graft polymerisation of vinyl fluoride to polyethylene, polypropylene, and polyisobutylene. Vinyl fluoride has been grafted to polyethylene (in film or powder form) from the vapour phase at 38°C and 27.5 atm [98,113] with dosage rates varying from 10 to 100 rad $s^{-1}$. The radiation-chemical yield fluctuates within the range 100–3800 mol./100 eV in the case of a film, and 870–9540 mol./100 eV for a powder. A graft copolymer containing <30% of poly(vinyl fluoride) is completely soluble in boiling toluene and in xylene [113]. With further increase in the content of the graft the solubility diminishes, and a gel is formed consisting of a graft copolymer of polyethylene containing very long poly(vinyl fluoride) side-chains. The grafting of vinyl fluoride increases the density of polyethylene to 1.082 g $cm^{-3}$ for a copolymer containing 50.2% of poly(vinyl fluoride). The splitting of the absorption band due to vibrations of the methylene group in the region of 720 and 730 $cm^{-1}$ in the infrared spectra of the copolymer [98] gradually disappears with increase in the poly(vinyl fluoride) content. This shows that grafting takes place both in amorphous and in crystalline regions of polyethylene, and leads to breakdown of the crystal structure of the latter. In graft copolymers containing ≥25% of poly(vinyl fluoride) fluidity is completely absent owing to cross-linking of the side-chains of the latter by the elimination of hydrogen fluoride under the influence of temperature [98].

As with polyethylene the modification of polypropylene by the grafting of vinyl fluoride increases its density while diminishing its solubility and swellability [329]. Graft copolymers of polyisobutylene with vinyl fluoride has been prepared in cyclohexanone with equimolecular proportions of polymer, monomer, and solvent and dosage rates of 9–126 rad $s^{-1}$. [338] As in the other cases, the poly(vinyl fluoride) content of the copolymer increases with the dose whatever the dosage rate. This is accompanied by increase in the heat and chemical resistance of the copolymer.

Vinyl fluoride has been grafted to polytetrafluoroethylene with the aim of improving the adhesive properties and diminishing the cold flow of the latter [338]. When polytetrafluoroethylene is irradiated in liquid vinyl fluoride, the homopolymer is formed preferentially. Better results are obtained by conducting the graft copolymerisation from the vapour phase. The resulting graft copolymers are readily wetted by polar liquids while retaining all the valuable properties of the original polytetrafluoroethylene.

Radiation grafting to poly(vinyl chloride) has been accomplished both in pure vinyl fluoride vapour and in the presence of vapours of various solvents [338–340], among which the presence of 1,1-dichloroethane gave the largest degree of grafting. With increase in the poly(vinyl fluoride) content of the copolymer from 6.7% to 35.8% the loss in weight in a vacuum and in air decreases by factors of 1.5–4, and 1.5–6 respectively [342]. Vinyl fluoride has been grafted also on khlorin fibre, obtained from chlorinated poly(vinyl chloride) [113,317,343]. The rate of the graft copolymerisation is proportional to the dosage rate to the power 0.61. Improvement in the heat, light, and chemical resistance of khlorin is noted.

Vinyl fluoride has been grafted on polystyrene [338], polyvinyl alcohol [98,113], poly(vinyl acetate) [98,338,340], and poly(methyl methacrylate) [98,337,338]. With polystyrene dosage rates of 9–126 rad $s^{-1}$ were used in 1,1-dichloroethane and chloroform. Increase in the poly(vinyl fluoride) content of the copolymer was accompanied by decrease in its swellability in toluene and fall in its glass point. A copolymer containing 5.6% of grafted poly(vinyl fluoride) decomposes at little more than one-sixth of the rate of decomposition of the original polystyrene.

Under identical conditions vinyl fluoride can be grafted considerably more rapidly to kapron than to polyvinyl alcohol [98,113]. This is explained by the low activity of the macroradical from the polymeric alcohol and by the formation of a very compact, oriented jacket on the surface of the fibre during its formation. Fluidity is completely absent from graft copolymers containing 28% of poly(vinyl fluoride), as from graft copolymers of polyethylene, owing to cross-linking at the time of the thermal test.

The radiation grafting of vinyl fluoride on poly(methyl methacrylate) has been accomplished in benzene and in 1,1-dichloroethane [98,338]. The glass points of the resulting graft copolymers were lower than that of the original methacrylate polymer, which is attributed to the plasticising action of the grafted chains. The grafting of vinyl fluoride on poly(vinyl acetate) strongly enhances the resistance of the latter to organic solvents and mineral acids [338], as well as raising the flow point. Thus graft copolymers containing 11.2% and 59.0% of poly(vinyl fluoride) have flow points of 116 and 198°C respectively.

Although poly(vinyl fluoride) has relatively good adhesive properties among fluorinated polymers, and can be dyed and processed comparatively readily, further improvement in these properties is of great practical interest. For this purpose styrene [343–346], methyl meth-

acrylate [344,346,347], vinyl acetate [346,347], and vinylidene chloride [344] have been grafted on a poly(vinyl fluoride) film, both under the influence of cobalt-60 $\gamma$-rays and by the use of an electron accelerator, and methyl methacrylate has been grafted on a copolymer of trifluoroethylene and vinyl fluoride under the influence of ultrasound [345]. Among these monomers methyl methacrylate gave the best graft [346], because of its high radiation sensitivity: almost all the methyl methacrylate was grafted during the first hour of irradiation. In the case of styrene the rate of grafting passes through a maximum with increasing time of exposure [343], which is attributed to the shielding effect of the more radiation-resistant grafted polystyrene.

These monomers form the sequence

vinyl acetate < styrene < methyl methacrylate

of increasing rate of grafting to poly(vinyl fluoride), which correlates with their sorption on the polymer [346]. The graft layer formed initially has a significant influence on the subsequent course of the process. Grafting obviously loosens the film surface, which facilitates diffusion of the monomers into the interior. Loosening of the structure of poly(vinyl fluoride) by grafting has been confirmed by X-ray diffraction and by a study of the density of graft copolymers [346,348].

The thermomechanical curves of graft copolymers containing up to 30% of methyl methacrylate or styrene are analogous to those of the original poly(vinyl fluoride) [346,347]. With further increase in the content of the grafted component segments appear in the curve corresponding to a vitreous state, rubberlike elasticity, and viscous flow.

Grafting the above monomers improves the wettability and dyeing properties of a poly(vinyl fluoride) film [346-348]. This effect is due firstly to the appearance on the film surface of functional groups that increase its affinity for liquids and secondly to diminished crystallinity of the polymer. With the same content of the grafted polymer the wettability by water increases in the sequence

poly(methyl methacrylate) < polystyrene < poly(vinyl acetate).

The increased adhesive power of modified poly(vinyl fluoride) is due [346] to the presence of the grafted side-chains, not to any other factor, in particular not to the influence of the $\gamma$-rays. The dyeability of the graft copolymers of poly(vinyl fluoride) increases in the sequence [348]

polystyrene < poly(methyl methacrylate) < poly(vinyl acetate).

This rule is due to the nature of the grafted polymers, since under identical conditions the dyeability of the polymers themselves also increases in the same sequence.

## VI. PROCESSING AND APPLICATION OF VINYL FLUORIDE POLYMERS

Poly(vinyl fluoride) can be processed into appropriate articles by all the methods that have been developed for and applied to other thermoplastic polymers, although its characteristic features must be taken into account. Injection moulding of poly(vinyl fluoride) above 200°C was suggested [12] for the production of films or monolithic articles possessing good impact strength. The possibility of film formation from solution was also examined [12]. A dimethylformamide solution containing 8% of the polymers was quite adequate for this purpose, and film formation was hindered from higher solution concentrations. However, the only method that found wide application for the production of poly(vinyl fluoride) films was extrusion. Various stabilisers must then be used to prevent thermal degradation [218,349].

The most convenient method has proved to be moulding in the presence of so called latent solvents, which tend to lower the melting point and diminish orientational stretching of the polymers, thereby preventing degradation [350]. Latent solvents, by causing partial dissolution and good swelling, promote high dispersion of the polymer. Homogeneous films containing up to 50% of poly(vinyl fluoride) have been prepared from such fine dispersions [81,93,351-357]. The latent solvent most often employed is dimethyl sulphoxide, either alone [350,358-360] or in the presence of an electroluminescent substance. Various lactones [351,353,361], tetramethylurea, triethyl phosphate [78], pyrrolidones [93], and piperidines [362,363] have also been proposed as latent solvents.

A method has been suggested for the production of both films and fibres from aqueous dispersions of poly(vinyl fluoride) in the presence of small quantities of a latent solvent [78,364,365]. Mixtures of water and sulpholan have also been proposed as dispersion medium [356]. The role of the latent solvent is aggregation of particles; although aggregates are formed from the accumulation of a few particles, they are separated from one another by a thin layer of solvent.

The processing of poly(vinyl fluoride) into films can be facilitated by preparing dispersions during the actual synthesis of the polymer in the presence of latent solvents. This avoids isolation and redissolution or redispersion of the polymer. Thus a film prepared from a 22% dispersion of poly(vinyl fluoride) synthesised in a medium containing 71% of dimethyl sulphoxide and 7% of water has good mechanical properties [366]. Opaque films devoid of lustre can be obtained by introducing into the dispersion an opalescent substance such as titania [367] or silica [368]. Various pigments, stabilisers, and plasticisers are also used in the preparation of poly(vinyl fluoride) films [152,369-377].

Several difficulties are involved in orienting the films at low temperatures: in all cases local stretching occurs, leading to non-uniformity of thickness over the area of the film [152]. These difficulties can be avoided by orienting films containing at least 35% of a latent solvent [377]. In this way a film 1.04 mm thick has been obtained from a sheet of poly(vinyl fluoride) 13.9 mm thick. At the present time films of this polymer are produced only in the USA, under the name Tedlar [378]. Several brands are available, differing in tensile strength—from the high value of 1265 kgf cm$^{-2}$ with great bending strength to the low value of 492 kgf cm$^{-2}$.

During recent years the possibility of obtaining fibres from poly(vinyl fluoride) has also been studied. Thus Knunyants et al. [379] developed methods for obtaining a technical fibre from the bulk polymer. A fibre can be prepared from the paste obtained by drying an emulsion of the polymer stabilised with partly hydrolysed adiponitrile [380], which acts also as a plasticiser. Monofilaments of tenacity 5 g denier$^{-1}$ can be formed from the polymer of reduced viscosity 1.25, by extruding a coalescing dispersion into a latent solvent [381].

The use of poly(vinyl fluoride) in coatings has proved especially fertile. They are distinguished by high adhesion, resistance to chemical reagents, abrasion, and weathering, and a wide range of working temperatures. The polymer composition for their production is prepared

by methods that are widely employed in the paint and varnish industry [350,382,383]. It contains not only the polymer and solvents but also pigments, stabilisers, fillers, and modifiers [180,350,384,385]. Pigments are selected on the basis of their thermal stability during baking and their behaviour in the final coating [350]. Various fillers, e.g. calcium silicate, magnesium silicate, and silicon dioxide, are also used [350].

Various viscosity modifiers are necessary ingredients in obtaining polymer coatings [350]. They should be soluble in an inert solvent and thermostable, and should neither prevent adhesion nor exert an adverse influence on the properties of the coating. Various acrylate polymers and poly(vinyl acetate) are generally used as modifiers [385]. In isolated cases the dispersion obtained during emulsion polymerisation can be used directly to obtain coatings [386]. A properly prepared and applied dispersion of poly(vinyl fluoride displays excellent adhesion to metals, without the need to use an organic primer. The dispersions are applied with spraying equipment, by means of reversing rollers, by dipping, and by centrifugal casting [350]. Procedures have been suggested for applying the powdered polymers in a stream of gas flowing at 100 m $s^{-1}$. [387]

Various compositions have now been developed for definite fields of application—to obtain transparent protective coatings, chemically stable and corrosion-resistant pigmented coatings and linings, pigmented architectural claddings [350]. In agriculture poly(vinyl fluoride) films can successfully replace those of the chloride and polyethylene for covering hotbeds and for protecting plantings from early spring frosts [388].

Poly(vinyl fluoride) can be widely applied in the building industry [165,168,350]. Panels coated with the polymer are used as external and internal facings in residential and industrial buildings [389,390]. Films of the polymer are used also for coating ornamental laminated plastics [391-399], asbestos goods [400], rolls of aluminium foil [401], charts, dials, signs and other decorative items, window and door fittings, and furniture upholstery. The useful life of such a coating functioning in the open air exceeds 25 years.

A film of poly(vinyl fluoride) in combination with polystyrene is used in the construction of luminous panels [402]. If a poly(vinyl fluoride) film 0.025 mm thick is attached to the inner surface of luminous polystyrene panels, they will function for at least 20 years.

A new brand of poly(vinyl fluoride) Delvar is also widely used for coating various articles, including those used in the building industry [403]. It is a component of the chemically resistant coating Delbon, which is unlike Tedlar film in being applied to a surface without a priming or an adhesive. Veneers having coloured poly(vinyl fluoride) coatings are manufactured under the name Welwood PF-L, [404-406] and asbestos-cement panels under the names Colorbest and Ternol [407]. Because of its great chemical resistance this polymer is used also to protect various cement structures from leaching, marine salts, and water vapour [408].

The good dielectric properties and retention of flexibility at low temperatures are recommendations for the use of poly(vinyl fluoride) film in the manufacture of electric batteries intended to function at low temperatures [409]. A more thermostable polymer, partly dehydrofluorinated and containing 26–38 wt.% of fluorine, is used as an insulator to separate two electrodes, acting as a capacitor [410]. Copolymers of vinyl fluoride with alkyl vinyl ethers have also proved suitable for this purpose [411]. Poly(vinyl fluoride) has been used in making the diphragms of electrolytic cells for the manufacture of chlorine [412].

Poly(vinyl fluoride) is used in the automobile and shipbuilding industries for coating various copper, brass, steel, and aluminium articles [166,350,413-418]. It provides excellent protection from corrosion and does not affect the decorative effect of the main material. During recent years coatings based on the polymer and on various copolymers of vinyl fluoride have come to be widely used in the container industry, instrument-making [350], and solar energy equipment [419], as well as for infrared detectors [420].

Among various fluorinated polymers poly(vinyl fluoride) exhibits relatively high radiation resistance [421]. It has therefore found application in nuclear technology [422,423] and is used as a coating for the protection of spacecraft [350,382,424]. Another reason for its use in space technology is that its loss in weight is only 0.5% under a residual pressure of around $10^{-6}$ mmHg at ~150°C, while articles made of it retain their appearance and shape [425,426].

The small water adsorption and high elasticity have made possible the use of vinyl fluoride polymers and copolymers for the production of photographic films [427,428]. Chemical industry is a promising field for application of the polymer, which can be used to cover and line tubes, extractor fans, reservoirs for fresh and salt water, reaction vessels, drying units, etc. [429-431] Poly(vinyl fluoride) also provides a coating for external and internal surfaces of chemical plant to prevent corrosion by chlorine, hydrochloric acid, caustic soda, acetone, petrol, tetrachloromethane, and butan-2-one [350,432].

Poly(vinyl fluoride) and various copolymers especially modified with ultraviolet absorbers are widely used for coating polyethylene [148] and poly(ethylene terephthalate) [433] films, polychloroprene felt [282,377,434], wood, and textiles [49]; they are used also as lubricants and impregnants [435].

It is thus obvious that vinyl fluoride polymers are worthy of comprehensive examination as materials having an extremely wide range of application.

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# Structural Chemistry of Substituted Benzene Derivatives

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Structural data for substituted benzene derivatives (bond lengths and angles) are summarised. A structural scheme of the deformation of $\sigma$ bonds in the benzene ring under the influence of electron-donating and electron-accepting substituents is based on X-ray diffraction results. The general rule is revealed that the valence angle of a substituted carbon atom in the benzene ring increases with the nuclear potential of the substituents. A correlation is established between such angles and the Taft inductive constants. The structural characteristics of substituted benzenes are compared with those of metal complexes. A list of 258 references is included.

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## I. INTRODUCTION

The present Review is based on X-ray diffraction data for crystals of substituted benzene derivatives, and is confined to a discussion of the nature of the intramolecular interaction between atoms. Questions of the packing of molecules in a crystal and the interaction of non-bonded atoms are not considered. Special monographs[1] and reviews have been devoted to the latter problem.

The modern theory of organic chemistry interprets the properties of molecules in terms of the displacement of valency electrons by inductive and conjugative mechanisms[2,3]. The electronic nature of chemical substituents was first characterised quantitatively by Hammett's $\sigma_p$ and $\sigma_m$ constants[4]. These constants were subsequently separated by Taft and Lewis[5] into components representing inductive $\sigma_I$ and conjugative $\sigma_R$ effects. Dewar and Grisdale[6] have since suggested that five mechanisms should be distinguished--the field $\sigma$-induction, $\pi$-induction, mesomeric, and electromeric effects--but Hammett[4] considers that there is no need to introduce more than two structural variables.

It is of great importance to place the qualitative electronic theory of organic chemistry on a quantitative basis by establishing correlations[7] between the structure and the physicochemical properties of a molecule. The chemical shifts $\delta_H$ and $\delta_{^{19}F}$ of the nuclear magnetic resonance spectra are adopted as sensitive measures of the effects of substituents on the distribution of electron density in the benzene ring. A correlation has been found between the chemical shifts and the Hammett constants.

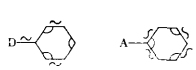
X-Ray structural investigations of the nature of the donor–acceptor interaction in organic molecules provide the most direct information for establishing a correlation between structure and physicochemical properties.

## II. STRUCTURAL SCHEME OF SUBSTITUTED BENZENES

The benzene molecule is a regular hexagon in which the angles between the bonds are 120° and the carbon–carbon bond lengths are 1.392(4) and 1.398 Å according to X-ray[8] and neutron[9] diffraction respectively. The mean carbon–carbon bond lengths in aromatic compounds are 1.398(5)–1.395(3) Å.[10,11]

The influence of an acceptor substituent A on the geometry of a substituted benzene molecule was first established for nitro-derivatives by Trotter[12], Bailey and Prout[13], Carter, McPhail, and Sim[14], and many later investigators. The valence angle of the substituted carbon atom C($NO_2$) in the ring has increased to a value that is independent of the angle of deflection of the nitro-group from the plane of the benzene ring, while the ($NO_2$)C–C bond length is shorter than in unsubstituted benzene. In a paper at the Ninth International Congress of Crystallography Hamilton[15] pointed out that donor substituents D—nitrogen, phosphorus, and antimony—diminish the C(D) bond angles and increase the (D)C–C bond lengths in the benzene ring. Papers both at the First All-Union Conference on Organic Crystal Chemistry[16] and at the Tenth International Congress of Crystallography[17] reported that the C(D,A) angles increase with the electronegativity of the elements along a period on passing from $\sigma$ donors to $\sigma$ acceptors, and also that they correlate with the Taft $\sigma_I$ inductive constants.

A scheme of deformation of $\sigma$ bonds in the benzene ring under the influence of electron-donating and electron-accepting substituents D and A was based[18] on X-ray diffraction data. According to the scheme the structure of such substituted benzenes can be represented as



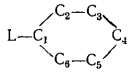

where a tilde represents a shortened carbon-carbon bond length, and an arc an increased valence angle at a carbon atom, in the ring. A consequence of the rehybridisation of $\sigma$ bonds is an increased proportion of the $p$ state of the hybrid $sp^2$ orbital of the carbon atom in an exocyclic A–C bond, with a resultant increase in the proportion of the $s$ state in the adjacent (A)C–C bonds forming an angle exceeding 120° in the benzene ring. The increased proportion of the $s$ state of the carbon atom leads to contraction of the bond. In an exocyclic D–C bond the proportion of the $s$ state of the hybrid orbital of the carbon atom is increased, and also the proportion of the $p$ state in the (D)C–C cyclic bonds, so that the angle they form is $< 120°$, while the (D)C–C bond becomes longer.

Such a view of the nature of atomic interaction in substituted benzenes reflects the general character of the structure of molecular compounds and is consistent with several published communications. As Bent showed[19], the *s* component of a hybrid orbital has a tendency to concentrate in those orbitals that are directed towards electropositive atoms. This conclusion is based on the results of a microwave spectral analysis of molecules of general formula HCO.R (where R = H, $CH_3$, OH, $OCH_3$, F), in which increase in the electronegativity of the substituent R is accompanied by contraction of the C–H and C=O bonds and increase in the H–C=O angle. A similar conclusion can be reached by quantum-chemical calculation[20]: formation of a D–A σ bond leads to decrease in the proportions of the *s* state of the electropositive atom D and of the *p* state of the electronegative atom A in comparison with the D–D and A–A σ bonds. Hence the populations of σ bonds can be written D(*p*)–(*s*)C and A(*s*)–(*p*)C. Since *p* electrons are more weakly bound to the atomic nucleus than are *s* electrons, an acceptor A acquires a *p* electron preferentially from the carbon atom, but a donor D donates a *p* electron preferentially to the carbon atom.

## III. STRUCTURAL CHARACTERISTICS (BOND LENGTHS AND ANGLES)

In the most exact modern X-ray structural work the accuracy of the determination of interatomic distances and bond angles is respectively ±0.001–0.003 Å and ±0.1–0.3 deg. More detailed information on the accuracy of individual data can be found in the references cited. Systematic information on the crystal structures of organic molecules is given in works of reference[21-24]. The above structural scheme of the deformation of σ bonds in the benzene ring enables conclusions on the σ donor–acceptor character of a substituent L in any structure to be reached directly from the angle at the substituted carbon atom C(L) in the benzene ring.

### 1. Monosubstituted Benzene Derivatives



Experimental values are averages for the chemically equivalent valence angles at $C_{(2)}$ ($C_{(6)}$) and $C_{(3)}$ ($C_{(5)}$) and bond lengths $C_{(1)}$–$C_{(2)}$ ($C_{(1)}$–$C_{(6)}$), $C_{(2)}$–$C_{(3)}$ ($C_{(5)}$–$C_{(6)}$), and $C_{(3)}$–$C_{(4)}$ ($C_{(4)}$–$C_{(5)}$). It is difficult to judge from experimental results the extent to which the alternation of bond lengths and angles is transmitted to all atoms in the benzene ring. One difficulty is the thermal oscillation of the atoms, which becomes stronger on passing from the centre of gravity of the molecule to the terminal atoms, producing a tendency for their bonds to contract. In any case, changes in bond angles and lengths are more clearly defined for the three carbon atoms nearest the substituent. The changes in the angle at the substituted atom C(L) provide a considerably more sensitive criterion for regarding the substituent L as a donor D or an acceptor A than do the changes in bond lengths.

Alkyl substituents produce a sharp decrease below 120° in the cyclic angle at the carbon atom, and are thus strong σ donors. In tetraphenylmethane[25], triphenylmethane[26], diphenylaminotriphenylmethane[27], *N*-1′-phenylcyclohexylpiperidinium chloride[28], 3-diphenylacetoxy-1-ethylpiperidinium chloride[29], (+)-benzylmethyl-1-methyl-2-*N*′-phenylpropionamidoethylammonium bromide[30], and tribenzylamine[31] this angle is respectively 117.5°, 117.8°, 117.9°, 117.6°, 117.4°, 116.8°, and 117.4°.

Although hyperconjugation of methyl groups has been discussed in the literature, structurally the need for this hypothesis does not arise. In several cases it is advisable to use instead a mechanism of σ rehybridisation, since with donor substituents D the two mechanisms—σ rehybridisation and π conjugation—have the same effect on the structural characteristics of the benzene ring: the D–$C_{(1)}$ and $C_{(2)}$–$C_{(3)}$ bonds contract, the (D)$C_{(1)}$–$C_{(2)}$ bond becomes longer, and the cyclic $C_{(1)}$(D) angle becomes smaller.

Substituents containing multiple bonds C=C and C≡C also have a well defined σ-donor character. In structures possessing a substituent vinyl group—tetraphenylethylene[27], 1,2-diphenylcyclopentene[32], tetraphenylcyclopenta-1,3-diene[33], *trans*-stilbene[34], 2,3-diphenylindole[35], 2,5-distyrylpyrazine[36], *cis*-1,*cis*-3-distyrylazulene[37], anthr-9-yl styryl ketone[38], β-*p*-tolylthio-*trans*-cinnamic acid[39], chalcone[40], 1,6-diphenylocta-1,2,4,5-tetraene[41], and dicinnamyl disulphide[42]—the C(C :C) angles are respectively 118.7°, 117.6°, 118.3°, 118.1°, 118.9°, 117.7°, 118.2°, 118.5°, 118.6°, 118.2°, 117.5°, and 118.4°. The substituted carbon atoms in biphenyl[43], terphenyl[44], and quaterphenyl[45] have bond angles of 117.9°. In 1,8-bisphenylethynylnaphthalene[46] C(C :C) angle is 119.2°. Thus the vinyl group is a stronger σ donor than the ethynyl group, a result that is consistent with the chemical properties of these molecules.

The σ-acceptor power increases on passing from the vinyl to the carbonyl group. The C(C :O) angle in benzamide[47], acetyl benzoyl peroxide[48], ethylene dibenzoate[49], hippuric acid[50], and 2-hydroxy-4-methoxybenzophenone[51] is respectively 120.1°, 119.7°, 119.9°, 120.1°, and 119.8°. In *N*-diphenylmethyleneaniline[52] the C(C :N) and C(N :C) angles are respectively 119.2° and 119.9°; and in αα-*N*-triphenylnitrone[53] the C(C=N→O) and C(O←N=C) angles are 118.2° and 122.0°: the angle in the benzene ring is larger when the substituents bind through a nitrogen atom than through a carbon atom. Clearly, the nitrone group can act both as a strong σ donor and as a strong σ acceptor.

Table 1. Bond angles C(D,A) and nuclear potentials $z^*/r$ of elements in monosubstituted benzene derivatives.

| D, A | C(D, A), ° | $z^*/r$ | D, A | C(D, A), ° | $z^*/r$ |
|---|---|---|---|---|---|
| B | 116.7 | 3.13 | Al | 116.4 (113.7) | 2.78 |
| C | 117.5 | 4.21 | Si | 116.1 | 3.55 |
| N | 119.4 | 5.27 | P | 118.9 (117.6) | 4.36 |
| O | 120.5 | 6.23 | S | 120.2 | 5.24 |
| F | 123.4 | 7.32 | Cl | 122.4 | 6.14 |
| Ga | 116.9 | 3.97 | | | |
| Ge | 118.3 | 4.62 | | | |

With respect to the donor–acceptor characteristics of heteroatoms differing in their electronic nature, Table 1 summarises the C(D,A) bond angles with donor D and acceptor A substituents, and compares them with the nuclear potentials of the elements $z^*/r$ (where $z^*$ is the effective charge on the nucleus and $r$ the covalent radius

of the atom). Values of the angle are given for triphenylborane[54], tetraphenylmethane[25], aniline[55], phenol[56], fluorobenzene[57], di-μ-phenylbisdiphenylaluminium[58], tetraphenylsilane[59], pentaphenylphosphorane[60], diphenyl disulphide[61], chlorobenzene[62], triphenylgallane[63], and tetraphenylgermane[64,65].

The general rule is that the cyclic angle at the substituted carbon atom C(D,A) increases with the nuclear potentials of the substituents along a series in the Periodic System:

$$C(B)<C(C)<C(N)<C(O)<C(F)$$

$$C(Al)<C(Si)<C(P)<C(S)<C(Cl).$$

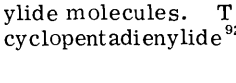
The C(D,A) angles of elements in the third and fourth periods are smaller than those in the second and fourth periods. The reason for such behaviour is that $z^*/r$ increases monotonically along a period, and changes abruptly within a group[66,67].

In the main, Table 1 correctly reflects the trends in the variation of the bond angles of the elements. These tendencies can be revealed by analysing the experimental results for complicated structures. As examples the C(Si) angles in phenyl-triphenylsilyldiazomethane[68], chlorobis-π-cyclopentadienyl-triphenylsilylzirconium(IV)[69], 2,2-diphenyl-2-silaindane[70], and acetyltriphenylsilane[71] are respectively 117.1°, 117.0°, 117.6°, and 117.5°; the C(P) angles in *p*-dimethylaminophenyldiphenylphosphine[72], bisdiphenylphosphinoacetylene[73], and dimethylphenylphosphine[74] are 118.1°, 118.8°, and 117.7°; the C(Ge) angles in acetyltriphenylgermanium[75] and triphenylgermanium *p*-t-butylphenyl sulphide[76] are 118.3° and 118.9°; and the C(N.N) angles in tetraphenylhydrazine[27] and 1-phenyl-thiosemicarbazide[77] are 119.1° and 119.2°. The number of known structures containing elements of the fifth series as substituents is still small.

The formation of double bonds with carbon, oxygen, and sulphur atoms increases the σ-acceptor power of heteroatoms. This is observed in the structures of methylenetriphenylphosphorane[78] (in which the C(P:C) angle is 119.1°), bistriphenylphosphoranylidenemethane[79] C(P:C:P) 119.2°, triphenylphosphine oxide[80] C(P:O) 118.9°, *p*-chloro- and *p*-bromo-phenyldiphenylphosphine oxides[81,82] and the corresponding phosphine sulphides[83,84]—C(P:O) 119.1° and 119.7°; and C(P:S) 119.5° and 119.2°—phenylsulphinylacetamide[85] C(S:O) 121.6°, diphenyl disulphone[86] C($SO_2$.$SO_2$) 122.5°, and 3-methyl-3-phenylsulphinylbutan-2-ol[87] C(S:O) 120.3°.

A significant increase in σ-acceptor power occurs with increase in the positive charge on the heteroatom. In the case of the nitrogen atom, however, the same effect may be produced by loss of π conjugation with the benzene ring due to steric hindrance. We note increases in the C(N.C:O) angle in *N*-phenylacetanilide[88], (+)-benzylmethyl-1-methyl-2-*N'*-phenylpropionamidoethylammonium bromide[30], *N*-methylacetanilide[89], and isonitrosoacetanilide[90] (120.2°, 120.2°, 122.8°, and 120.2°); and the C(N.C:S) angle in 4-phenyl-thiosemicarbazide[91] is larger than the C(N.N) angle in 1-phenyl-thiosemicarbazide[77] (121.1° and 119.2°).

The fact that the charges on substituents influence the deformation of the benzene ring has been established in ylide molecules. The structure of triphenylphosphonium cyclopentadienylide[92] shows an increase in the



angle 119.6° in conformity with the charge on the phosphorus atom of +0.69 e, found by phostoelectronic spectroscopy. Still larger increases in angles have been established in triphenyl-*N*-toluene-*p*-sulphonyliminophosphorane[93] C($P^+$.$N^-$) 120.1° and *SS*-diphenyl-*N*-toluene-*p*-sulphonylsulphidimine[94] C($S^+$.$N^-$) 121.1°.

The C($As^+$) angle of 121.7° in tetraphenylarsonium triiodide[95] and the C($P^+$) angles of 119.9° and 120.0° in tetraphenylphosphonium[96] and methyltriphenylphosphonium bistetracyanoquinodimethanes[97] suggest that positively charged arsenic and phosphorus atoms lose their σ-donor properties. The positively charged iodine atom in diphenyliodonium nitrate[98] remains a strong σ acceptor with C($I^+$) 122.4°, but negatively charged boron and indium atoms remain strong σ donors, as is indicated by C($B^-$) angles of 114.1° and 116.3° in π-cyclopentadienyl-η-ruthenium(II) tetraphenylborate[99] and bis(trimethyl phosphito)-rhodium(I) tetraphenylborate[100] and by a C($In^-$) angle of 118.2° in sodium tetraphenylindate[101]. The dependence of the C(P) angles on the partial charges on the phosphorus atoms in substituted benzenes has been reported[102].

The accurate experimental data that have now accumulated are still insufficient as a basis for quantitative conclusions on the σ bonds of all metals in the Periodic System. Evidence that the atoms of transition metals are among the strongest σ donors is provided e.g. by the angles C(Zn) 115.8°, C(Ni) 115.9°, and C(Cr) 115.2° in bis[phenyl(acetylacetonato)zinc]-bis(acetylacetonato)zinc[103], phenyl-(π-cyclopentadienyl)(triphenylphosphine)nickel[104], and *cis*-diphenylbis-2,2'-bipyridylchromium iodide[105].

## 2. Disubstituted Benzene Derivatives

It is of interest to trace the changes in structural characteristics as the number of substituents is successively increased. The donor–acceptor characteristics of disubstituted benzenes differ according to the orientation of the substituents. The structures of *para*-substituted benzenes have been the most thoroughly studied.

### *para*-Disubstituted derivatives

As in monosubstituted benzene derivatives the angles at the carbon atoms in *para*-disubstituted derivatives indicate that alkyl substituents are strong σ donors. Thus the C($CH_3$) and C($CH_2$) angles in di-*p*-tolyl disulphide[106], *p*-bitolyl[107], toluic acid[108], nitrotoluene[109], cresol[110], 1,1-di-*p*-tolylethylene[111], di-*p*-tolylcarbodi-imide[112], the enolic form of ω-*p*-tolylacetophenone[113], β-*p*-tolylthio-*trans*-cinnamic acid[39], ethyl *N*-methyl-*N*-*p*-tolylsulphonylmethylcarbamate[114], (+)-methyl *p*-tolyl sulphoxide[115], propenyl *p*-tolyl sulphone[116], triphenyl-*N*-toluene-*p*-sulphonyliminophosphorane[93], [8]paracyclophane-4-carboxylic acid[117], trisdiphenylmethane-*pp'*-diamine[118], and acetotoluidine[119] are respectively 117.3°, 117.8°, 118.5°, 117.5°, 117.8°, 118.0°, 117.7°, 118.2°, 117.8°, 118.8°, 118.2°, 118.6°, 117.5°, 117.6°, 118.6°, and 117.5°. Similarly to monosubstituted benzene derivatives, the C(C≡C) angle of 119.4° in *p*-diethynylbenzene[120] is larger than the C(C:C) angle in the presence of a vinyl group in 1,1-di-*p*-tolylethylene[111], diethylstilboestrol[121], [2.2](2,6)pyridinoparacyclophane-1,9-diene[122], and 1,6-di-*p*-chlorophenyl-3,4-dimethylhexatriene[123]—117.9°, 118.2°, 117.5°, and 118.0°.

An advantage of X-ray structural analysis in comparison with other methods—both physical and chemical—is that comparison of the angles at the carbon atoms in the benzene

ring provides an exceptional opportunity for determining the relative σ donor–acceptor characteristics of different substituents in the same molecule. Thus in tetra-*p*-tolyltin[124] the σ-donor power of the tin atom exceeds that of the methyl group: C(Sn) 116.4° and C($CH_3$) 117.3°. The structure of trisdiphenylmethane-*pp'*-diamine-sodium chloride[118], with angles C($CH_2$) 118.6° and C($NH_2$) 119.2°, shows that methylene is a stronger σ donor than is the amino-group. Examination of the structures of *p*-dimethylaminophenyldiphenylphosphine[72] and *p*-dimethylaminophenyl phenyl sulphide[125] reveals that in the former the phosphorus atom is a stronger σ donor than is the dimethylamino-group, for C(P) 116.9° and C[$N(CH_3)_2$] 117.5°, and that in the latter structure the dimethylamino-group is a stronger σ donor than is the sulphur atom, since C[$N(CH_3)_2$] 117.8° and C(S) 118.4°.

**Table 2.** Bond angles C(D) and C(A) in *para*-substituted hydroxy- and alkoxy-benzenes.

| Compound | D | A | C (D), ° | C (A), ° |
|---|---|---|---|---|
| Cresol[110] | $CH_3$ | OH | 117,8 | 120,4 |
| Anisidine[128] | $NH_2$ | $OCH_3$ | 118,4 | 120, 2 |
| Diethylstilboestrol[121] | C=C | OH | 118,2 | 120, 2 |
| *trans-pp'*-Diethoxyazobenzene[129] | N=N | $OC_2H_5$ | 119,5 | 120,5 |
| Hydroxyacetanilide[130] | N—$COCH_3$ | OH | 119,8 | 120,2 |
| Hydroxyacetanilide[131] | COOH | OH | 117,7 | 120,3 |
| Methoxybenzoic acid[132] | COOH | $OCH_3$ | 119,7 | 120,4 |
| Ethoxybenzoic acid[133] | COOH | $OC_2H_5$ | 118,7 | 120,4 |
| n-Butoxybenzoic acid[134] | COOH | $OC_4H_7$ | 118,9 | 120,2 |
| Potassium hydrogen bis-*p*-hydroxybenzoate monohydrate[135] | COOH | OH | 119,6 | 120,7 |
| Pyridinium hydroxybenzoate[136] | $COO^-$ | OH | 118,2 | 119,5 |

Further, comparison of the angles in terephthalic acid[126] and γ-quinol[127]—C(COOH) 120.4° and C(OH) 121.0°—shows that hydroxyl is a stronger σ acceptor than is carboxyl. This is confirmed by Table 2, which indicates that hydroxyl, methoxyl, ethoxyl, and butoxyl are weak σ acceptors in comparison with such σ donors as methyl, amino, ethylenic, azo, acetylimino, and carboxyl groups.

**Table 3.** Bond angles C(D) and C($NO_2$) in *para*-substituted nitrobenzenes.

| Compound | D | C (D), ° | C ($NO_2$), ° |
|---|---|---|---|
| Nitrotoluene[109] | $CH_3$ | 117,5 | 122,7 |
| Nitrobenzoic acid[141] | COOH | 119,8 | 122,6 |
| α-Nitrophenol[142] | OH | 120,9 | 122,3 |
| β-Nitrophenol[143] | OH | 120,5 | 122,0 |
| α-Di-*p*-nitrophenyl disulphide[144] | S | 119,0 | 122,7 |
| 1,1-Di-*p*-nitrophenylethylene[145] | C=C | 118,3 | 122,2 |
| Nitrobiphenyl[146] | $C_6H_4$—$C_6H_4$ | 118,6 | 122,2 |
| *syn-p*-Nitrobenzaldehyde oxime[147] | C=N—OH | 119,2 | 122,7 |
| Nitroacetophenone[148] | $COCH_3$ | 118,4 | 121,7 |
| Nitrophenyl acetate[149] | $COOCH_3$ | 120,7 | 121,5 |
| D-*p*-nitrophenylcarbodi-imide[150] | N=C=N | 120,4 | 122,1 |
| *N*-Ethyl-*N*-*p*-nitrophenylcarbamoyl chloride[151] | N($C_2H_5$)COCl | 120,5 | 123,8 |

As in monosubstituted benzene derivatives, the silicon atom is one of the strongest σ donors. Therefore the C(Si) angle in *p*-bistrimethylsilylbenzene[137] is 115.8°. The azoxy-group in *p*-azoxyanisole[138] has a dual role: it acts both as a σ donor with C(N :NO) 119.1° and C($OCH_3$) 119.6°, and as a σ acceptor, with C(NO :N) 121.1° and C($OCH_3$) 119.9°. The σ-acceptor properties of the azo-group are exhibited in *S*-methyldithiazone[139], with C(N :N) 120.2° and C(N.N) 119.1°, and especially in benzenediazonium-*p*-sulphonate[140], with C($N^+$≡N) 125.4° and C($SO_3^-$) 121.0°. Data on the C($NO_2$) angles in *para*-substituted nitrobenzenes are listed in Table 3.

Sulphonyloxy, sulphonyl, and sulphinyl groups act as σ acceptors: in *cis*-4-t-butylcyclohexyl toluene-*p*-sulphonate[152] C($SO_3$) 120.6° and C($CH_3$) 117.7°, ethyl *N*-methyl-*N*-*p*-tolylsulphonylmethylcarbamate[114] C($SO_2$) 121.1° and C($CH_3$) 118.8°, propenyl *p*-tolyl sulphone[116] C($SO_2$) 120.7° and C($CH_3$) 118.6°, β-sulphanilamide[153] C($SO_2NH_2$) 120.5° and C($NH_2$) 118.7°, and in (+)-methyl *p*-tolyl sulphoxide[115] C(SO) 120.3° and C($CH_3$) 118.2°. However, in *N*-dimethylsulphoniotoluene-*p*-sulphonamide[154] C($SO_2.N^-.S^+$) 119.7° and C($CH_3$) 118.9°, and in triphenyl-*N*-toluene-*p*-sulphonyliminophosphorane[93] C($SO_2.N^-.P^+$) 119.7°, so that the sulphonyl group has lost its σ-acceptor properties in structures of the ylide type.

The C($SOCH_3$) angle of 120.3° in (+)-methyl *p*-tolyl sulphoxide, indicating that the sulphinyl group is not a strong σ acceptor, was inconsistent[115] with the Hammett $\sigma_p$ constants, according to which the acceptor power of the methylsulphinyl group exceeds that of the chlorine atom. This discrepancy remains even with the Taft constants: $\sigma_I(Cl) = +0.40$ and $\sigma_I(SO.CH_3) = +0.49$. The C(Cl) angle of 122.1° in γ-*p*-chlorobenzene[155] shows that the chlorine atom is a strong σ acceptor. Closely similar C(Cl) angles were obtained in *p*-chlorobenzoic acid[156] C(Cl) 122.1° and C(COOH) 119.9° and in α-chlorophenol[157] C(Cl) 122.4° and C(OH) 121.1°. The C(Cl) angle in the latter compound coincides with C(Br) in 1-*p*-bromophenylbutane-1,3-dione[158]: C(Br) 122.4° and C(C :O) 119.3°.

**Table 4.** Mean bond angles C(D,A) for elements in the second period.

| D, A | C (D, A), ° | D, A | C (D, A), ° | D, A | C (D, A), ° |
|---|---|---|---|---|---|
| $B^-(C_6H_5)_3$ | 114.1 | $COCH_3$ | 118.8 | $N^+H_3$ | 121.6 |
| $N(CH_3)_2$ | 117.2 | $CONH_2$ | 119.8 | CN | 121.8 |
| $C_6H_5$ | 117.6 | COOH | 119.8 | $NO_2$ | 122.1 |
| $CH=CH_2$ | 118.0 | $OCH_3$ | 119.9 | F | 123.4 |
| $CH_3$ | 118.1 | N=N—$C_6H_5$ | 120.0 | $N^+\equiv N$ | 124.9 |
| $NH_2$ | 118.4 | OH | 120.2 | | |

It is worth noting the mean angles C(D,A) for elements of the second period in the structures of monosubstituted and *para*-disubstituted benzene derivatives (Table 4) given in a paper[17] and in a review[159]. The standard deviations of the angles are 0.1–0.2 deg. However, there are certain discrepancies. In particular, the σ-donor power of the methyl group exceeds that of the vinyl group[7]—$\sigma_I(CH_3) = -0.08$ and $\sigma_I(CH :CH_2) = +0.01$—so that the C($CH_3$) angle should be smaller than the C($CH :CH_2$) angle.

A linear relation has been reported in a review[160] between the mean C–D and C–A bond lengths and the C(D) and C(A) angles for elements in the third period: silicon (1.8683 Å, 116.98°), phosphorus (1.8276–1.7908 Å, 118.50–119.78°), sulphur (1.708–1.7534 Å, 119.73–121.19°), and chlorine (1.7404 Å, 121.37°). Table 1 shows that the

correlation between C–(D,A) and C(D,A) is due to the increase in the nuclear potential $z^*/r$ caused by the decrease in the radius $r$ and the increase in the effective charge on the nucleus $z^*$ for the atoms along the period.

*meta*-Disubstituted derivatives

Available data on the structures of *meta*-disubstituted benzene derivatives confirms the σ-donor nature of the methyl group in cresol[161] C($CH_3$) 118.7°, the amino-group in nitroaniline[162] C($NH_2$) 119.6°, the dimethylamino-group in nitro-*NN*-dimethylaniline[163] C[$N(CH_3)_2$] 117.7°, the carboxy-group in isophthalic acid[164] C(COOH) 119.8°, and the amino-group in *o*-*m'*-trifluoromethylanilinobenzoic acid[165] C(NH) 118.8°. In contrast to this, a σ-acceptor nature has been found for the amino-group in aminophenol[166] C($NH_2$) 120.9°, the hydroxy-group in resorcinol[167], cresol, aminophenol, and hydroxybenzamide[168] C(OH) 121.1°, 121.7°, 121.5°, and 120.5°, the chlorine atom in potassium hydrogen bis-*m*-chlorobenzoate[169] C(Cl) 122.4°, the iodine atom in *p*-*m'*-iodophenylbenzoic acid[170] C(I) 121.3° and C($C_6H_4$) 117.6°, the ammonio-group in *m*-carboxyanilinium chloride[171] C($NH_3^+$) 121.7°, the nitro-group in dinitrobenzene[172], *m*-nitroperchlorylbenzene[173], nitroaniline, and nitro-*NN*-dimethylaniline C($NO_2$) 123.6°, 124.1°, 122.3°, and 124.4°, the trifluoromethyl group in *o*-*m'*-trifluoromethylanilinobenzoic acid[165] C($CF_3$) 121.8°, and the sulphamoyl group in *m*-sulphamoylanilinium chloride[174] C($SO_2NH_2$) 121.7°.

*ortho*-Disubstituted derivatives

Significant steric hindrance is present between *ortho*-substituents. The σ donor–acceptor characteristics of donor D and acceptor A substituents differ more markedly when their mutual orientation is *ortho* than in the *para*- and *meta*-derivatives. The close proximity of the D and A substituents is responsible for an increase in the C(A) angle and a related decrease in the C(D) angle. Thus among the cresols the difference between these angles diminishes on passing from the *ortho*- to the *meta*- and the *para*-isomers: C(OH) 121.7°, 121.7° and 120.4° respectively; and C($CH_3$) 117.0°, 118.7°, and 117.8°.[175] In *o*- and *p*-nitrobenzoic acids[176] the C($NO_2$) angle is respectively 123.7° and 122.8°, while C(COOH) is 116.2° and 121.2°: i.e. the difference between corresponding angles C(A) and C(D) increases on passing from the *para*- to the *ortho*-derivative, although the angle $\varphi$ of rotation of the plane of the nitro-group relative to that of the benzene ring is larger in the *ortho*- than in the *para*-isomer (54.3° and 24.1°).

Data on the structure of *o*-ethoxybenzoic acid[177] — C($OC_2H_5$) 120.8° and C(COOH) 118.0° — are consistent with results for the *para*-derivatives: i.e. the ethoxy-group surpasses the carboxy-group in σ-acceptor power. This is observed also in salicylic acid[167,178] — C(OH) 119.5° and C(COOH) 119.1° — though the difference is less marked. As was to be expected, a still larger difference between the angles C(OH), C($OCH_3$), C(COOH) and the angles C($CH_3$), C(CH), C($CH_2$) has been established in cresol[175], 1,1,2,2-tetrakis-*o*-methoxyphenylethane[179] C($OCH_3$) 120.5° and C(CH) 117.4°, and in toluene-α,2-dicarboxylic acid[180] C(COOH) 120.3° and C($CH_2$COOH) 116.1°. In salicylaldehyde oxime[181] the angles are C(OH) 119.6° and C(C :N.OH) 118.0°, since the hydroxyimino-group occupies a position intermediate between the carboxyl and methyl groups. It is noteworthy that, despite the difference between the angles of rotation of the carboxylate groups around carbon-carbon bonds (32° and 71°), both the C($COO^-$) angles in diammonium phthalate[182] are 119.3°.

The identity of the cyclic angles at the substituted carbon atoms in *o*-hydroxymethanesulphonanilide[183] — C(OH) 120.6° and C($NHSO_2$) 120.8° — suggests approximate equality of the σ-acceptor powers of the substituents. There are examples of variation in the angles of nitrogen-containing substituents: thus in *trans*-*oo'*-dichloroazobenzene[184] C(N.N) 118.6° and C(Cl) 121.3°, *o*-chlorohydroxyiminoacetanilide[185] C(N.C :O) 118.6° and C(Cl) 121.0°, *o*-ethoxyhydroxyiminoacetanilide[186] C(N.C :O) 120.3° and C($OC_2H_5$) 119.8°, *o*-phenylenediamine hydrochloride[187] C($NH_3^+$) 122.3° and C($NH_2$) 117.1°, *NN*-dimethylanthranilic acid[188] C[$N^+H(CH_3)_2$] 122.5° and C($COO^-$) 117.0°, potassium *o*-nitrophenoxide hemihydrate[189] C($NO_2$) 122.5° and C($O^-$) 115.2°, nitrobenzamide[190] C($NO_2$) 122.1° and C($CONH_2$) 118.8°, and 4-acetyl-2'-nitrobiphenyl[191] C($NO_2$) 123.3° and C($C_6H_4$) 115.6°. Since the iodine atom is a weaker σ acceptor than is the nitro-group, a smaller difference between the angles C(A) and C(D) is observed in *p*-*o'*-iodophenylbenzoic acid[192] — C(I) 122.6° and C($C_6H_4$) 117.9° — than in the corresponding nitro-derivative.

The structures of the racemate[193] and an optically active form of (–)-*o*-methylsulphinylbenzoic acid[194], with C(S :O) 119.8°, 119.5° and C(COOH) 118.0°, 118.4°, orthanilic acid[195] C($SO_3^-$) 119.2° and C($NH_3^+$) 120.6°, and sulphobenzoic acid trihydrate[196] C($SO_3^-$) 119.6° and C(COOH) 118.4° clearly show that the sulpho and sulphinyl groups are σ donors.

It is significant that the introduction of two acceptors in the *ortho*-position leads to a mutual weakening of their σ-acceptor power. Thus in *o*-phenylenediammonium dichloride[197] and dibromide[198] the C($NH_3^+$) angles are respectively 120.1° and 119.4°. The hydroxyls in catechol[199] are weaker σ acceptors than are those in resorcinol and quinol: C(OH) 119.9°, 121.1°, and 121.0°.

3. Trisubstituted Benzene Derivatives

Trisubstituted benzenes retain the characteristic features of the variation in bond angles inherent in *meta*- and *ortho*-derivatives. Closely similar C($NO_2$) angles (123.4° and 123.6°) have been found in 1,3,5-trinitrobenzene[200] and in *m*-dinitrobenzene[172]. The acetyl group remains a weak σ donor in 1,3,5-triacetylbenzene[201] C($COCH_3$) 119.8°. As was to be expected, the σ-acceptor power of nitro- and hydroxy-groups and of fluorine and chlorine atoms is increased by the introduction of σ donors into the *ortho*-position. This is readily seen from a comparison of the C(A) and C(D) angles in *N*-methyl-*m*-nitro-*p*-toluidine[202] with C($CH_3$) 114.3°, C($NO_2$) 124.1°, and C($NHCH_3$) 117.3°, 2,5-dimethylphenol[203] C(OH) 121.5° and C($CH_3$) 116.6° and 117.3°, (±)-2-(2-fluorobiphenyl-4-yl)propionic acid[204] C($CC_6H_5$) 117.1°, C(F) 123.9°, and C(C) 119.6°, and 3-chloro-*NN*-dimethyl-4-nitrovinylaniline[205] C(C :C) 113.0°, C(Cl) 125.7°, and C[$N(CH_3)_2$] 116.6°. Another striking fact is that the σ-acceptor power of the bromine atom is diminished by the introduction of an *o*-nitro-group and an *o*-sulpho-group respectively in 4-bromo-*N*-methyl-3-nitroaniline[202], with C(Br) 116.1°, C($NO_2$) 122.4°, and C($NHCH_3$) 118.0°, and in the trihydrate of 2,5-dibromobenzenesulphonic acid[206] C(Br) 120.2° and 122.8° and C($SO_3^-$) 119.9°, since the C(Br) angle *ortho* to C($SO_3^-$) is smaller than the *meta*-C(Br) angle.

Among 1,2,3-derivatives pyrogallol[207]—C(OH) 120.7°, 119.8°, and 121.2°—has C(OH) angles at positions 1 and 3 that are closely similar to those (121.0° and 121.1°) in γ-quinol and resorcinol, whereas the C(OH) angle at position 2 is close to those in catechol (119.9°). In hemimellitic acid dihydrate[208], despite the marked difference in angles of rotation of the planes of the carboxyls relative to that of the benzene ring (the angles φ at positions 1–3 are respectively 9.6°, 87.2°, and 4.1°), the C(COOH) angles are also larger at positions 1 and 3 (119.7° and 120.0°) than at position 2 (118.9°).

Hydroxyl, ethylenic, and methyl groups undergo greater increase in σ-donor power when located between two σ acceptors: in 2,6-dinitrophenol[209] C(OH) 116.0° and C($NO_2$) 122.3° and 121.9°; in 1-(2,6-dichlorophenyl)-4-phenylbuta-*trans*-1,*trans*-3-diene[210] C(C :C) 114.6° and C(Cl) 122.8° and 123.9°; and in 3-bromo-2-methylphenol[211] C($CH_3$) 114.4°, C(OH) 124.9°, and C(Br) 124.5°.

Comparison of the structures of 2,3-dimethylphenol[211, 202]—C(OH) 122.4° and C($CH_3$) 118.1° and 119.7°—and of 2,3-dimethylbenzoic acid[212]—C(COOH) 121.3° and C($CH_3$) 117.4° and 120.3°—clearly shows, as a consequence of the location of hydroxy- and carboxy-groups *ortho* to the methyl groups, the sequence OH > COOH > $CH_3$ according to their σ-acceptor power, which is consistent with conclusions reached from mono- and di-substituted derivatives.

The difference between the C(O) angles is especially clearly developed in the oxygen bridge in 1-t-butyl-2-(2,6-dinitrophenoxy)benzene[213]: *ortho* to the t-butyl group as σ donor C(O) 123.9°, but *ortho* to two σ-acceptor nitro-groups C(O) 116.2°.

## 4. Tetrasubstituted Benzene Derivatives

Among 1,2,4,5-tetrasubstituted benzene derivatives—tetra-t-butylbenzene[214], durene[215], pyromellitic acid dihydrate[216], and tetracyanobenzene[217]—the σ-acceptor power increases in the sequence

C($C(CH_3)_3$) 115.1°<C($CH_3$) 118.2°<C(COOH) 119.7°<C(CN) 121.3°.

In 3,4,5-trimethylbenzoic acid[218], of course, the C(COOH) angle is 119.7°, but when the hydroxyl is located *ortho* to two t-butyl groups in 2,6-t-butyl-4-methylphenol[211], and a carboxyl is *ortho* to two methyl groups in mesitoic acid[219], the C(OH) angle increases to 122.6°, and C(COOH) to 120.7°. Similarly, the arrangement of a nitro-group *ortho* to two methyl groups in 3,5-dimethyl-4-nitrobenzoic acid[220] has increased the C($NO_2$) angle to 124.8°, and diminished the C($CH_3$) angles to 116.6°. The introduction of two nitro-groups or two chlorine atoms yields the respective angles—in 4-methyl-3,5-dinitrobenzoic acid[221] C($CH_3$) 114.1° and C($NO_2$) 124.3°, in 2,6-dichloro-4-nitroaniline[222] C($NH_2$) 115.2° and C(Cl) 123.0°, and in 2,4,6-trichlorobenzonitrile[223] C(C≡N) 117.6° and C(Cl) 123.6°.

In 1,2,3,5-tetrasubstituted benzenes containing three nitro-groups the presence of such strong σ acceptors at positions 1 and 3 leads to smaller angles at position 2 substituted by a σ-donor or a weaker σ-acceptor substituent. Therefore in picryl chloride[224], *NN*-difluoro-2,4,6-trinitroaniline[225], 2,4,6-trinitrophenetole[226], *N*-methyl-2,4,6-trinitroacetanilide[227], and in the anion of 2,4,6-trinitrobenzenesulphonic acid tetrahydrate[228] $H_5O_2^+C_6H_2(NO_2)_3SO_3^-$. $2H_2O$, as the angle at position 1 decreases—C(Cl) 117.0°, C($NF_2$) 116.8°, C(OR) 116.4°, C(N.C :O) 115.4°, and C($SO_3^-$) 115.1°—the angles at positions 2 and 6 correspondingly increase: C($NO_2$) 122.4°, 122.6°, 122.8°, 123.5°, and 123.7°.

Variation in σ donor–acceptor characteristics is clearly exhibited in a series of structures containing bridging substituents[229–233]. Thus in methyl 3-nitro-4-(2,4,6-trimethylbenzyl)benzoate, 3-nitro-4-(2,4,6-trimethylbenzoyl)benzoate, 4-mesitylthio-3-nitrobenzoate, 4-mesitylsulphinyl-3-nitrobenzoate, and 4-mesitylsulphonyl-3-nitrobenzoate the C($CH_2$), C(C :O), C(S), C(S :O), and C($SO_2$) angles are respectively 119.5°, 120.6°, 121.5°, 121.6°, and 121.5° with these groups *ortho* to two methyl groups, but 114.8°, 116.7°, 115.5°, 117.9°, and 117.7° when *ortho* to the nitro-group.

A comparison[227] of structures differing in the angle of rotation of the N–C=O group relative to the plane of the benzene ring—acetanilide[234] (N–$C_{Ar}$ 1.413 Å, C(N.C :O) 119.6°, and φ = 17.6°), *N*-methyl-2,4,6-trinitroacetanilide (1.417 Å, 115.4°, and 61°), and *N*-methylacetanilide (1.481 Å, 122.8°, and 90°)—has shown that the $N^{\delta+}$–C=$O^{\delta-}$ group develops strong σ-acceptor power in the third structure as a consequence of the absence of π conjugation, but in the second structure the overlap of the π orbitals of the nitrogen atom and the ring carbon atom is less than one-quarter of the maximum value (cos 60° = 0.25), so that the decreases in the C(N.C : O) angle and the N–$C_{Ar}$ bond length must be attributed to the σ-acceptor power of the nitro-groups. A similar effect is observed in 2-chloro-4,6-dinitrophenol[235], since the O–C bond is shorter than in phenol (1.333 and 1.383 Å) owing to the decrease in the C(OH) angle from 120.5° to 116.7°. A linear relation has been established between the acid strength p$K_a$ and the C–OH bond length in substituted benzenes[235]. For example, the dissociation constant increases by a factor of $10^8$ on passing from phenol to 2-chloro-4,6-dinitrophenol. It may be supposed that an increase in the contribution by the *s* state of the hybrid orbital of the carbon atom in the C–OH bond leads to an increase in the acid strength.

## 5. Penta- and Hexa-substituted Benzene Derivatives

On passing further sterically overcrowded molecules having five or six substituents in the benzene ring, we again see mainly a trend to preservation of the cyclic angles characteristic of the σ nature of electron-donating and electron-accepting substituents. The typical features of *ortho*-substituents noted in preceding subsections are also maintained.

In 2,4,6-trinitro-1,3-xylene[236] the angles are C($CH_3$) 114.2° in the 1 and 3 positions, with C($NO_2$) 127.2° (φ = 75.2°) at the 2 position and 122.4° (35.7°) at the 4 and 6 positions; in 4-bromo-*N*-methyl-2,6-dinitro-3-toluidine[237] C($NHCH_3$) 112.0°, C($CH_3$) 115.0°, C(Br) 123.5°, and C($NO_2$) 127.0° (φ = 73°) and 122.5° at positions 2 and 6. Hence the ring angles at nitro-substituted carbon atoms differ from those at atoms substituted by methyl and by a methylamino-group by 13° and 15° respectively, in agreement with their tendency to maintain the σ-bond angles of D and A substituents. An analogous phenomenon is observed in the structure of 2,4,6-trimethyl-3-pivaloylbenzoic acid[238]: C($CH_3$) 117.6°, 117.3°, and 116.7°, C(COOH) 121.7°, and C(CO) 121.8°.

In hexasubstituted benzenes steric hindrance also has a significantly weaker effect than has σ rehybridisation. Thus in pentafluorobenzoic acid[219] the C(COOH) angle of 116.7° has diminished, and the C(F) angles of 121.7° at

positions 2 and 6 are larger than the C(F) angles of 119.9–120.0° at positions 3, 4, and 5; in tetrakispentafluorophenylgermanium[239] C(Ge) 115.6° and C(F) 122.7° and 119.0–120.3°; and in decafluorobiphenyl[240] C($CF_5$) 116.3° and C(F) 122.1° and 119.7–120.1°. In 3-amino-6-ethylpyromellitonitrile[241] the angles increase in the sequence C($NH_2$) 116.2°, C($C_2H_5$) 116.3°, and C(CN) 121.3° and 122.4°.

Further refinement of the structure of hexachlorobenzene[242] has established that the carbon–carbon bond lengths (1.393 ± 0.002 Å, with temperature correction 1.401 Å) differ insignificantly from those in the unsubstituted benzene molecule. The carbon–chlorine bond lengths in substituted aromatic and quinonoid rings[243] are significantly shorter (mean distance 1.709 Å) when in the *ortho*-position and when more distantly separated or when isolated (mean 1.737 Å). The carbon–chlorine bond length in the overloaded hexachlorobenzene molecule (1.715 ± 0.002 Å, with temperature correction 1.722 Å) is shorter than an isolated bond. The steric effect should have increased the bond lengths in the overloaded molecules owing to mutual repulsion of the chlorine atoms. It is more correct to suppose that the possibility of σ rehybridisation is greater for well separated or isolated bonds, since the increase in the proportion of the *p* state of the carbon atom in the bonds is balanced, as a consequence of the strong σ-acceptor power of the chlorine atom, by an increase in the proportion of the *s* state of the carbon atom in the benzene ring. In hexachlorobenzene such a possibility of σ rehybridisation is excluded because all the carbon bonds in the ring are 120.0°, so that the carbon–chlorine bonds remain shortened owing to the excess content of the *s* component of the carbon atom in them. For the same reason the carbon–chlorine bond length should be increased by increase in the C(Cl) angle, as is observed on comparing the structure of picryl chloride C(Cl) 117.0° and C–Cl 1.709 Å with that of 2,6-dichloro-4-nitroaniline 123.0° and 1.743 Å. In decachlorobiphenyl[244], in which the dihedral angle between the phenyl rings is 86.7°, and the bond angles are C($C_6H_5Cl_5$) 118.7° and C(Cl) 121.0°, 118.9°, and 121.7°, the mean carbon–chlorine bond length somewhat exceeds the bond length in hexachlorobenzene (1.718 and 1.715 Å).

**Table 5.** Bond lengths (Å) and angles (°) in *para*-substituted anilines with the Hammett $\sigma_p$ constants of the substituents.

| Substituent | N–$C_1$ | $C_1$–$C_2$ | $C_2$–$C_3$ | $C_3$–$C_4$ | $C_5$–$C_1$–$C_6$ | $C_1$–$C_2$–$C_3$ | $C_2$–$C_3$–$C_4$ | $C_3$–$C_4$–$C_5$ | $\sigma_p$ |
|---|---|---|---|---|---|---|---|---|---|
| $NH_2$ | 1.408 | 1.389 | 1.377 | 1.389 | 117.1 | 121.4 | 121.4 | 117.1 | −0.47 |
| COOH | 1.380 | 1.399 | 1.375 | 1.398 | 119.3 | 120.8 | 121.1 | 118.3 | +0.38 |
| SCN | 1.376 | 1.393 | 1.373 | 1.385 | 118.1 | 121.1 | 119.8 | 119.6 | +0.52 |
| $SO_2NH_2$ | 1.385 | 1.402 | 1.381 | 1.393 | 118.7 | 120.8 | 119.7 | 120.5 | +0.55 |
| $NO_2$ | 1.371 | 1.412 | 1.375 | 1.390 | 118.9 | 120.5 | 119.5 | 121.2 | +0.76 |

## IV. X-RAY σ CONSTANTS

It appears reasonable to adopt the structural characteristics of molecules as the basis for constants representing their reactivity. We shall apply the special term "X-ray σ constants" to the C(D) and C(A) bond angles, the problem of which requires special discussion.

A linear dependence exists between the mean bond angles C(D,A)[17,160] and the Taft induction constants $\sigma_I$ (Fig. 1), values of which have been taken from a monograph[7]. Comparison of these angles in various structures has established relative series of σ-acceptor and σ-donor substituents.

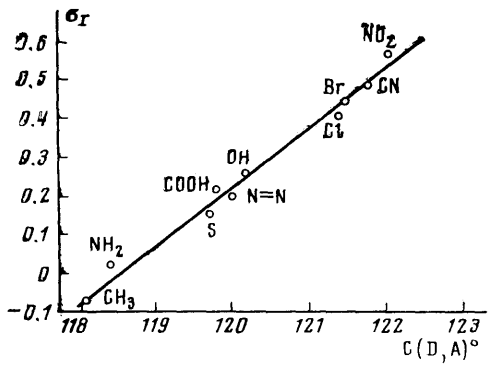



Figure 1. Dependence of induction constants $\sigma_I$ on bond angles C(D,A).

Insignificant π conjugation of the nitro-group with the benzene ring can be assumed in *p*-nitrotoluene and *p*-nitrobenzoic acid (C–$NO_2$ 1.482 and 1.491 Å). However, the data in Table 5[245–249] are consistent with the view that D and A substituents influence the distribution of C(A) bond angles in *para*-substituted anilines (C–$NH_2$ 1.408–1.371 Å) even when π interaction is superimposed on σ interaction.

When π conjugation of D and A substituents with the benzene ring is insignificant, the bond angles C(D,A) will obviously determine directly the induction effect $\sigma_I$ of the substituent. Such π conjugation is most strongly developed among elements in the second period, especially by the nitrogen atom. The plot of carbon–nitrogen bond length against the C(N) angle (Fig. 2) has a straight segment indicating a linear relation between σ rehybridisation and π conjugation. Hammett's equation $\lg(K/K_0) = \rho\sigma$ (where $K$ and $K_0$ are equilibrium constants of the chemical reaction) is based[252] on the linear relation between changes in free energy. The hypothesis[253] of a linear dependence between σ rehybridisation and π conjugation enables the bond angles C(D,A) to be used instead of Hammett σ constants. The correctness of this approach is supported by the linear correlation of the C(D,A) angles[160] with the nuclear potentials $z^*/r$ for elements in the second, third, and fourth periods (Fig. 3). Hence these angles obey a periodic law. The C(N) and C(O) angles plotted in Fig. 3 relate to compounds in which the contribution of π conjugation is insignificant.

A change of 0.5 deg in the C(N) angle is accompanied by a change in the Hammett $\sigma_p$ constant[3,7] by ~ 0.2 (Fig. 4). Modern X-ray techniques enable C(D,A) angles to be determined to 0.1–0.3 deg, and C–D,A bond lengths to 0.001–0.003 Å. X-Ray diffraction thus provides the most accurate method for determining constants characterising the reactivities of molecules.

Fig. 2 shows that the linear relation between the carbon–nitrogen bond length and the C(N) angle breaks down in *p*-thiocyanatoaniline and in 2-*p*-dimethylaminobenzylidenindane-1,3-dione, where strong direct polar $\pi$ conjugation is present, as well as in the presence of the saturation effect in *p*-phenylenediamine. For this reason the Hammett $\sigma$ constants should be replaced by other parameters.

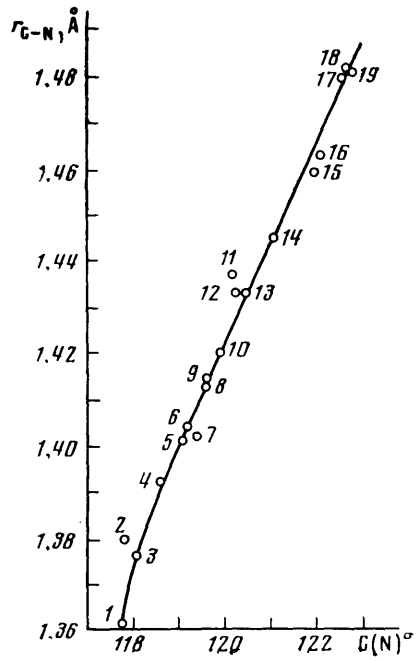
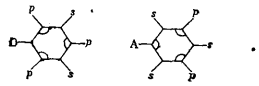



**Figure 2.** Correlation between C–N bond lengths and C(N) angles for: 1) 2-*p*-dimethylaminobenzylidenindane-1,3-dione; 2) *p*-dimethylaminophenyl phenyl sulphide; 3) *p*-thiocyanatoaniline; 4), 5), 13) anilinophenylphthalimide; 6) 1-phenyl-thiosemicarbazide; 7) aniline; 8) acetanilide; 9) *NN'*-diphenyl-*p*-phenylenediamine[250]; 10) *N*-diphenylmethylenaniline; 11) *N*-phenylacetanilide; 12) azobenzene[251]; 14) 4-phenyl-thiosemicarbazide; 15) $\alpha\alpha N$-triphenylnitrone; 16) mean values for *p*-nitrobenzenes[159]; 17) *p*-nitrobenzoic acid; 18) *p*-nitrotoluene; 19) *N*-methylacetanilide.

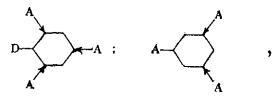
A review[160] has shown that the C(D, A) bond angles (denoted $\alpha$ by the reviewers) of elements in the third period are related to the Pauling[254] electronegativities $\chi$ by the linear formula $\alpha = 3.33\,\chi + 111.4$. On Pauling's thermochemical scale, however, the electronegativity sequence of the elements C > Si = Ge = Sn = Pb and N > P > As > Sb = Bi does not correspond to the bond angles and nuclear potentials of the elements.

Considering the structural aspect of the reactivity of the benzene molecule, we note that, according to the scheme of $\sigma$ rehybridisation of bonds in Section II, increase in the bond angle of a carbon atom in the benzene ring implies an increase in the proportion of the *s* state of this atom in the cyclic carbon–carbon bonds and hence an increase in the proportion of the *p* state of this atom in the exocyclic carbon–hydrogen bond. The distribution of predominant *s* and *p* components of $\sigma$-hybrid bonds of carbon atoms in the exocyclic bonds of monosubstituted derivatives can be represented

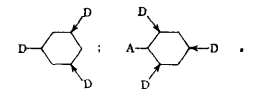


As a result, electrophilic-acceptor substituents will be oriented in conformity with the excess of *p* electrons, and nucleophilic-donor substituents according to the excess of *s* electrons:

electrophilic substitution



nucleophilic substitution



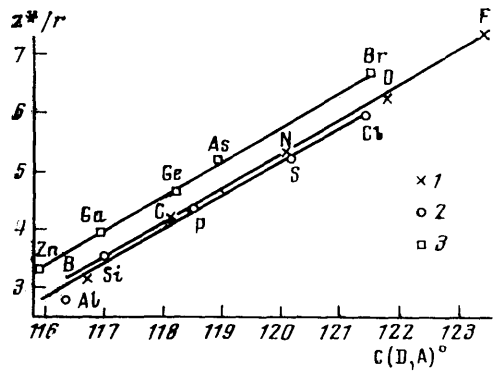



**Figure 3.** Dependence of bond angles C(D, A) on nuclear potentials $z^*/r$ of elements in different periods: 1) second; 2) third; 3) fourth.

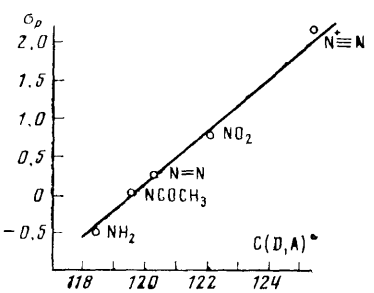



**Figure 4.** Dependence of the constants $\sigma_p = \sigma_I + \sigma_R$ on the bond angles C(D, A).

Thus the structural scheme of substituted benzenes is fully consistent with experiment: a donor D orients electrophilic substituents to *ortho* and *para*-positions, and nucleophilic substituents to the *meta*-position; but an

acceptor A orients electrophilic substituents to the *meta*-position, and nucleophilic substituents to *ortho*- and *para*-positions. Since σ bonds with excess of the *p* state are less stable than those with excess of the *s* state, electrophilic substitution should occur more readily than nucleophilic substitution. Thus the structural scheme of σ rehybridisation explains the main features of the reactivity of substituted benzenes, and hence σ bonds are of decisive significance for establishing the orienting effect of substituents.

## V. COMPARISON OF STRUCTURAL CHARACTERISTICS OF SUBSTITUTED BENZENES AND OF METAL COMPLEXES

It is of interest to compare the structural characteristics found for substituted benzenes with X-ray results obtained for metal complexes containing the same substituents as ligands in the coordination sphere. In the modern theory of the *trans*-effect in complex compounds of metals widespread use is made of the concept of the σ rehybridisation of orbitals of the central metal atom, according to which an increase in the proportion of a given component (*s*, *p*, or *d*) in the hybrid bond of the metal atom implies a decrease in an adjacent bond of the metal[255].

The scheme of population of σ bonds suggested for substituted benzenes D(*p*)–(*s*)A(*p*)– operates also in metal complexes. The *trans*-effect of ligands L, which has been most thoroughly studied in complex platinum compounds, is evident in the lability of the platinum–chlorine bond along the L–Pt–Cl axis: D(*p*)–(*s*,*d*)Pt(*p*)–Cl. Thus the platinum–chlorine bond length should increase on passing from acceptor ligands A to donor ligands D because of the increased fraction of the *p* state of the platinum atom in the platinum–chlorine σ bonds. Table 6 shows that decrease in the C(D,A) bond angle[160] is accompanied by an increase in the platinum–chlorine bond length[256].

Table 6.

| L | O | Cl | $PR_3$ | $CR_3$ | $SiR_3$ |
|---|---|---|---|---|---|
| Pt—Cl, Å | 2.28 | 2.30 | 2.37 | 2.415 | 2.45 |
| C(D, A)° | 121.8 | 121.4 | 118.5 | 118.1 | 117.0 |

Several deductions can be made from the above structural characteristics. According to the platinum–chlorine bond lengths the Taft induction constant $\sigma_I$ for the methyl group should exceed that for a trialkylsilyl group. This is supported by a comparison of the C(C) bond angle in triphenylmethane with C(Si) in tetraphenylsilane (117.8° and 116.1°). These results suggest that the sequence of the $\sigma_I$ constants of methyl and silyl groups (–0.08 and +0.01)[3] should evidently be refined.

The X-ray spectra of platinum complexes indicate[257] that the polarity of the platinum–chlorine bond is enhanced by the *trans*-effect of a ligand L. This is quite consistent with the concept of σ rehybridisation. The polarity of the platinum–chlorine bond would increase because *p* electrons are more weakly bound to the nucleus than are *s* electrons. Hence the ultimate cause of the enhanced bond polarity is an increase in the proportion of the *p* component of the platinum atom in this bond.

Similar ideas enable us to understand the relative stabilities of bonds involving other metals. For example, more substantial changes in bond lengths involving metal atoms are observed in tin than in platinum complexes[258].

We note in conclusion that the variation of the effect of substituents in benzene derivatives is paralleled by that of the *trans*-effect of the corresponding ligands in metal complexes. This is due to the important role of σ bonds in both classes of chemical compounds, resulting from the influence of donor–acceptor substituents (ligands) on the σ rehybridisation of (D,A)–C and (D,A)–M bonds. As a result, the influence of such donors D or acceptors A is apparent in the thermodynamic lability or stability of the C–H and M–L bonds involved in substitution. The reason for such behaviour of substituents (ligands) lies in the general rule that the length of a D–A bond decreases with fall in the nuclear potential $z^*/r$ of the donor atom D and rise in that of the acceptor atom A.[66,67]

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# Gas Chromatography with Organic Eluents

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The characteristics of the use of organic gases and vapours as the mobile phases in the elution gas chromatography as well as additives to the usual carrier gases are considered. Methods are described for the preparation of the eluents and detection, and the role of the eluent as the factor permitting the regulation of the retention of the sorbate and the shape of the chromatographic band is discussed. The considerable advantages of organic gases and the vapours of organic compounds as eluents in preparative chromatography are demonstrated.
The bibliography includes 100 references.

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## I. INTRODUCTION

In the elution version of gas chromatography, the mobile phase (carrier gas) plays as a rule merely the role of a transporting agent; the concentration of the sorbate analysed in this phase is determined by the vapour pressure of the sorbate at the working temperature and the nature of the sorbent. The first studies on gas chromatography with organic eluents and with organic additives to the usual carrier gases were published as early as 1956–1959.[1-10] It was shown that the use of organic and mixed eluents makes it possible to change significantly the pattern of the chromatographic separation of substances; thus the nature of the mobile phase becomes a factor which determines to a large extent both the retention of the chromatographic band and the shape of the recorded peak.

Together with their role as transporting agents, organic eluents and additives can perform the following "active" functions: (1) the blocking of the active centres of solid carriers (polar eluents) with formation of symmetrical bands of polar sorbates; (2) adsorption on the surface of the adsorbent and formation of a liquid layer which alters the partition coefficient of the sorbate in the mobile phase—sorbing medium system and hence the retention (the latter is usually decreased); (3) dissolution in the stationary liquid and formation of a binary stationary phase whose composition determines the retention of the sorbates; (4) the shift of the phase equilibrium of the sorbate in the mobile phase (it is manifested to the greatest extent with increase of the pressure)†; (5) the formation of volatile derivatives of involatile substances (particularly metals), which can be transported along the column; (6) the increase in some cases of the sensitivity of the detectors in relation to the substances analysed.

The above characteristics of organic eluents make it possible to extend the scope of gas chromatography as a method for the analysis of polar and high-boiling compounds.

† The above phenomena are observed also when a vapour eluent is used. The relevant studies have been reviewed[11].

Other advantages of organic eluents are noteworthy: (1) the ease of condensation (which enables them to be used in preparative chromatography without the need for low-temperature cooling of the traps); (2) the availability of hydrocarbon gases in petrochemical undertakings (this facilitates the employment of these gases as eluents in industrial control). The vapour of the stationary liquid which is volatile under the selected working conditions can be used as the eluent or its component and the analysis can be carried out both under the conditions of circulation chromatography[7,8] and with continuous saturation (before the column) of the carrier gas by the vapour[9]. Thus the range of the stationary phases employed is extended to include more volatile substances.

Table 1 presents data for the conditions in the chromatographic process with organic or mixed eluents. Methane and its mixture with hydrogen were used for the first time as carrier gases in 1956 by Taramasso[1,2]. In many instances, this proved to be convenient and economical in industrial monitoring (naturally, provided that safety precautions are taken), which was subsequently confirmed[12]. Furthermore the use of methane as the carrier gas instead of nitrogen increases the sensitivity of the katharometer because of the greater thermal conductivity of methane.

In 1959 Dumazert and Ghiglione[5] suggested that the chromatographic process be carried out in ethanol vapour, which influenced significantly the nature of the sorption of the substances analysed in the column and hence also the retention and shape of the concentration bands. Thus the eluent ceased to be merely a transporting agent; its nature became a factor influencing the phase equilibrium. A year earlier, Knight[6] showed that the introduction of small amounts of polar organic additives into the usual carrier gases ensures symmetrical peaks of polar sorbates and thus reduces the requirement for the inertness of solid carriers with respect to adsorption, since polar additives block their active centres. Subsequent studies on these lines were performed by Ackman and coworkers[14-16]. Organic additives were used in 1960 to increase the sensitivity of ionisation detectors with respect to inorganic gases[39] and in 1971 in order to form volatile adducts with metals[40].

**Table 1.** Conditions in the separation of substances in a stream of organic eluents or their mixtures with ordinary carrier gases.

| Substance | Eluent | Sorbent | Column Temp., °C | Detector | Ref. |
|---|---|---|---|---|---|
| Natural gas ($C_1$-$C_4$) | methane, methane with an admixture of hydrogen | n-hexadecane, dinonyl phthalate on Celite | 25 | katharometer | 1,2 |
| Methane | acetylene | wood charcoal | 25 | katharometer | 3 |
| Lower alcohols, water, allylamines | helium saturated by a mixture of water and n-hexylamine | di-isodecyl phthalate, tricresyl phosphate, triethylene glycol, $\beta\beta'$-oxydipropionitrile, poly(propylene glycol), DC-550 silicone on refractory brick | 25-60 | katharometer | 4 |
| $C_2$-$C_5$ acids | ethanol | liquid paraffin and stearic acid on refractory brick | 100-110 | katharometer | 5 |
| Nitrogen, ethylene, propane | methane | silica gel, dibutyl phthalate on silica gel | 75 | katharometer | 6 |
| Acetone, n-heptane, toluene, n-hexane, n-octane, benzene, cyclohexane, methylcyclohexane | helium with added solvent vapour | methanol, aniline on C-22 refractory brick | 20-150 | katharometer | 7,8 |
| $C_4$-$C_8$ hydrocarbons, oxygen compounds | helium with added solvent vapour | n-octane, n-decane on C-22 refractory brick | 30,60 | katharometer | 9 |
| $C_5$-$C_7$ hydrocarbons, $C_1$-$C_5$ alcohols | methane, ethane, ethylene, n-pentane | $\beta\beta'$-oxydipropionitrile, Paraplex, UCON-LB-550-X, Apiezon L, di-iso-decyl phthalate on Chromosorb W | 100 | katharometer | 12 |
| Isoalkenes | hydrogen, nitrogen with added solvent vapour | methanol, ethanol, acetone, ethyl methyl ketone, dioxan on a solid carrier | 28-45 | katharometer | 13 |
| Volatile $C_2$-$C_6$ aliphatic acids | helium with added formic acid vapour | ethyl formate, ethyl acetate, n-hexane, cyclohexane, ethylene glycol sebacate on Chromosorb W, Porapak QS, Chromosorb-101 | 160-200 | FID | 14-16 |
| Oxygen, argon, neon, helium | nitrogen with added iso-$C_5$ vapour | 5 Å molecular sieves | – | FID | 17 |
| Methane, propane, n-decane, n-heptane | methane, methane-propane mixture | n-decane, n-heptane on a solid carrier | – | katharometer | 18 |
| n-Pentane, isopentane, hexane, 2-methylpentane, 2,2-dimethylbutane | methane, ethane | squalane on Celite | 25,50 | katharometer | 19 |
| Toluene, 1-propanol, 1,2-dichloroethane, benzene, carbon tetrachloride | nitrogen, hydrogen with added benzene and 1,2-dichloroethane vapours | toluene, 1-propanol, 1,2-dichloroethane, benzene, carbon tetrachloride on Fluon, Haloport, Teflon-6 | 30-65 | FID | 20 |
| Barbiturates | nitrogen with added formic acid vapour | Apiezon L on Chromosorb | 185 | FID | 21 |
| Pentane, hexane, heptane benzene, toluene, ethanol, propanol, isobutyl alcohol, acetone, water | nitrogen with added n-octane, n-nonane, n-decane, hexanol, and dibutyl phthalate vapours | ethanol, propanol, isobutyl alcohol, heptane, octane, benzene, *p*-xylene on Chromosorb and INZ-600 | | katharometer | 22,23 |
| Isopropylbenzene | inorganic carrier gas with added solvent vapour | dioctyl phthalate on a solid carrier | – | – | 24 |
| $C_1$-$C_7$ hydrocarbons, oxygen compounds | methanol, ethanol, isopropyl alcohol, heptane, hexane, ethyl acetate, n-butyl chloride, chloroform, and dichloroethane vapours<br>mixtures of ethanol with methanol, heptane, benzene, hexane, and iso-octane | dioctyl phthalate on Chromosorb W A W, Porapak S and Q, activated alumina, silica gel, diethylene sebacate, silicone oil, poly(ethylene glycol) on C-22 refractory brick | 80, 140-230 | katharometer, u.v.cell | 25-30 |
| $C_9$-$C_1$ hydrocarbons, $C_4$-$C_6$ aliphatic alcohols | ethanol and heptane vapours | Apiezon L on INZ-600 | 135, 160 | katharometer | 31 |
| Free $C_2$-$C_{18}$ aliphatic acids, $C_3$-$C_{18}$ aliphatic amines, ethylenediamine, ethanolamine | water vapour with added formic acid or hydrazine hydrate vapour | Chromosorb GAW, Corning GLC-100 porous glass beads | 125-200 | FID | 32 |
| $C_6$-$C_1$ hydrocarbons, amines, isomeric geranate esters, halogenoalkenes, free aliphatic acids | Freon, formic acid, and methanol vapours | poly(ethylene glycol), SKTV polydimethylpolysiloxane on Chromosorb A and Chromaton | 120-175 | FID, densitometer, electron capture detector | 33,34 |
| Acetone, methanol, ethanol, diethyl ether | inorganic carrier gas with added isopentyl and hexyl alcohol vapours | isopentyl alcohol, high-vacuum grease on Celite-545 | 50,70 | katharometer | 35 |
| Nitrogen, argon, carbon dioxide, sulphur dioxide | Freon-116 vapour | silica gel | – | FID | 36 |
| Aromatic hydrocarbons | water vapour with added organic vapour (ethanol, pentane-ethylene fraction) | poly(ethylene glycol adipate), n-butylamine on Spherochrome | 130 | katharometer | 37 |
| Nitrogen compounds | nitrogen with added ammonia, polyethylene-amine, tetraethylene-pentamine, tetra(hydroxyethyl)-ethylene-diamine | OV-1 silicone on Chromosorb | 235 | FID | 38 |

This review considers the possibility of employing organic eluents and organic additives to carrier gases in analytical and preparative chromatography and also in physicochemical measurements. Attention has been concentrated on experiments under the usual pressures. As regards fluid chromatography[41-56], which constitutes a very powerful means of increasing the mobility of involatile sorbates, only some of its aspects are discussed below, because a number of reviews have been devoted to this method[40-42,45,47]. Since the review is restricted to the discussion of elution gas chromatography, frontal and displacement versions, where the mobile phase usually consists of organic gases and vapours, and particularly chromatography without a carrier gas[57] (with the exception of the problem of the preparation of a fixed mobile phase which has a bearing on the subject of the review) remain outside its scope.

## II. PREPARATION OF THE ELUENT

The organic additives are introduced into the carrier gas in the following ways: (1) by passing the stream of carrier gas through a tube or vessel with an adsorbent or

solid carrier impregnated with the volatile organic liquid; (2) by bubbling a layer of the liquid with the carrier gas; (3) by passing the carrier gas over a layer of the liquid; (4) by injecting a portion of the volatile solvent into the metering device of the chromatograph.

Thus the carrier gas has been passed[9] through a vessel with Sil-o-cel impregnated with the corresponding volatile solvent, and, in order to ensure the complete saturation of the gas, the temperature of the vessel exceeded by several degrees the working temperature of the column; after coming into contact with the solvent, the gas was cooled to the working temperature and was introduced into the chromatographic column.

In order to evaporate a mixture of water and formic acid, Nonaka[32] used a modified evaporator in the chromatograph. The carrier gas is usually saturated with formic acid vapour by passing it over a layer of concentrated formic acid[14-16].

Virtually complete saturation of the carrier gas by the organic vapour takes place when the gas is bubbled through a layer of the liquid[37,58]. An apparatus has been described[58] for a vacancy-chromatographic study of the phase equilibrium constants in which a saturator is used to saturate the carrier gas with the organic sorbate by bubbling. A device described by Benedek and Ratkovics[59] was used as the saturator.

In order to create a mobile band of the volatile liquid phase in the column, a number of workers[23,24,35] introduced the solvent directly into the column through a metering device. Evaporators of different designs have been used to obtain individual eluent vapours. Thus the generation system in one investigation[31] incorporated two steel cylindrical containers heated to 200°C. The liquid was evaporated in the first container and the resulting vapour passed to the second container, which served as a damping device and which was provided with a manometer and a fine control valve. The vapour then passed to the column through a heated capillary.

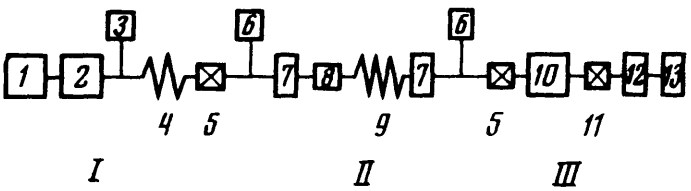



**Figure 1.** Schematic representation of the chromatographic apparatus with an organic vapour-phase eluent: I) gas-generating section; II) separating column; III) condenser for organic vapour-phase carrier; 1) vapour generator; 2) buffer reservoir; 3) manometer; 4) hydraulic resistance; 5) needle valve; 6) manometer; 7) detector; 8) evaporator; 9) column; 10) cooled trap; 11) cut-off valve; 12) trap with $CaCl_2$; 13) vacuum pump.

Fig. 1 illustrates schematically an apparatus where the vapour of an organic substance was used as the eluent (carbon tetrachloride, benzene, and ethanol)[26]. It consists of three parts: the gas generator, the column, and the condenser for the organic eluent. After the system had been evacuated, the reservoir *1*, containing the organic solvent, was heated to the required temperature (80° to 110°C); the vapour pressure reached 1–2 kgf $cm^{-2}$ at this temperature and the vapour was supplied to the separating column. The flow rate of the organic eluent was controlled by the inlet and outlet pressures in the column by means of a needle valve. The pressure in the column and the gas generator temperature were limited by the level of errors in the zero line. Before connection to the rest of the apparatus, the chromatographic system was conditioned for several hours in order to ensure equilibration. Because of its prior evacuation, the system usually operated at a reduced pressure. The flow rate of the organic eluent was calculated by dividing the dead volume of the saturating column by the retention time of the non-sorbed component.

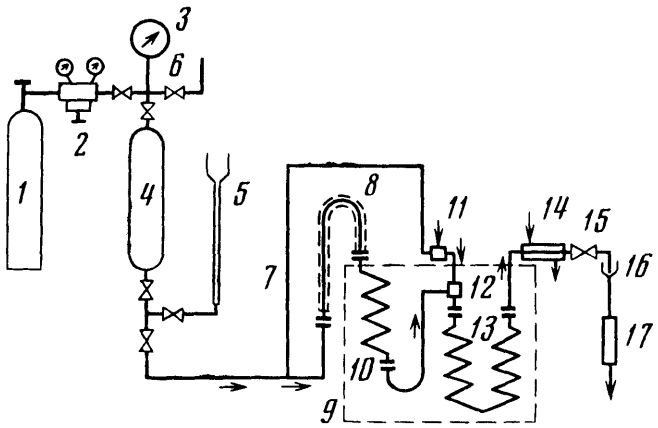



**Figure 2.** Schematic illustration of the apparatus for chromatography with hypercritical liquids: 1) gas cylinder; 2) reduction valve; 3) Bourdon manometer; 4) reservoir; 5) funnel; 6) valve; 7) side line; 8) heater; 9) air thermostat; 10) conditioning tube; 11) pneumatic injector; 12) three-way connector; 13) chromatographic column; 14) capillary tube; 15) needle valve; 16) degassing unit; 17) detector.

The apparatus usually employed to generate the vapours of organic eluents in fluid chromatography[45,47,48] is illustrated schematically in Fig. 2.[47] The mobile liquid phase is under nitrogen pressure in a stainless steel reservoir *4*, whence it passes to a heater *8*, where its temperature is adjusted to a value close to the critical temperature. The eluent is heated to the working temperature in the conditioning tube *10*, assembled, together with the chromatographic column *13*, in an air thermostat *9*. The pressure in the apparatus is regulated by the nitrogen pressure in the reservoir *4* and by the needle valve *15*. In later studies by the same workers[47], the pressure was generated by means of a pump.

## III. DETECTION

With some exceptions[1,2,36], organic eluents greatly reduce the sensitivity of the katharometer (K) and rule out the possibility of the application of a flame-ionisation detector (FID) for analysis; the above detectors are the

most widely used in traditional gas chromatography. In chromatography with organic eluents, the FID can be used only after the introduction into the usual carrier gas of small amounts of organic additives [38], which generate a small background current, or under conditions such that the detector does not record the organic substance (for example, when pure formic acid vapour is used as the eluent [34] and also when it is added to a usual carrier gas [14-16,21]), or under special conditions, for example as the carrier gas in the analysis of inorganic gases [17,60].

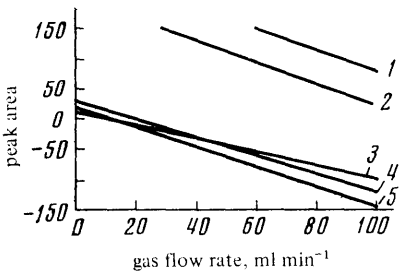



Figure 3. The influence of the flow rate of different carrier gases on the sensitivity of the katharometer to n-pentane ($t_c$ = 100°C): 1) hydrogen; 2) helium; 3) ethane; 4) methane; 5) nitrogen.

Despite the above limitations, the katharometer is widely used in this version of chromatography, both because a sufficient difference between the thermal conductivities of the eluent and the sorbate is achieved and because of the lack of an alternative. Fig. 3 [12] illustrates the influence of the nature of the carrier gas and of its flow rate on the sensitivity of the katharometer.

In order to improve the sensitivity of the usual katharometer, it is necessary to increase the current passed through the detector, which is impossible when the thermal conductivity of the organic vapour is low. In recent years studies have been published [61-63] in which an improved version of the katharometer with a constant filament temperature is proposed. The suggested version is free from the above disadvantages and the use of eluents with a low thermal conductivity actually increases its sensitivity [61].

An ultraviolet cell, which is selectively sensitive to aromatic compounds, has been used in studies by Tsuda and coworkers [25,27-30], whose work has been most productive in chromatography employing organic eluents. The ultraviolet cell is also widely used in fluid chromatography. The possibility of its successful employment up to 290 atm without reducing the pressure before its inlet has been demonstrated [53]. However, as stated above, its application is limited owing to its selectivity.

Despite the fact that examples of the use of the densitometer [33] and the electron capture detector [34] have been described in the literature, the katharometer and the ultraviolet cell will probably remain in the immediate future the most convenient detectors for this version of gas chromatography.

A comparative analysis of the results obtained with the aid of the ultraviolet cell and the katharometer in experiments where they were incorporated in the system in succession has been published [27]. The detectors operated in the linear range; the widths of the recorded peaks at the level of half their heights for a specific flow rate of the eluent vapour (ethanol) were approximately the same. The sensitivities of the detectors to substances containing one benzene ring are likewise approximately identical; the ultraviolet cell is more sensitive (approximately by a factor ten) to polycyclic aromatic compounds. The minimum amount of substance detected by the ultraviolet cell is 10–100 ng. A two-channel scheme with two detectors, one universal and the other selective with respect to the class of compounds investigated, is available and is suitable also for eluents in the vapour phase. Fig. 4 [27] presents chromatograms for the same mixture of substances obtained with the aid of these two detectors. The ratios of the peak heights of the same substance on the u.v. and K chromatograms are 1.4, 0.1, and 15 for derivatives of benzene, olefins or ketones, and naphthalenes respectively. The *b*, *d*, and *f* peaks correspond to olefins or ketones, the *c*, *e*, *g*, *h*, *i*, and *j* peaks correspond to benzene derivatives, and the *a* peak corresponds to a saturated hydrocarbon.

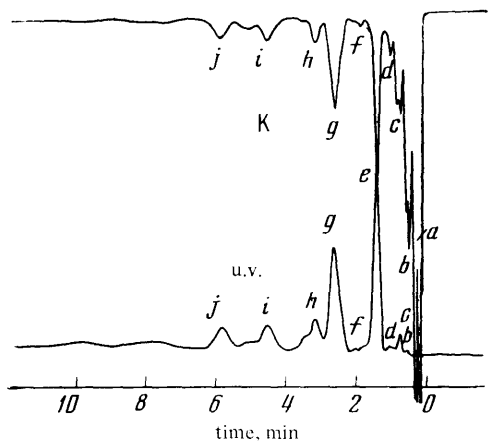



Figure 4. Combination of two detectors: sorbate—0.2 ml of petrol; column with 20 wt.% of dioctyl phthalate; $t_c$ = 120°C.

Ionisation detectors are relatively insensitive to inorganic gases. When an organic substance is introduced into the stream of carrier gas and an inorganic gas is then injected into the detector, the ionisation current is reduced to a greater extent than after the introduction of single gas into the stream of pure carrier [39]. Methods have been developed on this basis for the chromatographic determination of inorganic gases by ionisation detectors [17,36,39,60,64-67] (with a sensitivity of $0.5 \times 10^{-4}$% to $H_2$, $O_2$, and $CH_4$ and of $1 \times 10^{-4}$% to nitrogen [39]).

A universal detector meeting the requirements of fluid chromatography has not yet been devised. When traditional chromatographic detectors are used, it is necessary to reduce the pressure to atmospheric before the detector, which leads to the condensation of the mobile phase or to its degassing. As already stated, the majority of workers use the ultraviolet cell. Detectors which do not require the reduction of pressure beyond the chromatographic column have been proposed [44,54].

## IV. SORBENTS

In experiments with organic and mixed eluents, it is possible to use all the liquid phases and adsorbents which are employed in ordinary chromatography with inorganic carrier gases. Furthermore, in the presence of polar organic eluents and additives, requirements for the inertness of solid carriers become less stringent, and the set of possible liquid phases is extended by the inclusion of volatile solvents. Data concerning the application of liquid phases and adsorbents are presented in Table 1.

Having noted that organic eluents and additives affect the retention times of the substances analysed and the shape of the peaks, a number of workers [14-16,21,25,30,31,38,68-74] expressed different views concerning their influence on the mechanism of the interaction of the sorbate with the sorbent. The view that a thin liquid film is formed from the eluent vapour on the adsorbent surface, altering its sorption properties, is generally accepted. On the other hand, in the gas–liquid version, four factors, believed to be responsible for the change in the mechanism of the interaction of the liquid phase with the sorbate, have been isolated: (1) the formation of a liquid film on the surface of the liquid phase; (2) the formation of binary liquid phases; (3) temporary modification of the solid carrier by the molecules of the vapour phase; (4) the interaction between the sorbate and the eluent in the gas phase.

When organic eluents are used, all the above factors operate, but the role of each can be estimated only when account is taken of the specific experimental conditions: temperature, pressure, and the nature of the liquid phase or adsorbent and the eluent.

Berezkin et al. [31] analysed mixtures of alcohols and hydrocarbons in a stream of ethanol and heptane vapours and in nitrogen using Apiezon L as the liquid phase. At a high column temperature (160°C), nitrogen and ethanol vapour yielded virtually identical retention characteristics, because at an elevated temperature an eluent film is not formed on the surface of the liquid phase and a binary liquid phase is not produced, since ethanol is almost insoluble in Apiezon L. This also shows that, under the given conditions, the interaction in the gas phase does not have a significant influence on the retention. On the other hand, in the presence of heptane the retention volumes are altered, as a result of the dissolution of heptane in Apiezon L and the formation of a binary liquid phase with modified sorption properties.

An increase or decrease of the retention of propanol, octane, and toluene in ethanol and benzene vapours at a lower temperature (125°C) and using poly(ethylene glycol), dioctyl phthalate, and silicone as the stationary phases, relative to the retention of the same sorbates in a stream of nitrogen, has been explained [26] by the formation of a surface layer of condensed eluent, which prevents the mass transfer process and also by the dissolution of a small amount of the eluent in the stationary liquid. It is noteworthy that these explanations are in many respects contradictory, and the observed phenomena require a more detailed study. The retention volumes obtained in a number of studies [26,31] are listed in Table 2.

The process occurring in the column is in many respects determined by the temperature. When volatile solvents are used as the stationary phase by their partial condensation on an inert carrier in the column, a change in column temperature alters not only the partition coefficient of the sorbate in the gas–liquid system but also the thickness of the surface layer of the eluent, i.e. the amount of the stationary phase [7,8,22,23,35].

When the liquid phase and the eluent are only slightly miscible, a thick liquid film is formed on the surface of the liquid phase (according to Tsuda et al. [30], the thickness of the film corresponds to approximately 2–10 molecules when ethanol and alumina are used as the carrier vapour and adsorbent respectively at a column temperature of 100–150°C); on the other hand, when the liquid phase and the eluent are miscible, a binary phase is formed. Since the thickness of the film is determined by the sorption capacity of the support, the film is naturally thicker on an adsorbent than on a solid carrier; on the other hand, the adsorbent influences significantly the retention and the shape of the peaks.

Table 2. The ratios of the retention volumes of the sorbates for different carrier gases and liquid phases to the retention volumes for the nitrogen carrier gas [26,31].

| Liquid phase | Poly(ethylene glycol) | | Dioctyl phthalate | | Silicone | | Apiezon L | |
|---|---|---|---|---|---|---|---|---|
| Carrier gas | $C_2H_5OH$ | $C_6H_6$ | $C_2H_5OH$ | $C_6H_6$ | $C_2H_5OH$ | $C_6H_6$ | $C_2H_5OH$ | $n\text{-}C_7H_{16}$ |
| Ethanol | — | — | — | 1.7 | — | 1.9 | — | — |
| 1-Propanol | 0.9 | 1.0 | 0.8 | 1.2 | 0.7 | 1.4 | — | — |
| 1-Butanol | — | — | — | — | — | — | 0.9 | 1.7 |
| 1-Pentanol | — | — | — | — | — | — | 1.0 | 1.5 |
| 1-Hexanol | — | — | — | — | — | — | 1.0 | 1.3 |
| n-Octane | 0.7 | 0.8 | 0.8 | 1.0 | 0.5 | 1.3 | 0.9 | 1.1 |
| Toluene | 0.7 | 0.9 | 0.7 | 1.0 | 0.6 | 1.1 | — | — |
| n-Nonane | — | — | — | — | — | — | 1.0 | 1.2 |
| n-Decane | — | — | — | — | — | — | 1.0 | 1.3 |

Pressure has a significant influence on the chromatographic process only when it is greatly increased, although there is some change in the retention characteristics when the pressure is altered, but not to an extent sufficient to affect the chromatographic separation pattern. Thus Tsuda et al. [26] showed that, when the pressure is increased by a factor of seven (from 100 to 700 mmHg), the retention of octane and toluene increases by a factor of 1.3, while that of propanol remains unchanged. A different situation is observed with increase of pressure during the condensation of the eluent vapour on the adsorbent surface. According to Rakhmankulov and Vigdergauz [75] (they used water vapour as the eluent, alumina as the adsorbent, and a column temperature of 170°C), an increase of pressure from 1.6 to 7.2 atm entails a sharp decrease of retention—by a factor of several tens for high-boiling paraffins, and significantly smaller for polar sorbates soluble in water. An analogous effect obtains also in the presence of an organic-vapour eluent [12,28,30].

In fluid chromatography, the fluid has a very strong influence on the retention, displacing the phase equilibrium in the direction of the mobile phase. In fluid–liquid chromatography, stationary liquids such as Apiezon M and UCON-50-HB-2000 are eluted from the column in several minutes [49], which necessitates the use of high-molecular-weight liquids as stationary phases. One can instead saturate the mobile phase with the vapour of the stationary liquid, or the liquid phase can be grafted onto a solid carrier [44,50,51,53].

The formation of a liquid film with a simultaneous increase of partition coefficients is also observed in fluid-adsorption chromatography under certain conditions [45].

## V. THE SHAPE OF THE PEAKS AND RETENTION

The use of vapour-phase eluents permits in many instances a significant improvement of the separation as a result of the improvement in the shape of the peaks of the components to be separated and in view of the possibility of regulating the selectivity of the chromatographic column. In ordinary chromatography, the shape of the peaks is determined mainly by two factors: the influence of active adsorption centres of the carrier leading to the spreading of the rear sections of the peaks, and diffusion in the mobile phase, influencing the overall spreading. The use of vapour-phase eluents makes the peaks narrower and more symmetrical as a result of the suppression of the adsorption centres and decrease of the diffusion-induced spreading, since the extent of diffusion in vapour–vapour systems is smaller than in vapour–gas systems.

Table 3. Ratios of the retention volumes of the sorbates for different carrier gases to the retention volumes for the nitrogen or helium carrier gas [28].

| Liquid phase | Carrier gas | Sorbate | Ratio of retention volumes |
|---|---|---|---|
| Dioctyl phthalate, 20 wt.% Silicone, 25 wt.% | $CCl_4$, He | ethylbenzene, n-decane | 1.7–1.6 |
| | $CCl_4$, $N_2$ | 1-propanol, n-octane, toluene | 1.2–0.9 |
| | $C_2H_5OH$, $N_2$ | ditto | 0.7–0.5* |
| | $C_6H_6$, $N_2$ | " | 1.4–1.1* |
| Porapak S | $CCl_4$, He | n-hexane, cyclohexane, benzene | 0.18–0.15 |
| Porapak Q | $CCl_4$, $N_2$ | benzene | 0.4 |
| Alumina | $C_2H_5OH$, $N_2$ | benzene | 0.01 |

*Data of Tsuda et al. [30]

Table 4. The influence of the carrier gas (and the liquid phase) on the absolute specific retention volumes [12].

| Sorbate | Liquid phase—15% UCON-LB-550-X oil on Chromosorb W (60–80 mesh) | | | Liquid phase—15% Apiezon on Chromosorb W (50–80 mesh) | | |
|---|---|---|---|---|---|---|
| | He | $N_2$ | $CH_4$ | He | $N_2$ | $CH_4$ |
| n-Pentane | 5.9 | 5.8 | 4.8 | 6.0 | 5.2 | 3.9 |
| n-Hexane | 10.6 | 10.0 | 9.6 | 11.2 | 10.0 | 9.2 |
| n-Heptane | 19.2 | 18.2 | 18.0 | 22.0 | 18.7 | 19.7 |
| Hex-1-ene | 7.8 | 9.1 | 10.0 | 9.9 | 9.5 | 8.7 |
| Cyclohexane | 20.3 | 17.8 | 17.5 | 20.7 | 20.0 | 19.7 |
| Ethylcyclohexane | 52.4 | 51.1 | 50.8 | 67.7 | 64.5 | 64.5 |
| Cyclohexene | 19.9 | 20.6 | 24.1 | 23.2 | 22.2 | 21.2 |
| Benzene | 22.3 | 21.4 | 20.6 | 19.8 | 18.7 | 17.8 |
| Toluene | 42.6 | 38.8 | 39.8 | 41.0 | 39.2 | 31.8 |
| *p*-Xylene | 75.1 | 74.1 | 72.7 | 81.9 | 78.0 | 78.0 |
| *o*-Xylene | 91.1 | 88.0 | 87.6 | 96.6 | 92.4 | 92.0 |
| Isopropylbenzene | 102.5 | 101.4 | 99.8 | 103.9 | 102.6 | 100.7 |
| Methanol | 3.5 | 3.6 | 2.6 | 1.7 | 1.2 | 0.8 |
| Ethanol | 5.9 | 5.9 | 5.3 | 3.5 | 2.6 | 1.9 |
| 1-Propanol | 10.9 | 10.3 | 10.1 | 6.9 | 6.1 | 4.8 |
| 1-Butanol | 18.8 | 17.8 | 19.7 | 14.2 | 13.1 | 12.0 |
| 1-Pentanol | 38.7 | 36.5 | 38.5 | 30.6 | 30.9 | 28.4 |
| Isopropyl alcohol | 5.9 | 5.2 | 5.7 | 5.6 | 3.9 | 2.9 |
| Isobutyl alcohol | 15.6 | 15.1 | 13.6 | 12.5 | 9.6 | 9.6 |
| Isopentyl alcohol | 30.9 | 29.7 | 28.5 | 25.4 | 23.1 | 22.2 |
| t-Butyl alcohol | 6.6 | 6.7 | 6.1 | 6.0 | 5.2 | 4.8 |
| s-Butyl alcohol | 13.3 | 12.7 | 12.3 | 12.1 | 8.3 | 7.7 |

The change in the retention of substances when vapour-phase eluents are used is caused by the formation of binary stationary phases or surface films of the eluent and also by the formation of compounds more volatile than the initial sorbates (particularly in the analysis of metals) [40,76–81]. For example, the addition of aluminium chloride vapour to helium (carrier gas) made it possible to analyse metal chlorides having boiling points up to 2000°C (for $t_c$ = 150 to 500°C), which had not been analysed previously by gas chromatography [76].

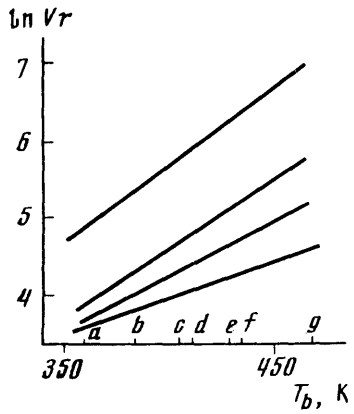



Figure 5. The influence of the nature of the carrier gas on the retention volumes in a column with activated alumina; vapour phase carrier: 1) n-hexane; 2) n-butyl chloride; 3) ethyl acetate; 4) ethanol; sorbates: *b*) toluene; *c*) chlorobenzene; *d*) ethylbenzene; *e*) bromobenzene; *f*) n-propylbenzene; *g*) iodobenzene; $t_c$ = 150°C; vapour flow rate 200 μl $min^{-1}$; sensitivity of u.v. detector 0.32 or 0.16 OD. The retention volumes are quoted with allowance for the pressure drop in the column; 75 cm column with activated alumina.

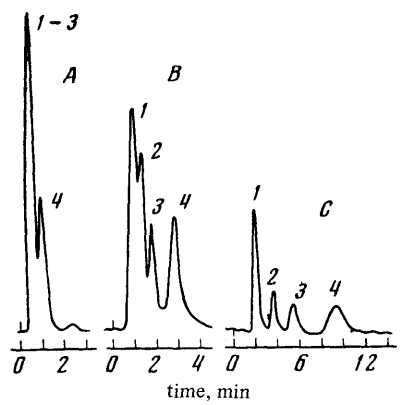



Figure 6. Chromatogram obtained using ethanol (*A*), ethyl acetate (*B*), and n-hexane (*C*) vapours as eluents. 75 cm column with activated alumina (100–300 mesh); column temperature 150°C; sample size 1–3 μl of ethanol containing 1% of different additives: 1) benzene; 2) toluene; 3) ethylbenzene; 4) n-propylbenzene.

Tables 3 and 4 and Figs. 5 and 6 [30] present data demonstrating the influence of the nature of the carrier gas on the retention volumes and chromatographic separation. When ethanol vapour and alumina are used as the carrier gas and adsorbent respectively, the retention volume of

benzene is 1/100 of the retention volume when nitrogen is used as the carrier gas in the presence of the same adsorbent.

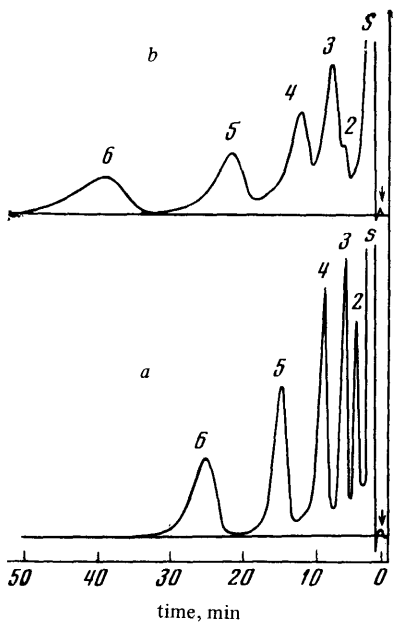



**Figure 7.** Chromatograms of a mixture of $C_2-C_6$ acids with (*a*) and without (*b*) addition of formic acid to the carrier gas; column with silicone; $t_c = 138°C$; helium flow rate 8 $cm^3\ min^{-1}$; *s*—acetone peak; the numerals against the peaks denote the number of carbon atoms.

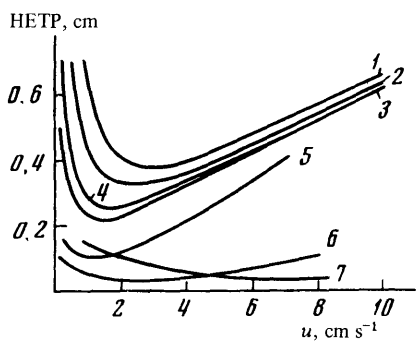



**Figure 8.** Variation of column efficiency (HETP) with the linear flow rate *u* and the nature of the carrier gas: 1) hydrogen; 2) helium; 3) methane; 4) nitrogen, ethane, ethylene ($t_c = 100°C$);[12] 5) carbon tetrachloride ($t_c = 90°C$);[28] 6) nitrogen; 7) helium[81].

As an illustration of the influence of the polar organic additive (formic acid) on the shape of the peaks and the degree of separation, Fig. 5 [15] presents chromatograms for the separation of volatile $C_2-C_6$ aliphatic acids on a column with silicone. Fig. 8 [12,28,82] illustrates the variation of HETP with the flow rate of eluents of different types. With increase of the molecular weight of the eluent, i.e. with decrease of the diffusion coefficient of the sorbate–eluent mixture (the diffusion coefficients of the hydrocarbons ethane, butane, and benzene are 0.6–0.8 $cm^2\ s^{-1}$ at 120–190°C in helium, or approximately 0.1 $cm^2\ s^{-1}$ in chloroform, carbon tetrachloride, and dichloroethane vapours at the same temperatures[28]), the HETP minimum is displaced towards lower linear flow rates of the eluent.

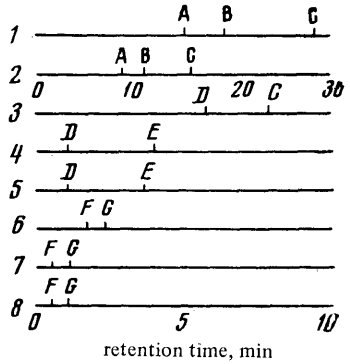



**Figure 9.** The influence of the nature of the carrier gas on the retention time; vapour-phase carrier: 1) benzene; 2) mixture of 10% of benzene and ethanol; 3) and 6) mixture of 1% of ethanol and iso-octane; 4) and 7) ethanol; 5) and 8) mixture of 1% of water and ethanol; flow rate 200 $\mu l\ min^{-1}$; A) phenol; B) *o*-cresol; C) *m*-cresol; D) *p*-di-isopropylbenzene; E) admixture of *p*-di-isopropylbenzene; G) cumene; F) admixture of cumene; 1) and 2) adsorbent—K-923 silica gel, column length 50 cm, internal diameter 3 mm, $t_c = 140°C$; 3)–8) adsorbent—HS-Pellumina, column length 1 m, internal diameter 2 mm, $t_c = 150°C$.

It is also possible to use multicomponent vapour-phase eluents and the components of such mixtures may be not only the vapours of organic substances but also permanent gases, water vapour, ammonia, etc. This approach makes it possible to regulate the selectivity of the chromatographic system (the stationary liquid–vapour-phase eluent system) by selecting the composition of the eluent. Thus, when the eluent was a mixture of ethanol and water vapours [30] (this method was first proposed by Mar'yakhin and Vigdergauz [37]) in the analysis of a mixture of $\alpha$- and $\beta$-naphthols on a column with silica gel, the retention time of the naphthols increased by 5–8 min compared with the experiment where the carrier gas was the vapour of pure ethanol. Similar effects have also been observed when the vapours of mixtures of ethanol with methanol, iso-octane, benzene [30], and hexane [25] were used.

The influence of the nature and composition of the eluent on the retention of sorbates is illustrated by the data in Fig. 9. [30]

## VI. DETERMINATION OF PHYSICOCHEMICAL PROPERTIES

Organic eluents may be used widely in the determination of the physicochemical properties of substances. The gas-chromatographic methods for the determination of physicochemical constants are based on the interaction between the sorbate, the liquid phase, and the carrier gas, so that an increase of the number of substances used as carrier gases greatly extends the range of interactions investigated.

The use of organic eluents in the corresponding systems does not affect the existing methods for the determination of diffusion coefficients [26,83-85], virial coefficients, and activity coefficients [9,18-20,22,86-93]. Thus Kobayashi and coworkers [18,89-93] investigated the gas–liquid equilibria in multicomponent systems, including gaseous and liquid hydrocarbons, and determined the diffusion coefficients [85] up to 136 atm. The employment of organic eluents makes it possible to simplify or modify some of the physicochemical methods (for example the determination of molecular weights [94-96] or of heats of desorption [30]) and to devise new ones, for example the procedure for the determination of complex-formation constants [87].

In particular, when a liquid film is formed on the surface of the adsorbent, the determination of the heat of desorption in chromatography with an organic eluent requires a modification of the method used in traditional chromatography [97]. Tsuda et al. [30] suggested that there is a relation in this case between the heats of desorption and the boiling point of the individual component analogous to Trouton's rule and obtained on this basis an approximate formula for the heat of desorption

$$\Delta H = K_2 T_b,$$

where $K_2 = K_1 T_c$, $T_b$ is the boiling point of the individual substance (in degrees Kelvin), $T_c$ the column temperature (in degrees Kelvin), and $K_1$ is determined from the slope of the linear plot based on the equation

$$\ln V_R = K_1 T_b + A_1 \quad (V_R \text{— is the retention volume}).$$

Using the equation obtained, the authors confirmed the presence of a liquid film on the adsorbent and concluded that the use of ethanol vapour is to be preferred in the analysis of high-boiling mixtures.

## VII. PREPARATIVE CHROMATOGRAPHY

Only a few studies have been made on the use of organic eluents in preparative gas chromatography [33,37,98-100], although the advantages of their employment (as well as water vapour [11]) are quite evident, since, apart from the possibility of modifying the sorption properties of the stationary phase, vapour-phase eluents ensure the virtually complete recovery of the products separated.

In order to increase the degree of recovery of benzene, Tsuda and Ishii [98] added to the carrier gas (nitrogen) a stream of toluene vapour, which condensed in a cooled trap together with the benzene issuing from the column. The degree of recovery of benzene depended on the ratio of the nitrogen and toluene streams and on the rate at which they passed through the column, exceeding 90% under optimum conditions.

Vigalok and coworkers [99,100] achieved a preparative separation of *m*- and *p*-xylenes on a column with a modified synthetic zeolite at 200°C in a stream of benzene vapour. Virtually complete recovery of the high-purity products was achieved (up to 99% after the removal of benzene). Naturally, the recovery did not require low temperatures.

Vigdergauz and Mar'yakhin [37] used, together with water vapour, its mixtures with various organic vapours in preparative chromatography. After their emergence from the column (3.2 m long and with an internal diameter of 20 mm), the mixed eluents were fully condensed (together with the substances isolated in traps cooled by tap water). The version where the eluent is a mixture of water and hydrocarbon vapours is of interest [37]. By varying the composition of this eluent, it is possible to regulate the selectivity and separating capacity of the preparative column. Furthermore, aqueous and hydrocarbon layers are formed in the traps and the substances isolated may concentrate in one of them (depending on their solubility).

Freons have been used in preparative chromatography [33] on a 15 m column having an internal diameter of 10 mm with poly(ethylene glycol) on Chromosorb A, where isomers of geranate ester were separated. Another version [33] involves the use of nitrogen as the carrier gas and the injection of small amounts of Freon into the gas stream directly before entering the trap.

In connection with the considerable progress in the improvement of the productivity of preparative chromatographic apparatus and the transition from preparative chromatography to semi-industrial and industrial chromatographic processes, the use of organic vapour-phase eluents, mainly readily available pure hydrocarbons and petroleum fractions, may serve as a basis for further advances in this field.

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# The Electron Affinities of Organic Electron Acceptors

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The principal methods used to determine the electron affinities of organic molecules are examined and the published data in this field are analysed. Briegleb's series, used in the majority of instances, yields absolute values which are too low. The most probable absolute electron affinities are quoted for the majority of organic electron acceptors investigated and their dependence on substituents and structural features is analysed.
The bibliography includes 121 references.

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## I. INTRODUCTION

The electron affinities of organic molecules and ions are nowadays essential for the interpretation of the results in a very wide variety of research fields, associated mainly with the study of the properties of charge-transfer complexes and their role in organic, catalytic, and biological processes [1-7] as well as the study of one-electron transfer reactions [6,8], organic semiconductors [9-11], and organic materials with metallic conduction [12,13]. The publication of the handbook of Gurvich et al. [14] made available a large number of experimental electron affinities of organic acceptors but did not in any way solve the problem of their utilisation, since the results obtained by various workers for the same acceptors frequently differ by more than 1 eV.

The aim of the present review is to select from the available experimental data the most reliable electron affinities of organic acceptors. We also hope that the review will draw the attention of new investigators to the problem of the determination of electron affinities, which will directly assist in its final solution.

Since this review deals with compounds having fairly distinct electron-accepting properties, aromatic hydrocarbons, heterocyclic compounds, and other compounds with a negative or small positive electron affinity are excluded.

Among the methods for the determination of electron affinities, quantum-mechanical calculations are not considered, since we believe that they should be the subject of a separate review.

## II. FUNDAMENTAL CONCEPTS

Electron capture in the gas phase can be most conveniently treated in relation to a neutral diatomic molecule AB. This process can be regarded as a transition between two vibronic levels [15], one of which characterises the neutral molecule AB and the other the corresponding

radical-anion $AB^{\cdot-}$. Case *a* (Fig. 1) represents dissociative electron capture. Electrons whose kinetic energy varies from $E_1$ to $E_2$ are captured, while those having other kinetic energies are scattered. In case *b* (Fig. 1), the capture of electrons with a kinetic energy in the range $E_4 < E_{kin} < E_3$ leads to vibrational excitation of the radical-anion $AB^{\cdot-}$, which is stabilised in collisions with other species. The potential energy curve for the radical ion has a minimum. In case *c*, the molecule can capture an electron only in a vibrationally excited state and the radical-ion is stabilised in subsequent collisions between molecules.

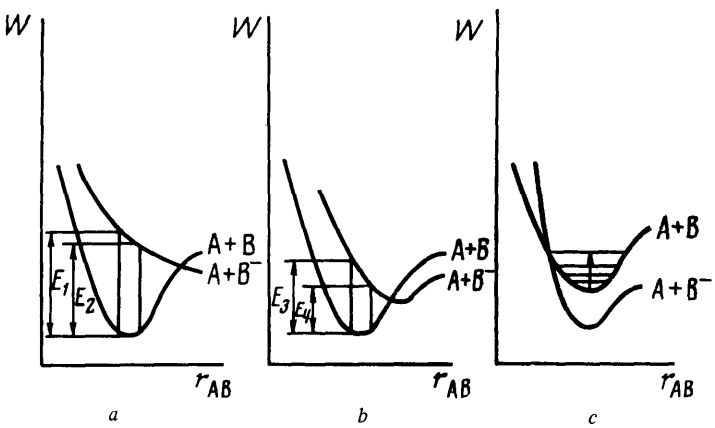



Figure 1. Electron capture by a diatomic molecule AB.

It is noteworthy that only in the last case does the molecule AB have a positive electron affinity ($EA$). Electron affinity is an energetic characteristic of electron capture processes and is equal to the amount of energy consumed or evolved when an electron is added to a gas-phase molecule in the state with minimum energy. Depending on whether the electron adds to a radical-ion in the ground (equilibrium) or vibrationally excited state, adiabatic (thermodynamic) and vertical electron affinities are distinguished. All the foregoing considerations may be expressed by the following equations:

$$AB + e \rightleftarrows AB^{\cdot-},$$
$$EA\ (\text{adiabatic}) = E(AB^{\cdot-}, r_{AB^{\cdot-}}) - E[(AB, r_{AB}) + e],$$
$$EA\ (\text{vertical}) = E(AB^{\cdot-}, r_{AB}) - E[(AB, r_{AB}) + e],$$

where $E$ is the total energy of the $AB^{\cdot-}$ and AB species in the equilibrium ($AB^{\cdot-}$, $r_{AB^{\cdot-}}$ and AB, $r_{AB}$) and vibrationally excited ($AB^{-}$, $r_{AB^{-}}$) states.

By definition, the adiabatic ionisation potential ($IP$) of the radical-anion $AB^{\cdot-}$ is expressed as follows:

$$-IP_{ad}(AB^{\cdot-}) = E[(AB, r_{AB}) + e] - E(AB^{\cdot-}, r_{AB^{\cdot-}})$$

and

$$EA_{ad}(AB) = IP_{ad}(AB^{\cdot-}).$$

The above relation is invalid for vertical processes.

Examination of processes of this kind for polyatomic molecules does not entail fundamental difficulties, although it is much more complex owing to the larger number of degrees of freedom. In principle, a molecule can combine not only with the first electron to form a radical-anion, but also with a second electron to form a dianion. In the latter case, one is dealing with the second electron affinity. In the gas phase, such processes are extremely improbable, but they are known in the condensed phase, where their occurrence is promoted by the strong solvation of charged species.

Electron affinities in the gas and condensed phases are also distinguished. In the condensed phase, the electron affinity does not characterise an individual molecule but a molecule in a crystal lattice or a solvation shell and is correspondingly increased by the polarisation ($P$) or solvation[9] ($E_{solv}$) energy:

$$EA_{cr} = EA + P$$
$$EA_{solv} = EA + EA^{\cdot-}_{solv} - E^{A}_{solv}.$$

## III. METHODS FOR THE DETERMINATION OF ELECTRON AFFINITY

The fundamental methods for the determination of electron affinity have been examined in a number of monographs and reviews[15-23]. Most of them are indirect, permitting the calculation of electron affinity from the general energetics of the given process. Some of them are related to the study of the given electron-accepting molecule in a condensed medium.

### Photochemical Elimination of Electrons from Negative Ions (The Photoabstraction Method)

This is a direct and most accurate method for the determination of electron affinities[20,21,24,25]. After their generation, capture, and detection, negative ions are irradiated with monochromatic light having a smoothly varying frequency. When the threshold photon energy is reached, the photoabstraction of electrons from the negative ions $A^{\cdot-}$ begins:

$$A^{\cdot-} + h\nu \rightarrow A + e.$$

The efficiency curves or the curves of the relative cross-sections for the photoabstraction of electrons plotted as a function of the energy of photons make it possible to determine the threshold photon energies from which the electron affinities of the acceptors A are determined. Considerable progress has been achieved in the development of apparatus for the method and increasingly more complex ions[26-28], including aromatic ions[29], are being investigated.

### Mass Spectrometry of Negative Ions

This procedure has been recently used with increasing frequency. Measurements of the appearance potentials ($AP$) of negative fragments under electron or photon impact permit the calculation of the electron affinities of radicals coupled with the negative ions formed[23,30,31]. The principle of this method can be described by the following equations:

(1) dissociative electron capture:

$$R_1{-}R_2 + e \rightarrow R_1^{-} + R_2^{\cdot},$$
$$EA(R_1^{\cdot}) = D(R_1 - R_2) - AP(R_1^{-}) + KE + IE;$$

(2) the formation of an ion pair:

$$R_1 - R_2 \xrightarrow{e,h\nu} (R_1{-}R_2)^{*} \rightarrow R_1^{+} + R_2^{-},$$
$$EA(R_2) = AP(R_2^{-}) - D(R_1{-}R_2) - IP(R_1^{\cdot}) - KE - IE,$$

where $D(R_1 - R_2)$ is the homolytic bond dissociation energy and $KE$ and $IE$ are the kinetic and internal energies of the species involved. The necessity for the determination of $D$, $KE$, $IE$, and $IP$ complicates the application of this method.

A method involving the mass spectrometric investigation of the equilibria in proton transfer reactions has also been used to determine the electron affinities of organic free radicals [32].

### The Method of Collision Ionisation of Alkali Metal Atoms

This procedure is promising. The electron affinities are calculated from the threshold value for the reaction

$$M + A \rightarrow M^+ + A^-,$$

where M is an alkali metal, usually caesium. The threshold value is determined by studying the dependence of the relative reaction cross-section on the translational energy of the reactants [33]. It is equal to the difference between the ionisation potential of the alkali metal and the electron affinity of the acceptor A. The method yields reliable results and has no fundamental limitations except that the process must lead to the formation of the molecular ion $A^-$ and not its decomposition products. The accuracy of the method [34-36] does not usually exceed ±0.1 eV. Electron transfer to the acceptor can be achieved also with the aid of other electron donors with known ionisation potentials [36,37].

### The Electron Capture or Thermal Equilibrium Method [15,19]

The method reduces to the investigation of the equilibria in reactions involving the capture of thermalised electrons by the acceptor in the gas phasa:

$$e + A \xrightarrow{K} A^- .$$

The steady-state concentration of electrons varies exponentially with the acceptor concentration in the system:

$$[e] = [e_0]e^{-\varkappa[A]},$$

where $\varkappa$ is the electron capture coefficient. The method is based on the determination of the electron capture coefficients. When $[e] \gg [A]$, we have $\varkappa = K$. At fairly high temperatures, $\ln \varkappa T^{3/2}$ varies linearly with $1/T$ and the slope of the straight line is $EA/K$. The intercept which the plot makes on the ordinate axis is not constant. It is believed that the temperature variation of $\varkappa$ is required for the correct determination of $EA$. At low temperatures, $\varkappa$ becomes approximately constant. Many $EA$ values for organic compounds have also been determined using the relative [19] electron capture constant $\varkappa'$.

Thermalised electrons are obtained in the form of secondary electrons when a mixture of gases, usually of methane and argon, is irradiated. Apart from thermalised electrons, radicals and positively charged ions, whose concentration does not vary under standard conditions even when the amounts of the acceptor investigated are small, are generated. The presence of the test gas influences only the concentration of the thermalised electrons. The experimentally determined quantities are [e] and [A]. Their separate determination is based either on the different mobilities of the electron and the acceptor molecule or on the magnetron effect. The latter requires special consideration, since the method based on this effect has come to be called the "magnetron method". The method, introduced for the first time by Sutton and Mayer [38,39], has been used particularly successfully by Page and coworkers [17,40]. The experimental apparatus consists of a cathode, a grid, and an anode mounted within a solenoid. The test substance is introduced in the gaseous state (vapour pressure $10^{-4}$–$10^{-2}$ mmHg). Thermalised electrons are generated by the heated cathode. In the absence of a magnetic field, both the electrons and the radical-anions $A^-$ reach the anode. The magnetic field forces the electrons to move along a circular orbit and they are captured by the grid. The magnetic field has little effect on the motion of $A^-$. Thus it is possible to measure separately the currents generated by the streams of electrons ($i_e$) and radical-anions ($i_i$). Since

$$i_e/i_i = K \cdot \exp(-EA/RT) \quad \text{and}$$

$$-\frac{R\, d\ln(i_e/i_i)}{d(1/T)} = EA(\bar{T}),$$

the slope of the straight line defined by the equation $Rd\ln(i_e/i_i) = cd(1/T)$ is equal to the electron affinity at a temperature $T$. The latter is determined as the average temperature of the cathode in the range where the measurements are made. The electron affinity at 0 K is obtained from the relation $EA_0 = EA(\bar{T}) - {}^3/_2 R\bar{T}$.

The method is unreliable, because the negative ion corresponding to the given species for which $EA$ is to be determined is not identified, which may lead to erroneous results [41]. Small amounts of impurities and products of thermal reactions can also bind electrons and can lead to considerable errors.

### The Method of Charge-Transfer Complexes (CTC)

It is based on the determination of the charge-transfer (CT) energy for complexes of a series of donors with the electron acceptor investigated [19]. The CT energy is usually determined from the CT band maximum. According to Mulliken's theory [5], the CT energy for a weak interaction between the donor and the acceptor can be expressed by the following equation:

$$h\nu_{CT} = IP - EA + G_0 - C + X_1 + X_0 \quad , \qquad (1)$$

where $G_0$ is the energy of all types of interactions between the donor and the acceptor in the ground CTC state, with the exception of the donor–acceptor interaction, $C$ is the energy of the Coulombic interaction between the components in the excited CTC state, and $X_0$ and $X_1$ are the energies of the resonance interaction between $\psi(D, A)$ and $\psi(D^+, A^-)$ in the ground and excited CTC states.

Using the expressions for $X_0$ and $X_1$, it is possible to obtain the following equation:

$$h\nu_{CT} = IP - EA - C - G_0 + \frac{\beta_0^2 + \beta_1^2}{IP - EA - C - G_0},$$

where $\beta_0 = H_0 + S_{01}W_0$ and $\beta_1 = H_{01} - S_{01}W_1$. The latter equation may be simplified because $C$ and $G_0$ can be assumed to be constant for CTCs of the same type with a fairly satisfactory degree of approximation. For a weak interaction between the donor and the acceptor, the overlap integral $S_{01}$ is small, so that $\beta_0$ and $\beta_1$ can also be regarded as approximately constant. Thus we obtain [1]

$$h\nu_{CT} = IP - (EA + E) + \frac{C_1}{IP - (EA + E)}.$$

For small values of $C_1$ and fairly high ionisation potentials, this equation acquires an even simpler form, which is frequently used in investigations [1-4,42-45]:

$$h\nu_{CT} = IP - EA - W, \qquad (2)$$

where $W$ is an approximately constant quantity for the given class of CTC.

In principle, Eqn. (2) can be used directly to calculate the electron affinities of acceptors, provided that $W$ is known. Since its exact value is not known, one usually starts with Eqn. (2), obtaining in this way the following expression for complexes of a common donor with a series of acceptors [19]:

$$h\nu_{CT}^{x} - h\nu_{CT}^{0} = \overset{0}{EA} - EA^{x} + W^{0} - W^{x}, \quad (3)$$

where $EA^0$ and $EA^X$ are the electron affinities of the reference acceptor and the test acceptor respectively.

It is frequently assumed [1-4,19] that $W^0 - W^X = 0$ and Eqn. (3) is simplified in this way is used to calculate $EA^X$. This is apparently justified only for acceptors having a similar structure and when, instead of a single donor, a series of donors are used in order to eliminate specific interactions of the components, since it has been shown [46] that the error resulting from the introduction of the last approximation can reach as much as 0.4 eV. Aromatic hydrocarbons, whose first and second ionisation potentials differ little in terms of energy, are most suitable as donors. *p*-Chloranil is most often employed as the reference acceptor [3,19,47].

## The Method Based on the Study of the Equilibrium Between the Radical-Ion and the Neutral Molecule

It is based on the determination of the equilibrium constant for the reaction

$$A^{\bar{\cdot}} + B \overset{K}{\rightleftarrows} B^{\bar{\cdot}} + A, \quad (4)$$

using spectroscopic analytical methods for this purpose. If the medium is insufficiently polar and ion pairs are present, another equilibrium actually obtains:

$$(A^{\bar{\cdot}}, K^{+}) + B \overset{K'}{\rightleftarrows} (B^{\bar{\cdot}}, K^{+}) + A$$

$$K' = K\frac{K_{diss}(A^{\bar{\cdot}}, K^{+})}{K_{diss}(B^{\bar{\cdot}}, K^{+})},$$

where $K_{diss}$ are the dissociation constants of the ion pairs. In solutions of radical-ions, more complex equilibria can also occur [48]. The enthalpy of reaction (4) is correlated with the difference between the values of $EA$ for the acceptors A and B. The less well-founded equation

$$-RT \ln K' = EA(A) - EA(B).$$

is usually employed [49].

## The Potentiometric Method [15]

The method is based on the measurement of the potential arising in the $A/A^{\bar{\cdot}}$ redox system. A modified method, resembling potentiometric titration, has found the most extensive applications. Measurements are made of the potential between two platinum electrodes, one of which is immersed in a standard redox system $A_0/A_0^{\bar{\cdot}}$ and the other in a solution containing the test redox system $A_X/A_X^{\bar{\cdot}}$. The redox system investigated is obtained by titrating a solution of $A_X$ with a standard solution of $A_0/A_0^{\bar{\cdot}}$. The half-wave potential $\epsilon$ is determined from the titration curve. According to Jagur-Grodzinski et al. [50], it is given by the expression

$$\varepsilon = \varepsilon_0 + 0.03 \ln (K_{A_0}/K_{A_x}) + 0.03 \ln \frac{[A_x, K^{+}]_t}{[A_0, K^{+}]_t}$$

where $\epsilon_0$ is the standard potential of the reaction $A_0^{\bar{\cdot}} + A_X \rightleftharpoons A_X^{\bar{\cdot}} + A_0$, $K_{A_0}$ and $K_{A_X}$ are the dissociation constants of the corresponding ion pairs, and $[A^{\bar{\cdot}}, K^{+}]_t$ is the sum of $(A_0^{\bar{\cdot}}, K^{+})$ and $(A_X^{\bar{\cdot}}, K^{+})$.

The standard potential $\epsilon_0$ is equal to the difference between the electron affinities of $A_X$ and $A_0$, i.e. the method yields the relative electron affinities. The relative electron affinities thus obtained are satisfactorily correlated with the corresponding absolute values for the gas phase, the slope of the straight line being close to unity [15].

## The Polarographic Method

The reversible one-electron reduction of the acceptor A is determined by the following process:

$$A_{solv} + e \rightleftharpoons A_{solv}^{\bar{\cdot}} \quad .$$

The half-wave potential is given by the expression [51]

$$E_{1/2} = E_0 - \frac{RT}{F} \ln \frac{D_1}{D_2},$$

where $E_0$ is the formal or standard potential, $R$ the gas constant, $F$ the Faraday, and $D_1$ and $D_2$ are the diffusion coefficients of the oxidised and reduced forms in the layer near the electrode.

$E_0$ is determined by the energetic characteristics of many processes [19], including the electron affinity of the acceptor A:

$$EA = E_{1/2} - \Delta E_{solv} - 5.07 + \frac{RT}{F} \ln D_1/D_2,$$

where $\Delta E_{solv}$ is the difference between the solvation energies of $A^{\bar{\cdot}}$ and A.

Since the diffusion coefficients $D_1$ and $D_2$ cannot differ by more than 1-2 orders of magnitude, the last term of this equation is negligibly small and can be rejected. Consequently the relation between the electron affinity in the gas phase and the half-wave potential of the reversible one-electron reduction is given by the equation

$$EA = E_{1/2} - \Delta E_{solv} + 5.07 \text{ (eV)} \quad . \quad (5)$$

Since the solvation energies of neutral molecules are small, the quantity $\Delta E_{solv}$ is determined mainly by the solvation energy of the corresponding radical-anion, i.e. $\Delta E_{solv} \simeq E_{solv}^{A^{\bar{\cdot}}}$. The study of the radical-anions of aromatic hydrocarbons [19,51,52] and of other electron acceptors [19] has shown that the solvation energies of radical-anions do not vary significantly with the structure of the delocalised radical-ion. According to Briegleb [19], the differences between the values of $\Delta E_{solv}$ for a series of different electron acceptors in acetonitrile do not exceed ±0.15 eV. A change of solvent can alter the solvation energy to a greater extent and hence also the values of $E_{1/2}$. Thus, when acetone is replaced by dichloromethane [53], the values of $E_{1/2}$ for a series of different acceptors change by 0.31 ± 0.05 V, i.e. the changes in the solvation energies for different radical-ions are approximately the same on passing from one solvent to another. The following equation can therefore be used with an adequate degree of approximation to calculate the electron affinities of acceptors forming delocalised radical-ions:

$$EA \simeq E_{1/2} + C \quad ,$$

$$\Delta EA \simeq \Delta E_{1/2},$$

where $C$ is a constant and $E_{1/2}$ the half-wave potential for polarographic reduction under the same condition.

Apart from the methods described above, other procedures are also available for the determination of electron affinities[21,54], but are not considered here.

## IV. ELECTRON AFFINITIES OF NEUTRAL ELECTRON ACCEPTORS

The vast majority of experimental data have been obtained by methods which do not yield directly the absolute electron affinities, but permit their calculation, provided that one can estimate in some way the remaining unknowns in the equations used to determine $EA$. It is therefore not surprising that the polarographic and CTC methods lead to very different estimates of absolute electron affinities (Table 1) in studies by different investigators. If one considers relative electron affinities obtained for the same estimates of other unknowns, instead of their absolute values, the situation changes radically (Table 1) and the majority of values for a particular acceptor agree to within 0.15 eV. It is also found that the relative electron affinities are satisfactorily correlated (Figs. 2 and 3) with the absolute electron affinities obtained by independent methods (electron capture, magnetron, and mass-spectrometric methods), the slope of the straight lines being close to unity.

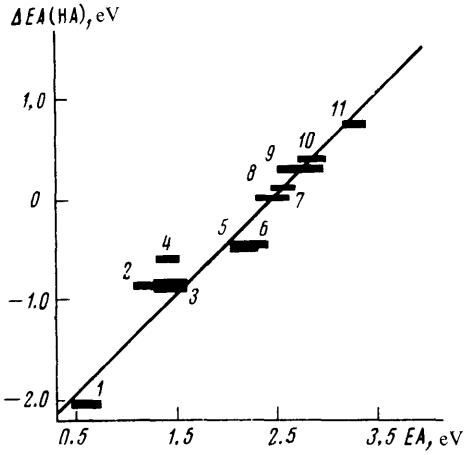



**Figure 2.** Relation between the relative (CTC method, reference acceptor–$p$-chloranil) and absolute electron affinities: 1) acceptor 45, electron capture method; 2) acceptor 144, magnetron method; 3) acceptor 11, mass spectrometric method; 4) acceptor 100, magnetron method; 5) acceptor 104, magnetron method; 6) acceptor 40, magnetron method; 7) acceptor 129, magnetron method; 8) acceptor 44, magnetron method; 9) acceptor 8, magnetron method; 10) acceptor 168, magnetron method; 11) acceptor 10, magnetron method (the acceptors are numbered in accordance with Table 1).

Consequently the problem of determining the absolute electron affinities can be solved by determining the relative electron affinities of different acceptors and by selecting the most probable absolute electron affinity of the reference acceptor–$p$-chloranil (HA). The absolute electron affinities of $p$-chloranil, obtained by the magnetron method, are also listed in Table 1. The validity of the latter results can be assessed in several ways. One of these involves the comparison of the results obtained by different methods using the relative electron affinities; the required data are presented in Table 2.

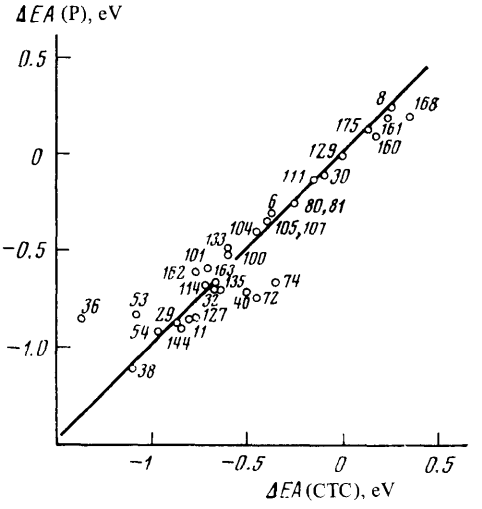



**Figure 3.** Comparison of the results obtained by the CTC and polarographic methods (the acceptors are numbered in accordance with Table 1).

Tbe absolute electron affinity of $p$-chloranil can also be inferred from a more detailed analysis of the results obtained by the polarographic method. Here the principal difficulty consists in the estimation of the solvation energies of the radical-anions arising in the one-electron reduction of the acceptor. Although much attention has been devoted to the determination of the solvation energies of charged species, their exact values are unknown[23,110,111]. This is particularly true of organic radical-anions and is the reason why the polarographic method has yielded two series[14] of electron affinities, differing by 1 eV.

One can assume with a satisfactory degree of approximation that the lower limit to the solvation energies of organic ions in polar solvents is given by the polarisation energies[9] in crystals of non-polar aromatic hydrocarbons, which are of the order[9,112] of 1.5 eV. Since the polarisation energy of negative ions is approximately 0.2 eV higher than that of positive ions and the negative charge of the radical-anions of acceptors is largely localised on the heteroatoms, one can assume that the lower limit to the solvation energies of the radical-anions of organic electron acceptors is approximately 2 eV. Since the solvation energy depends markedly on the charge density, the solvation energy of the iodide ion should probably be regarded as the upper limit, assuming that the charge is more delocalised in any organic radical-anion with a fairly well developed $\pi$-electron system. In aprotic polar solvents, incapable of specific solvation of anions, the solvation energy of the iodide ion[110,113] is approximately 2.5–3 eV. Since $\Delta E_{solv}$ is somewhat smaller than $E_{solv}$, it follows that, in conformity with Eqn. (5), the most probable electron affinity of $p$-chloranil exceeds 2.2 eV.

**Table 1.**

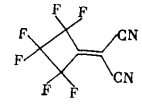
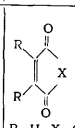
| No. | Compound | *EA*, eV | $\Delta EA^*$, eV | *EA* (abs.), eV | Method** and references |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 1. | Tetranitromethane  | 1.8 | — | 1.8 | EC (Ref.55) |
| 2. | $R_1$=$R_2$=$R_3$=$R_4$=H | −1.8 | — | — | QC (Ref.56) |
| 3. | $R_1$=$COOC_2H_5$; $R_2$=$R_3$=$R_4$=H | 0.25 | — | 0.25 | EC (Ref.19 |
| 4. | $R_1$=$R_3$=$COOC_2H_5$; | 0.6 | — | 0.6 | EC (Ref.19) |
| | $R_2$=$R_4$=H (*trans-*) | 0.8±0.1 | — | 0.8 | MM (Ref.57) |
| 5. | $R_1$=$R_3$=CN; $R_2$=$R_4$=H | — | −0.4 | 2.1 | CTC (Ref.19) |
| 6. | $R_1$=$R_4$=CN; $R_2$=$R_3$=COOH | — | −0.3 | | P (Ref.14,58) |
| 7. | $R_1$=$R_2$=CN; $R_3$=$R_4$=$CF_3$ | — | −0.1 | 2.35 | CTC (Ref.59) |
| | | 2.89±0.1 | — | — | MM (Ref.57) |
| 8. | $R_1$=$R_2$=$R_3$=$R_4$=CN | 1.6 | — | 2.75 | EC (Ref.60) |
| | | — | +0.3 | — | CTC (Ref.19,61) |
| | | — | +0.34 | — | CTC (Ref.62) |
| | | | +0.25 | — | P (Ref.19) |
| 9. |  | | −0.42 | 2.05 | CTC (Ref.59) |
| 10. | Hexacyanobutadiene | 3.3±0.1 | — | 3.2 | MM (Ref.57) |
| | | | +0.7 | — | CTC (Ref.63) |
| 11. |  R=H, X=O | — | −0.83 | — | P, CTC (Ref.19) |
| | | 1.43 | — | — | QC (Ref.64) |
| | | 1.4±0.2 | — | 1.4 | MS (Ref.65) |
| | | — | −1.25 | — | CTC (Ref.66) |
| 12. | R=Cl, X=O | 0.55 | −0.8 | 1.65 | CTC (Ref.66,67) |
| 13. | R=I, X=O | 0.45 | −0.9 | 1.55 | CTC (Ref.67) |
| 14. | X=S, R=Cl | 0.6 | −0.75 | 1.7 | CTC (Ref.68) |
| |  | | | | |
| 15. | R=Cl | 0.4 | — | 0.4 | EC (Ref.19) |
| 16. | R=Br | 0.4 | — | 0.4 | EC (Ref.19) |
| 17. | R=I | 0.54 | — | 0.5 | EC (Ref.19) |
| 18. | R=CHO | 0.43 | — | 0.5 | EC (Ref.69,70) |
| | | — | −1.85 | — | P (Ref.71) |
| 19. | $R=COOCH_3$ | 0.2 | — | ⩾0.2 | EC |
| 20. | R=COF | −0.42 | −1.85 | 0.6 | P (Ref.19,71) |
| 21. | R=COCl | 0.03 | −1.40 | ⩽1.05 | P (Ref.19, 71) |
| 22. | R=COBr | 0.20 | −1.20 | ⩽1.25 | P (Ref.19,71) |
| 23. | $R=NO_2$ | 0.54 | — | — | EC (Ref.19) |
| | | | −1.15 | ⩽1.3 | P (Ref.72) |
| |  | | | | |
| 24. | $R_1$=COCl, $R_2$=$OCH_3$ | −0.13 | −1.55 | ⩽0.9 | P (Ref.19,71) |
| 25. | $R_1$=COCl, $R_2$=$CH_3$ | −0.05 | −1.45 | ⩽1.0 | P (Ref.71) |
| 26. | $R_1$=COCl, $R_2$=$NO_2$ | 0.77 | −0.65 | ⩽1.8 | P (Ref.71) |
| 27. | $R_1$=$R_2$=CHO | 0.21 | −1.17 | ⩽1.3 | P (Ref.71) |
| | | 0.98 | — | — | QC (Ref.63) |
| | | 0.60 | — | — | EC (Ref.73) |
| 28. | $R_1$=$R_2$=COCl | 0.52 | −0.9 | ⩽1.55 | P (Ref.71) |
| 29. | $R_1$=$R_2$=COBr | 0.54 | −0.9 | 1.55 | P (Ref.71) |
| 30. | $R_1$=$R_2$=$COCH_3$ | 0.64 | — | 0.65 | EC (Ref.73) |
| | | 0.95 | −0.47 | 0.9 | P, CTC (Ref.71) |
| 31. | $R_1$=$R_2$=CN | — | −1.65 | — | P (Ref.74) |
| 32. | $R_1$=$R_2$=$NO_2$ | — | −0.7 | ⩽1.75 | P (Ref.75) |
| | | 0.7 | −0.67 | | CTC (Ref.19) |
| 33. | $R_1$=Cl $R_2$=$NO_2$ | — | −1.1 | 1.35 | P (Ref.75) |
| |  | | | | |
| 34. | $R_1$=$R_2$=$COCH_3$ | 0.55 | — | ⩾0.55 | EC (Ref.73) |
| 35. | $R_1$=$R_2$=CN | 1.1±0.13 | — | 1.1 | MM (Ref.57) |
| 36. | $R_1$=$R_2$=$NO_2$ | — | −0.84 | ⩽1.6 | P (Ref.75) |
| |  | | | | |
| 37. | $R_1$=$R_2$=$COCH_3$ | 0.55 | — | 0.55 | EC (Ref.73) |
| 38. | $R_1$=$R_2$=$NO_2$ | — | −0.9 | — | P (Ref.75) |
| | | 0.3 | −1.1 | — | CTC (Ref.19) |
| | | 1.5 | −1.1 | 1.35 | P (Ref.58) |
| | | — | −1.1 | — | CTC (Ref.76) |
| | | — | −1.2 | — | CTC (Ref.77) |
| |  | | | | |
| 39. | $R_1$=$R_3$=$R_5$=CN; $R_2$=$R_4$=$R_6$=H | 0.1 | −1.27 | 1.25 | CTC (Ref.19) |
| | | — | −1.20 | | CTC (Ref.78) |
| 40. | $R_1$=$R_2$=$R_4$=$R_5$=CN; $R_3$=$R_6$=H | — | −0.71 | — | P (Ref.79) |
| | | 0.4 | −0.97 | — | CTC (Ref.19) |
| | | 2.19±0.2 | — | 2.0 | MM (Ref.57) |
| | | 2.15 | — | — | MM (Ref.17) |

**Table 1 (cont'd.)**

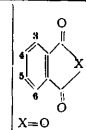
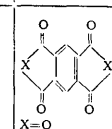
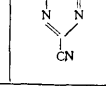
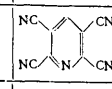
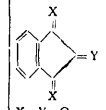
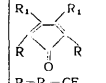
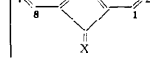
| No. | Compound | *EA*, eV | $\Delta EA^*$, eV | *EA* (abs.), eV | Method** and references |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 41. | $R_1$=$R_2$=CN; $R_3$=$R_4$=$R_5$=$R_6$=Cl | — | −1.0 | 1.45 | CTC (Ref.78 |
| 42. | $R_1$=$R_2$=$R_4$=$R_5$=CN; $R_3$=$R_6$=$CH_3$ | — | −0.8 | 1.65 | CTC (Ref.80) |
| 43. | $R_1$ to $R_5$ = CN; $R_6$ = $CH_3$ | — | −0.3 | 2.15 | CTC (Ref.80) |
| 44. | $R_1$ to $R_6$ = CN | 2.55 | — | — | QC (Ref.64) |
| | | 2.55 | — | 2.55 | MM (Ref.57) |
| | | — | +0.1 | — | CTC (Ref.89) |
| 45. | $R_1$ to $R_6$ = Cl | 0.58 | — | ⩾0.6 | EC (Ref.19) |
| 46. | $R_1$ to $R_6$ = F | — | −2.05 | ⩾0.4 | CTC (Ref.81) |
| 47. | $R_1$=$R_2$=$COCH_3$; $R_3$=$R_4$=$R_5$=$R_6$=Cl | 0.77 | — | 0.8 | EC (Ref.73) |
| 48. | $R_1$=$R_2$=$NO_2$ $R_3$=$CH_3$; $R_4$=$R_5$=$R_6$=H | — | −1.27 | 1.2 | CTC (Ref.19) |
| 49. | $R_1$=$R_2$=$NO_2$ $R_3$=F; $R_4$=$R_5$=$R_6$=H | — | −0.9 | 1.55 | P (Ref.75) |
| 50. | $R_1$=$R_2$=$NO_2$ $R_3$=$R_4$=F; $R_5$=$R_6$=H | — | −0.85 | 1.60 | P (Ref.75) |
| 51. | $R_1$=$R_2$=$NO_2$ $R_3$=OH; $R_4$=$R_5$=$R_6$=H | 0.6 | — | ⩾0.6 | EC (Ref.19) |
| 52. | $R_1$=$R_3$=$R_5$=$NO_2$; $R_2$=$R_4$=$R_6$=H | — | −0.6 | 1.75 | P (Ref.75) |
| | | 0.7 | −0.7 | — | P, CTC (Ref.19) |
| | | 1.86 | −0.74 | | P (Ref.58) |
| | | 2.63 | — | — | MM (Ref.17) |
| | | — | −0.75 | — | CTC (Ref.62) |
| 53. | $R_1$=$R_3$=$R_5$=$NO_2$; | 1.78 | −0.82 | 1.4 | P (Ref.58) |
| | $R_2$=$OCH_3$; $R_4$=$R_6$=H | — | −1.08 | | CTC (Ref.82) |
| | | | | | CTC (Ref.19) |
| 54. | $R_1$=$R_3$=$R_5$=$NO_2$; | 0.6 | −0.77 | | P (Ref.58) |
| | $R_2$=$CH_3$; $R_4$=$R_6$=H | 1.69 | −0.9 | 1.55 | P (Ref.58) |
| 55. | $R_1$=$R_3$=$R_5$=$NO_2$; | 1.7 | −0.9 | 1.95 | CTC (Ref.86) |
| | $R_2$=Cl; $R_4$=$R_6$=H | — | −0.45 | — | CTC (Ref.84) |
| 56. | $R_1$=$R_3$=$R_5$=$NO_2$; | — | −0.25 | 2.2 | |
| | $R_2$=CN; $R_4$=$R_6$=H | | | | |
| 57. | $R_1$=$R_3$=$R_5$=$NO_2$ | — | −0.97 | 1.45 | CTC (ref.19) |
| | $R_2$=$R_4$=$CH_3$; $R_6$=H | | | | |
| |  | | | | |
| 58. | X=O | 0.1 | −1.3 | 1.15 | P (Ref.19) |
| 59. | X=S | 0.38 | −1.0 | ⩽1.45 | CTC (Ref.68) |
| 60. | X=O 3,4,5,6-tetrachloro- | 0.55 | −0.82 | — | CTC (Ref.19) |
| | | — | −0.85 | 1.65 | CTC (Ref.78) |
| | | 1.8 | −0.8 | — | P (Ref.58) |
| 61. | X=O; 3,5-dinitro- | — | −0.34 | 2.1 | CTC (Ref.85) |
| 62. | X=NH | 1.5 | −1.1 | 1.35 | P (Ref.70) |
| |  | | | | |
| 63. | X=O | 0.8 | −0.55 | 1.9 | P, CTC (Ref.19) |
| 64. | X=O, dibromo- | 1.15 | −0.32 | 2.15 | P, CTC (Ref.19) |
| 65. | X=S | — | −0.95 | 1.5 | CTC (Ref.68) |
| 66. |  | — | −0.25 | 2.2 | CTC (Ref.78) |
| 67. |  | 2.18±0.07 | — | 2.2 | MM (Ref.37) |
| |  | | | | |
| 68. | X=Y=O | — | −0.3 | 2.15 | CTC (Ref.86) |
| 69. | X=O; Y=$C(CN)_2$ | — | 0 | 2.45 | CTC (Ref.86) |
| 70. | X=$C(CN)_2$; Y=O | — | +0.2 | 2.65 | CTC (Ref.86) |
| |  | | | | |
| 71. | R=$CF_3$ | — | +0.15 | 2.60 | CTC (Ref.87) |
| 72. | R=$R_1$=Ph | — | −0.45 | 1.85 | CTC (Ref.86) |
| | | | −0.75 | — | P (Ref.88) |
| 73. | R=$C_6H_5OCO$; $R_1$=Ph | — | −0.35 | 1.95 | CTC (Ref.87) |
| 74. | R=Ph; $R_1R_1$=  | — | −0.35 | 1.95 | CTC (Ref.87) |
| | | — | −0.65 | — | P (Ref.88) |
| 75. | R=$C_2H_5OCO$ $R_1R_1$=  | — | −0.15 | 2.15 | CTC (Ref.87) |
| |  X=O | | | | |

**Table 1** (cont'd.)

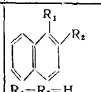
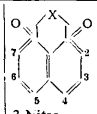
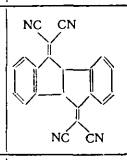
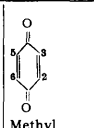
| No. | Compound | *EA*, eV | $\Delta EA^*$, eV | *EA* (abs.), eV | Method** and references |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 76. | 2,7-Dinitro- | — | −0.65 | 1.85 | P (Ref.89) |
| 77. | 3,6-Dinitro- | — | −0.53 | 1.95 | P (Ref.89) |
| 78. | 2,4,7-Trinitro- | — | −0.45 | 2.05 | P (Ref.89) |
| 79. | 2,4,5,7-Tetranitro- X=C(CN)$_2$ | — | −0.3 | — | CTC (Ref.19) |
| | | | −0.25 | 2.2 | P (Ref.89) |
| 80. | 2,4-Dinitro- | — | −0.25 | 2.2 | P, CTC (Ref.89) |
| 81. | 2,5-Dinitro- | — | −0.25 | 2.2 | P, CTC (Ref.89) |
| 82. | 2,6-Dinitro- | — | −0.2 | 2.25 | CTC (Ref.89) |
| 83. | 2,7-Dinitro- | — | −0.25 | 2.2 | CTC (Ref.89) |
| 84. | 3,6-Dinitro- | — | −0.15 | 2.3 | CTC (Ref.89) |
| 85. | 2,4,7-Trinitro- | — | 0 | 2.45 | CTC (Ref.89) |
| | | — | +0.1 | — | CTC (Ref.90,91) |
| 86. | 2,4,5,7-Tetranitro- | — | +0.1 | 2.55 | CTC (Ref.89) |
| |  | | | | |
| 87. | $R_1$=$R_2$=H | 0.15 | — | 0.15 | EC (Ref.92) |
| 88. | $R_1$=COH; $R_2$=H | 0.67 | — | 0.7 | EC (Ref.92) |
| 89. | $R_2$=COH; $R_1$=H | 0.62 | — | 0.6 | EC (Ref.92) |
| |  X=O | | | | |
| 90. | 3-Nitro- | — | −0.67 | 1.8 | CTC (Ref.93,94) |
| 91. | 4-Nitro- | — | −0.67 | 1.8 | CTC (Ref.93) |
| 92. | 3,6-Dinitro- | — | −0.37 | 2.1 | CTC (Ref.93) |
| 93. | 4,5-Dinitro- | — | −0.27 | 2.2 | CTC (Ref.93) |
| 94. | 2,4,5,7-Tetranitro- X=NC$_2$H$_5$ | — | +0.4 | 2.85 | CTC (Ref.93 |
| 95. | 3,6-Dinitro- | — | −0.55 | 1.9 | CTC (Ref.93) |
| 96. | 4,5-Dinitro- | — | 0.45 | 2.0 | CTC (Ref.93) |
| |  | | | | |
| 97. | R=H | 0.57 | — | 0.6 | EC (Ref.95) |
| 98. | R=COH | 1.0 | — | 1.0 | EC (Ref.69) |
| 99. |  | — | +0.1 | 2.55 | P (Ref.96) |
| 100. |  | 1.4 | — | 1.85 | MM (Ref.14,97) |
| | | 1.94 | — | | QC (Ref.64) |
| | | 0.64 | — | | EC (Ref.19) |
| | | | −0.60 | | CTC (Ref.19) |
| | | | −0.52 | | P (Ref.19) |
| | | | −0.7 | | CTC (Ref.3) |
| 101. | Methyl | — | −0.71 | 1.75 | CTC (Ref.19) |
| | | — | −0.6 | | P (Ref.19) |
| 102. | Methoxy- | — | −0.63 | 1.70 | P (Ref.70) |
| 103. | Dimethylamino- | — | −0.76 | 1.60 | P (Ref.70) |
| 104. | Fluoro- | 2.16 | — | 2.05 | MM (Ref.17) |
| | | — | −0.45 | | CTC (Ref.14,19) |
| | | — | −0.39 | | P (Ref.70) |
| 105. | Chloro- | — | −0.35 | 2.05 | P (Ref.19) |
| | | — | −0.37 | | CTC (Ref.19) |
| 106. | Bromo- | — | −0.37 | 2.05 | P (Ref.19) |
| 107. | Iodo- | — | −0.4 | 2.05 | CTC (Ref.19) |
| 108. | Methoxycarbonyl | — | −0.40 | 2.05 | CTC (Ref.70) |
| 109. | Acetyl- | — | 0.32 | — | P (Ref.70) |
| | | — | −0.32 | 2.1 | CTC (Ref.19) |
| | | — | −0.4 | — | CTC (Ref.70) |
| 110. | Trifluoromethyl | — | −0.25 | 2.2 | CTC, P (Ref.70) |
| 111. | Cyano- | — | −0.15 | 2.3 | CTC (Ref.19) |
| | | — | −0.15 | — | P, CTC (Ref.70) |
| 112. | Nitro- | — | +0.1 | 2.55 | P, CTC (Ref.70) |
| | | — | +0.1 | — | CTC (Ref.19) |
| 113. | Phenyl- | — | −0.50 | 1.95 | P, CTC (Ref.70) |
| 114. | 2,6-Dimethyl- | — | −0.77 | 1.65 | CTC (Ref.19) |
| 115. | 2,6-Dichloro- | — | −0.17 | — | CTC (Ref.19) |
| | | — | −0.19 | 2.25 | P (Ref.19) |
| 116. | 2,6-Dibromo- | — | −0.2 | 2.25 | CTC (Ref.19) |
| 117. | 2,6-Dicyano- | — | +1.0 | ⩽3.4 | CTC (Ref.98) |
| 118. | 2,6-Dinitro- | — | +0.38 | 2.85 | CTC (Ref.19) |
| 119. | 2,5-Dimethyl- | — | −0.7 | 1.75 | P, CTC (Ref.19) |
| 120. | 2,5-Di-t-butyl | — | −0.51 | 1.95 | P (Ref.19) |
| 121. | 2,5-Dichloro- | — | −0.22 | 2.25 | CTC (Ref.19) |
| | | — | −0.19 | | P (Ref.19) |
| 122. | 2,5-Dicyano- | — | +0.3 | 2.75 | CTC (Ref.98) |
| 123. | 2,3-Dichloro- | — | −0.27 | 2.2 | CTC (Ref.19) |

**Table 1** (cont'd.)

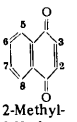
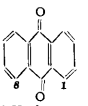
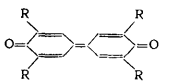
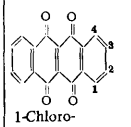
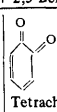
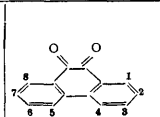
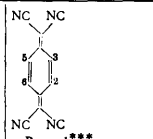
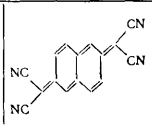
| No. | Compound | *EA*, eV | $\Delta EA^*$, eV | *EA* (abs.), eV | Method** and references |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 124. | 2,3-Dicyano- | — | +0.33 | 2.75 | CTC (Ref.19) |
| | | — | +0.26 | — | CTC (Ref.3) |
| | | — | +0.38 | — | CTC (Ref.49) |
| 125. | 2,3,5-Trimethyl- | — | −0.7 | 1.75 | CTC (Ref.19) |
| 126. | 2,3,5-Trichloro- | — | −0.1 | 2.35 | P, CTC (Ref.19) |
| 127. | Tetramethyl | — | −0.80 | 1.65 | P, CTC (Ref.19) |
| 128. | 3,5,6-Trifluoro-2-methyl | — | −0.25 | 2.2 | P, CTC (Ref.70) |
| 129. | Tetrachloro-(HA) | 2.4 | — | 2.45 | MM (Ref.17) |
| | | 2.46 | — | — | MM (Ref.46) |
| | | 2.59 | — | — | MM (Ref.46,99) |
| | | 2.05 | — | — | MM, CTC (Ref.100) |
| 130. | Tetrabromo- | — | 0 | 2.45 | P, CTC (Ref.19) |
| 131. | Tetrafluoro- | — | −0.05 | 2.4 | P (Ref.102) |
| 132. | Tetraiodo- | — | 0 | 2.45 | P, CTC (Ref.19) |
| 133. | 2,3-Dichloro-5,6-dicyano- | — | +0.54 | 3.0 | CTC (Ref.60) |
| | | — | +0.58 | — | CTC (Ref.19) |
| | | — | +0.5 | — | P (Ref.19) |
| | | — | +0.62 | — | CTC (Ref.49) |
| 134. | Tetracyano- | — | +0.43 | 3.40 | CTC (Ref.19) |
| | | — | +0.97 | — | CTC (Ref.80,98) |
| 135. |  | — | 0.6 | 1.75 | CTC (Ref.87) |
| | | — | −0.67 | — | CTC (Ref.19) |
| | | — | −0.72 | — | P (Ref.19) |
| | | 1.6 | — | — | QC (Ref.64) |
| 136. | 2-Methyl- | — | −0.75 | 1.7 | P (Ref.14) |
| 137. | 2-Hydroxy- | — | −0.82 | 1.65 | CTC (Ref.19) |
| 138. | 5-Hydroxy- | — | −0.5 | 1.9 | P, CTC (Ref.19) |
| 139. | 2-Amino- | — | −0.93 | 1.5 | P (Ref.19) |
| 140. | 2,3-Dichloro- | — | −0.40 | 2.05 | CTC (Ref.46) |
| 141. | 2,3-Dichloro-5-nitro- | — | −0.22 | 2.25 | CTC (Ref.46) |
| 142. | 2,3-Dicyano- | — | +0.28 | 2.70 | CTC (Ref.46) |
| 143. | 2,3-Dicyano-5-nitro | — | +0.33 | 2.80 | CTC (Ref.46) |
| 144. |  | — | −0.87 | 1.55 | CTC (Ref.19) |
| | | — | −0.8 | — | CTC (Ref.87) |
| | | — | −0.95 | — | P (Ref.19) |
| | | 1.15 | — | — | MM (Ref.14) |
| 145. | 1-Hydroxy- | — | −0.67 | 1.75 | CTC (Ref.19) |
| | | — | −0.78 | — | P (Ref.19) |
| 146. | 1,8-Dihydroxy- | — | −0.5 | 1.95 | CTC (Ref.19) |
| 147. | 1,4-Anthraquinone | — | −0.76 | 1.7 | P (Ref.102) |
| 148. | 5,12-Tetracenequinone | — | −0.9 | 1.55 | CTC (Ref.87) |
| 149. | 6,13-Pentacenequinone | — | −1.05 | 1.40 | CTC (Ref.87) |
| |  | | | | |
| 150. | R=H | — | −0.25 | 2.20 | P (Ref.102) |
| 151. | R=Cl | — | +0.34 | 2.8 | CTC (Ref.103) |
| 152. | R=Br | — | +0.36 | 2.8 | CTC (Ref.103) |
| 153. |  | — | +0.05 | 2.5 | CTC (Ref.104) |
| 154. | 1-Chloro- | — | +0.05 | 2.5 | CTC (Ref.105) |
| 155. | 2-Chloro- | — | +0.15 | 2.6 | CTC (Ref.105) |
| 156. | 2-Methoxy- | — | +0.05 | 2.5 | CTC (Ref.105) |
| 157. | 1,2,3,4-Tetrachloro- | — | +0.05 | 2.5 | CTC (Ref.105) |
| 158. | 2,3-Benzo- | — | 0 | 2.45 | CTC (Ref.105) |
| 159. |  | — | −0.32 | 2.15 | P (Ref.102) |
| 160. | Tetrachloro- | — | +0.18 | 2.6 | CTC (Ref.19) |
| | | — | +0.1 | — | P (Ref.19) |
| 161. | Tetrabromo- | — | +0.23 | 2.65 | CTC (Ref.19) |
| | | — | +0.2 | | P (Ref.19) |
| 162. | 3,4-Benzo- | — | −0.77 | 1.85 | CTC (Ref.19) |
| | | — | −0.6 | — | P (Ref.102) |
| | | 1.55 | — | — | QC (Ref.64) |
| 163. |  | — | −0.67 | 1.75 | CTC (Ref.19,14) |
| | | — | −0.67 | — | P (Ref.19) |
| 164. | 3,6-Dinitro- | — | −0.15 | 2.3 | CTC (Ref.14) |
| | | — | −0.2 | — | P (Ref.14) |
| 165. | 2,7-Dinitro- | — | −0.2 | 2.25 | CTC (Ref.14) |
| | | — | −0.30 | — | P (Ref.14) |
| 166. | 2,5-Dinitro- | — | −0.25 | 2.20 | CTC (Ref.14) |
| | | — | −0.35 | — | P (Ref.14) |
| 167. | 2,4,7-Trinitro- | — | −0.1 | 2.35 | P, CTC (Ref.14) |

Table 1 (cont'd.)

| No. | Compound | $EA$, eV | $\Delta EA$*, eV | $EA$ (abs.), eV | Method** and references |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 168. |  | 2.8±0.1 | — | 2.8 | MS (Ref.106) |
| | | — | +0.35 | | CTC (Ref.19) |
| | | — | +0.20 | — | P (Ref.19) |
| | | 2.88±0.2 | — | — | MM |
| 169. | n-Propyl*** | — | +0.12 | — | P (Ref.107) |
| | | — | +0.1 | 2.8 | P (Ref.107) |
| 170. | 2,5-Dimethyl | — | +0.01 | 2.7 | P (Ref.107) |
| 171. | 2,5-Di-isopropyl | — | +0.11 | 2.8 | P (Ref.107) |
| 172. | 2,5-Dicyano- | — | +0.60 | 3.3 | P (Ref.107) |
| 173. | Tetrafluoro- | — | +0.50 | 3.2 | P (Ref.107) |
| 174. | 2,5-Dicyano-3,6-difluoro- | — | +0.74 | 3.4 | P (Ref.107) |
| 175. | 2,3-Benzo- | — | +0.13 | 2.7 | P, CTC (Ref.108) |
| 176. |  | — | +0.2 | 2.9 | P (Ref.109) |

*$\Delta EA$ = EA(X) - EA(HA), where EA(X) and EA(HA) are the electron affinities of the test acceptor and *p*-chloranil respectively, determined by the same method.

**QC = quantum-mechanical calculation; EC = electron capture; MM = magnetron method; CTC = charge-transfer complex method; P = polarography; MS = mass spectrometry.

***For acceptors 169–176, the values of $EA$(abs.) were estimated from the $E_{1/2}$ using tetracyanoquinodimethane as the reference acceptor.

The CTC method constitutes yet another possibility for an approximate estimation of the absolute electron affinity of *p*-chloranil. It is assumed[5] that Eqn. (1) can be simplified to the following expression with a satisfactory degree of approximation for weak $\pi-\pi$ complexes:

$$EA = IP - h\nu_{CT} + g_1 + x_1. \qquad (6)$$

Table 2. Estimation of the electron affinities of *p*-chloranil relative to the absolute electron affinities of other electron acceptors.

| Acceptor | $EA$, eV | Method of determination of $EA$ | $\Delta EA = EA$ (X) $- EA$ (HA), eV | $EA$ (HA), eV |
|---|---|---|---|---|
| Hexachlorobenzene | 0.55 | EC | −2.05 | 2.6 |
| Benzaldehyde | 0.43 | EC | −1.85 | 2.3 |
| Naphthalene | 0.15 | EC | −2.45 | 2.6 |
| Anthracene | 0.57 | EC | −1.95 | 2.5 |
| Maleic anhydride | 1.4±0.2 | MS | 0.85 | 2.25±0.2 |
| 7,7',8,8'-Tetracyano-quinodimethane | 2.88±0.2 | MM | 0.37 | 2.50±0.2 |
| | 2.80±0.1 | MS | 0.37 | 2.43±0.1 |

*CT and CTC methods of determination.
**$EA_{av}$(HA) = 2.45 eV.

The first of the two unknowns $g_1$ and $x_1$ makes the greatest contribution, which in the case of $\pi-\pi$ complexes consist entirely of the Coulombic interaction energies ($C$) between the oppositely charged radical-ions in the excited CTC state. The latter can be estimated and then, using Eqn. (6) in the form

$$EA \geqslant IP - h\nu_{CT} - C, \qquad (7)$$

the absolute electron affinities of the acceptors can be inferred. Several models have been used to estimate $C$.[3,19,114] The model of point charges at the centres of the donor and acceptor molecules must be regarded as the least satisfactory approximation. The use of localised charge models[5,114] showed that the average values of $C$ for $\pi-\pi$ complexes are of the order of 3.3 eV. It follows from Eqn. (6) that $EA$(HA) ≥ 2.3 eV.

Another method for the determination of the absolute electron affinities of $\pi$-electron acceptors may be used on a comparison of the CT energies of their complexes with the CT energies of CTC acceptors of halogen atoms. Comparison of the results of the study of CTC of acceptors differing so greatly may appear incorrect at first sight. However, the characteristics of the complexes belonging to these groups are extremely similar. Thus the enthalpies of formation of the benzene–iodine[114,115] and *o*-xylene–iodine[116] complexes are 0.09 and −0.19 eV respectively. The distances between the components in the CTC of $\pi$-electron donors[115,116] are as follows: 3.36 Å for $Br^-$ complexes[61] and 3.7 Å for $I^-$ complexes[117]. All these characteristics are within the limits of the corresponding characteristics of the $\pi-\pi$ complexes[3]. Consequently the stabilisation energies of the excited CTC states of the $\pi-\pi$ and $\pi$-halogen atom complexes should not differ greatly and the differences between the CT energies (in the presence of a common donor) are approximately equal to the differences between the electron affinities. The electron affinities of the $Br^-$ and $I^-$ acceptors are known fairly well, although the data quoted by different workers[118] vary somewhat: 3.38–3.55 eV for $Br^-$ and 3.08–3.25 eV for $I^-$. According to Buchel'nikova[21], higher values should be used: 3.66 and 3.29 eV. The relevant data are presented in Table 3.

Table 3. Estimation of the electron affinity of *p*-chloranil.

| Donor | Acceptor | | | | $h\nu_{CT}$(X) − $h\nu_{CT}$(HA), eV | $EA$(HA), eV** |
|---|---|---|---|---|---|---|
| | $Br^-$ | | HA (3) | | | |
| | $h\nu_{CT}$, eV | solvent | $h\nu_{CT}$, eV | solvent | | |
| Benzene | 2.21–2.32 | Benzene (Ref.119) | 3.71 | $CCl_4$ | −1.39 – −1.50 | 2.2–2.3 |
| Toluene | 2.15 | Toluene (Ref.119) | 3.25 | $CCl_4$ | −1.10 | 2.56 |
| Naphthalene | 1.82 | | 2.61 | $CCl_4$ | −0.80 | 2.86 |
| | $I^-$ | | | | | |
| Benzene | 2.48–2.67 | Benzene (Ref.119) | 3.71 | $CCl_4$ | −1.03 – −1.23 | 2.2–2.3 |
| Benzene | 2.88 | In gas phase (Ref.12) | 3.90* | In gas phase | −1.0 | 2.3 |
| Toluene | 2.39–2.41 | Toluene (Ref.119) | 3.25 | $CCl_4$ | 0.85 | 2.44 |
| *o*-Xylene | 2.18 | *o*-Xylene (Ref.119) | 3.06 | $CH_2Cl_2$ | 0.88 | 2.41 |
| Mesitylene | 2.10 | Mesitylene (Ref.119) | 2.89 | $CH_2Cl_2$ | 0.79 | 2.50 |

*The polarisation energy was used[121].
**$EA_{av}$(HA) = 2.45 eV.

The data in Tables 1–3 show that the most probable value of the absolute electron affinity of *p*-chloranil is 2.45 ± 0.15 eV. It has been used to calculate the electron affinities of the acceptors for the determination of which there are no data obtained by absolute methods and to refine the electron affinities of the acceptors for which such data are available [Table 1, the values of $EA$(abs.)].

Comparison of the results obtained by different methods (Figs. 2 and 3) makes it possible in its turn to infer the errors; they do not appear to exceed 0.2 eV and in those cases where reliable results found by several methods are available, the error is much smaller.

It is well known that the introduction of substituents can alter greatly the electron affinity. The amino-, methoxy-, and alkyl groups reduce electron affinities, while the nitro-, cyano-, acyl, and alkoxycarbonyl groups as well as halogens increase them. The problem of the possible utilisation of the increments due to various substituents has remained unresolved due to the inaccuracy of the $EA$ values themselves [19]. Nevertheless the employment of empirical increments for substituents would provide the easiest and possibly the most accurate method at the present time for the estimation of the electron affinity of a compound, since quantum-mechanical calculations for large systems with heteroatoms by the Hückel and PPP methods using the Koopmans theorem do not yield reliable results.

The increments due to substituents may be determined by comparing the affinities of the monosubstituted and unsubstituted compounds. We adopted *p*-benzoquinone as the standard system, since a fairly large number of monosubstituted *p*-benzoquinones have been investigated (Table 1, acceptors Nos. 100–113) and the following increments were obtained: −0.15 eV ($CH_3O$); −0.05 eV ($CH_3$); +0.13 eV (F); +0.18 eV (Cl); + 0.19 eV (Br); +0.17 eV (I); +0.20 ($CH_3OCO$); +0.25 eV ($CH_3CO$); +0.30 eV ($CF_3$); +0.43 eV (CN); +0.70 eV ($NO_2$).

The electron affinities of polysubstituted acceptors can be calculated from the general equation

$$EA = EA_0 + C_1 \sum_n I_n - C_2 C_1 \sum_n I_n,$$

where $EA_0$ is the electron affinity of the initial unsubstituted acceptor, $C_1$ a coefficient characterising the sensitivity of the given system to the introduction of substituents, which is determined from measurements for monosubstituted compounds and is unity for *p*-benzoquinones, $I$ are the increments of the substituents, and $C_2$ is a coefficient taking into account the effects of the interaction of the substituents, i.e. the non-additivity in the case of polysubstituted compounds; for monosubstituted compounds, $C_2 = 0$.

It was found that $C_2 = 0.1$ for polysubstituted *p*-benzoquinones and remains constant for a series of other compounds, i.e. the equation for the calculation of the electron affinities of polysubstituted acceptors can be formulated as follows:

$$EA = EA_0 + 0.9C \sum_n I_n \,. \qquad (8)$$

Eqn. (8) and the above series of increments can be used without modification to estimate the electron affinities only in those systems where the effects of the substituents in different positions are approximately the same and the introduction of a new substituent does not alter appreciably the steric structure of the acceptor molecule (the substituent has a small steric effect). Such systems proved to be the derivatives of fluorenone (Table 1, Nos. 76–79) and dicyanomethylenefluorene (Nos. 80–86 with $C_1 = 0.25$), 1,4-naphthoquinone ($C_1 = 0.29$ for substituents in the 5-, 6-, 7-, and 8-positions, and $C_1 = 1.08$ for substituents in the 2- and 3-positions; Nos. 135–143), 7,7′,8,8′-tetracyanoquinodimethane ($C_1 = 0.63$; Nos. 168–174), the anhydride of phthalic acid ($C_1 = 0.75$; Nos. 11–13), *o*-benzoquinone ($C_1 = 0.7$; Nos. 159–161), diphenoquinone ($C_1 = 0.92$; Nos. 150–152), trinitrobenzene with electron-accepting substituents (with small steric effects; $C_1 = 1.1$; Nos. 52, 55, and 56), and ethylene ($C_1 = 1.9$; Nos. 3, 4, 5, 7, and 8).

Among the 45 compounds for which tests were made, the discrepancy between the experimental and calculated electron affinities did not exceed ±0.05 eV for 34 compounds and ±0.1 eV for 8 compounds, exceeding 0.1 eV for only three compounds. This shows that equations of this kind are very promising for the specific synthesis of new electron acceptors. Eqn. (8) also makes it possible to estimate the electron affinities of the unsubstituted initial compounds. A fairly unexpected result is obtained for ethylene: $EA = 0.2$ eV.

An increase of the π-electron system of the acceptor leads to a decrease of the electron affinity, despite the fact that in systems without heteroatoms the opposite behaviour is observed. This shows that, in systems with heteroatoms (they are all powerful electron acceptors), the lowest vacant molecular orbital is to a large extent localised in the part of the molecule which is directly linked to the heteroatom and its additional delocalisation leads to an increase of its energy. Thus the changes observed on passing from maleic anhydride (Table 1, No. 11) to phthalic anhydride (No. 58) and from 7,7′,8,8′-tetracyanoquinodimethane (No. 168) to 11,11′,12,12′-tetracyano-1,4-naphthoquinodimethane (No. 175) are associated with a decrease of the electron affinity by 0.25 and 0.2 eV respectively. In the series of *ortho*-quinones (No. 159, 162, and 163), an increase of the system by one benzene ring reduces the electron affinity on average by 0.2 eV. The linear condensation of benzene rings in *p*-benzoquinone derivatives (Nos. 100, 135, 144, 147, 148, 149) leads to a decrease of the electron affinity on average by 0.1–0.15 eV (per benzene ring) and this behaviour holds satisfactorily throughout the series. On the other hand, an increase of the conjugated π-electron system between the electron-accepting groups leads to an increase of electron affinity (see Nos. 168 and 176).

The replacement of the carbonyl group by the dicyanomethylene group increases electron affinity by 0.25–0.45 eV (Table 1, Nos. 68, 69, 70, 76, 83, 77, 84, 78, 85; 79, 86; 100, 168, 135, 175). In quinonoid systems, the increase is a maximum and is close to 0.45 eV for each dicyanomethylene group (Nos. 100, 168; 135, 175).

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# Compounds of Two-coordinated Phosphorus

N.I.Shvetsov-Shilovskii, R.G.Bobkova, N.P.Ignatova, and N.N.Mel'nikov

A systematic account is given of the available literature data on phosphorus(III) compounds with multiple bonds. The methods of synthesis, the physicochemical properties, and the chemical properties of phosphamethinecyanines, phosphorins, (phosphabenzenes), 1,2,3-diazaphospholes (phosphadiazoles), and other compounds of two-coordinated compounds are considered. The bibliography includes 100 references

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## I. INTRODUCTION

Compounds containing two-coordinated phosphorus were virtually unknown until 1964. It was believed that structures with multiple bonds involving a tervalent phosphorus atom are unstable. The diatomic molecules with one-coordinated phosphorus described previously, namely $P_2$, PN, and PO, were detected only by spectroscopic methods at high temperatures [1-3]. Methinophosphide (phospha-acetylene, carbophosphil) HC≡P could be isolated in the form of a white solid stable at the temperature of liquid nitrogen, but polymerising above −120°C, [4-6] Apart from methinophosphide, its halogeno-, amino-, and hydroxy-derivatives were described [7]. The author demonstrated the monomeric nature of these derivatives by the fact that the phosphorus signals in the $^{31}P$ NMR spectra consist of narrow singlets. Evidence confirming the molecular weight adopted is not quoted in the relevant paper.

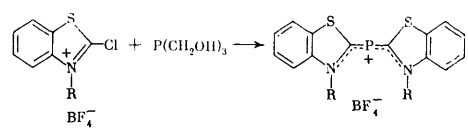
Kirby and Warren [8] compared phosphorus with carbon and nitrogen and adduced a number of causes which explain the greater difficulty of the formation of multiple bonds involving phosphorus(III). The conditions for sufficient overlapping of the orbitals and the formation of $\pi$-bonds are apparently more favourable for the $2p$ orbitals of the atoms of Second Period elements, separated by $2p_\sigma$-bonds, than for the more diffuse $3p$ orbitals of the atoms separated by the longer $3p_\sigma$-bonds. Furthermore the repulsion of the filled inner electron shells of the atoms of the Third Period elements constitute an additional obstacle, hindering the decrease of the bond length required for the formation of strong $p_\pi$-bonds [9]. Hudson [10] and Mulliken [11] suggest that the relative instability of the $\pi$-bonds involving Third Period elements is also caused by the greater energy of their $\sigma$-bonds, in particular by the contribution of the $d\sigma$-orbitals.

Nevertheless, a number of acyclic and cyclic compounds containing two-coordinated phosphorus in CPC (phosphamethinecyanines and phosphorins), CPN (diazaphospholes), and NPN [bis(trimethylsilyl)aminotrimethylsilyliminophosphine and triazaphospholes)] fragments have been synthesised recently.

## II. ACYCLIC COMPOUNDS

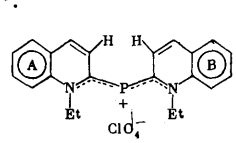
### 1. PHOSPHAMETHINECYANINES

The first compounds of two-coordinated phosphorus–phosphamethinecyanines–were obtained from *N*-alkylated benzothiazolyl fluoroborates and tris(hydroxymethyl)phosphine in the presence of ethyldi-isopropylamine in dimethylformamide [12]:



Symmetrical and asymmetric phosphamethinecyanines were synthesised analogously from benzothiazolium and quinolinium fluoroborates and perchlorates [12-14]. Instead of tris(hydroxymethyl)phosphine, tris(trimethylsilyl)-phosphine may be used to obtain phosphamethinecyanines.[15] The stability of structures with two-coordinated phosphorus is apparently due to the involvement of the phosphorus atom in conjugation. An X-ray diffraction study of the structure of bis-(*N*-ethyl-2-benzothiazolyl)phosphamethinecyanine showed that the planes of both benzothiazole rings are in the *cis*-positions relative to the phosphorus atom and are rotated relative to one another only by 6°. The C–P–C angle is 104.6°. Both C–P bonds have the same length, amounting to 1.76 Å, i.e. they are longer than the P=C bonds in phosphinylides (1.65–1.68 Å) and shorter than the P–C bonds in triphenylphosphine (1.83 Å).[13]

The replacement of benzothiazole by quinoline in phosphamethinecyanines leads to an appreciable change of molecular geometry, as was to be expected from steric considerations [the close proximity of the hydrogen atoms attached to $C_{(3)}$] [16]:

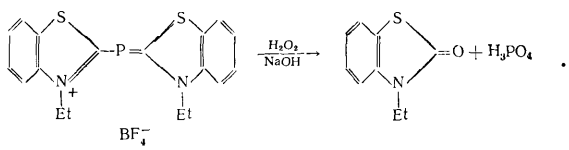


Thus the planes of the quinoline rings A and B are inclined at angles of 40° and 24° relative to the C–P bonds of the cyanine plane. As a result of this, conjugation in the cyanine cation is hindered, which leads to some increase in the length of the C–P bonds, to 1.81 and 1.77 Å, The C–P–C angle in bis-(1-ethyl-2-quinolinyl)-phosphamethinecyanine is 100.4°.

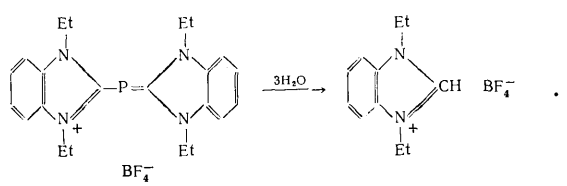
The chemical shift of phosphorus in the $^{31}P$ NMR spectra is −24.9 p.p.m. for bis-(*N*-ethylbenzothiazolyl)-phosphamethinecyanine and −48.8 p.p.m. for the bis-quinolinyl derivative (relative to 85% $H_3PO_4$).

The electronic spectra of phosphamethinecyanines resemble those of monomethine- and monoazamethine-cyanines, the position of $\lambda_{max}$ corresponding to the lower electronegativity of phosphorus compared with carbon and nitrogen [13,14].

The majority of reactions of two-coordinated phosphorus are associated with oxidations involving the phosphorus atom. Phosphamethinecyanines are decomposed by oxidising agents. When treated with 30% hydrogen peroxide in an alkaline solution, the salts of bis-(*N*-alkyl-2-benzothiazolyl)- and bis-(*N*-alkyl-2-quinolinyl)-2-phosphamethinecyanines are smoothly oxidised to 2-benzothiazolone and 2-quinolone derivatives and phosphates. A large number of unidentified radicals are formed at intermediate stages [16]:



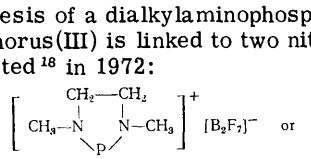
Like methinecyanines, phosphamethinecyanines are protonated by strong acids with formation of colourless dications, which can be reconverted into phosphamethinecyanines by treatment with weak bases [17]. When benzimidazolylphosphamethinecyanine was treated with silver tetrafluoroborate in methanol, colourless crystalline silver complexes, decomposed by an excess of methanol, were isolated. Mercury chloride forms similar complexes with phosphamethinecyanines. Water decomposes phosphamethinecyanines [17]:



## 2. BIS(TRIMETHYLSILYL)AMINOTRIMETHYLSILYLIMINOPHOSPHINE

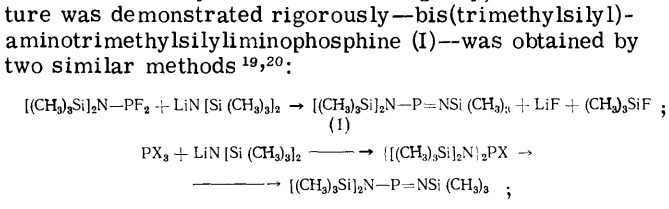
Compounds of two-coordinated phosphorus(III) with a phosphorus–nitrogen multiple bond were unknown until 1972. The reasons for the difficulty of the formation of $p\pi-p\pi$ bonds involving phosphorus(III) were noted above. One need only point out that, whereas the difference between the energies of the σ- and π-bonds for the phosphorus–carbon linkage amounts to 18 kcal mole$^{-1}$, the difference for the P–N linkage is 23 kcal mole$^{-1}$.

The synthesis of a dialkylaminophosphonium cation, in which phosphorus(III) is linked to two nitrogen atoms, was briefly reported [18] in 1972:



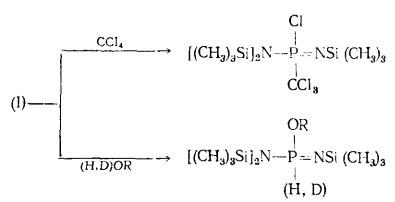
A downfield shift of the $^{31}P$ signal, which is unusual for organophosphorus compounds was noted in the $^{31}P$ NMR spectrum of this cation: $\delta_{^{31}P}$ = −274 p.p.m. (in toluene) and −264 p.p.m. (in 1,2-dichloroethane). The magnitude of this shift constituted the only argument justifying the structure adopted.

The first compound with a –P=N group, whose structure was demonstrated rigorously—bis(trimethylsilyl)-aminotrimethylsilyliminophosphine (I)—was obtained by two similar methods [19,20]:

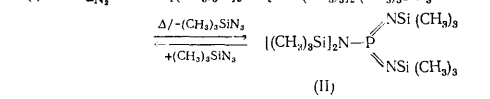


Compound (I) is a yellow-green liquid sensitive to hydrolysis, which is fairly stable in a pure form at temperatures below 0°C and in the absence of light. The composition and structure of the aminoiminophosphine (I) were demonstrated by elemental analysis, mass-spectrometry, and infrared and NMR spectroscopy. The chemical shift of phosphorus is −325.5 p.p.m. This range of chemical shifts had not been reached by any of the phosphorus compounds known hitherto.

The phosphorus atom in bis(trimethylsilyl)aminotrimethylsilyliminophosphine is highly electrophilic, which is manifested in a number of exothermic 1,1-addition reactions [19]:



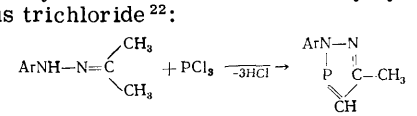
The interaction of bis(trimethylsilyl)aminotrimethylsilyliminophosphine with trimethylsilyl azide leads to phosphine di-imide(II), the first representative of compounds with a three-coordinated phosphorus(V) atom [21]:



## III. FIVE-MEMBERED HETEROCYCLES

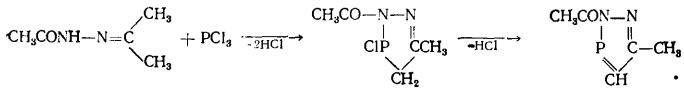
### 1. DIAZAPHOSPHOLES

The first derivatives of 1,2,3-diazaphospholes were synthesised by the reaction of acetone arylhydrazones with phosphorus trichloride [22]:

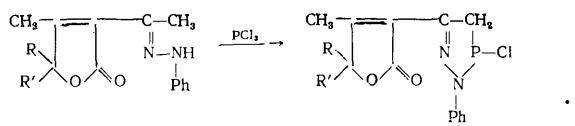


The excess initial phenylhydrazone or triethylamine serves as the hydrogen chloride acceptor. The phenylhydrazones of alkyl methyl ketones and acetaldehyde, β-cyanoethyl-, benzoyl-, and butoxycarbonyl-hydrazones of acetone, and β-cyanoethylhydrazones of acetophenone and *p*-bromoacetophenone react similarly with phosphorus trichloride[22-28].

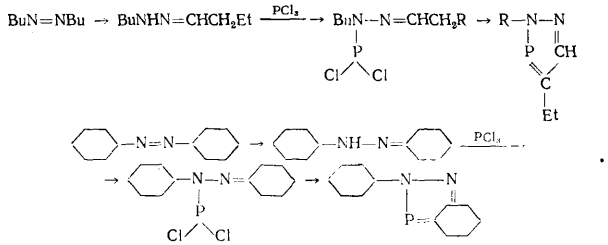
The reaction of phosphorus trichloride with acetone acetylhydrazone under the same conditions leads to 2-acetyl-3-chloro-5-methyl-1,2,3-diazaphospholine, which is converted into 1,2,3-diazaphosphole by additional treatment with triethylamine[24,26-29]:



The formation of 3-chlorodiazaphospholines was also observed when the phenylhydrazones of 2-acetyl-2-but-4-enolides reacted with phosphorus trichloride[30]:



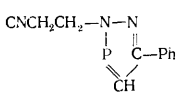
A new method of synthesis of diazophospholes from azo-compounds and phosphorus trichloride was published in 1974. The reaction mechanism involves the isomerisation of the azo-compound to hydrazones[31]:



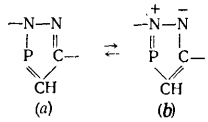
It is interesting to note that, having replaced phosphorus trichloride by arsenic trichloride in the reaction with hydrazones, Märkl obtained a series of arsadiazoles[32,33].

## (a) Physicochemical Properties

An X-ray diffraction study of 2-(β-cyanoethyl)-5-phenyldiazaphosphole[34]



showed that the five-membered heterocycle and the benzene ring are planar (the maximum deviation of the atoms from their average planes does not exceed 0.01 Å), the mutual rotation of the planes of the rings is by an angle of only 16.1°, and the $C_{(2)}-C_{(3)}$ bond is coplanar with the planes of both rings, so that the conjugation between the two fragments is unaffected. The P–N and P=C bond lengths are respectively 1.676 and 1.702 Å, i.e. corespond to partial double bond character. The C=N bond length (1.34 Å) is comparable to the value (1.32 Å) found for the diazomethane molecule and the N–N bond length (1.34 Å), although appreciably smaller than the value corresponding to a single bond, is nevertheless characteristic of the bonds between nitrogen atoms of the type =N–N=. Finally, $C_{(1)}-C_{(2)}$ (with a length of 1.41 Å) is a typical linkage with a bond order of 1.5. The observed distribution of bond lengths in the diazaphosphole ring corresponds to partial delocalisation of electrons with structure *a* predominating to some extent:



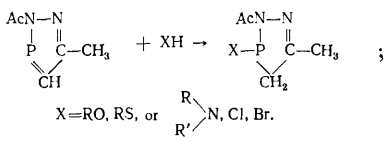
X-Ray diffraction analysis confirmed that 2-(β-cyanoethyl)-5-phenyldiazaphosphole is not dimeric, since the atoms of the closest molecules in the unit cell are separated by a distance greater than the van der Waals radius. The results of the X-ray diffraction study of 2-(β-cyanoethyl)-5-phenyldiazaphosphole are consistent with earlier electron-diffraction data[23,29] for 2-acetyl-5-methyldiazaphosphole and 5-methyl-2-phenyldiazaphosphole.

The ultraviolet spectra of diazaphosphole are similar to those of the corresponding triazoles. There is a bathochromic shift due to the lower electronegativity of phosphorus compared with nitrogen. The wavenumber of the most intense band (1295 $cm^{-1}$) in the infrared spectra of diazaphospholes was assigned to the pulsating (puckering?) vibration of the ring. The lower value of this wavenumber compared with those of the pulsating vibrations of pyrazoles, triazoles, and oxadiazoles can be explained by the greater mass of the phosphorus atom in the ring[22].

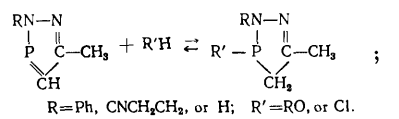
The chemical shift of phosphorus, determined by the method of double phosphorus–proton resonance, is −225 p.p.m. for 2-phenyldiazaphosphole and −238 p.p.m. for 2-acetyldiazaphosphole.

## (b) Chemical Properties

A wide variety of compounds with an active hydrogen atom readily add to the multiple bonds of diazaphospholes, which has been investigated in greater detail for 2-acetyl-4-methyldiazaphosphole. The latter reacts readily with alcohols, amines, phenols, mercaptans, nitrogen-containing heterocycles, and hydrogen halides[28]:



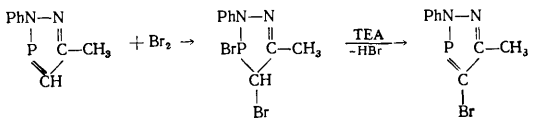
When alcohols and hydrogen chloride add to 2-phenyldiazaphosphole and when alcohols add to 2-(β-cyanoethyl)-diazaphosphole and diazaphospholes unsubstituted in the 2-position, the products are diazaphospholines, which are thermally unstable and are readily reconverted into the initial compounds[35]:



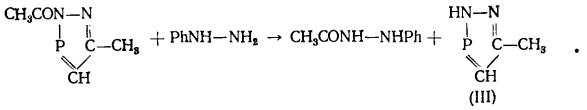
On treatment with an excess of alcohol or alkali, diazaphospholes decompose to hydrazones and phosphites.

Bromine also adds to the C=P bond of 2-phenyldiazaphosphole, giving rise to the unstable 3,4-dibromo-5-methyl-2-phenyldiazaphosphole, the formation of which was confirmed by the PMR method. On treatment of the

reaction mixture containing the above compound with triethylamine (TEA), 4-bromo-5-methyl-2-phenyldiazaphosphole was obtained[35]:



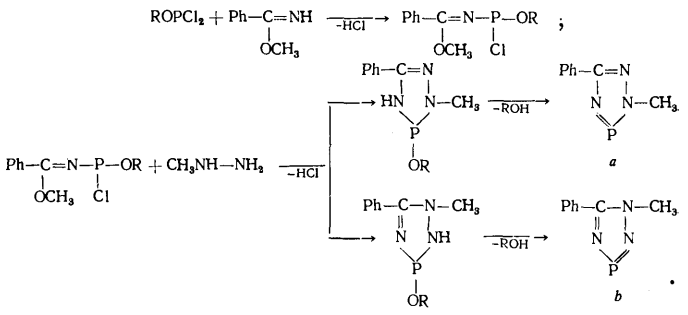
The reaction of 2-acetyl-5-methyldiazaphosphole with phenylhydrazine leads to β-acetylphenylhydrazine and a diazaphosphole unsubstituted in the 2-position: 5-methyldiazaphosphole(III):



The structure of compound (III) was demonstrated by infrared spectroscopy, NMR, and mass spectrometry[35].

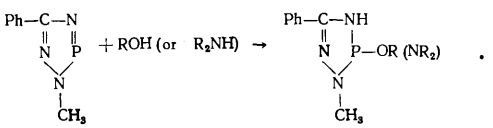
## 2. TRIAZAPHOSPHOLES

Triazaphospholes were synthesised from *O*-methyl iminobenzoate, phosphorodichloridite, and methylhydrazine[36]:



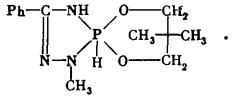
Structure *a* and *b* were attributed on the basis of NMR spectra to the isomeric substances obtained, the ratio of the isomers being 6 : 1. The chemical shifts of the triazaphospholes are −256.1 and −261 p.p.m. respectively.

One of the isomeric triazaphospholes (isomer *a*) is involved in the 3,4-addition reaction with certain alcohols and amines:

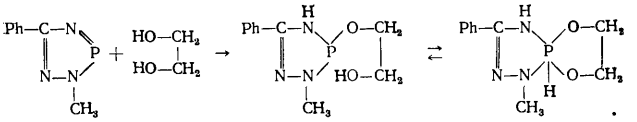


The occurrence of this reaction was inferred[36] from the change in the signals in the $^{31}P$ NMR spectra. When an attempt is made to vacuum-distill them, the addition products are reconverted into the initial triazaphosphole.

The reaction of triazaphospholes with catechol and pinacone leads to spirophosphoranes:



The reaction with ethylene glycol results in the formation of an equilibrium mixture[36]:



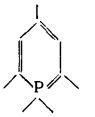
## IV. SIX-MEMBERED HETEROCYCLES

### 1. PHOSPHORINS

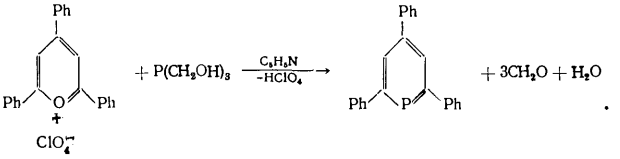
#### (a) Methods of Preparation

The majority of phosphorin derivatives have been obtained by the reaction of pyrylium salts with phosphines. The general methods for the synthesis of phosphorins also includes the thermolysis of 1-substituted dihydrophosphorins and 1,1-disubstituted phosphorins, the rearrangement of methylenephosphacyclohexadienes, and the reaction of 1,1-dibutyl-1,4-dihydrostannanes with phosphorus tribromide.

Phosphorin derivatives with a phosphorus(V) atom have been synthesised by Märkl[37,38] from cyclic phosphonium salts and by Price[39] from pyrylium fluoroborates by reaction with phenylphosphine:



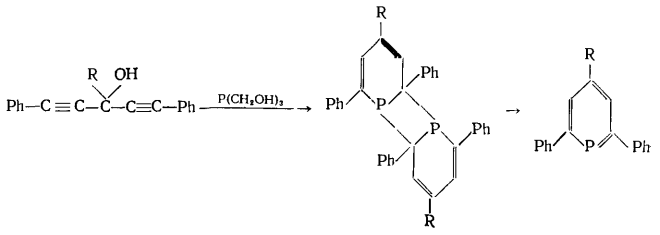
Using tris(hydroxymethyl)phosphine instead of phenylphosphine in the reaction with pyrylium fluoroborate and pyridine as the base and solvent, Märkl synthesised 2,4,6-triphenylphosphorin:



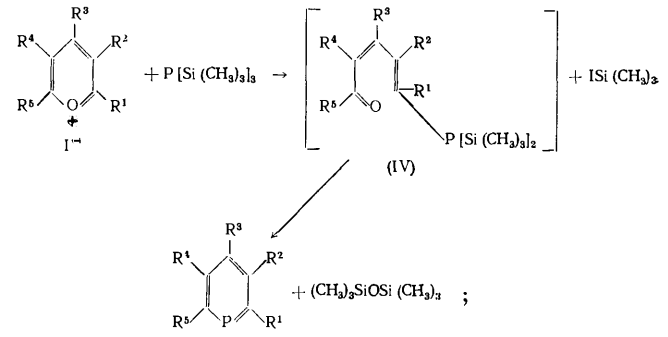
2,4,6-Triphenylphosphorin is a pale-yellow crystalline substance with a melting point of 172–173°, which is readily soluble in organic solvents[40,41]. Tolmachev and Kozlov[42] obtained by the same procedure, involving the reaction of 2,4,6-triarylpyrylium perchlorate with tris-(hydroxymethyl)phosphine, and almost simultaneously with Märkl, a series of arylphosphorins. 4-Indolyl- and 4-pyrrolylpyrylium salts react similarly with tris(hydroxymethyl)phosphine[42,44].

The first phosphorin derivative containing only aliphatic substituents was obtained from 2,4,6-tri-t-butylpyrylium tetrafluoroborate and tris(hydroxymethyl)phosphine[45]. The reaction of tris(hydroxymethyl)phosphine with 1,5-diphenylpenta-1,4-diyn-3-ol gave a phosphorin

dimer, which can be cleaved to the monomeric phosphorin by thermal and photochemical reactions[46]:



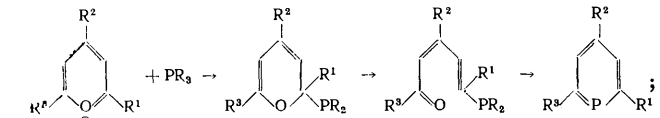
Märkl et al.[15] suggested that tris(trimethylsilyl)phosphine be used to obtain phosphorin derivatives instead of tris(hydroxymethyl)phosphine. In this case there is no need for solvents with basic properties and the yield of substituted phosphorins increases:



$R^1=R^5=$Ph, $p$-$CH_3C_6H_4$, $p$-$CH_3OC_6O_4$; $R^2=R^4=$H,Ph; $R^3=$Ph, or $p$-$CH_3OC_6H_4$ .

However, when tris(trimethylsilyl)phosphine is used to synthesise phosphorin derivatives, the second reactants can be only pyrylium iodides. The fluoroborates and perchlorates are unsuitable in view of the weak nucleophilic properties of the anions. The intermediate compound (IV) was not isolated, since spontaneous elimination of hexamethyldisiloxane leads to ring closure with formation of a substituted phosphorin.

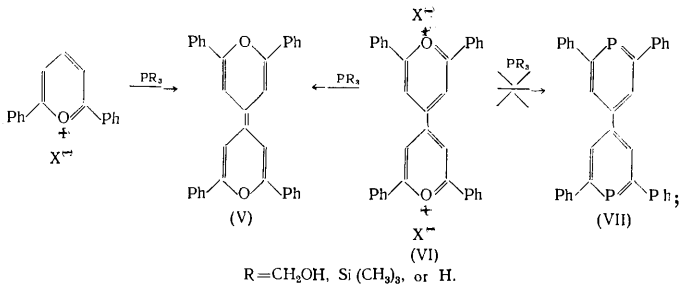
Together with tris(hydroxymethyl)- and tris(trimethylsilyl)-phosphines, unsubstituted phosphine can also be used to synthesise substituted phosphorins. 2,4,6-Trialkylphosphorins, the synthesis of which is hindered by steric factors, have been obtained with the aid of unsubstituted phosphine. The greater the difference between the dimensions of the substituents in the pyrylium salt and of the phosphine molecule, the easier the nucleophilic attack by phosphine on the carbon atom in the 2-position of the pyrylium salt. Subsequently the reaction leads to the formation of a substituted phosphorin:



R=$CH_2OH$, Si $(CH_3)_3$, or H; $R^1$, $R^2$, $R^3$=$CH_3$, or Ph.

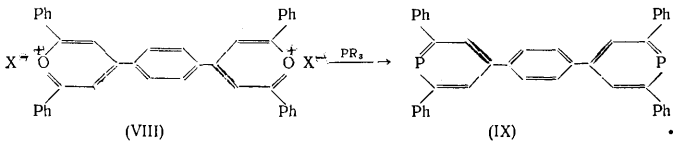
The use of unsubstituted phosphine, whose molecule is much smaller than those of tris(hydroxymethyl)- and tris(trimethylsilyl)-phosphines, extended the scope of the method for the synthesis of phosphorin derivatives. The reaction with unsubstituted phosphine is carried out under the conditions of acid catalysis at 120–130°C.[47]

The method of synthesis of phosphorin derivatives by the reaction of pyrylium salts with phosphines is unsuitable for salts without a substituent in the 4-position. In this case the $C_{(4)}$ atom is involved in the reaction and 2,2′,6,6′-tetraphenyldipyrylene (V) is formed[48,49]:



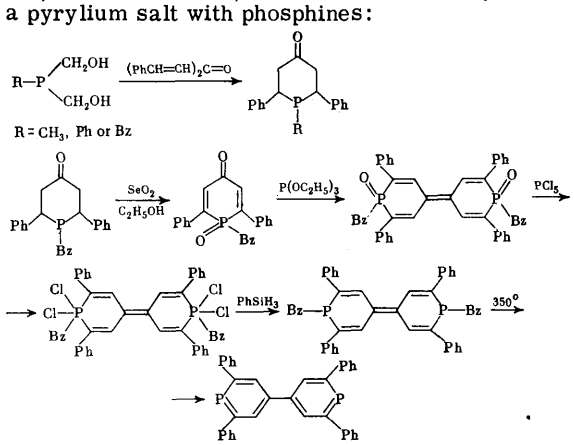
R=$CH_2OH$, Si $(CH_3)_3$, or H.

On reaction with tris(hydroxymethyl)phosphine, tris-(trimethylsilyl)phosphine, and unsubstituted phosphine, the bispyrylium salt (VI) is reduced to the dipyrylene (V) and does not give rise to the diphosphapyrylene (VII). On the other hand, the pyrylium salt (VIII) reacts under analogous conditions to form the phosphorin derivatives (IX) in a low yield (up to 15%):

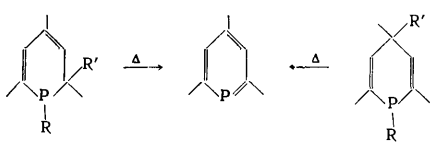


The authors[48,49] attribute this finding to the difference between the redox potentials of compounds (VI) and (VIII).

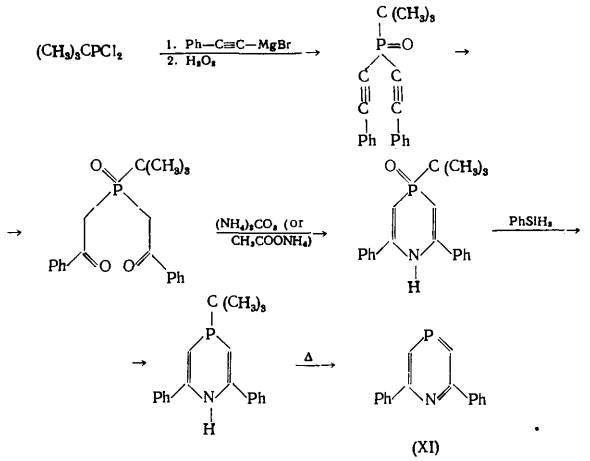
**Thermolysis of 1-substituted dihydrophosphorins and 1,1-disubstituted phosphorins.** Märkl et al.[49] proposed the following cycle of reactions for the synthesis of diphosphapyrylene (VII), which, as stated above, cannot be obtained by the reaction of a pyrylium salt with phosphines:



The thermolysis of 1,1′-dibenzyl-1,1′-diphospha-4,4′-pyrylene (X) is the first example of the synthesis of phosphorins with a two-coordinated phosphorus atom from 1-substituted dihydrophosphorins[45]. The reaction is general, which Märkl and coworkers showed in relation to the thermolysis of a series of 1-substituted 1,4- and 1,2-dihydrophosphorins:

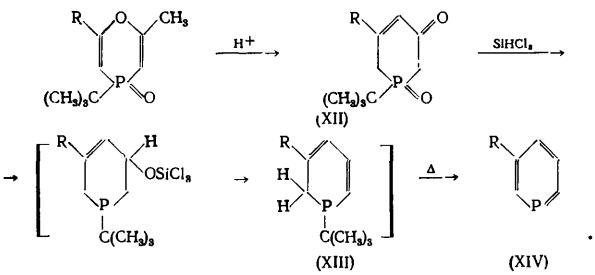


This procedure made it possible to synthesise a wide variety of substituted phosphorins, many of which had been unknown previously[49-52]. Thus a heterocyclic compound containing a nitrogen atom in the six-membered ring together with a two-coordinated phosphorus atom—2,6-diphenyl-1,4-azaphosphorin or phosphapyridine (XI)—was obtained by Märkl and Matthes[50] by means of a scheme based on the thermolysis of 1-substituted 1,4-dihydrophosphorins:



(XI)

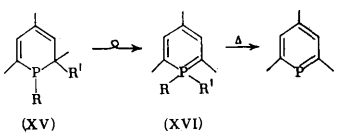
3-Arylphosphorins (XIV), which cannot be synthesised by the reaction of pyrylium salts with phosphines, can be obtained[53] from the readily available 1-t-butyl-3-R-phosphacyclohex-3-ene-1,5-diones (XII) [54]:



(XII) (XIII) (XIV)

The resulting 1-t-butyl-3-R-1,2-dihydrophosphorin (XIII) apparently undergoes thermolysis in the last stage of the reaction.

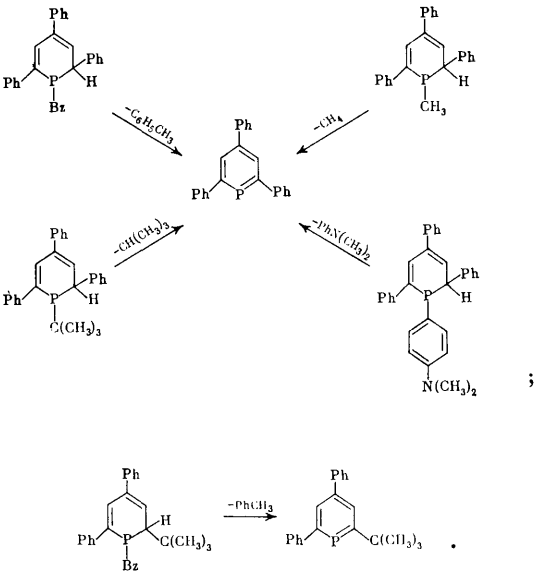
Märkl and Merz[51] showed that the thermolysis of 1-substituted 1,2-dihydrophosphorins involves the migration of the substituent from the 2-position and the formation of 1,1-disubstituted phosphorins in the first stage:



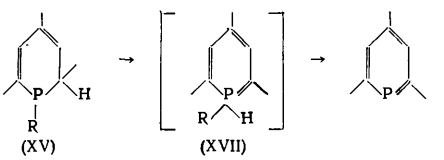
(XV) (XVI)

A similar rearrangement of 1-substituted 1,2-dihydrophosphorins (XV) to 1,1-disubstituted phosphorins (XVI) is the first example of the transformation of tertiary phosphines into phosphinoalkylenes and can be accounted for solely by the stabilisation of the phosphorin system as a result of conjugation. The conditions for the rearrangement depend on the substituents R and R′. Thus the temperature of the rearrangement is 220° for R = $C_6H_5$ and R′ = $CH_2C_6H_5$, 180°C for R = R′ = $CH_2C_6H_5$, 220°C for R = $C_6H_5$ and R′ = $CH_2CH{=}CH_2$, and 25°C for R = $CH_2C_6H_5$ and R′ = $C(C_6H_5)_3$.

1-Alkyl- and 1-aryl(2*H*)-dihydrophosphorins are cleaved similarly to phosphorins:



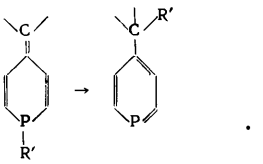
According to the authors[51], the mechanism of this reaction when the latter involves compounds (XV, R′ = H) also consists of the conversion of 1-alkyl(aryl)-2*H*-dihydrophosphorins into 1-alkyl(aryl)-1*H*-phosphorins with subsequent synchronous 1,1-elimination:



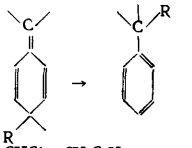
(XV) (XVII)

The authors draw an analogy between this process and the spontaneous N–H → P–H isomerisation of cyclophosphazadienes to cyclotriphosphazenes[55]. Since the formation of 1-R-1*H*-phosphorins (XVII) has not been demonstrated unambiguously hitherto, one cannot rule out the possibility of 1,2-elimination.

Rearrangement of methylenephosphacyclohexadienes to phosphorins. Continuing the investigation of the thermal behaviour of phosphorus-containing heterocycles, Märkl and Fischer[56] found yet another method for the synthesis of phosphorin derivatives substituted in the 4-position. This involves the rearrangement of methylenephosphacyclohexadienes to phosphorins:

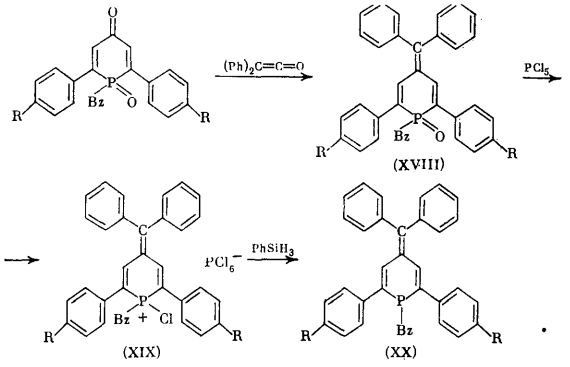


A similar rearrangement of carbocyclic compounds has been known for a long time[57]:

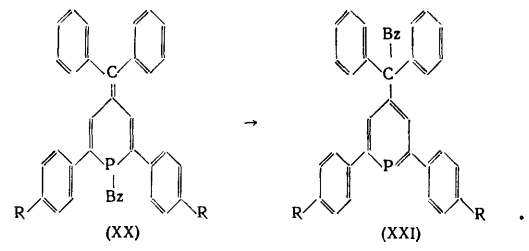


R=$CCl_3$, $CHCl_2$, $CH_2C_6H_5$, or $CH_2CH{=}CH_2$.

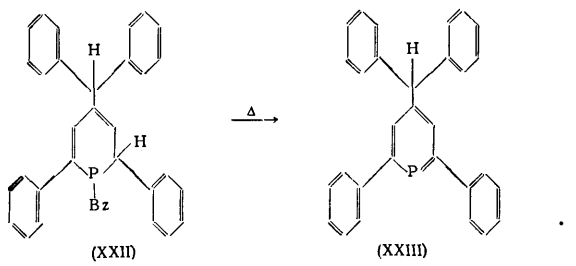
Märkl and Fischer[56] studied the thermolysis of 1-benzyl-4-methylene-1-phosphacyclohexa-2,5-diene (XX), synthesised via the following scheme:



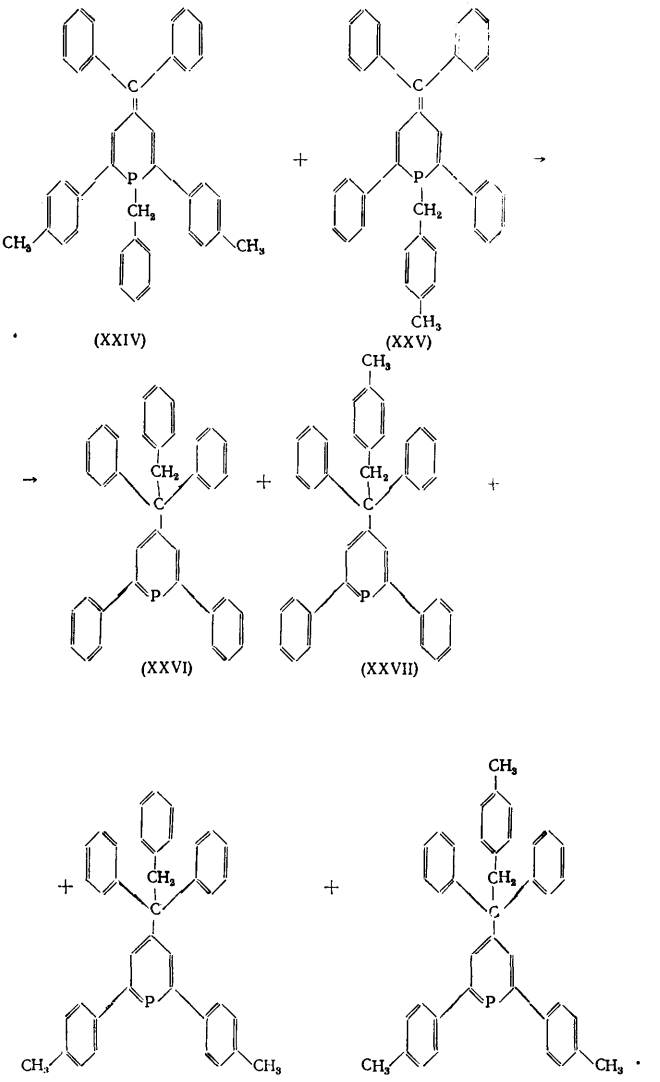

At the melting point (250°C), the resulting methylenephosphacyclohexadiene (XX) undergoes the above rearrangement. This leads to the quantitative formation of a phosphorin derivative (XXI) with a two-coordinated phosphorus atom:




It is interesting to note that the reaction of the oxide (XVIII) in which R = H with phosphorus pentachloride unexpectedly does not lead to the dark-red hexachlorophosphate (XIX) and gives rise instead to yellow hygroscopic salt of unknown structure, whose reduction with phenylsilane gives the 1,2-dihydrophosphorin derivative (XXII). The latter undergoes thermolysis, like the dihydrophosphorin described above, with elimination of toluene and the formation of the phosphorin (XXIII)[56]:



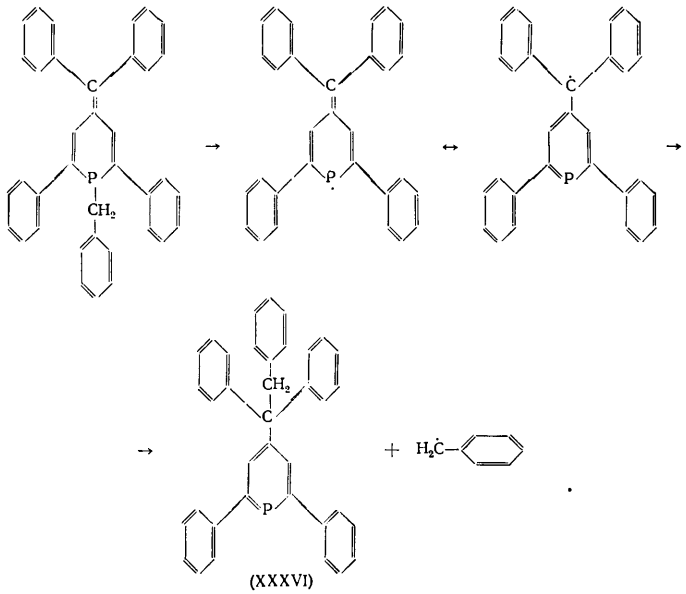

A mass-spectrometric study[58] of the thermolysis products of a mixture of 1-benzyl-4-diphenylmethylene-2,6-di-*p*-tolyl-1-phosphacyclohexa-2,5-diene (XXIV) and 2,6-diphenyl-4-diphenylmethylene-1-*p*-xylylphosphacyclohexa-2,5-diene (XXV) revealed the presence of four reaction products, which supports an intermolecular mechanism of the rearrangement:




The rearrangement probably has a radical mechanism. This hypothesis is based on the analogies, in the first place, with tertiary phosphines, for which thermal heterolytic dissociation of the P–C bond is unknown, and, in the second place, with 1,1-dibenzylphosphorins, the thermolysis of which results in the formation of bibenzyl, which demonstrates the formation of benzyl radicals. The radical mechanism of the rearrangement has been confirmed by experimental data.

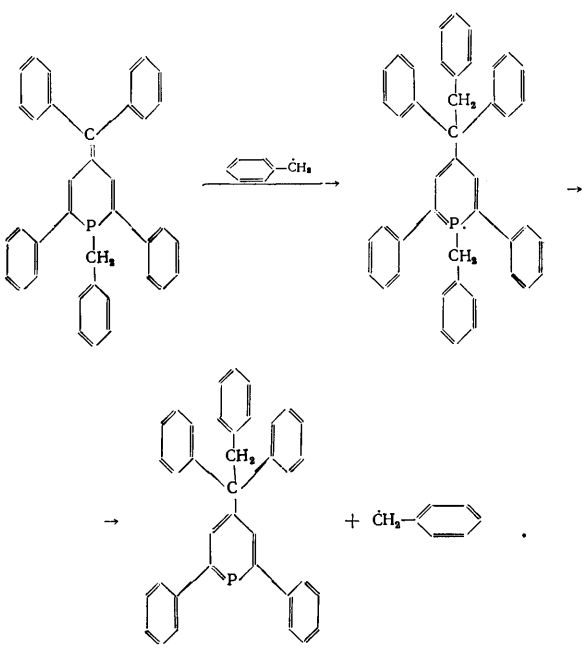
The benzyl radicals formed from Hg $(CH_2C_6H_5)_2$ are capable of becoming involved in the rearrangement of methylene phosphacyclohexadiene. Thus the rearrangement of 1-*p*-xylyl-1-phosphacyclohexadiene (XXV) in the presence of $Hg(CH_2C_6H_5)_2$ entails the formation of the benzylphosphorin (XXVI) together with the xylylphosphorin

(XXVII). The probable mechanism of this rearrangement is as follows[58]:

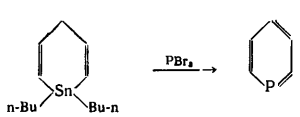


(XXXVI)

According to the authors, the benzyl radical formed reacts immediately with 1-benzyl-1-phosphacyclohexadiene, by analogy with the carbocyclic "semibenzene–benzene" rearrangement, which has been thoroughly investigated:

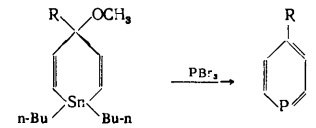


The reaction of phosphorus tribromide with 1,1-dibutyl-1,4-dihydrostannanes. The hitherto unknown unsubstituted phosphorin was synthesised by the reaction of phosphorus tribromide with 1,1-dibutyl-1,4-dihydrostannane[59]:

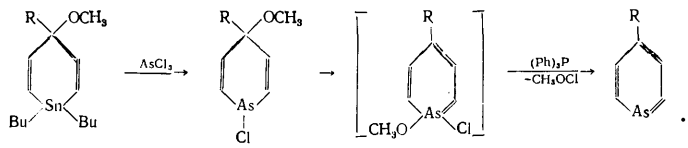


Unsubstituted phosphorin is a colourless liquid, unstable in air, with the characteristic smell of phosphine[59]. In this compound, the properties of the ring are not masked by the effect of substituents, which were to some extent responsible for the interest in its synthesis.

The above method was used by Märkl and Kneidl[60] to obtain previously unknown 4-monosubstituted phosphorins from 4-substituted 4-methoxy-1,4-dihydrostannanes:



The mechanism of the reaction was examined in relation to the synthesis of arsenic compounds–arsenines, obtained when phosphorus tribromide is replaced by arsenic trichloride:



(b) Physicochemical Properties

The ultraviolet, infrared, and PMR spectra of unsubstituted phosphorin are similar to those of pyridine[59]. The magnetic anisotropy of the heteroatom is manifested by a downfield shift of the signals of $\alpha$-protons in the PMR spectrum and an upfield shift of the signals of the protons attached to $C_{(3)}$ and $C_{(4)}$. The 1515 and 1395 $cm^{-1}$ lines in the infrared spectrum of phosphorin have been assigned to the ring vibrations. $\lambda_{max}$ = 213 $\mu$m ($\epsilon$ = 19 000) and 246 $\mu$m ($\epsilon$ = 8500) as well as a shoulder at 290 $\mu$m ($\epsilon$ = 250) have been noted in the ultraviolet spectrum of phosphorin, i.e. there is a bathochromic shift relative to pyridine and benzene, which is associated with the fact that phosphorus is less electronegative than nitrogen and carbon.

An X-ray diffraction study of 2,6-dimethyl-4-phenylphosphorin showed that the molecule has 2($C_2$) symmetry, the symmetry axis passing through the phosphorus atom and the most remote carbon atom of the phenyl substituent. Both six-membered rings are planar within the limits of the accuracy of the X-ray diffraction analysis. The dihedral angle between the rings is 38.8°C, i.e. approaches the angle of 42° found for biphenyl. The C–P–C angle is 103° and may be compared with the values found for triphenylphosphine (103°) and phosphamethinecyanines. Since the phosphorin ring is planar, the remaining P–C–C and C–C–C angles are greater than 120°. A similar increase of the angles occurs also in the pyridine molecule. The P–C bond length is 1.75 Å, i.e. is comparable to the 1.76 Å bond length found for bis-(*N*-ethyl-2-benzothiazolyl)phosphamethinecyanine. The C–C bond lengths are virtually the same as in benzene[61,62].

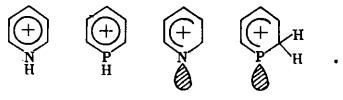
In the ultraviolet spectra of substituted phosphorins, $\lambda_{max}$ is in the range 258–299 $\mu$m and there is also a bathochromic shift relative to the analogous pyridines and aromatic hydrocarbons. The chemical shift $\delta_{^{31}P}$ in the NMR spectra is −178.2 p.p.m. for 2,4,6-triphenylphosphorin and −178.5 p.p.m. for 2,4,6-tri-t-butylphosphorin

(relative to 85% $H_3PO_4$).[40,63] Such a large downfield displacement of the signal is explained by the effect of the magnetic anisotropy of the $-P=C\langle$ multiple bond.

The introduction of nitrogen into a system containing a two-coordinated phosphorus atom leads, as expected, to a downfield shift of the $^{31}P$ signals. Thus $\delta_{31P} = -245.4$ p.p.m. for 2,6-diphenyl-1,4-azaphosphorin (XI).[50]

NMR, ultraviolet spectroscopic, and X-ray diffraction data led to the conclusion that phosphorins are aromatic. This has bene confirmed by calculations of the electronic structures of phosphorins by the CNDO/2 method, which showed that the main contribution to $\pi$-bonding comes from the $3p_z$ orbital of phosphorus together with an appreciable contribution of the $d_\pi$ orbitals[64-66].

The CNDO/2 method also made it possible to estimate the basicity of phosphorin[65]. By analogy with pyridine, basic properties might have been expected for phosphorin, but calculations disproved this hypothesis. The calculated proton affinities of pyridine and phosphorin are 328 and 232 kcal mole$^{-1}$ respectively. Since the true experimental proton affinities of these molecules are unknown, Oehling and Schweig[65] obtained "experimental" values of 213 kcal mole$^{-1}$ for pyridine and 192 kcal mole$^{-1}$ for phosphorin by comparing the experimental and theoretical proton affinities of $NH_3$ and $PH_3$. The difference between the proton affinities of 21 kcal mole$^{-1}$ corresponds to a difference of 15 units between the $pK_a$ values. Thus it is found that the basicity of two-coordinated phosphorus(III) in phosphorin is just as low as that of the perchlorate and iodide anions ($pK_a = -9$ for $HClO_4$ and $pK_a = -8$ for HI). However, the low $pK_a$ predicted for the phosphorinium ion protonated at the phosphorus atom [the ion (XXVII)] does not imply that phosphorin cannot be more easily protonated at other atomic centres. Indeed primary [preliminary] calculations have shown that protonation in the 2-position is much more preferable for phosphorin [the ion (XXVIII)]:



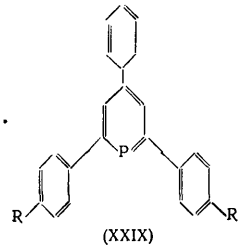
(XXVII) (XXVIII)

Data obtained from the photoelectronic spectra of substituted phosphorins permitted certain conclusions[89]. As was to be expected, phosphorins ionise more readily than the corresponding pyridines, but, the energies of the molecular orbitals of pyridines and phosphorins differ little. The authors suggest that the difference between the energies of molecular orbitals in the pyridine and phosphorin series is probably associated with the contribution of the atomic orbitals of the heteroatom and the neighbouring carbon atoms. The highest occupied molecular orbital (HOMO) of phosphorin is a molecular $\pi$-orbital, while in pyridine it is the orbital of the free electron pair of the nitrogen atom. The free electron pair of the phosphorus atom has a greater amount of *s* character than that of the nitrogen atom in pyridine. The electron pair of phosphorus occupies a more diffuse orbital than that of nitrogen. The sequence of $\pi$-orbitals in the phosphorin system differs from that in pyridine.

Molecular $\pi$-orbitals with a non-zero coefficient at the heteroatom have a higher energy than the molecular $\pi$-orbitals with a node at the heteroatom[64-66].

(c) Chemical Properties

Oxidation. The oxidation of 2,4,6-triphenylphosphorin (XXIXa) by various phenoxy-radicals proceeds via a radical mechanism[69], which is confirmed by the ESR spectrum where the constant for the hyperfine interaction of the unpaired electron with the nucleus of the phosphorus atom $a_p = 23.2$ G.

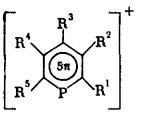


(*a*) R=H; (*b*) R=$OCH_3$

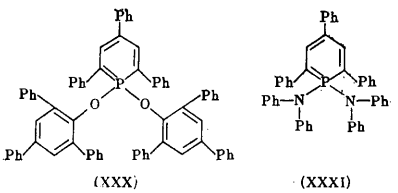
(XXIX)

The spectrum is independent of the structure of the oxidant, which leads to the conclusion that there is no linkage between the phenoxy-group and the phosphorus-containing group.

2,4,6-Tri-t-butylphenoxy-a and 2,6-di-t-butyl-4-phenylphenoxy-radicals do not oxidise 2,4,6-triphenylphosphorin. Probably either the t-butyl group causes steric hindrance to the reaction or the oxidation-reduction potential of the phenoxy-radical is insufficient. The decrease of the oxidation-reduction potential of compound (XXIX) as a result of the introduction of two *p*-methoxy-groups into the phenyl substituents [compounds (XXIXb)] makes it possible to carry out the oxidation even with lead dioxide. This leads to the formation of the analogous phosphorus-containing radical. According to Dimroth et al.[70], this species has the structure of a radical-cation:

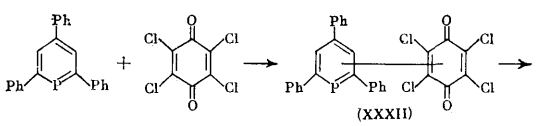


When 2,4,6-triphenylphosphorin reacts with two moles of 2,4,6-triphenylphenoxy-radicals, the product is 2,4,6-triphenyl-1,1-bis-(2,4,6-triphenylphenoxy)phosphorin (XXX). The reaction of tetraphenylhydrazine with 2,4,6-triphenylphosphorin yields 2,4,6-triphenyl-1,1-bis-(diphenylamino)phosphorin (XXXI)[71]:

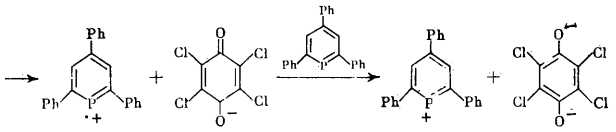


(XXX) (XXXI)

Dimroth and Stade[71,72] investigated the oxidation of triphenylphosphorin by tetrachloro-*p*-benzoquinone. The complex (XXXII) without electron transfer is apparently formed initially, but, when a polar solvent, for example acetonitrile, is added, a doublet with $a_p = 23.2$ G due to the radical-cation (XXXIII) appears in the ESR spectrum:

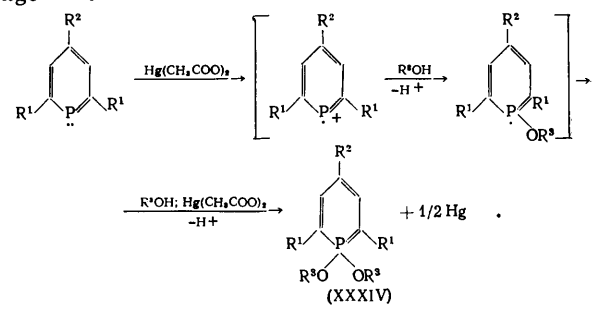


(XXXII)



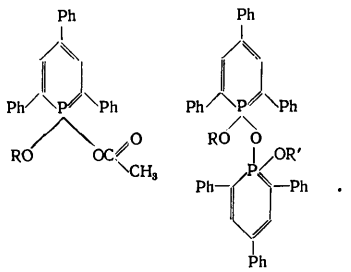
(XXXIII)

When 2,4,6-trisubstituted phosphorins are oxidised by mercury (II) acetate in the presence of an excess of an alcohol of phenol, mercury is liberated and 1,1-dialkoxy- or 1,1-diaryloxy-phosphorins (XXXIV) are formed. The process also probably proceeds via a radical-cation stage [72,73]:

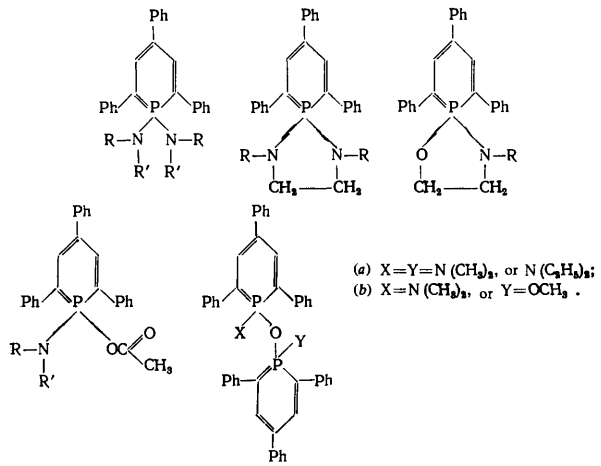


(XXXIV)

A change in the conditions of this reaction leads to the formation of phosphorins belonging to new classes: 1-acetoxy-1-alkoxyphosphorins and substituted bis-(1-alkoxy)hydroxyphosphorins [74]:

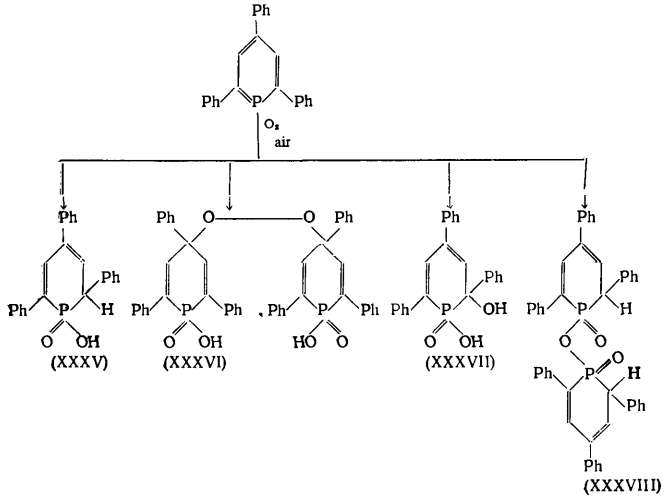


Compounds of the first type described above are formed from trisubstituted phosphorins on oxidation with mercury(II) acetate in dry benzene with one equivalent of alcohol. Those of the second type have been obtained in the presence of 1.5 equivalents of alcohol and one equivalent of water. Depending on the reaction conditions, the following types of compounds have been obtained on oxidation with mercury(II) acetate in the presence of amines [74]:



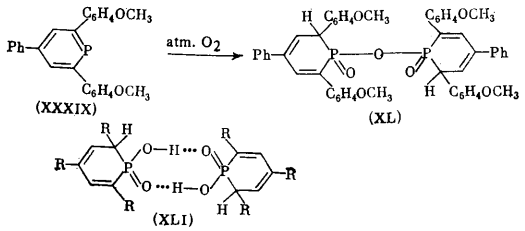
(a) X=Y=N(CH$_3$)$_2$, or N(C$_2$H$_5$)$_2$;
(b) X=N(CH$_3$)$_2$, or Y=OCH$_3$.

Several 2,4,6-trisubstituted phosphorins have been oxidised by atmospheric oxygen [75,76]. The oxidation of 2,4,6-triphenylphosphorin in benzene solution has been examined in greatest detail [76]; it led to the isolation of compounds (XXXV), (XXXVI), and a substance of unknown structure having the composition $C_{46}H_{36}O_3P_2$. In an earlier investigation [75], the structures of the 2-hydroxyphosphinic acid (XXXVII) and the phosphinic acid anhydride (XXXVIII) were attributed to the products of the oxidation of 2,4,6-triphenylphosphorin by atmospheric oxygen:



(XXXV) (XXXVI) (XXXVII) (XXXVIII).

Compound (XL) is formed from 2,6-bis-(4-methoxyphenyl)-4-phenylphosphorin (XXXIX) on oxidation with atmospheric oxygen, while 2,4,6-triphenyl- and 2,4,6-tri-t-butylphosphorins give rise to the dimer (XLI) under the same conditions:

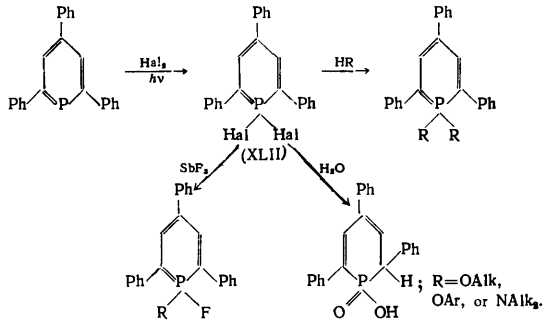


(XXXIX) (XL)

(XLI)

Compounds (XLI) were obtained also on oxidation of 2,4,6-tri-t-butyl- and 2,4,6-triphenyl-phosphorins with hydrogen peroxide in acetone [75,76]. Hydrogen peroxide in ethanol cleaves 2,4,6-tri-t-butylphosphorin, which entails the formation of tri-t-butyl 3,5-di-t-butyl-2-furyl ketone in 30% yield [45].

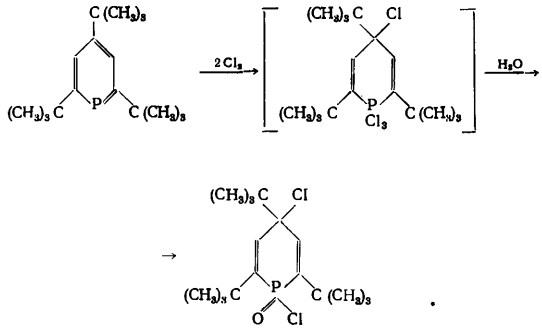
Kanter and Dimroth [77] oxidised 2,4,6-triphenylphosphorin with bromine and chlorine in the light and obtained 1,1-dihalogenophosphorins (XLII), which readily undergo nucleophilic substitution reactions with water, alcohols, amines, and antimony trifluoride:



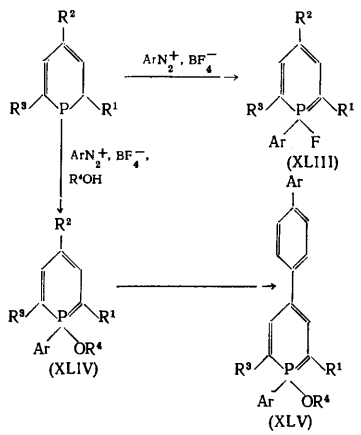
(XLII)

R=OAlk, OAr, or NAlk$_2$.

It was shown earlier that 2,4,6-tri-t-butylphosphorin may combine with two moles of chlorine [77]. This involves the formation of 2,4,6-tri-t-butyl-1,1,1,4-tetrachlorophosphorin, which readily hydrolysss and gives rise to a 4-chlorophosphinyl chloride:



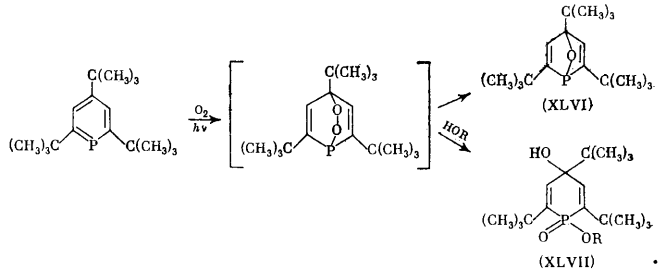
The interaction of trisubstituted phosphorins with aryldiazonium tetrafluoroborates results in the evolution of nitrogen and the formation of 1-aryl-1-fluorophosphorins (XLIII).[78] If the reaction is carried out in the presence of an alcohol, the products are 2,4,6-trisubstituted 1-alkoxy-1-arylphosphorins (XLIV):



The authors [78] suggest that the phosphorin is oxidised initially by the aryldiazonium ion. The oxidation product (a radical cation) then reacts with the aryl radical and the nucleophile (alcohol or $F^-$ ion derived from $BF_4^-$) to form a 1,1-addition product. In alcohol in the presence of an excess of aryldiazonium tetrafluoroborate, the doubly arylated phosphorin (XLV) is formed together with compound (XLIV). The former can also be obtained directly from compound (XLIV) and the diazonium salt.

When 2,4,6-tri-t-butylphosphorin was oxidised in dry cyclohexane using a mercury lamp in the presence of eosin as the sensitiser, two crystalline compounds were obtained in 15% yield. The structures (XLVI) and (XLVII) were attributed to them on the basis of the results of elemental analysis and infrared and ultraviolet spectroscopic, NMR, and mass-spectrometric measurements [79].

Compound (XLVII) is also obtained when 2,4,6-tri-t-butylphosphorin is oxidised with a mixture of nitric and phosphoric acids. Photochemical oxidation of 2,4,6-triphenylphosphorin leads to a large number of products which are difficult to separate.



Attempts to use concentrated perchloric and sulphuric acid solutions as oxidants for triphenylphosphorin have been described in the literature. Oxidation did occur under these conditions, but the reaction products could not be isolated [75].

Thus the mode of oxidation of phosphorins depends on the oxidant employed, the reaction conditions, and the nature of the substituents in the phosphorin ring. Depending on these factors, the oxidation either involves the phosphorus atom with formation of 1,1-disubstituted phosphorins, or it involves the 1,2- or 1,4-positions with formation of oxidised derivatives of 1,2- or 1,4-dihydrophosphorins, or the phosphorin ring is disrupted.

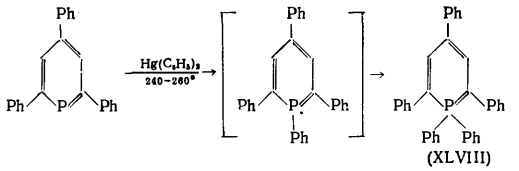
Reduction of phosphorin. Phosphorin derivatives are capable of being reduced to radical-ions [80]. ESR has shown that, when 2,4,6-triphenylphosphorin is reduced with a potassium mirror or a sodium–potassium alloy in tetrahydrofuran, stable radical-anions are formed with a constant for hyperfine interaction of the unpaired electron with the phosphorus nucleus $a_P = 32.4$ G. When a benzene solution of the radical-cation (with $a_P = 23.2$ G),[69] obtained by oxidising triphenylphosphorin, is added to a solution of the radical-anion, the signals of both radicals in the ESR spectra vanish and triphenylphosphorin is reformed.

On being reduced, 2,4,6-triphenylphosphorin can combine with three electrons in succession and the reaction products can likewise give up three electrons in succession. In the absence of air, all three reduction products (radical monoanions, non-radical dianions, and radical-trianions) persist for a long time.

Electrophilic properties of the phosphorin system. As noted above, theoretical calculations by the CNDO/2 method established the presence of weak basic properties in phosphorins. Märkl and coworkers [40] demonstrated experimentally that phosphorins do not exhibit nucleophilic properties. Thus 2,4,6-triphenylphosphorin is not alkylated by methyl iodide or triethyloxonium fluoroborate, reacting instead with nucleophiles and radical reagents.

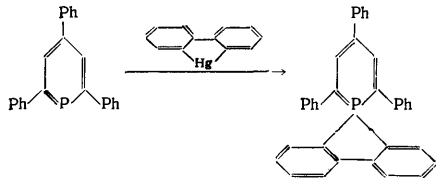
The reaction of triphenylphosphorin with diphenylmercury, involving the formation of 1,1-diarylphosphorins (XLVIII), probably proceeds via a radical mechanism.

Such oxidative arylation probably takes place via the formation of the 1,2,4,6-tetraphenylphosphorinyl radical:

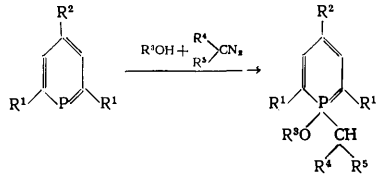


(XLVIII)

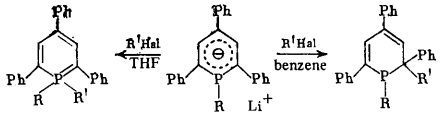
The reaction of diphenylenemercury with 2,4,6-triphenylphosphorin gives a 20% yield of spiro-1,1-diphenylene-2,4,6-triphenylphosphorin[81]:



Trisubstituted phosphorins readily react with diazoalkanes[82] to form 1-alkoxy-1-alkylphosphorins in the presence of alcohols and phenols. It is suggested that the reaction begins with nucleophilic attack by diazoalkanes on the phosphorus atom:

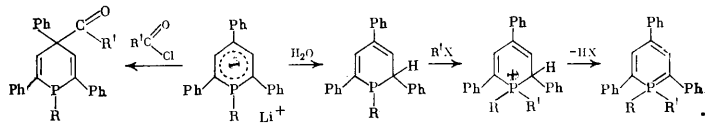


Powerful nucleophiles such as alkyl- and aryl-lithium and organomagnesium compounds react with 2,4,6-triphenylphosphorin even at room temperature[15,83]. The base adds directly to the phosphorus atom with formation of the anion (XLIX), which has ambident properties and has reaction centres in the 1-, 2-, 4-, and 6-positions[84]. In complex-forming solvents such as tetrahydrofuran and 1,2-dimethoxyethane, electrophilic substitution by reaction with alkyl halides takes place preferentially in the 1-position with formation of a 1,1-disubstituted phosphorin (L). In non-polar solvents, for example in benzene, a 2-alkyl-1,2-dihydrophosphorin (LI) is formed:



(L) (XLIX) (LI)

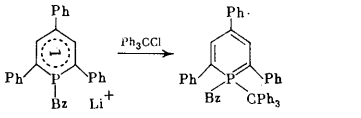
Electrophilic substitution as a result of reaction with acid chlorides takes place in the 4-position and the products are 4-acyl-1,4-dihydrophosphorins (LII). Hydrolysis of the anion (XLIX) leads to 1,2-dihydrophosphorins (LIII):



(LII) (XLIX) (LIII)

The alkylation of the anion (XLIX) by alkyl halides apparently proceeds both via an $S_E1$ and an $S_E2$ mechanism. The reaction involving the $S_E2$ mechanism proceeds via the more nucleophilic centre—the phosphorus atom; when the $S_E1$ mechanism operates, centres with a higher electron density react, i.e. the carbon atoms in the 2-, 4-, and 6-positions. The reaction mechanism depends not only on the solvent used but also on the nature of the alkyl halide. The reaction with alkyl halides via the $S_E2$ mechanism leads to the formation of 1,1-disubstituted phosphorins (L, R′ = $CH_3$ or $C_2H_5$). In the reactions with alkyl halides forming a stabilised carbonium ion, alkylation takes place in the 2-position and leads to the dihydrophosphorins (LI, R′ = $CH_2C_6H_5$ or $CH_2$–CH=$CH_2$).[84]

As noted above[49], 1-substituted 1,2-dihydrophosphorins (LI) are capable of rearranging to 1,1-disubstituted phosphorins (L), while the reverse rearrangement of compounds (L) to (LI) is impossible. This probably accounts for the, at first sight, unexpected formation of the 1,1-disubstituted phosphorin (LV) in the reaction of the anion (LIV) with chlorotriphenylmethane. The structure of the alkyl halide suggested that in this case the reaction should proceed via the $S_E1$ mechanism with formation of a 1,2-disubstituted 1,2-dihydrophosphorin[84]:

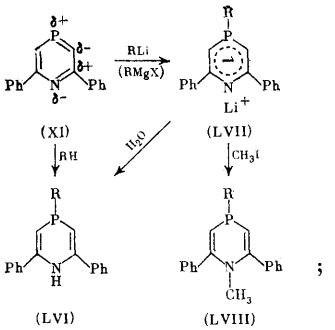


(LIV) (LV)

Presumably the 1,2-dihydrophosphorin formed immediately rearranges to a 1,1-disubstituted phosphorin (LV).

The replacement of carbon by nitrogen in the phosphorin enhances the electrophilic properties of the system[50]. Thus 2,6-diphenyl-1,4-azaphosphorin (XI) reacts readily not only with organometallic compounds but also, in contrast to phosphorins, with weaker nucleophiles such as phenols, alcohols, amines, and mercaptans. In the latter case, addition in the 1,4-positions takes place with formation of the corresponding 1,4-dihydro-derivatives (LVI).

The azaphosphorin (XI) reacts with organometallic compounds to form initially the mesomeric anion (LVII), which then interacts with water and is alkylated, also with formation of the 1,4-dihydro-derivatives (LVI) and (LVIII):

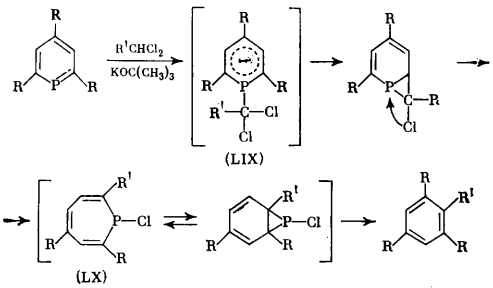


(XI) (LVII) (LVI) (LVIII)

R = R′O, R′S, or $R'_2N$ .

The reactions of phosphorins with carbenes. When 2,4,6-triphenyl-, and 2,4,6-tri-t-butyl-phosphorins react with the halogenomethanes $CH_2Cl_2$, $CHCl_3$, and $C_6H_5CHCl_2$ in the presence of potassium

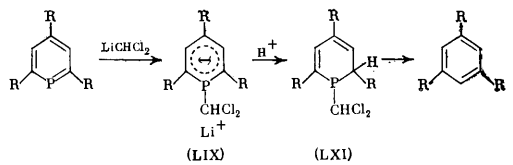
t-butoxide, phosphorus is eliminated and benzene derivatives are formed[85]. On the basis of a series of analogies, the authors suggest the following reaction mechanism:



(LIX)

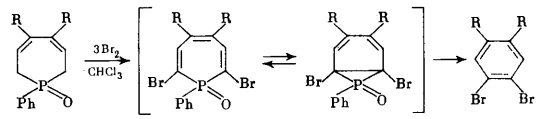
(LX)

The intermediate anion (LIX) is probably formed via a process resembling the reaction of 2,4,6-triphenylphosphorin with dichloromethyl-lithium. The dark-red 1-dichloromethylphosphorin anion (LIX) is formed in tetrahydrofuran at −80°C. Its protonation by glacial acetic acid gives 1-dichloromethyl-2,4,6-triphenyl-1,2-dihydrophosphorin (LXI), which was identified by PMR.[85] This compound is unstable and is readily converted into an aromatic hydrocarbon:



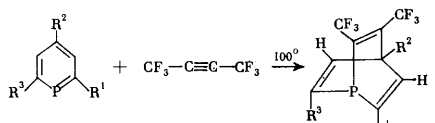
(LIX) (LXI)

As for the reaction of the intermediate phosphepin (LX), the authors found that the reaction of 4,5-dimethoxycarbonyl-1-oxo-1-phenyldihydrophosphepin (LXII) with bromine results in the formation of a 4,5-dibromophthalate ester (LXIII):



(LXII) (LXIII)

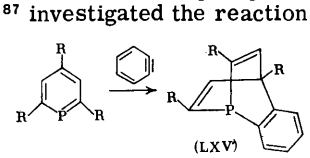
The Diels–Alder reaction in the series of phosphorin derivatives. 2,4,6-Trisubstituted phosphorins are involved in diene synthesis only with highly reactive dienophiles but under milder conditions than aromatic hydrocarbons. For example, hexafluorobutyne reacts[86] with substituted phosphorins at 100°C, while the reactions with benzene and durene take place only at 200°C:



(LXIV)

Apart from hexafluorobutyne, the Diels–Alder reactions of dicyanoacetylene, diethyl acetylenedicarboxylate, and maleic anhydride with phosphorins were investigated[86]. In all cases cycloaddition takes place exclusively in 1,4-positions with formation of 1-phosphabarrelenes (LXIV).

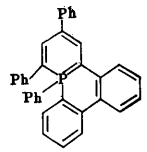
Märkl et al.[87] investigated the reaction of phosphorin with arynes:



(LXV)

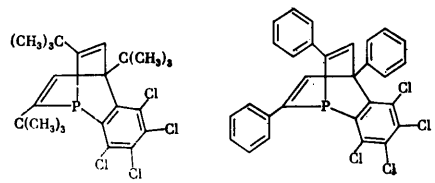
They suggest that the reaction may proceed via the intermediate formation of ambident phosphorin anions.

The reaction of 2,4,6-triphenylphosphorin with dehydrobenzene yields, in addition to the phosphabarrelene (LXV), a 1 : 2 adduct to which the structure (LXVI) was attributed on the basis of spectroscopic data:



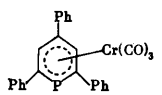
(LXVI)

Pentachlorophenyl-lithium reacts with 2,4,6-tri-t-butyl- and 2,4,6-triphenyl-phosphorins, again forming benzophosphabarrelenes [compounds (LXVII) and (LXVIII)]:



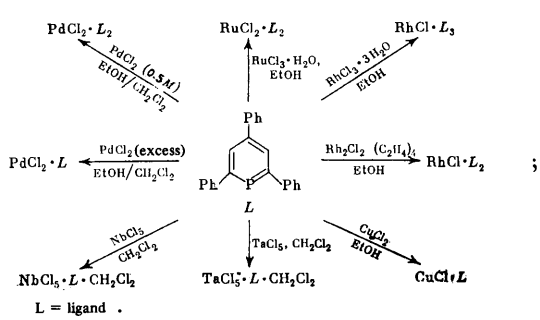
(LXVII) (LXVIII)

Electron-donating properties of phosphorins. In contrast to pyridine derivatives, aryl- and alkyl-phosphorins cannot be protonated by strong acids which are not oxidants, such as, for example, trifluoroacetic acid. However, trisubstituted phosphorins are capable of forming complexes with transition metal salts. For example, 2,4,6-triphenyl- and 2,4,6-tri-t-butylphosphorins react with chromium hexacarbonyl, forming π-complexes. The structure of the π-complex (LXIX) obtained from 2,4,6-triphenylphosphorin was confirmed by X-ray diffratcion analysis[88]:



(LXIX)

In an inert atmosphere, 2,4,6-triphenylphosphorin also forms complexes with transition metal chlorides[89]:

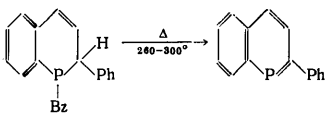


L = ligand .

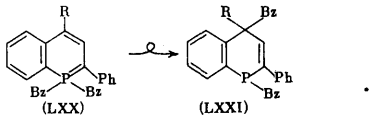
## 2. COMPOUNDS WITH CONDENSED RINGS

### (a) Phosphanaphthalenes

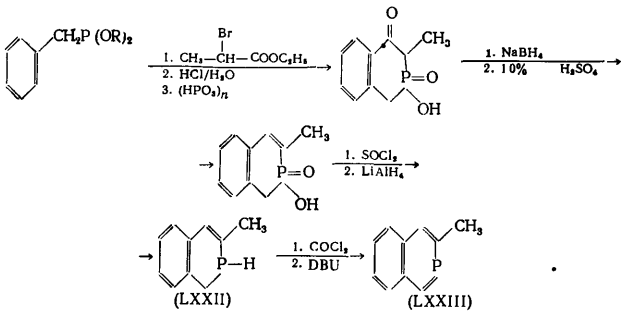
Three phosphanaphthalene derivatives have now been obtained, namely: 2-phenyl-1-phospha- and 3-methyl-2-phospha-naphthalenes as well as unsubstituted 2-phosphanaphthalene. 2-Phenylphosphanaphthalene is obtained similarly to phosphorin, by the thermolysis of 1-substituted dihydro-derivatives [90]:



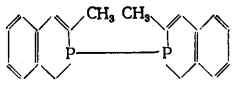
In contrast to phosphorin derivatives, phosphanaphthalenes cannot be obtained by the thermolysis of 1,1-disubstituted phosphanaphthalenes. Thus 1,1-dibenzylphosphanaphthalene (LXX) rearranges at 230–250°C to 1,4-dibenzyl-1,4-dihydrophosphanaphthalene (LXXI) [91]:



3-Methyl-2-phosphanaphthalene (LXXIII) is synthesised by the dehydrochlorination of the appropriate chlorodihydro-derivatives with the aid of 1,5-diazabicyclo[5,4,0]-undec-5-ene (DBU) [92]:



The chlorophosphine formed in the reaction of the secondary phosphine (LXXII) with phosgene is treated with DBU without being isolated. After the separation of the DBU hydrochloride and the vacuum sublimation of the residue, white crystals of compound (LXXIII) are obtained in a low yield. Apart from this product, the dimer



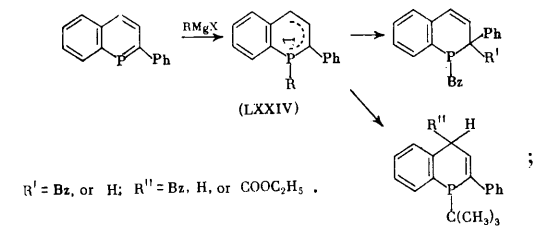
is also formed in the reaction.

The attempt to obtain by this procedure the unsubstituted 2-phosphanaphthalene was not altogether successful, since it could not be isolated in a pure form [92]. The presence of 2-phosphanaphthalene in the reaction mixture was only inferred from ultraviolet spectroscopic data. In another paper [93] devoted to this compound, the method of preparation is not described.

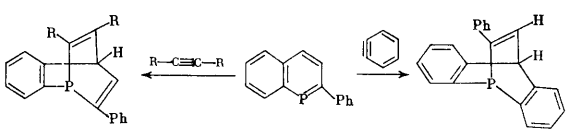
The structure of phosphanaphthalene derivatives has been demonstrated by ultraviolet spectroscopy and NMR. The chemical shift and the spin–spin interaction constants are consistent with the values for phosphorins. A bathochromic shift is observed in the ultraviolet spectra of phosphanaphthalenes relative to the corresponding aromatic hydrocarbons, for example $\lambda_{max}$ = 332 nm for 2-phenyl-1-phosphanaphthalene compared with 322 nm for 2-phenylquinoline. [92]

The chemical properties of phosphanaphthalenes have been studied comparatively little. When 2-phosphanaphthalene is reduced with metallic potassium in tetrahydrofuran, a radical-anion similar to that obtained in the reduction of phosphorin is formed [93].

2-Phenyl-1-phosphanaphthalene reacts with organomagnesium compounds and gives rise to the anion (LXXIV), which is capable of reacting with dialkyl halides [94]:

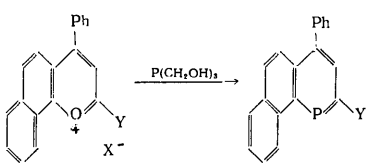


2-Phenyl-1-phosphanaphthalene combines with arynes and alkynes, forming benzo- and dibenzo-phosphabarrelenes [95]:

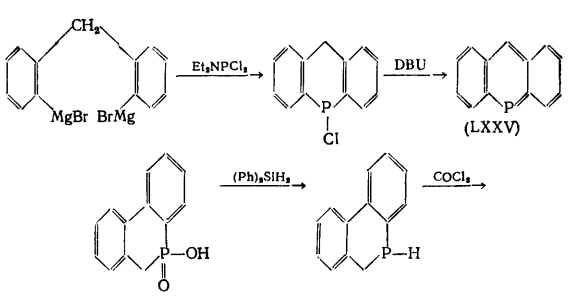


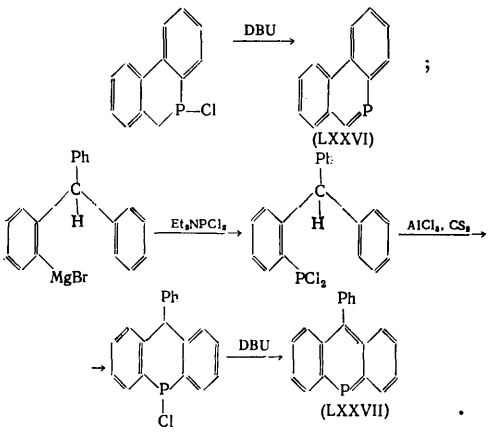
### (b) Phospha-anthracenes and Phosphaphenanthrenes

The above derivatives of phosphorin with condensed rings are synthesised, like phosphorin, from substituted pyrylium salts [96,97]:



Dibenzo[*b*, *e*]phosphorin (LXXV), dibenzo[*c*, *e*]phosphorin (LXXVI), and 10-phenyldibenzo[*b*, *e*]phosphorin (LXXVII) can be obtained similarly to 3-methyl-2-phosphanaphthalene [92], by the dehydrochlorination of chlorodihydro-derivatives with the aid of DBU [98–100]:






Compounds (LXXV) and (LXXVI) are unstable and their formation has been demonstrated mainly by spectroscopic methods. Compound (LXXVII) is stable and can be sublimed at 160°C and $10^{-3}$ mmHg. The PMR and ultraviolet spectra of condensed phosphorins are consistent with those observed for the non-condensed systems [100]. An X-ray diffraction study of 4-aryl-2-t-butyl-5,6-dihydro-1-phosphaphenanthrene showed that the phosphorus-containing ring in this compound is also planar and has the same bond lengths and angles as in substituted phosphorins [97].

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# Advances in the Chemistry of Azulene

V.B.Mochalin and Yu.N.Porshnev

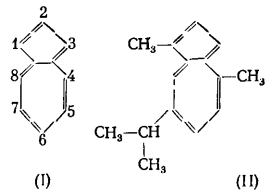
The chief methods of preparation and the chemical properties of azulene hydrocarbons are described. Attention is paid mainly to the most recent papers, not covered in previous reviews. Certain aspects of the application of azulene compounds are also considered. A list of 315 references is included.

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## I. INTRODUCTION

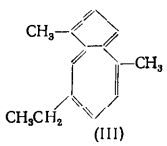
Forty years have passed since Pfau and Plattner finally established the structure of azulene hydrocarbons[1]. The parent of this class of non-benzenoid aromatic compounds is bicyclo[5,3,0]decapentaene, azulene (I). Azulene hydrocarbons are present in various natural oils, where they are formed by the dehydrogenation and dehydration of bicyclic sesquiterpenoid alcohols. Specific names have been retained for many azulene hydrocarbons isolated from natural sources: guaiazulene (II) is 7-isopropyl-1,4-dimethylazulene, obtained by dehydrogenating the oil from the wood of *Guaiacum officinale* L., patchouli oil from *Pogostemon patchouli*, and eucalyptus oil from *Eucalyptus globulus*; chamazulene (III) is present in camomile oil from *Matricaria camimilla* L., oil of yarrow *Achillea millejolun* L., oil of wormwood *Artemisia absinthium* L., and certain other oils; lactaroviolin (IV) is an aldehyde contained in edible fungi; and vetivazulene (V) and zierazulene (VI) are dehydrogenation products of the sesquiterpenoid ketones vetivone and zierone[2]. Azulene hydrocarbons are also present in many other plant species, but in extremely small amounts.



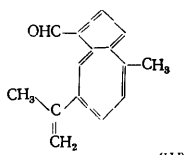
(I)



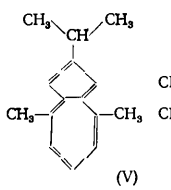
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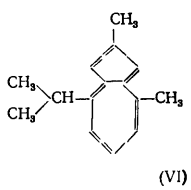
(III)



(IV)



(V)



(VI)

Azulene and its simple homologues are deeply coloured compounds of high boiling point, volatile in steam, which dissolve in hydrocarbon solvents and crystallise well. The simplest azulene hydrocarbons absorb light in the range 550–650 nm.[2,4] They are stable in air up to 300–350°C, and only above this temperature do they begin to be converted into valence isomers of benzenoid structure, naphthalene and its homologues[2]. Azulene compounds can also undergo photoisomerisation[5].

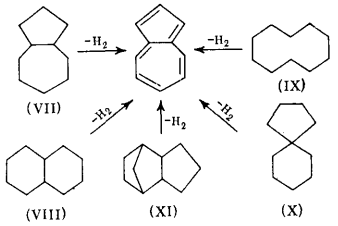
The unusual physical and chemical properties of azulene hydrocarbons have long attracted the attention of many investigators, but until the end of the 1950s these compounds were extremely inaccessible, and only after the development by Hafner and by Nozoe of effective methods for the synthesis of azulenes did their widespread study become possible. The most complete survey of the literature on the structure and the chemistry of azulenes appeared in 1959 [3] (translated into Russian in 1963 [2]). Subsequent reviews[6,7] contained data only on individual problems of the synthesis or the reactivity of azulenes. Therefore the present Review, devoted to methods of preparation, chemical properties, and prospects for the application of azulene derivatives, covers mainly the literature from 1959 to 1975. The large number of publications that appeared during this period prevent the inclusion of several aspects—(i) methods for the isolation, purification, and identification of azulene compounds, (ii) the physical and physicochemical characteristics of azulenes, and (iii) the chemical properties and methods of preparation of heteroazulene compounds, in which one or more methine groups have been replaced by heteroatoms[8]—which all, without doubt, deserve special discussion.

## II. METHODS OF PREPARATION OF AZULENE COMPOUNDS

### 1. Methods involving Dehydrogenation

Dehydrogenation of bicyclic precursors of azulene having the bicyclo[5,3,0]decane structure (VII) or of the corresponding partly unsaturated compounds was historically the first (and for a long time the only) method for obtaining azulene and its alkyl homologues. Both natural oils containing sesquiterpenoid precursors and synthetic bicyclic derivatives were used. Although guaiazulene,

chamazulene, and vetivazulene have hitherto been obtained mainly by the dehydrogenation of natural oils, substituted bicyclo[5,3,0]decanes have rarely been used for preparing other azulene derivatives owing to the complexity and the multistage character of the process[2]. Azulenes have been obtained by dehydrogenation not only of bicyclo[5,3,0]-decane (VII) derivatives[9] but also of compounds of the cyclodecane (IX),[2,10,11] decahydronaphthalene (VIII),[12] tetrahydrodicyclopentadiene (XI),[12] and spiro[4,5]decane (X)[13] series.




However, the complexity of the preparation of most such compounds, the formation of mixtures of isomeric azulenes from substituted derivatives of (VIII)–(X), and—the most important—the low yields (1–10%) at the dehydrogenation stage have resulted in the extremely rare use of these methods also. Such yields are greatly increased when highly unsaturated hydrocarbons such as dihydroazulenes are used, so that "partial" dehydrogenation remains an important method of preparation in the chemistry of azulenes. Dehydrogenation is sometimes employed also to prove the structure of a sesquiterpene hydrocarbon.

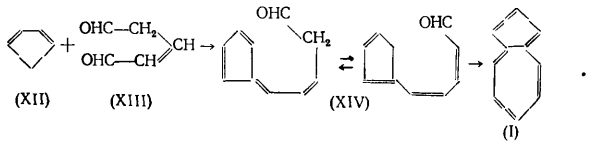
Sulphur, selenium, 5–10% palladium on carbon, chloranil, and diphenyl disulphide are widely employed as dehydrogenating agents. Dehydrogenation with sulphur is accomplished on heating (200°C), with yields usually not exceeding 10%[14,15] and only in isolated cases reaching 30–50%.[16,17] Acyl- and alkyl-azulenes may form thienoazulenes on dehydrogenation with sulphur[17–19]. The use of selenium[20–22] or palladium[23–25] for liquid-phase dehydrogenation requires higher temperatures (280–300°C), which often leads to migration of hydrocarbon substituents or even partial isomerisation of the azulene into the naphthalene system[26]. Yields of azulenes are 1–10%. Catalytic dehydrogenation in the gas phase over palladium on carbon, molybdenum sulphide, or other catalysts frequently gives higher yields, but requires careful selection of optimum conditions in each specific case[9,12,27]. Little information is available on the dehydrogenating action of diphenyl disulphide; it has been successfully used for the preparation of guaiazulene[28].

Recently chloranil has been the hydrogenating agent used most often[29–33]. Dehydrogenation occurs under very mild conditions, but a high degree of unsaturation is required in the compounds to be dehydrogenated.

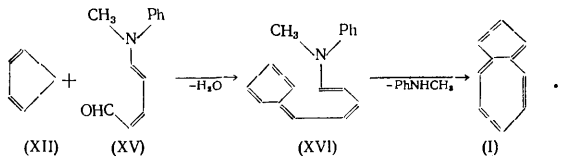
The complexity of the directed preparation of hydrogenated precursors of azulene and the low yields obtained in their dehydrogenation have led to the development of fundamentally new ways of obtaining azulene that avoid dehydrogenation.

## 2. Cyclisation of Polymethinium Salts and Fulvenes

In 1955 Ziegler and Hafner[34], and almost simultaneously Rösler and König[35], reported a new synthesis of azulene systems that eliminated the dehydrogenation stage. The general principle consisted in obtaining fulvene (XIV) from cyclopentadiene (XII) and glutaconaldehyde (XIII) and cyclising the product to azulene (I):

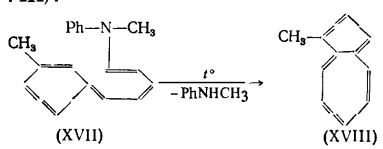



However, this form of the process has not yet been accomplished: in practice the relatively unstable glutaconaldehyde is replaced by a derivative, Zincke's aldehyde (XV), which is converted into the fulvene (XVI). In the presence of a base such as benzidine or trishydroxyethylamine at 200–300°C this fulvene is cyclised to azulene, which sublimes as it is formed:

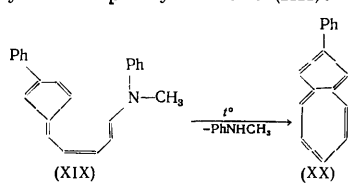



The high yield of azulene (up to 70%) makes this method most promising for industrial application[34].

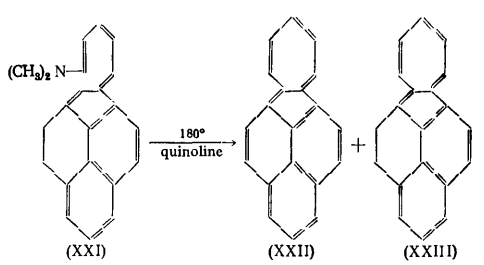
Azulenes substituted in the five-membered ring can be obtained by the same method. Cyclisation of the fulvene (XVII) obtained from methylcyclopentadiene gives 1-methylazulene (XVIII):[36]




However, the corresponding cyclisation of the phenylated fulvene (XIX) yields 2-phenylazulene (XX):[37]

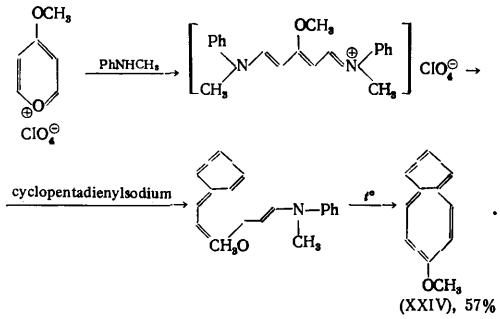



Such a difference in the course of cyclisation is probably due to both electronic and steric factors. A 62% yield of azuleno[1,2,3-*cd*]phenalene (XXII) has recently been obtained[38] by cyclisation of the corresponding fulvene (XXI), with separation of the dihydro-derivative (XXIII) as a byproduct:



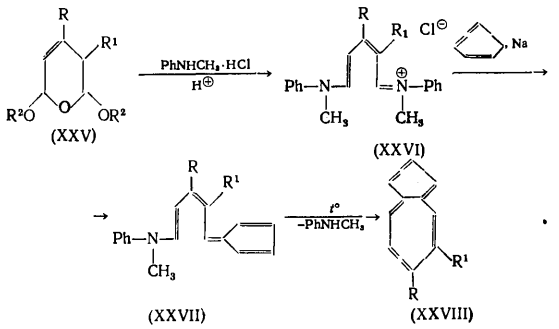

Azulenes substituted in the seven-membered ring can be obtained by reaction between cyclopentadiene and substituted Zincke aldehydes, but the cleavage of mono- and poly-alkylated pyridines to the desired glutaconaldehyde derivatives presents certain difficulties[39]. Since pyrylium salts are cleaved considerably more readily by amines, they may serve as convenient starting materials

for obtaining several difficultly accessible azulenes, e.g. 6-methoxyazulene (XXIV):[39]



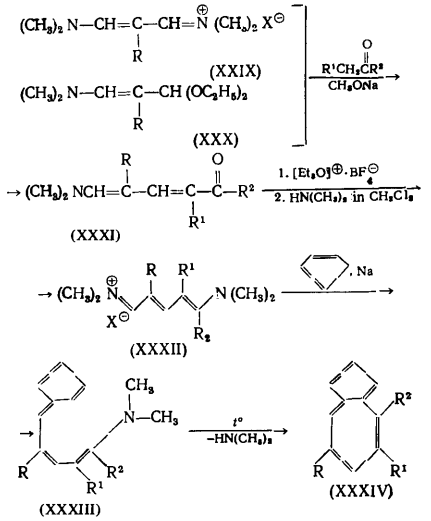
(XXIV), 57%

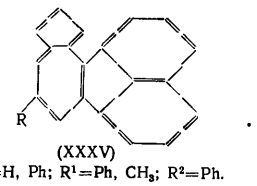
6(5)-Arylated azulenes (XXVIII) can be obtained from 2,6-dialkoxy-4(5)-aryl-$\Delta^3$-dihydropyrans (XXV)[40] via the *N*-methyl chlorides (XXVI) and fulvenes (XXVII):



This method has been used to obtain 6-phenyl-,[41] 6-thien-2′-yl-,[42] and 5-phenyl-azulenes[43].

Another method of obtaining substituted pentamethinammonium salts—derivatives of glutaconaldehyde—is based on condensation of a malonaldehyde derivative (XXIX) or (XXX) with a carbonyl compound containing an active methylene group[44]. The resulting amino-dienone (XXXI) is converted into the pentamethinammonium salt (XXXII) by treatment with triethyloxonium tetrafluoroborate followed by dimethylamine. The subsequent action of cyclopentadienylsodium forms the fulvene (XXXIII), which when heated to 180–190°C is converted into the azulene (XXXIV) substituted in the seven-membered ring (yield 15–35%):

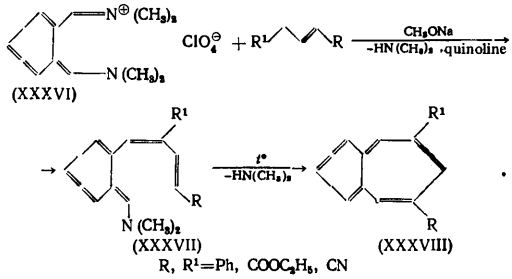




(XXXV)
R=H, Ph; $R^1$=Ph, $CH_3$; $R^2$=Ph.

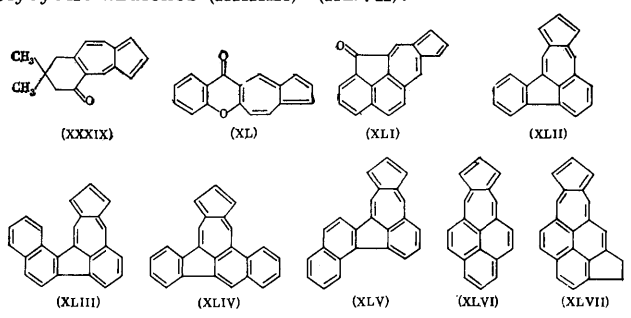
The presence of bulky substituents $R^1$ and $R^2$ in the fulvene (XXXIII) prevents formation of an azulene, probably owing to hindrance to establishment of the *cis*-configuration necessary for cyclisation. Application of this method to acenaphthenone yields fused pentacyclic compounds of the azuleno[4,5-*a*]acenaphthylene series (XXXV).[44]

The salt (XXXVI), containing a dimethylaminofulvene group, became very valuable as initial compound for the synthesis of polycyclic azulene hydrocarbons[45-50]. It reacts with derivatives of glutaconic or 4-phenylbut-3-enoic acid in the presence of sodium methoxide to give fulvenes (XXXVII) capable of cyclisation with high yields into 5,7-disubstituted azulenes (XXXVIII):[44]

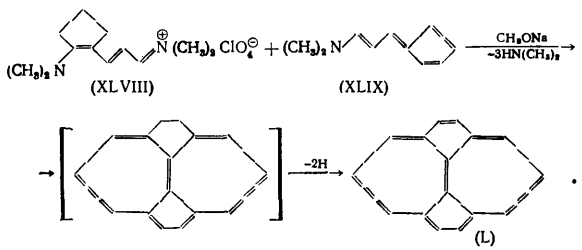


R, $R^1$=Ph, $COOC_2H_5$, CN

Replacement in this reaction of derivatives of glutaconic acid by isophorone, 2-methylchromone, acenaphthenone, fluorene, benzofluorenes[44], phenalene[51], and 1,2-dihydro-5*H*-cyclopenta[*c*, *d*]phenalene[52] gave the corresponding polycyclic azulenes (XXXIX)–(XLVII).

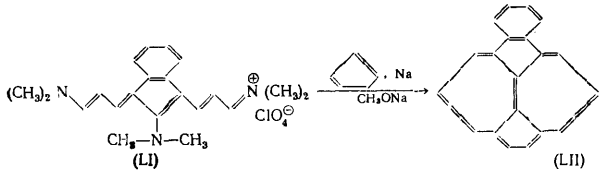


Jutz and Schweiger[53] suggested a method of double cyclisation of the pentamethinammonium salt (XLVIII)[54] with the fulvene (XLIX) in the presence of sodium methoxide to give an approximately 5% yield of the extremely difficultly accessible pyraceheptylene (L):



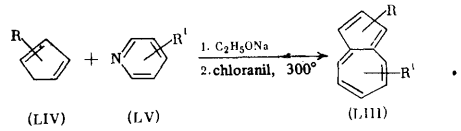
Condensation of cyclopentadiene with the salt (LI) obviously involves both formation of a fulvene and its subsequent

double cyclisation with the further elimination of two molecules of dimethylamine to give a 2.5% yield of benzo[*a*]-pyraceheptylene (LII):[53]



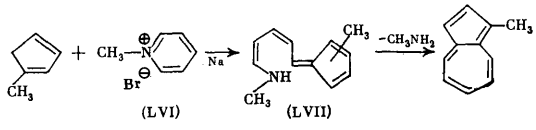

3. Syntheses from Pyridinium and Pyrylium Salts

The relationship between glutaconaldehyde and pyridine enabled Hafner[55] to synthesise azulene (LIII) by the condensation of substituted cyclopentadienes (LIV) with substituted pyridines (LV) followed by cyclisation and dehydrogenation at an elevated temperature:



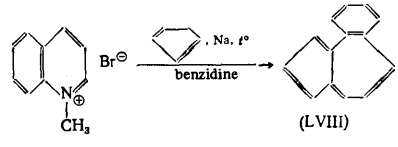

This method was used to obtain 1-, 4-, and 5-methylazulenes, 4,8-dimethylazulene, 1-isopropylazulene, 1-diphenylmethylazulene, and also 1,2-benzazulene,

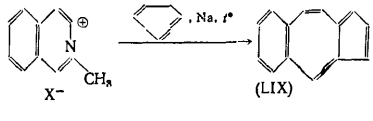
However, quaternary pyridinium and homologous salts have been more widely used. For example, reaction between *N*-methylpyridinium bromide (LVI) and methylcyclopentadienylsodium in liquid ammonia enabled Ziegler and Hafner to obtain the fulvene (LVII), which cyclised thermally into 1-methylazulene in 55% yield[56]:




1,2,3-Triphenylazulene was obtained similarly from 1,2,3-triphenylcyclopentadiene[57].

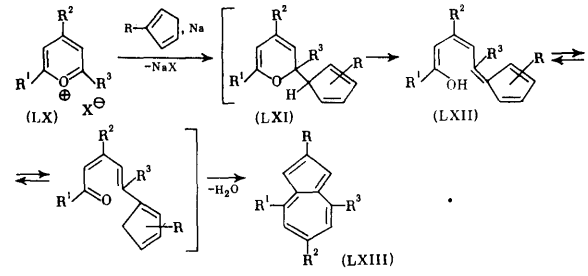
Cyclopentadienylsodium reacts with quinolinium[58] and isoquinolinium[59] salts to give low yields of respectively 4,5-benzazulene (LVIII) and 5,6-benzazulene (LIX):



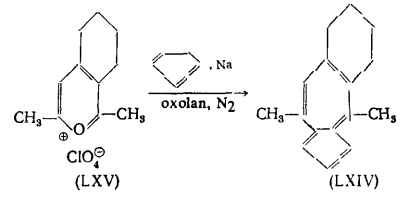




The syntheses are fairly complicated when used as methods of preparation, and published yields are not always reproducible.

Considerably better results are obtained by replacing pyridinium by pyrylium salts. Hafner showed[60] that several salts (LX) form with cyclopentadienylsodium even at room temperature azulenes substituted in the seven-membered ring, in yields that in individual cases are nearly theoretical. The hypothetical intermediate products (LXI) and (LXII) could not be isolated. The alkyl group in the cyclopentadiene appears at position 2 in the azulene (e.g. 2,4,6,8-tetramethylazulene (LXIII: R = $R^1$ = $R^2$ = $R^3$ = $CH_3$) is formed):

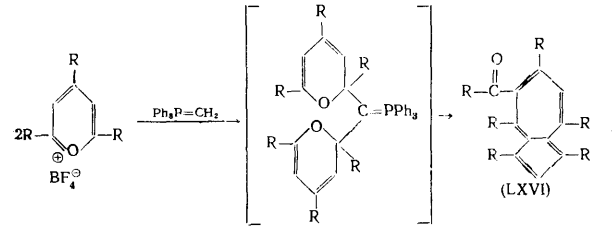



Various substituted azulenes—4,6,8-trimethyl, 4,8-dimethyl-6-t-butyl, 4-methyl-6,8-diphenyl, 4,8-dimethyl-6-phenyl, 6-methoxy-4,8-dimethyl, and several other analogues—have been obtained by this reaction[61], but it is not universally applicable to the synthesis of substituted azulenes. Thus 5,6,7,8-tetrahydro-4,10-dimethylbenz-[*f*]azulene (LXIV) was obtained from the salt (LXV) in only 3.3% yield[59]:




Unsubstituted pyrylium perchlorate[62] and 4-unsubstituted 2,6-dialkylpyrylium salts do not form azulenes when treated with cyclopentadienylsodium. Nor can 2,4,6-triphenylpyrylium and 4-phenyl-2,6-distyrylpyrylium perchlorates, as well as several other pyrylium salts, serve as sources of azulenes. Clearly, unsubstituted pyrylium salts on reaction with the cyclopentadienyl anion readily undergo condensation involving the carbon atoms at positions 2, 4, and 6, with the formation of a large number of unstable side-products. 2,4,6-Triarylated pyrylium salts do not undergo cleavage by the cyclopentadienyl anion under mild conditions, because of their stability due to conjugation[61].

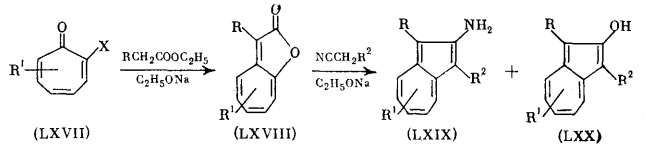
Another interesting route to azulene compounds was suggested in 1963 by Dimroth et al.[63] In this synthesis both azulene rings are formed from a pyrylium salt. The action of excess of methylenetriphenylphosphorane on a pyrylium salt produces in a single stage a substituted 5-acylazulene (LXVI) in ~30% yield:




Thus, despite certain limitations, the use of pyrylium salts provides a most effective method for synthesising azulenes, because of the acceptability of the initial compounds, the mild reaction conditions, and the high yields.

### 4. Tropones, Tropolones, and Heptafulvenes in the Synthesis of Azulenes

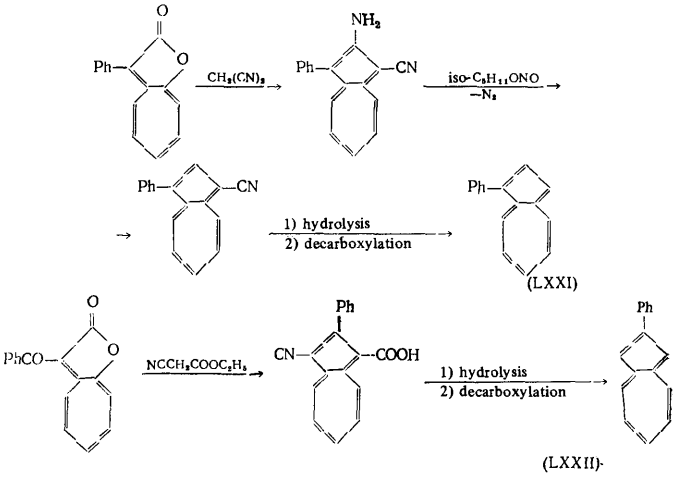
Another method of forming azulene compounds that has been studied in detail[64] involves closure of a five-membered ring in compounds that already contain a cycloheptatriene system. One such process is the action of esters containing an active methylene group on tropones substituted at the 2 position by halogen[64-68], arenesulphonyloxyl[69], or alkoxyl[70] (LXVII):



(LXVII) (LXVIII) (LXIX) (LXX)

X = Cl, Br, $OSO_2Ar$, $OCH_3$, $OC_2H_5$; R = CN, $COOC_2H_5$, $C_6H_5$, $C_6H_5CO$;
$R^1$ = Alk, Ar; $R^2$ = CN, $COOC_2H_5$

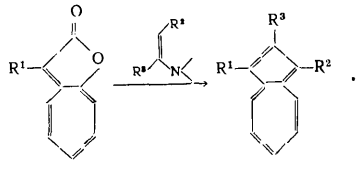
In the presence of sodium ethoxide substituted cycloheptafuranones (LXVIII) are readily formed, and are then converted into azulenamines (LXIX). Application of a twofold excess of cyanoacetic ester enables good yields of diethyl 2-aminoazulene-1,3-dicarboxylates (LXIX: R = $R^2$ = $COOC_2H_5$) to be obtained; the use of malononitrile gives the 1,3-dicyanoazulen-2-amine (LXIX: R = $R^2$ = CN). Low yields of the 2-hydroxy-derivatives (LXX: R = CN; $R^2$ = $COOC_2H_5$ or CN) are formed as secondary products. The nitrile and ester groups can be removed by hydrolysis followed by decarboxylation[66], and the amino-group replaced by hydrogen by diazotisation with isopentyl nitrite in alcohol in the presence of sulphuric acid[68]. These reactions can be illustrated by the preparation of 1- and 2-phenylazulenes (LXXI) and (LXXII):



(LXXI)

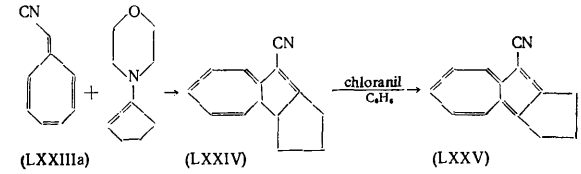
(LXXII)

Cycloheptafuranones (LXVIII) can be converted into azulenes by a different route—by cycloaddition with vinylamines[71,72]:



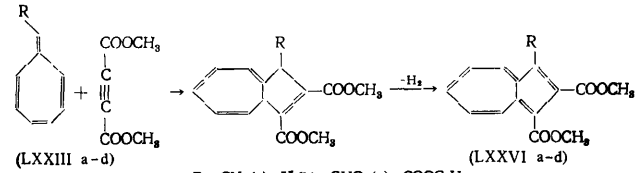
1,2-Propano-, 1,2,butano-, and 1,2-pentano-azulenes, 1- and 2-phenylazulenes[71], indeno[2,1-*a*]azulene, indeno-[1,2-*a*]azulene, and their 3-cyano-derivatives[72] have been obtained in this way.

Cycloheptafuranones (LXVIII) are heptafulvene derivatives. Heptafulvenes themselves are also able to undergo cycloaddition with enamines. For example, the condensation of 8-cyanoheptafulvene (LXXIIIa) with N-cyclopentenylmorpholine leads to formation of the dihydroazulene derivative (LXXIV), whose dehydrogenation by chloranil gives 3-cyano-1,2-propanoazulene (LXXV):[73]



(LXXIIIa) (LXXIV) (LXXV)

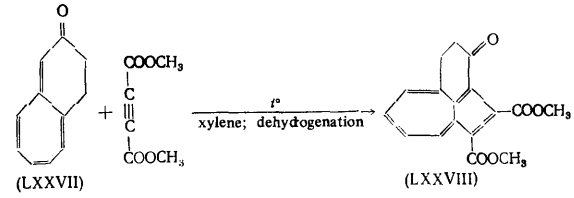
The 1,3-cycloaddition† of acetylenedicarboxylic esters to heptafulvene and its derivatives leads to formation of the five-membered ring of the dihydroazulene system, whose dehydrogenation readily gives azulene derivatives. Thus the heptafulvenes (LXXIIIa–d) have given the azulene-1,2-dicarboxylic ester (LXXVIb),[24] as well as the corresponding 3-aldehyde (LXXVIc), the tricarboxylic ester (LXXVId),[74] and the 3-cyano-derivative (LXXVIa):[73]



(LXXIII a–d) (LXXVI a–d)

R=CN (a), H(b), CHO (c), $COOC_2H_5$ (d)

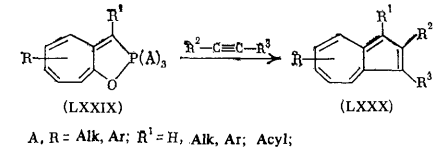
Similarly, the heptafulvene derivative (LXXVII) yields dimethyl 11-oxo-1,8-propanoazulene-2,3-dicarboxylate (LXVIII)



(LXXVII) (LXXVIII)

which is then converted into the fully conjugated tricyclic 3-benz[*c*, *d*]azulenone system[75].

The phosphoranes (LXXIX) are also able to undergo a similar reaction with acetylenes containing electron-accepting substituents, to form substituted azulenes (LXXX) with simultaneous elimination of trialkyl- or triarylphosphine oxides[76]:



(LXXIX) (LXXX)

A, R = Alk, Ar; $R^1$ = H, Alk, Ar; Acyl;
$R^2$, $R^3$ = CN, COOR .

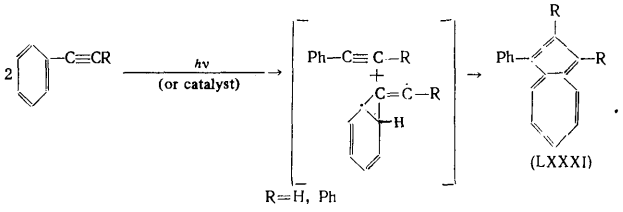
Methods based on the use of troponoid compounds readily yield azulene derivatives functionally substituted in the five-membered ring, and thus a useful supplement to preparations based on pyridinium, pyrylium, and Zincke salts. Many 2-substituted azulene derivatives—with chloro, iodo, amino, cyano, carboxy, methoxy,

† It would have been more correct to term this reaction *1,8-cycloaddition*, since it takes place at the ends of the conjugated chain (in heptafulvene this chain comprises eight atoms).

hydrazino, or other functional group—completely inaccessible by other routes, have been obtained from troponoid compounds[77]. Tri- and tetra-cyclic azulenoid systems, containing fused pyridine, pyridazine, pyrazole[78-80], and thophen[81] rings, have been obtained similarly.

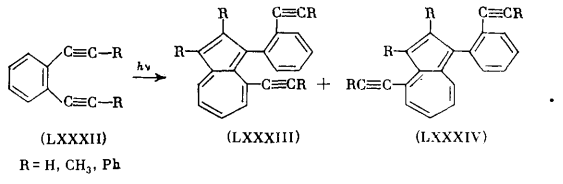
## 5. Cyclisation of Acetylenic Compounds and Other Methods

Formation of the azulene system from acetylenic compounds was observed as early as 1948 by Reppe and his coworkers[82], who reported the appearance of small quantities of azulene in the preparation of cyclo-octatetraene from acetylene. Such processes usually involve active species formed e.g. on cleavage of the benzene ring in phenylacetylene and similar in structure to heptafulvene; cycloaddition of such a species at the triple bond entails closure of the five-membered ring of the azulene system. The reactions are initiated photochemically, and sometimes can be accomplished also by means of certain catalysts. An illustration is the conversion of phenylacetylene into 1-phenylazulene (LXXXI: R = H):[83]

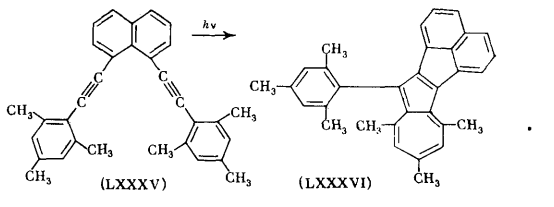



Diphenylacetylene undergoes a similar reaction also in the presence of 2,4-dinitrophenylsulphenyl chloride and anhydrous aluminium chloride or bromide, to give an approximately 25% yield of 1,2,3-triphenylazulene (LXXXI: R = $C_6H_5$).[84,85] The same reaction is effected also by palladium chloride, with which diphenylacetylene forms the complex compound $2C_6H_5C{:}CC_6H_5 \cdot PdCl_2 \cdot C_2H_5OH \cdot HCl$.[86] Cyclisation of acetylenes into azulenes can probably occur by both radical and ionic mechanisms.

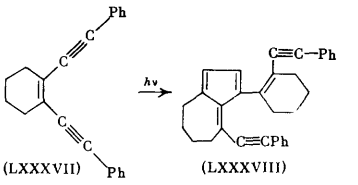
Diacetylenes (LXXXII) undergo an analogous reaction to form mixtures of the structurally isomeric azulene hydrocarbons (LXXXIII) and (LXXXIV):[87,88]



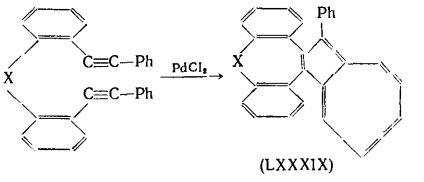

Intramolecular cyclisation of 1,8-dimesitylethynylnaphthalene (LXXXV) on ultraviolet irradiation gives the polycyclic azulene hydrocarbon (LXXXVI):[89]




In connection with the mechanism of such reactions it is interesting that 1,2-diphenylethynylcyclohexene (LXXXVII) is converted by radiation into a hydrogenated azulene derivative (LXXXVIII)[88]

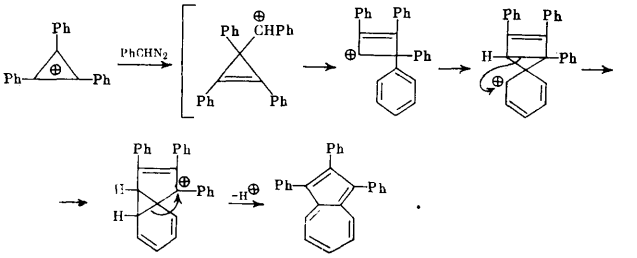



dehydrogenation of which by chloranil yields the corresponding azulene. Intramolecular cyclisation has been employed to obtain polycyclic azulene derivatives (LXXXIX) containing a silicon or sulphur atom in one of the fused rings[90,91]:

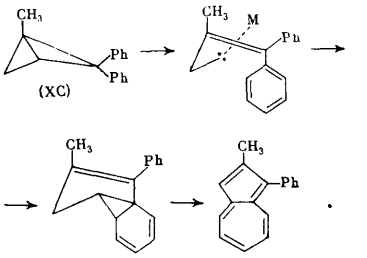



X=SO, Si $(CH_3)_2$ .

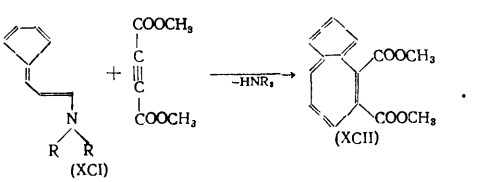
Another method of obtaining azulene derivatives—from arylcyclopropenylium salts[92-94]—also involves expanding the ring of a phenyl substituent:




A further synthetic approach to azulenes involving intramolecular cycloaddition is based on rearrangement of a phenylated bicyclo[1,1,0]butane (XC) initiated by a transition-metal carbonyl[95]:

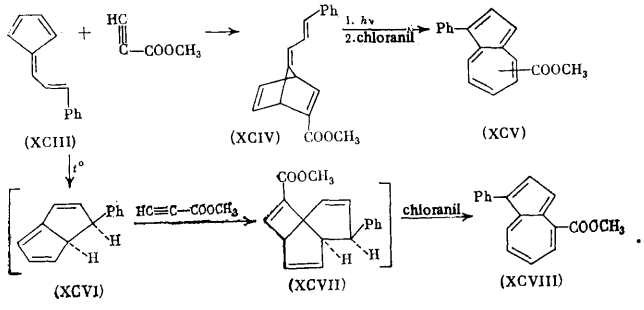



Like heptafulvenes (§II, 4) aminovinylfulvenes (XCI) are able to undergo cycloaddition with acetylenedicarboxylic esters, to give azulene-4,5-dicarboxylic esters (XCII):[96]

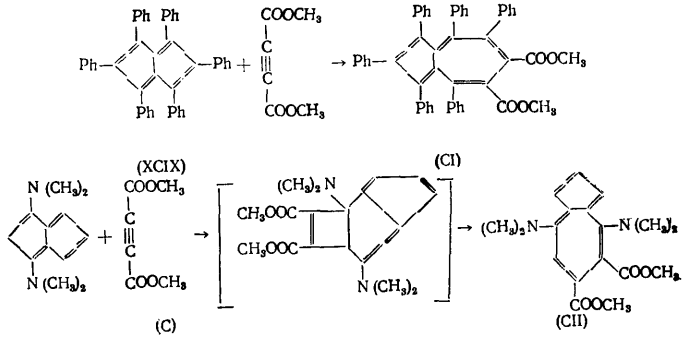



6-Styrylfulvene (XCIII) undergoes diene synthesis with methyl propiolate to form an adduct (XCIV) that rearranges into a mixture of phenyldihydroazulenecarboxylic esters;

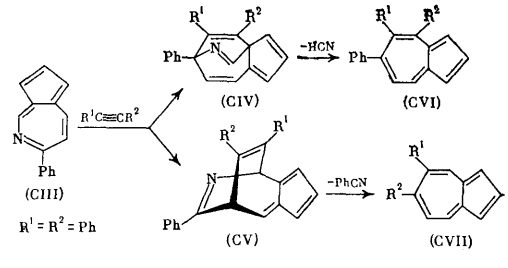
the latter are readily dehydrogenated by chloranil, forming a mixture of methyl 1-phenylazulene-4(8)-carboxylates (XCV). When heated the fulvene (XCIII) isomerises into phenyldihydropentalene (XCVI); cycloaddition of the propiolic ester produces the cyclobutene derivative (XCVII), which on dehydrogenation is converted into the individual methyl 1-phenylazulene-4-carboxylate (XCVIII).[29]



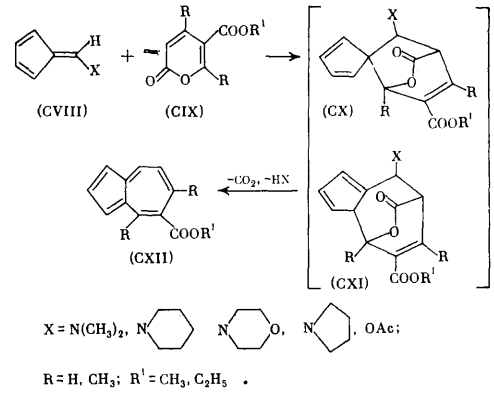

This mechanism is supported by the well known methods of converting the substituted pentalenes (XCIX) [97] and (C) [98] into the corresponding azulenes (CI) and (CII) by the action of acetylenedicarboxylic ester:




The cyclic analogue of styrylfulvene, 6-phenyl-5-aza-azulene (CIII), also undergoes cycloaddition with acetylenic compounds[99], when both possible adducts (CIV) and (CV) are formed; these eliminate hydrocyanic acid or benzonitrile to give a mixture of the corresponding azulene derivatives (CVI) and (CVII):

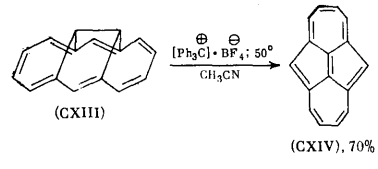



Cycloaddition of dialkylaminofulvenes (CVIII) to coumalic esters (CIX) gives the adducts (CX) and (CXI), which are aromatised into azulenes (CXII) with elimination of carbon dioxide and the dialkylamine[100]:

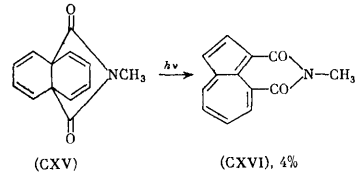



Syntheses of azulene compounds based on cycloaddition have been actively studied during recent years, and their possibilities are probably far from exhausted.

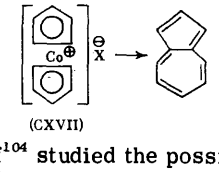
A few other methods of obtaining azulene compounds have been described which, although of no great synthetic value, provide a good illustration of the stability of the aromatic azulene system. Thus 1,6:8,13-ethanediylidene-[14]annulene (CXIII) is converted in high yield into dicyclohepta[*c*,*d*:*g*,*h*]pentalene (CXIV), a novel non-benzenoid isomer of pyrene[101]:



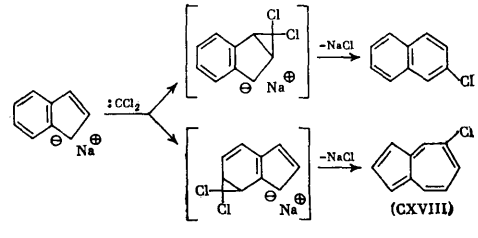

When the propellane (CXV) is exposed to ultraviolet radiation, *N*-methylazulene-1,8-dicarboximide (CXVI) is formed in 4% yield together with other compounds[102]:



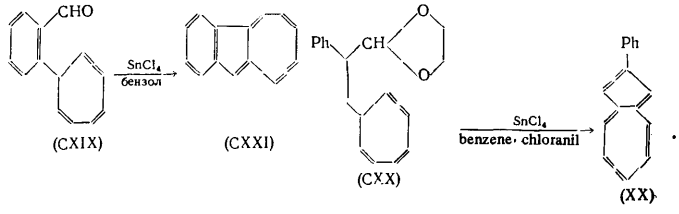

Cobalticinium hexafluorophosphate (CXVII) forms azulene in low yields when treated with bases[103]:




Parham and Reiff[104] studied the possibility of obtaining azulene compounds from indenylsodium by the addition of dichlorocarbene; they found the course of the reaction to be ambiguous, giving 5-chloroazulene (CXVIII) in only about 0.5% yield:

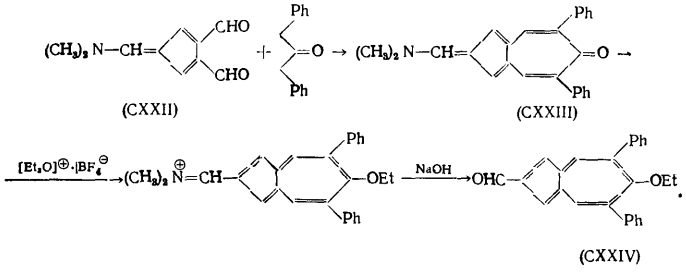


Syntheses of azulene compounds by closure of a five-membered ring in aldehydes or acetals of the cycloheptatriene series (CXIX) and (CXX) have also been reported[105]. Low yields of 1,2-benzazulene (CXXI) and 2-phenylazulene (XX) have been obtained by this method; in the latter case the intermediate dihydro-derivative was dehydrogenated by means of chloranil:




(CXIX) (CXXI) (CXX) (XX)

Another method of condensation of aldehydes involves closure of the seven-membered ring of the azulene system[48]. Borrowed from the chemistry of tropones, it converts the substituted cyclopentadiene dialdehyde (CXXII) into the azulenequinonemethide (CXXIII), which can then be transformed into the azulene derivative (CXXIV):




(CXXII) (CXXIII) (CXXIV)

The methods described in this Section have been used to synthesise various azulenoid polycyclic compounds containing 3–7 fused rings, not only carboxylic azulenoid systems[106–127] but also fused heterocyclic azulene compounds containing nitrogen[128–134], sulphur[135–140], or oxygen[141] as heteroatom.

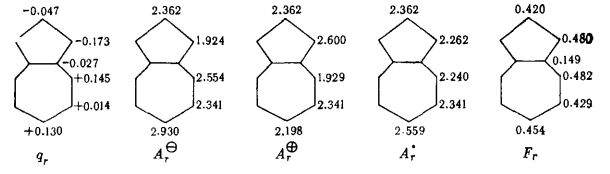
It must be noted in conclusion that no universal method is yet available for the synthesis of substituted azulene hydrocarbons. Many of the above processes cannot be used to prepare azulene and its homologues, both because of the inaccessibility of the initial compounds and because of the low yields. The search for effective new syntheses of azulenes is therefore still continuing at the present time.

## III. CHEMICAL PROPERTIES OF AZULENE COMPOUNDS

### 1. Structure and Reactivity of Azulene

The chemistry of azulene compounds has been intensively developed mainly during the past two decades; certain theoretical views on the reactivity of the azulene system have been elaborated in parallel with or even preceding the synthetic investigations. In spite of the difficulties involved in assessing the contribution of polar structures, even the simplest LCAO-MO calculations[142–152] showed high electronegativity of the five-membered ring and a deficiency of electrons on the atoms of the seven-membered ring.

The charges $q_r$, localisation energies $A_r$, and free valency indices $F_r$ calculated by the Hückel method are



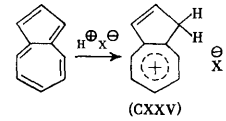

The calculated results lead to several conclusions: (i) the liability to electrophilic attack should decrease either in the sequence of carbon atoms 1(3) > 2 > 5(7) > 6 > 4(8) according to the charges, or in the sequence 1(3) > 5(7) > 2 > 4(8) > 6 according to the localisation energies; (ii) the reactivity towards nucleophilic attack should diminish in the sequence of carbon atoms 4(8) > 6 > 5(7) > 2 > 1(3); and (iii) homolytic reactions should take place at carbon atoms 4(8) [142] or 1(3).[153] As will be shown later, the results of synthetic investigations exhibit in the main good agreement with these theoretical ideas.

### 2. Electrophilic Substitution

A consequence of the high electron density on the carbon atoms forming the five-membered ring is that the aromatic azulene system is highly reactive towards various electrophilic reagents. Azulene and its derivatives readily form $\pi$ complexes with various electron-deficient compounds—trinitrobenzene, trinitrotoluene, picric acid[4,154], tetracyanoquinodimethane[155], tetracyanoethylene[156,157], and several other similar compounds[158]—and trinitrobenzene complexes are often used for the isolation, purification, and identification of azulenes, since they readily break down into their components when chromatographed on aluminium oxide. Complexes of azulenes with metal carbonyls have also been described[159–162].

#### (*a*) Reactions of azulenes with acids

The strongly basic character of azulenes leads to the formation of azulenium salts (CXXV) on treatment with mineral acids[163–165]:




(CXXV)

The ability of azulene and its derivatives to dissolve with salt formation in 60% sulphuric and 85% phosphoric acids[15] is used in several cases to isolate azulene compounds, since dilution of the acid solution with water leads to hydrolysis of the salt with separation of the initial azulene. Salts can be formed by azulenes also with aprotic acids[166], which leads in several cases to the appearance of secondary products when Friedel–Crafts catalysts are used.

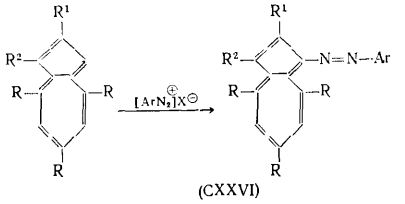
The active hydrogen atoms at positions 1 and 3 exchange readily for deuterium[167,168], whereas the remaining hydrogen atoms exchange only under severe conditions[169].

(*b*) Nitration, nitrosation, and azo-coupling

Because of the sensitivity of the ring system to strong acids, azulene and its homologues cannot be nitrated with a nitrating mixture. However, the nitration of unsubstituted azulene can be easily accomplished by means of acetyl[170], copper[171], or urea[172] nitrate. The use of tetranitromethane in pyridine is especially convenient[173]. With urea nitrate azulene gives both 1-mono-.and 1,3-di-nitroderivatives, whereas with tetranitromethane only 5-nitroazulene is formed. Azulene derivatives containing isopropyl and t-butyl substituents at positions 1 and 3 are nitrated at position 5 in ~25% yield[32].

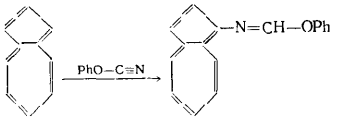
Azulene is nitrosated at position 1 by nitrosyl perchlorate to give the unstable 1-nitrosoazulene[174]. The corresponding nitroso-derivative of 4,6,8-trimethylazulene, obtainable in high yield, is considerably more stable. Nozoe et al.[175] effected the nitrosation of ethyl 2-aminoazulene-1-carboxylate with isopentyl nitrite with formation of ethyl 2-amino-3-nitrosoazulene-1-carboxylate.

1(3)-Unsubstituted azulene derivatives are able to undergo azo-coupling with such weak electrophiles as diazonium salts to give high yields of azo-dyes (CXXVI):[171,176-179]



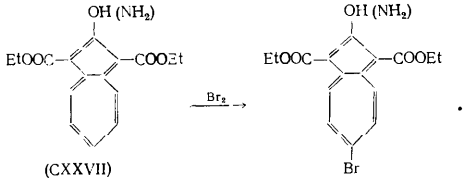
(CXXVI)

These dyes are readily reduced to azulenamines[179,180]. Azulene reacts also with phenyl cyanate[181]:



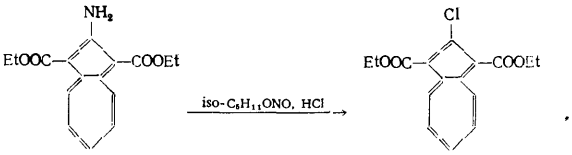
(*c*) Halogenation

The best halogenating agents for obtaining 1(3)-mono- and 1,3-di-halogenated azulenes are *N*-chlorosuccinimide[182-184], *N*-bromosuccinimide[183-185], and *N*-iodosuccinimide[184], which give high yields. Chlorinating agents producing good results are t-butyl hypochlorite[183], phosphorus pentachloride[183,186], phosphoryl chloride[183], and copper(II) chloride[187]; sulphur monochloride in the presence of aluminium chloride also has a chlorinating action[178]. Azulene compounds can be brominated also by means of dioxan dibromide[183], phosphorus pentabromide[183], phosphoryl bromide, pyridinium bromide–perbromide, cyanogen bromide[185], and copper(II) bromide[187]. 1,3-Dibromoazulene can be obtained also by the hypobromination of 1,3-diacetylazulene[170]. Unusually, dialkyl 2-hydroxy- and 2-amino-azulene-1,3-dicarboxylates (CXXVII) are brominated at the 6 position[188,189]:



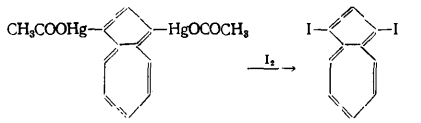
(CXXVII)

1,3-Dichloroazulene can be chlorinated by *N*-chlorosuccinimide at position 5 to give a 17% yield of 1,3,5-trichloroazulene[243]. 2-Chlorinated azulenes have been obtained by diazotising diethyl 2-aminoazulene-1,3-dicarboxylates in the presence of hydrochloric acid[190]:



6-Chloro-derivatives have been obtained from the corresponding azulen-6-ols[183].

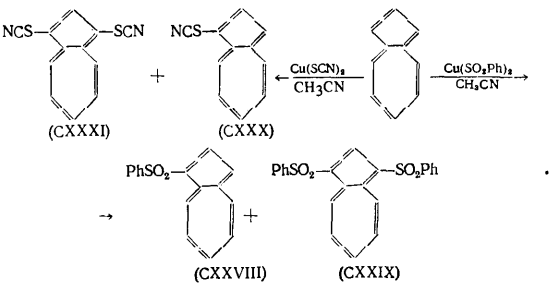
A complex of iodine chloride in dioxan[183] and iodine in the presence of copper acetate[187] have been used to obtain 1(3)-mono- and 1,3-di-iodoazulenes. Another method is exchange substitution of acetoxymercuric groups by treatment with iodine[46]:



1(3)-Halogenoazulenes form normal organomagnesium derivatives[4] and are able to exchange their halogen for the thiocyanato- or cyano-group when heated with the copper or silver salts[183]. Nucleophilic exchange of the halogen has been studied in 6-chloroazulenes[183] and 2-chloroazulenes[191].

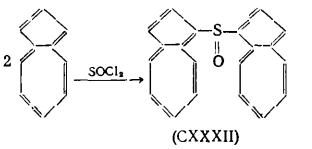
(*d*) Sulphonation, thiocyanation, and other reactions

Azulene is sulphonated by a solution of sulphuric acid in acetic anhydride or by dioxan–sulphur trioxide to the 1,3-disulphonic acid[185,192]. 1-Monosulpho-derivatives of azulene and its homologues have been obtained by sulphonation with copper sulphate in acetic anhydride[193] and with dioxan–sulphur trioxide[194]. The action of copper benzenesulphinate on azulene gives the azulenyl phenyl sulphone (CXXVIII) and the corresponding 1,3-disulphone (CXXIX);[193] methanesulphonyl chloride reacts with azulene to form azulenyl methyl sulphone[195]; and copper thiocyanate gives good yields of 1-cyanatoazulene (CXXX) and 1,3-dithiocyanatoazulene (CXXXI),[193] which had been obtained earlier from azulene and thiocyanogen[178]:



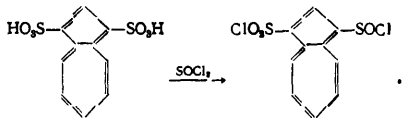
(CXXXI) (CXXX) (CXXVIII) (CXXIX)

At low temperatures azulene reacts with thionyl chloride to form diazulenyl sulphoxide (CXXXII), which on oxidation with sodium periodate is converted into diazulenyl sulphone[196]:



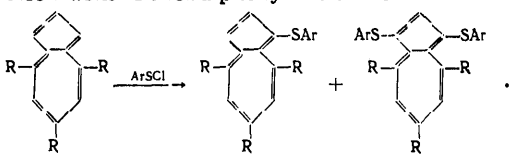
(CXXXII)

An unusual reaction takes place when the 1,3-disulphonic acid is treated with excess of thionyl chloride, for 3-chlorosulphinylazulene-1-sulphonyl chloride (CXXXIII) is formed[192]:



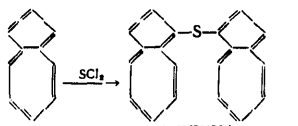
(CXXXIII)

Azulene and its derivatives readily give the 1-sulphides (CXXXIV) and the corresponding 1,3-bis-sulphides (CXXXV) on interaction with arenesulphenyl chlorides[174,178,195,197]:



(CXXXIV) (CXXXV)

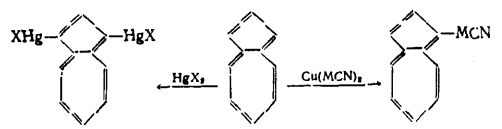
At −78°C sulphur dichloride acts on azulene to give diazulenyl sulphide (CXXXVI):[196]



(CXXXVI)

(*e*) Organoelementary azulene derivatives

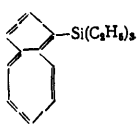
Azulene is readily mercurated by mercury(II) chloride to form azulene-1,3-dimercuric dichloride (CXXXVII):[198]



(CXXXVII) (CXXXVIII)

X=Cl, $OCOCH_3$; M=Se, Te

Mercury acetate is equally effective[192]. Monomercurated derivatives can also be obtained by varying the proportions of the reactants. The chloromercuri-derivatives are converted quantitatively into halogeno- or thiocyanato-derivatives by the action of copper(II) chloride, bromide, or thiocyanate[193]. Copper selenocyanate and tellurocyanate give good yields of the corresponding seleno- and telluro-cyanatoazulenes (CXXXVIII).[199] The organosilicon azulene derivative

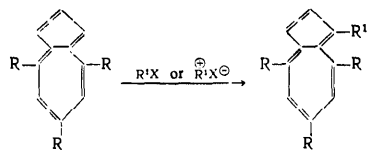


(CXXXIX)

was synthesised indirectly, not by direct substitution[200].

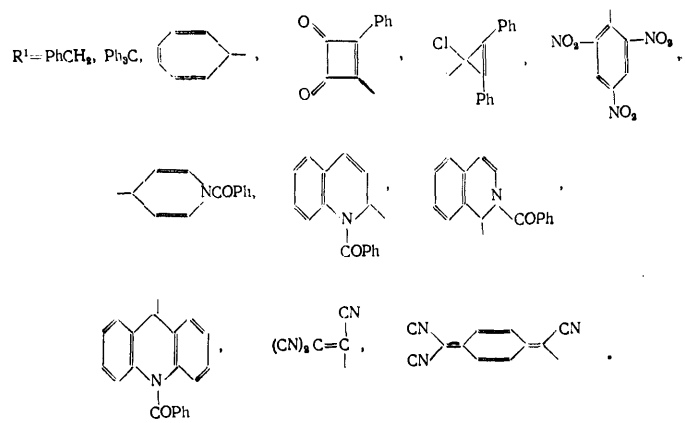
(*f*) Alkylation

Alkylation of azulene and its homologues under the conditions of Friedel–Crafts reaction takes place at positions 1 and 3, but such reactions give by no means high yields owing to the great sensitivity of azulenes to catalysts[166,198]: for example, benzyl chloride forms 1-benzylazulene in only 5.6% yield[198]. Alkyl halides give still poorer results[201,202]. However, compounds capable of forming stable carbonium ions—such as triphenyl chloromethane[203], tropylium bromide[204], 3-bromo-4-phenylcyclobutene-1,2-dione[205], and 3,3-dichloro-1,2-diphenylcyclopropene[206]—readily alkylate azulene at positions 1 and 3. Good results have been obtained by the action of picryl chloride and *p*-chloronitrobenzene on azulene hydrocarbons[166]; the condensation of azulene with pentaacetylbromoglucose has been described[207].



X=Cl, Br, CN;

R=H, $CH_3$;

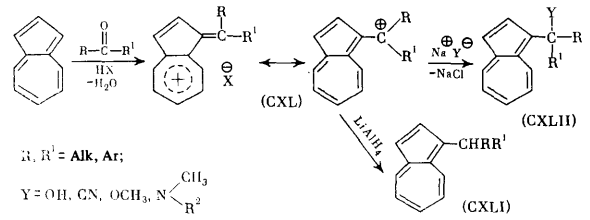


Di- and tri-phenylmethanols, their ethers or esters, or arylated ethylenes capable of forming stable carbonium ions have been used as alkylating agents[203,208] instead of alkyl halides. Tropylium and triphenylmethyl perchlorates are also effective alkylating agents[174,209]. 1-Ethyl-4,6,8-trimethylazulene has been obtained by alkylating 4,6,8-trimethylazulene with triethyloxonium tetrafluoroborate[174], but such a reaction could not be accomplished with unsubstituted azulene[198]. Yields of 40–60% have recently been obtained in the heteroarylation of azulene and its homologues with *N*-acylated pyridinium, quinolinium, isoquinolinium, and acridinium salts[210,211]. The $\pi$ complexes of azulene hydrocarbons with tetracyanoethylene and tetracyanoquinodimethane are converted into the 1-tricyanovinyl derivatives with the elimination of hydrogen cyanide[155–157].

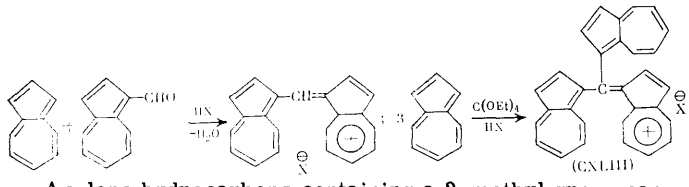
(*g*) Reactions with carbonyl compounds

In the presence of various mineral and organic acids azulene hydrocarbons condense with aromatic[165,212–219], heterocyclic[217,218,220,221], aliphatic[222,223], polyene[222,224], and azulene[212,214,222] aldehydes, ketones[206,225], and several dicarbonyl compounds[222]. The resulting mesomeric cations (CXL) can easily be reduced to the corresponding

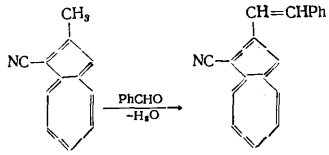
1-alkylazulenes (CXLI),[219,223] and are converted by bases into compounds of type (CXLII):[223]



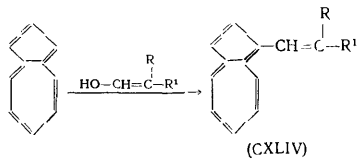
This reaction has been used to obtain azulenoid polymethine dyes[220,221]. Saltlike dyes of the diazulenylmethane series have been obtained by the interaction of azulene and 1-formylazulene[214,215,218,222]; and a triazulenylmethane dye (CXLIII) is produced by condensing azulene with orthocarbonic ester in acid medium[214]:



Azulene hydrocarbons containing a 2-methyl group can be condensed with benzaldehyde to form 2-styrylazulenes[226].



Enols alkylate azulene and its homologues in acid media with the elimination of water and the formation of vinyl derivatives (CXLIV):[222]

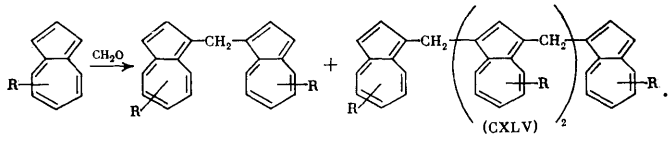


(CXLIV)

R=H, CN, $NO_2$, Ph, CHO; $R^1$=$COCH_3$, COPh

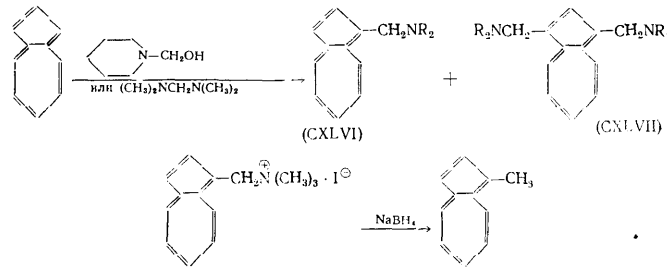
## (*h*) Aminomethylation

Chloromethylation and hydroxymethylation of azulene and guaiazulene by means of formaldehyde yield only products of diazulenylmethane structure[216] or of further condensation (CXLV),[227] not the corresponding chloromethyl or hydroxymethyl derivatives:



(CXLV)

However, the use of mild aminomethylating agents, such as aminomethanols[227,228] and methylenebisdialkylamines[229], made it possible to accomplish the Mannich reaction. Azulene is aminomethylated at positions 1 and 3 to give the unstable dialkylaminomethyl derivatives (CXLVI) and (CXLVII); with methyl iodide these form the more stable quaternary salts, which can be reduced by sodium tetrahydroborate to methylazulenes:

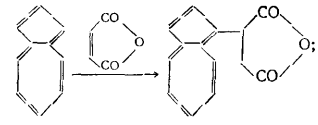


(CXLVI) (CXLVII)

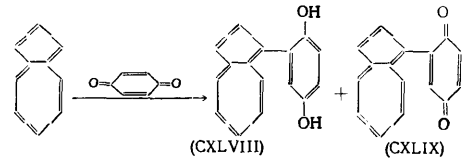
Reactions of these salts with alkali-metal phenoxides and cyanides have been described, as well as several other transformations of aminomethyl derivatives[137,228,230-232].

## (*i*) 1,2-Addition

Azulenes do not undergo diene condensation, but are able to add to active dienophiles—acetylenecarboxylic and azo-dicarboxylic esters[233], maleic anhydride[233,234], benzoquinone[233,234], 1,2-naphthaquinone[181]—with the formation of 1,2-addition products: e.g.



The product (CXLVIII) formed initially by the addition of benzoquinone to azulene may be oxidised by excess of the former reactant to the substituted quinone (CXLIX):[235]

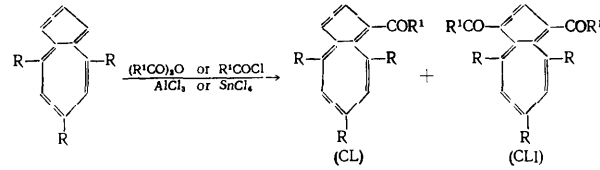


(CXLVIII) (CXLIX)

Azulene adds also to phenyl isocyanate to form azulene-1-carboxyanilide[181].

## (*j*) Acylation

Azulene is acylated by chlorides and anhydrides of carboxylic acids in the presence of aluminium chloride[171,201], perchloric acid[225], or tin tetrachloride[170] with the formation of 1-mono- and 1,3-di-acyl derivatives (CL) and (CLI):

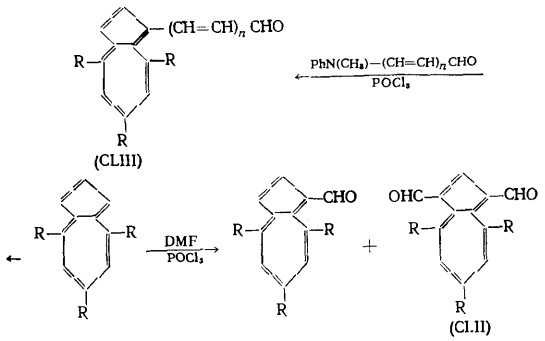


(CL) (CLI)

With trifluoroacetic anhydride the reaction goes almost quantitatively in the absence of a catalyst[236,237]. Acylation has been achieved with oxalyl[238-240], malonyl[241,242], and phenylacetyl[244] chlorides or bromides. Under the conditions of the Friedel–Crafts reaction carbonyl chloride forms diazulenyl ketones[212]. Guaiazulene may be formylated under the conditions of the Gattermann reaction[239]. In all the above cases acylation occurs at positions 1 and/or 3, at which the greatest electron density is concentrated; when these are occupied, position 5 becomes acylated.

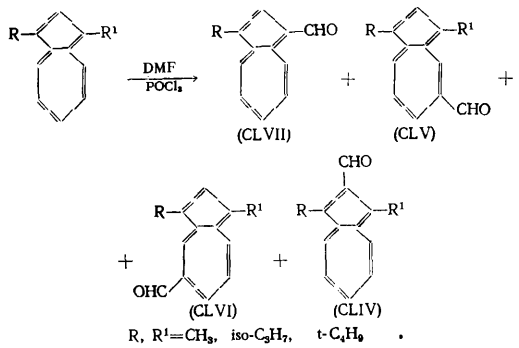
Substituents already present at the former positions—chloro[182,243], isopropyl[173], t-butyl[174]—often exchange simultaneously for an acyl group. 1- and 3-Acetyl groups may in turn be displaced by other electrophilic reagents[174], e.g. when heated with alcohols in acid media[225].

The Vilsmeier–Haack reaction is mostly used at the present time to obtain acyl and especially formyl derivatives of azulene hydrocarbons. Many diverse 1(3)-formyl derivatives of azulene have been prepared by this method[4,203,245-250]. The corresponding 1,3-dialdehydes (CLII) have also been obtained in good yields, and application of the reaction to unsaturated amino-aldehydes yields vinylogues of 1-formylazulene (CLIII):[117,224]




R=H, $CH_3$; n=1, 2 .

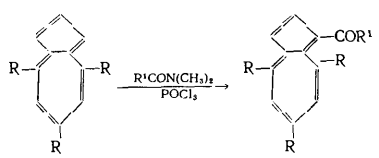
Treatment of 1,3-dialkylated azulenes with a complex of dimethylformamide and phosphoryl chloride gives a mixture of the 2-, 5-, and 7-formyl derivatives (CLIV)–(CLVI) together with the product (CLVII) of replacement of an alkyl by a formyl group[173]:




R, $R^1$=$CH_3$, iso-$C_3H_7$, t-$C_4H_9$ .

At a high temperature the formylating complex is able to displace the bromine atoms in 1,3-dibromoazulene[251] (see below).

Azulene can be formylated also by means of orthoformic ester in acid media[214]. Aldehydes have been obtained also by oxidising 1-dialkylaminomethylazulenes[228] and 1-methylazulene[260] with potassium permanganate. Treatment of azulene hydrocarbons with acylating complexes obtained from dimethylamides of acetic[18,127,248], chloroacetic[254], oxalic[253], benzoic[127,248], and several other acids have been used to prepare the corresponding 1(3)-acylazulenes (CL):



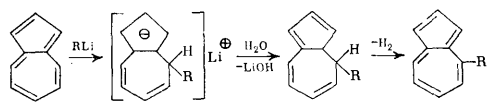

R=H, $CH_3$; $R^1$=$CH_3$, $CH_2Cl$, $CON(CH_3)_2$, $C_6H_5$ .

Azulene aldehydes and ketones are used as initial compounds for obtaining various classes of derivatives containing the azulene ring system[81,107,110,116-118,120,127,131,132,254-259].

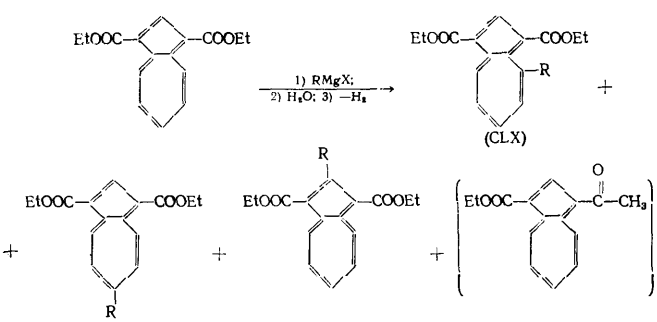
Displacement of substituents at positions 1 and 3 in the ring system is met quite often in the chemistry of azulene compounds and occurs readily under conditions of electrophilic attack. This phenomenon especially often accompanies formylation[173,251] and acylation[173,174,243], although it has been observed also during halogenation[186], nitrosation[175], and azo-coupling[174]. Groups that give stable carbonium cations are very easily replaced. Thus the ease of substitution of alkyl groups increases on passing from methyl to isopropyl, t-butyl, and then to triphenylmethyl and cycloheptatrienyl. Either one or both groups at positions 1 and 3 may undergo substitution. Not only alkyl groups but also the acetyl group[174] and halogens[243,251] may be replaced.

## 3. Nucleophilic Substitution

Considerably less study has been made of nucleophilic than of electrophilic substitution in azulene compounds. As LCAO-MO calculations have predicted, nucleophilic attack takes place at carbon atoms 4(8) and 6. Thus azulene reacts with organolithium compounds to give addition products (CLVIII), which on hydrolysis yield colourless dihydroazulene derivatives (CLIX), whose dehydrogenation by chloranil produces 4-substituted azulenes[30,32]:

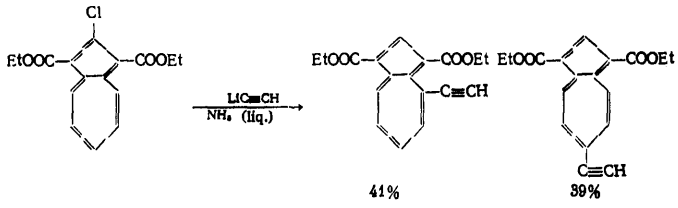



in which R = $CH_3$, $(CH_3)_3C$, $C_6H_5$, 1-$C_{10}H_7$, $C_6H_5CH_2$, 2-$C_4H_3S$, 2-$C_5H_4N$, or 2-$C_5H_4NCH_2$. 4,8-Disubstituted azulenes can be obtained similarly. It is interesting that diethyl azulene-1,3-dicarboxylate reacts with aliphatic and aromatic organomagnesium compounds without involvement of the ester groups, to form after hydrolysis and dehydrogenation a mixture of 4-, 6-, and 2-substituted azulenes (CLX)–(CLXII),[31,262] and in only one case has the product of interaction between an organomagnesium compound and an ethoxycarbonyl group (CLXIII) been detected:



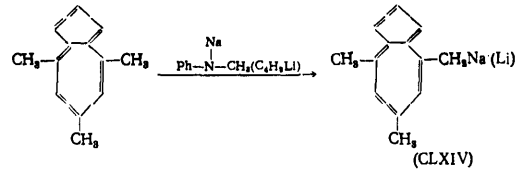

R=Alk, Ar .

An ethynyl group is readily introduced into the azulene ring system by the action of lithium acetylenide in liquid ammonia on 2-chloroazulenecarboxylic esters[261]:




Here, too, ethoxycarbonyl groups are unaffected, though their electron-accepting effect activates the azulene system to nucleophilic attack: unsubstituted azulene does not undergo such a reaction with acetylenides. The presence of halogen at position 2 makes it possible to eliminate the dehydrogenation stage, since the aromatic azulene structure is regenerated, by dehydrochlorination under the influence of ammonia, from the intermediate dihydro-derivatives formed by addition.

Metal derivatives of alkylated azulenes have been obtained by the action of the sodium derivative of *N*-methylaniline or of butyl-lithium on 4- or 6-methylated azulenes[244,262]:

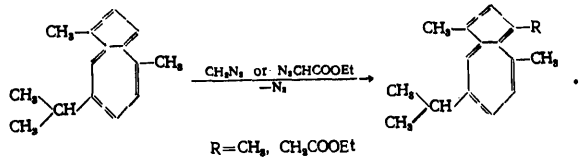



(CLXIV)

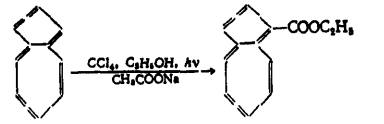
The organometallic derivatives (CLXIV) undergo the usual reactions with alkyl halides, carbon dioxide, and carbonyl compounds, forming various 4-substituted azulene derivatives[116,120,244,262–265]. Azulene is aminated at position 4 in low yield by sodamide[185]. Various nucleophilic reactions involving exchange of halogen in halogenated azulenes have been studied[183,266–268].

## 4. Radical Substitution

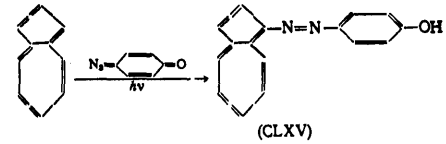
Calculated localisation energies suggest that radical reactions should occur at position 4 in azulene compounds[269], but the difference in energy of localisation at positions 1 and 4 is insignificant, and almost all known radical reactions take place at the 1-carbon atom. Such reactions, which have been studied with the alkylation of guaiazulene by diazomethane and diazoacetic ester as example[270], yield the corresponding substitution products:




A 15% yield of 1-phenylazulene has been obtained[216] by the action of nitrosoacetanilide on azulene. The radical benzylation of azulene[271] gives a mixture of the 1- and 2-isomers, the latter probably formed by secondary migration of the benzyl group under the severe reaction conditions (see below). Of preparative interest is the photoalkyoxycarbonylation of azulene[272] to give a 52% yield of ethyl azulene-1-carboxylate:

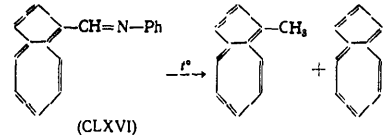



A high yield of the azo-dye (CLXV) is obtained by the action of *p*-diazoquinone on azulene during exposure to ultraviolet radiation[273]:



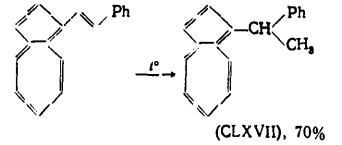

(CLXV)

Several thermal reactions of azulene derivatives resulting in modification of 1-substituents are probably also radical in character. Thus the Schiff base (CLXVI) when heated is converted into a mixture of 1-methylazulene and azulene in 36% and 24% yield respectively[274]:



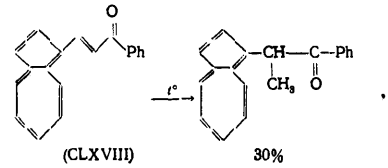

(CLXVI)

1-Styrylazulene is transformed in high yield into 1-α-methylbenzylazulene (CLXVII):[275]




(CLXVII), 70%

Azulenylvinyl phenyl ketone (CLXVIII) undergoes analogous rearrangement[276]:




(CLXVIII) 30%

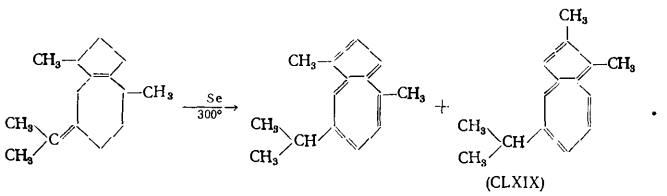
Reduction of the rearranged products is a consequence of partial decomposition of the azulene compounds. Although the yields in these processes are not always high, such reactions enable several difficultly accessible azulene derivatives to be obtained.

On irradiation 1-nitroazulene exchanges its nitro-group for a cyano- or a methoxy-group[277,278], a reaction of especial interest for obtaining the difficultly accessible 1-methoxyazulene. It is quite likely that the migration of various groups from 1 to the 2 position in the azulene ring system has a radical mechanism.

## 5. Migration of Substituents

The most common specific migration of groups is the conversion of 1- into 2-substituted azulenes, first observed by Plattner[279]; it has now been studied on several examples, and provides a route to 2-substituted azulenes, which are

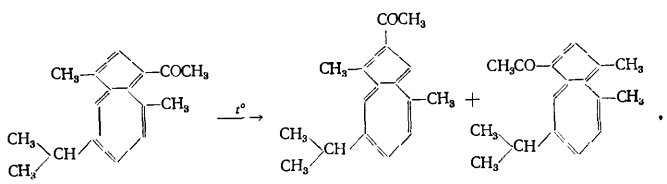
extremely difficult to obtain by other methods, although the yield is often diminished by secondary processes due to the high temperature of conversion. Dehydrogenation of guaiene with selenium at 300°C yields not only guaiazulene (II) but also the isomeric (CLXIX):[279,280]




(CLXIX)

Isopropyl[282], t-butyl[283], phenyl[281], acetyl[19,285,286], benzoyl[284], and formyl[252] groups migrate in this way. Ease of migration increases on passing from methyl to t-butyl[283].

This isomerisation is promoted by substituents at positions 4 and 8. Thus 1-formylazulene does not isomerise into the 2-aldehyde, whereas 1-formyl-4,6,8-trimethylazulene is converted into the 2-formyl derivative in 16% yield[252,287]. The reaction may be accompanied by exchange of the migrating group for hydrogen[283] and by intermolecular alkylation. A case of the simultaneous migration of two substituents is known[286]:




## IV. PRACTICAL APPLICATIONS OF AZULENE COMPOUNDS

Two main trends in the practical application of azulene derivatives have developed during recent years: the first is based on the broad spectrum of biological activity exhibited by azulenes and has led to the production of various medicinal preparations; the second exploits the peculiar electronic structure of azulene hydrocarbons, which enables these compounds to be used as dyes, optical sensitisers, and perhaps photosemiconductors. Many plants that are natural sources of azulene compounds have long been employed in folk and official medicine. A broad study of natural and synthetic azulenes has established that many of them possess high bacteriostatic[288,289], anti-inflammatory[290-295], antipyretic[70,129,133], sedative[134,296-298], antiallergic, antasthmatic[299-302], and several other types of activity. During recent years preparations possessing antineoplastic activity have been based on azulene compounds[141,179,204,303,304], although no statistical data on their application have appeared. The high anti-inflammatory activity of several azulene compounds has led to their widespread introduction as components of toothpastes, creams, and several other cosmetic materials[306]. For this purpose methods have been developed for producing stable emulsions and water-soluble formulations[295]. Azulene analogues of known medicinal preparations have been synthesised[307,308]. The influence of azulene compounds on several enzyme systems was studied[309] in order to elucidate the mechanism of their biological action. The carcinogenic effect of several fused polycyclic azulenes has been examined[310,311].

The ability of azulene derivatives to absorb in the visible led to an intensive study of azulene analogues of triphenylmethane[107] and polymethine[221,255,312] dyes, including those based on azulenylthiazole[254]. Photoconduction by azulene crystals has been studied[313]. Certain substituted heterocyclic azulenes are used as stabilisers for polymers[314]. The use of azulene in analytical chemistry has been reported[315].

In assessing the practical utilisation of azulenes we must emphasise that research on their application was held back for a long time by the absence of effective methods of synthesis, which have been developed only during the past two decades[305]. However, the results already available suggest that great prospects lie before this class of non-benzenoid aromatic compounds.

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# The Addition of Sulphenyl Chlorides to Unsaturated Compounds

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One of the aspects of the chemistry of sulphenyl chlorides, which is vigorously developing at the present time, is examined. It involves their interaction with unsaturated compounds. The application of modern physical research techniques has made it possible to investigate the addition of sulphenyl chlorides to asymmetric olefins, which results as a rule in the formation of a mixture of isomeric β-halogenoalkyl sulphides. The interconversions of the β-halogenoalkyl sulphides, associated with the vicinal positions of the halogen and sulphur atoms in the molecule, are considered. The high reactivity of the halogen and sulphur atoms in the molecule, are considered. The high reactivity of the halogen permits its ready nucleophilic substitution with formation of a series of new interesting compounds.
The bibliography includes 210 references.

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## I. INTRODUCTION

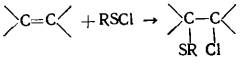
Reactive sulphenyl chlorides add readily and quantitatively to unsaturated compounds. The reaction constitutes a convenient method of synthesising various β-chloroalkyl sulphides, which are used as insecticides, fungicides, and bactericides or serve as the starting materials for the synthesis of aminomercaptans, monomers, etc. Certain β-chloroalkyl sulphides exhibit antitumour or mutagenic activities. The addition of sulphenyl chlorides to unsaturated compounds such as olefins, acetylenes, and steroids is also used for their characterisation and quantitative determination.

Certain reactions involving the addition of sulphenyl chlorides to unsaturated compounds are briefly reviewed in Kharasch's monograph[1], but many new data have been published in recent years, which necessitated significant modifications of the earlier ideas. Gundermann's review[2] deals with the involvement of the sulphur atom in nucleophilic substitution of the halogen in β-halogenoalkyl sulphides. Mueller[3] analysed the influence of steric and electronic factors, confirming the formation of the episulphonium ion as an intermediate in the addition of sulphenyl chlorides to unsaturated compounds and in the cleavage of thiirans by electrophiles. Kuhle[4] described methods for the preparation of sulphenyl chlorides and a wide variety of their reactions.

This review includes new studies on the addition of alkyl, aryl, acetylthio-, dialkoxyphosphoryl, alkoxyalkylphosphinyl, and alkylamino-derivatives of sulphenyl chlorides to olefins, dienes, allenes, acetylenes, and derivatives of αβ-unsaturated acids.

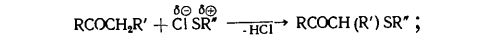
## II. ADDITION TO OLEFINS

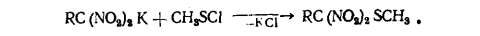
The first data on the addition of sulphenyl chlorides to olefins were published by Lecher et al.[5] in 1925:



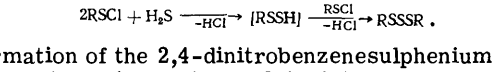
R = $C_6H_5$; *p*-$CH_3C_6H_4$; or *o*-$NO_2C_6H_4$.

The reaction drew attention, since, owing to their high reactivity, sulphenyl chlorides add easily and quantitatively to double bonds with formation of the corresponding β-chloroalkyl sulphides. According to modern ideas, the sulphenyl chloride molecule is polarised in such a way that the partial positive charge is localised at the sulphur atom. This structure is confirmed also by the interaction of sulphenyl chlorides with compounds containing a mobile hydrogen atom, such as malonic ester, acetoacetic ester, nitromethane, hydrogen cyanide, etc. The reaction leads to the formation of sulphides[6-8]:



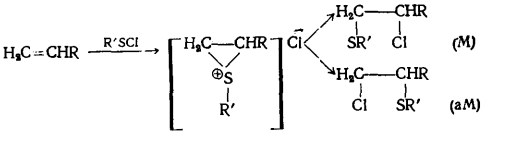


Sulphenyl chlorides react with hydrogen sulphide to form trisulphides[9,10]:



The formation of the 2,4-dinitrobenzenesulphenium cation $(NO_2)_2C_6H_3S^+$ on dissolution of 2,4-dinitrobenzenesulphenyl chloride in concentrated sulphuric acid has also been described[11,12].

Kharasch contributed much to the study of the mechanism of the addition of sulphenyl chlorides to unsaturated compounds. He was the first to suggest the formation in this reaction of the intermediate cyclic episulphonium ion (I). The subsequent opening of the ring by the chloride anion leads to the formation of β-chloroalkyl sulphides. With asymmetric olefins, adducts can be formed both in accordance with (designated subsequently by M) and contrary to (designated subsequently by aM) the Markovnikov rule[13]:



(I)

The study of the kinetics of the addition of sulphenyl chlorides to olefins showed that this is an electrophilic reaction [14,15]. The rate of addition of 2,4-dinitrobenzenesulphenyl chloride (DNBS) to *p*-substituted styrenes is influenced by those *p*-substituents which increase the electron density in the double bond of styrene [16]. The addition to cyclohexene is ten times faster than to styrene and three times faster than to *p*-methylstyrene [17-20]. The rate of addition of DNBS to 4,5-disubstituted cyclohexenes and to norbornene derivatives decreases with enhancement of the electron-accepting properties of the substituents [21]. Methanesulphenyl chloride adds faster to olefins containing methyl groups attached to the double bond. The influence of the nucleophilic properties of the double bond and steric factors on the relative rates on addition of sulphenyl chlorides has been demonstrated for olefin homologues and *cis*- and *trans*-isomers. Comparison of the reactivities of sulphenyl chlorides and chlorine in addition to olefins under analogous conditions showed that the formation of the intermediate sulphonium ion is less sensitive to changes in the nucleophilic properties of the olefins than in the case of chlorine and is extremely sensitive to steric factors. The relative reactivities of olefins with respect to electrophilic attack in non-polar solvents are given below:

| Olefin | $Cl_2$ | $CH_3SCl$ | Olefin | $Cl_2$ | $CH_3SCl$ |
|---|---|---|---|---|---|
| But-1-ene | 1.6 | 1.0 | Isobutene | 50 | 0.75 |
| *cis*-But-2-ene | 63 | 13.0 | Trimethylethylene | 11.000 | 8.26 |
| *trans*-But-2-ene | 58 | 0.72 | Tetramethylethylene | 430.000 | 12.90 |

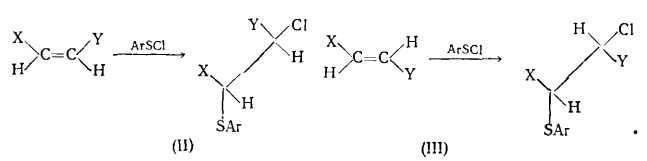
The rate of addition is also influenced by the geometry of the olefins; for example, *cis*-but-2-ene combines with methanesulphenyl chloride faster than its *trans*-isomer [22].

The nature of the substituent in the benzene ring of benzenesulphenyl chloride also affects the rate of addition. *p*-Methyl- and 2,4-dichloro-benzenesulphenyl chlorides add to but-2-ene faster than DNBS. [23] The study of the relative rates of addition of *p*-substituted *o*-nitrobenzenesulphenyl chlorides to cyclohexene led to analogous conclusions [24-26].

It is believed that the formation of the episulphonium ion is the rate-determining stage in the addition of DNBS to styrene [27], *p*-substituted styrenes [16], and cyclohexene [17]. The ionic reaction mechanism is also confirmed by data obtained in the study of the influence of the polarity of the solvent on the rate of addition of DNBS to cyclohexene. The reaction in nitrobenzene is 3000 times faster and in acetic acid 1400 times faster than in carbon tetrachloride [17].

The Hammett and Taft constants calculated for the addition of arenesulphenyl chlorides to olefins also point to the existence of an intermediate episulphonium ion rather than a carbonium ion [25,28].

The addition of sulphenyl chlorides to unsaturated compounds is strictly stereospecific [29]. Different arenesulphenyl chlorides yield respectively the racemic *threo*- and *erythro*-adducts (II) and (III) on interaction with the *cis*- and *trans*-isomers of 2-phenylbut-2-ene, [30] but-2-ene [23,31], stilbene [32-34], and 1-phenylprop-1-ene [35]:




(II) (III)

*cis*-Stilbene reacts more slowly than its *trans*-isomer. The two adjacent phenyl groups apparently prevent the formation of the intermediate episulphonium ion [32].

Kinetic studies on the addition of 2,4-dinitrobenzenesulphenyl chloride to the vapours of various 1-arylpropenes and the corresponding olefins also showed that all the *trans*-isomers of 1-arylalkenes are more reactive than the *cis*-isomers. On the other hand, the rate of addition of sulphenyl chlorides to *cis*-alkenes is approximately ten times higher than the rate of addition to the *trans*-isomers [36].

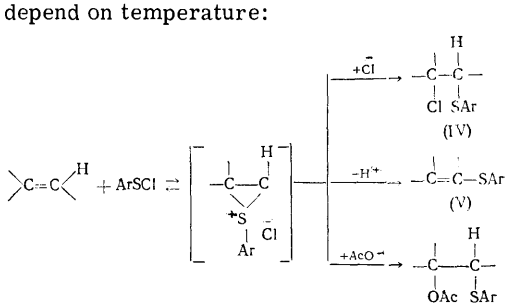
Data indicating the high stereospecificity of the addition of *p*-chlorobenzenesulphenyl chloride to *cis*- and *trans*-but-2-enes over a wide temperature range (from −34° to +180°C) also confirm the formation of an intermediate cyclic episulphonium ion. If an intermediate carbonium ion, which has presumably a planar configuration with free rotation about the central C=C bond, had been formed, the ratio of the *erythro*- and *threo*-adducts would have been identical for both *cis*- and *trans*-but-2-enes [37]. The addition of RSCl to cyclohexenes resulted in the formation of *trans*-adducts [31,38,40]. In some investigations, the configuration of the cyclohexene adducts was not determined [41-48]. *trans*-Adducts were also obtained with other cyclic compounds: norbornene [49,50], norbornadiene [51-54], and sulpholene [55].

Following the addition of benzenesulphenyl chloride to 7-chlorodibenzobicyclo[2,2,2]octatriene [54] and of 2,4-dinitrobenzenesulphenyl chloride to norbornene [56], the Wagner–Meerwein rearrangement was observed.

The *trans*-addition of methanesulphenyl chloride to acenaphthylene, of benzenesulphenyl chloride to 7,7-dimethylnorbornene [57-61], and of various alkanesulphenyl chlorides to dihydropyran [62,63] was confirmed by NMR spectra.

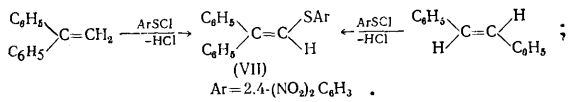
A single non-stereospecific example, involving the addition of 2,4-dinitrobenzenesulphenyl chloride to *cis*- and *trans*-anetholes in tetrachloroethane, has been described. *cis*-Anethole yields 70% of the *threo*-adduct and 30% of the *erythro*-adduct, while the *trans*-isomer gives rise to 5 and 95% of the two adducts respectively. A slow rearrangement was observed until the attainment of equilibrium with approximately equal proportions of the isomers (51.8% of the *erythro*-adduct and 48.2% of the *threo*-adduct) [64].

When arenesulphenyl chlorides react with anethole [13], *p*-methoxystyrene [16], and 3,3-dimethylbutene [65] in glacial acetic acid, several compounds are obtained, whose formation can be explained solely by the transformation of an intermediate episulphonium ion. The addition of the chloride anion to the intermediate episulphonium ion gives rise to a β-chloroalkyl sulphide, while the abstraction of a proton from the latter results in the formation of a vinyl sulphide and solvolysis with glacial acetic acid gives a β-acetoxyalkyl sulphide. The proportions of the compounds depend on temperature:




In the reaction involving *p*-methoxystyrene, the vinyl sulphide (V) and the β-acetoxyalkyl sulphide (VI) are formed from β-chloroethyl sulphide (IV) much more

slowly than in the direct addition of the arenesulphenyl chloride to the olefin [16]. In the addition of ArSCl to 1,1-diphenylethylene, HCl is evolved and the unsaturated sulphide (VII) is formed [13]; it was also obtained from *trans*-stilbene in boiling acetic acid [66]:

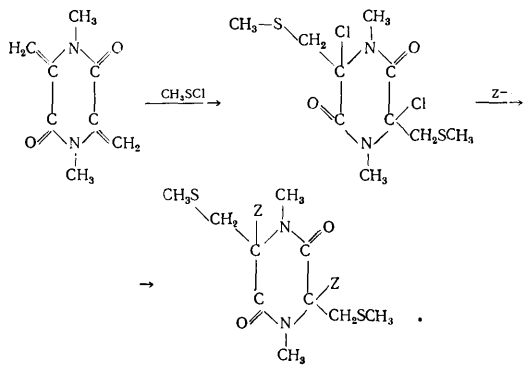


(VII)

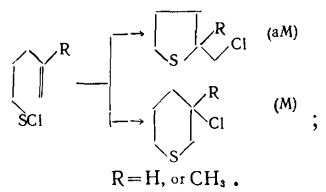
Ar = 2,4-$(NO_2)_2C_6H_3$ .

It has been shown that, when 2,3,5,6-tetrachloropyridine-4-sulphenyl chloride adds to asymmetric alkenes, the ratio of the M and the aM adducts is greatly influenced by steric factors and the solvent [67].

The addition of methanesulphenyl chloride to 1,4-dimethyl-3,6-dimethylenepiperazine-2,5-dione results in an adduct which loses HCl on prolonged storage with formation of three isomeric compounds. On treatment with nucleophiles, chlorine is readily substituted [68]:



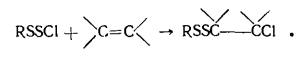
The intramolecular addition of a sulphenyl chloride with formation of a mixture of aM and M compounds has been achieved:



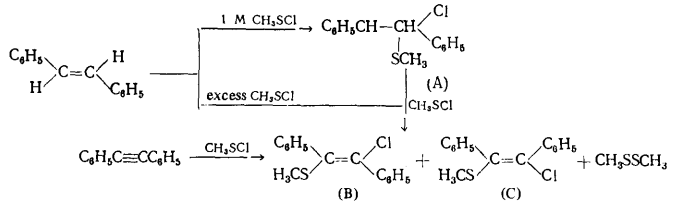
R = H, or $CH_3$ .

The aM adduct is first formed preferentially and then gradually isomerises to the M adduct. The structures were confirmed by NMR and by oxidation to sulphones [69].

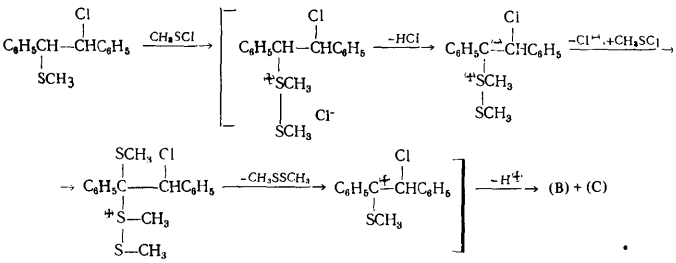
The addition of arenethiosulphinyl chlorides leads to the corresponding mixed β-halogenodisulphides [70]:



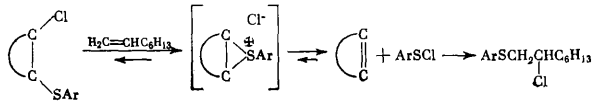
Interesting results were obtained in a study of the addition of methanesulphenyl chloride to *trans*-stilbene [71]. On treatment of *trans*-stilbene with one mole of methanesulphenyl chloride, the adduct (A) is formed, while on treatment with an excess of the reagent the product consists of a mixture of compounds (B) and (C). The same mixture was obtained following the addition of methanesulphenyl chloride to tolane:



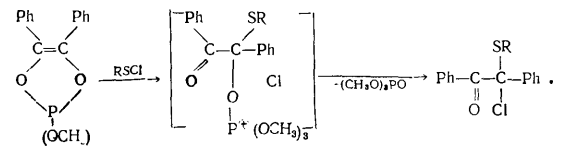
with *cis* : *trans* = 4 : 1. The authors suggested the following mechanism for the formation of compounds (B) and (C):



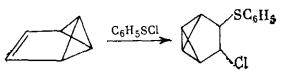
The exchange of sulphenyl chloride between olefins has been achieved [72]. It has been shown that the adducts obtained by the addition of 4-chlorobenzenesulphenyl chloride to cyclic or acyclic olefins exchange it with oct-1-ene on heating in tetrachloroethane:



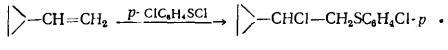
The addition of sulphenyl chlorides to 1,3,2-dioxaphospholen leads to the elimination of phosphate and the formation of α-chloro-α-thioketones [73]:



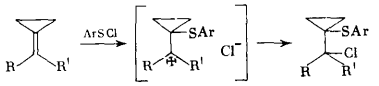
The addition of benzenesulphenyl chloride to benzvalene has been achieved [74]:



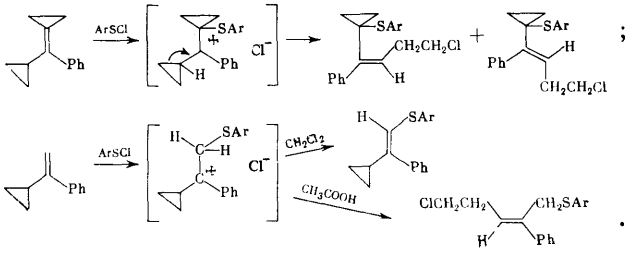
The effect of the cyclopropyl substituents on the rate of electrophilic addition has been investigated [75] and it has been shown that the rate of addition of β-chlorobenzenesulphenyl chloride to cyclopropylethylene is an order of magnitude higher than the rate of addition to n-butylethylene:



The addition of 2,3-dinitrobenzenesulphenyl chloride to phenylmethylenecyclopropanes and α-cyclopropylstyrene [76] has been studied. Phenylmethylenecyclopropanes with R = R′ = Ph and R = Ph, R′ = H normally combine with sulphenyl chlorides via the mechanism



In the reaction of phenylcyclopropylmethylenecyclopropane and α-cyclopropylstyrene, the unsubstituted cyclopropane ring rearranges to homoallyl adducts:

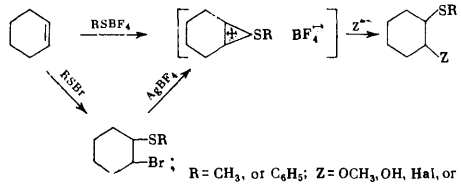


The tendency by the intermediate to lose a proton diminishes with increase of the acidity of the solution in the following sequence:

$$CH_3COOH \gg CH_3NO_2 > CH_2Cl_2 .$$

When sulphenyl chloride adds in acetic acid solution, chlorine is partly substituted by the acetoxy-group [76].

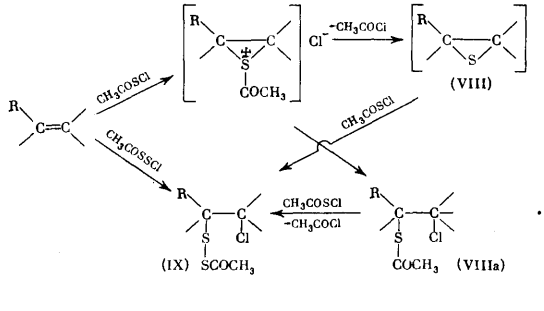
The possibility of addition to the multiple bonds of the more highly polarised sulphenyl fluoroborates has also been demonstrated [77,78]:



R = $CH_3$, or $C_6H_5$; Z = $OCH_3$, OH, Hal, or $NHCOCH_3$ .

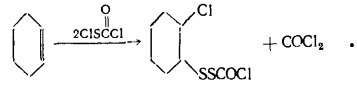
However, the authors were unable to isolate the intermediate in the form of a stable episulphonium salt; only the products of the subsequent nucleophilic substitution were isolated. Under these conditions, there was *trans*-addition to tetradeuterocyclohexene [79].

The addition of acetylsulphenyl chloride to olefins takes place in an unusual manner. It is suggested that here too an episulphonium ion is formed as an intermediate and is stabilised by ejecting acetyl chloride with formation of the thiiran (VIII). The latter is immediately cleaved by a second molecule of acetylsulphenyl chloride with formation of the β-chloroalkyl acetyl disulphide (IX), which is also obtained by the addition of acetylthiosulphenyl chloride to an olefin [80-82]. However it has been shown recently [83] that the *S*-acetyl-β-chloromercaptan (VIIIa) likewise readily reacts with acetylsulphenyl chloride to form compound (IX). Thus another mechanism is also possible in this instance:

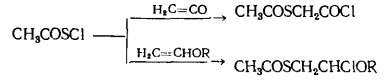


If the rate of addition of acetylsulphenyl chloride to olefins with the reactants taken in equimolar amounts is much higher than the rate of cleavage, only the normal adducts are formed—*S*-acetyl-β-chloromercaptans (VIIIa); on the other hand, if the rate of addition of acetylsulphenyl chloride is lower than the rate of cleavage of compound (VIIIa) by the sulphenyl chloride, only the disulphides (IX) are formed.

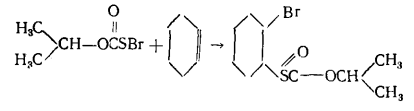
Chlorocarbonylsulphenyl chloride adds similarly to a cyclic olefin [84]:



Like other sulphenyl chlorides [85], acetylsulphenyl chloride reacts normally with ketones [81,86] and vinyl ethers [81] to form monoadducts:

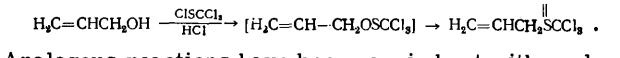


Isopropoxycarbonylsulphenyl bromide likewise reacts with cyclohexene to form a monoadduct [87]:

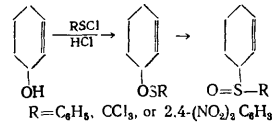


The addition of sulphenyl chlorides to enolic esters [88], allyl chloride [89,90], vinyl chloride [91] and the phthalimide derivative of allylamine [92] has been achieved.

Allyl alcohol reacts with sulphenyl chlorides preferentially via the hydroxy-group, forming unstable allyl sulphenates. The latter readily rearrange to the isomeric sulphoxide [93-95]:

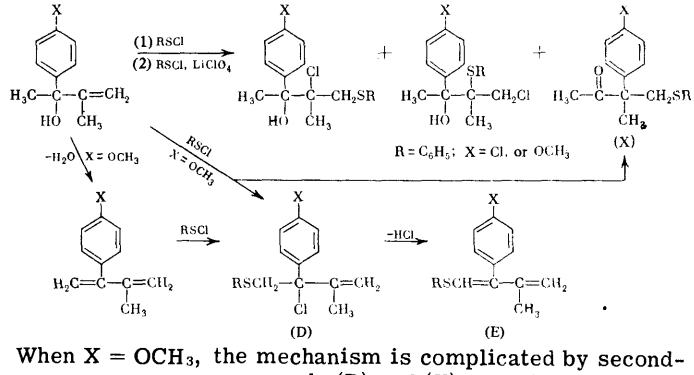


Analogous reactions have been carried out with cyclohexen-2-ol [96]:



R = $C_6H_5$, $CCl_3$, or 2.4-$(NO_2)_2C_6H_3$ .

However, sulphenyl chlorides normally add to the double bond of 3-methyl-2-(4-X-phenyl)but-3-en-2-ols. The subsequent rearrangement of the adduct gives the ketone (X), whose amount is much larger in the presence of $LiClO_4$ (51%):



When X = $OCH_3$, the mechanism is complicated by secondary processes; compounds (D) and (E) were isolated in addition to the ketone [97,98].

Kharasch was the first to note that the asymmetric olefins propene and pent-2-ene react with DNBS to form simultaneously two adducts, M and aM, the M adduct predominating (65%). The authors demonstrated the

structure of these isomeric β-chloroalkyl sulphides by converting them into alkyl aryl sulphones (XI):[13]

$$2,4\text{-}(NO_2)_2C_6H_3SCH_2CHClCH_3 \xrightarrow[(3)\ H_2/Ni]{\substack{(1)\ KMnO_4/CH_3COOH \\ (2)\ (C_2H_5)_3N \\ (4)\ C_6H_5COCl}} \rightarrow 2,4\text{-}(C_6H_5CONH)_2C_6H_3SO_2CH_2CH_2CH_3 .$$

(XI)

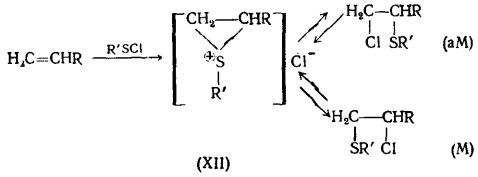
In a number of studies on the addition of sulphenyl chlorides to unsaturated compounds, the structures of the adducts were also determined solely by chemical methods: by converting them into sulphones[23,43,99], lactones, and thiolactones[100,101], by dehydrohalogenation[47,102], and by specific synthesis[48,49]. Some workers adopted the M structure solely on the basis of the Markovnikov rule[93-99].

**Table 1.** Dependence of the initial isomer ratio on the structure of the initial reactants.

| Initial olefin | Substituent R in RSCl | Adducts, % $CH_2-C(Cl)-SR$ (aM) | Adducts, % $CH_2-C(SR)-Cl$ (M) | References |
|---|---|---|---|---|
| $H_2C=CHCH_3$ | $CH_3$ | 82 | 18 | 59 |
| $H_2C=C(CH_3)_2$ | $CH_3$ | 80 | 20 | |
| $H_2C=CHCH(CH_3)_2$ | $CH_3$ | 94 | 6 | |
| $H_2C=CHC(CH_3)_3$ | $CH_3$ | 95 | 5 | |
| $H_2C=CHCH_3$ | $(CH_3)_2N$ | 78 | 22 | 110 |
| $H_2C=C(CH_3)_2$ | $(CH_3)_2N$ | 71 | 29 | |
| $H_2C=CHCH(CH_3)_2$ | $(CH_3)_2N$ | 90 | 10 | |
| $H_2C=CHC(CH_3)_3$ | $(CH_3)_2N$ | 95 | 5 | |
| $H_2C=CHCH_3$ | $C_6H_5$ | 68 | 32 | 59 |
| $H_2C=CHCH(CH_3)_2$ | $C_6H_5$ | 87 | 13 | |
| $H_2C=CHCH_3$ | $CH_3C(O)S$ | 60 | 40 | 82 |
| $H_2C=C(CH_3)_2$ | $CH_3C(O)S$ | 32 | 68 | |
| $H_2C=CHC(CH_3)_3$ | $CH_3C(O)S$ | 82 | 18 | |
| $H_2C=CHCH_3$ | $(CH_3O)_2P(O)$ | 50 | 50 | 59 |
| $H_2C=C(CH_3)_2$ | $(CH_3O)_2PO$ | 19 | 57* | |
| $H_2C=C(C_6H_5)_2$ | $CH_3$ | 10 | 90 | 59,82 |
| $H_2C=CHC_6H_5$ | $CH_3$ | 2 | 98 | |
| $H_2C=CHC_6H_5$ | $CH_3C(O)S$ | — | 100 | |
| $H_2C=CHCH_2CH(CH_3)_2$ | $2\text{-}NO_2\text{-}4\text{-}CH_3O\text{-}C_6H_3$ | 52 | 47 | 112 |
| $H_2C=CHCH_2CH(CH_3)_2$ | $2\text{-}NO_2\text{-}4\text{-}CH_3\text{-}C_6H_3$ | 47 | 51 | |
| $H_2C=CHCH_2CH(CH_3)_2$ | $2\text{-}NO_2\text{-}C_6H_4$ | 44 | 54 | |
| $H_2C=CHCH_2CH(CH_3)_2$ | $2,4\text{-}(NO_2)_2\text{-}C_6H_3$ | 38 | 61 | |

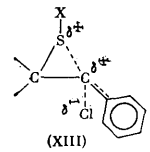
*21% of $RSCH_2-C(CH_3)=CH_2$ was also obtained.

The application of NMR for the determination of the structures of the adducts enabled Mueller and coworkers[58,59] not only to establish a number of characteristics of the addition of sulphenyl chlorides to unsaturated compounds but also to explain some of them. Thus, in order to prevent isomerisation, alkane- and arene-sulphenyl chlorides were added in the presence of calcium carbonate to asymmetric olefins in methylene chloride at a low temperature. It was established that aM adducts are formed preferentially in the first instance (Table 1). The selectivity of the formation of the aM adducts increases with increase of the size of the substituent at the double bond from methyl to t-butyl. This shows that the mode of addition of sulphenyl chloride depends not only on electronic factors but also on the steric influence of the substituents. In the intermediate episulphonium ions (XII), they direct the attack by the chloride anion to the less substituted carbon atom with formation of the aM adduct[57,59].



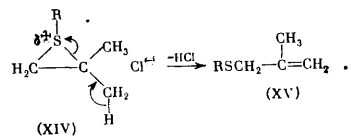
(XII)

Only the M adduct is formed in the reaction with styrene, while in the reaction with 1,1-diphenylethylene the proportion of M is up to 90% (Table 1) owing to the stabilisation of the positive charge of the α-carbon atom in the transition state (XIII):[59]



(XIII)

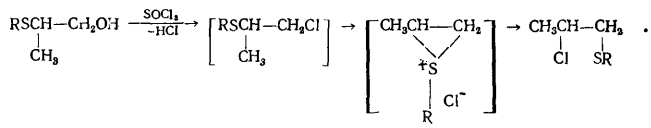
In the reaction with isobutene, the two methyl groups attached to the same carbon atom create conditions for the formation of an intermediate ion having some of the properties of a carbonium ion. On interaction with *OO*-dimethylphosphorylsulphenyl chloride, this olefin gives rise to the unsaturated sulphide (XV) apparently via the intermediate state (XIV) (Table 1). The electron-accepting phosphoryl group makes the sulphur less nucleophilic and facilitates the elimination of a proton from the methyl group[59,111]:



(XIV) (XV)

The ratio of the adducts in the reaction mixture is also influenced by the nature of the sulphenyl chloride (Table 1);[59,82,110-112] as the electron-accepting properties of the substituent R in the sulphenyl chloride become more marked, the amount of the M adduct increases. The explanation is that the electron-withdrawing group R in the intermediate episulphonium ion favours the formation of a positive charge on the substituted carbon atom, directing thereby the chloride ion to this atom.

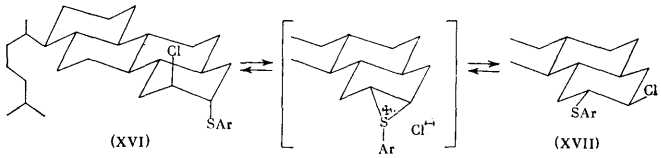
Fuson et al. described for the first time the isomerisation of β-chloroalkyl sulphides in which the chloro- and alkylthio- or arylthio-groups change places[99]. The authors postulated that the isomerisation proceeds via an episulphonium ion:



A similar isomerisation was later observed by other workers, who synthesised β-chloroalkyl sulphides by various methods[114,118].

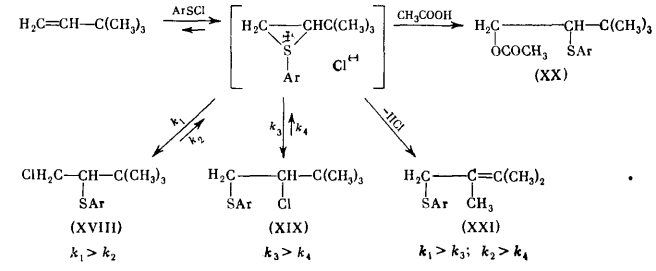
The rate of isomerisation of β-chloroalkyl sulphides in various solvents has been studied in relation to the adduct formed by arenesulphenyl chloride with 5-α-cholest-2-ene[119,120]. The addition reaction involves the initial formation of the diaxial adduct (XVI), which isomerises on heating to the diequatorial adduct (XVII). The isomerisation is accelerated by solvents promoting ionisation; for example, the isomerisation is 1600 times faster in butanol than in decalin. The introduction of the *p*-nitro-group into benzenesulphenyl chloride retards isomerisation in butanol to a greater extent than in decalin. This observation confirms the ionic mechanism of the

isomerisation process, which may proceed via an episulphonium ion:



(XVI) (XVII)

The variation of the rate of isomerisation of β-chloroalkyl sulphides with temperature and the duration of heat treatment has been studied in relation to the addition of 2,4-dinitrobenzenesulphenyl chloride to 3,3-dimethylbut-1-ene in glacial acetic acid[65]:



(XVIII) (XIX) (XXI) (XX)

$k_1 > k_2$ $k_3 > k_4$ $k_1 > k_3$; $k_2 > k_4$

It is suggested that the activation energy for the stage involving the formation of the initial adduct (XVIII) is smaller than the activation energy for the formation of compound (XIX). At lower temperatures and for shorter reaction times, the kinetically controlled aM adduct (XVIII) is therefore formed, while at higher temperatures and for longer reaction times the product is the thermodynamically stable M adduct (XIX). This is accompanied by the simultaneous acetolysis and elimination of HCl with formation of compounds (XX) and (XXI).

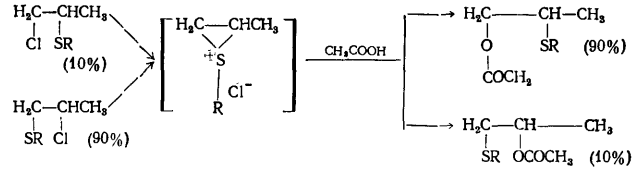
The ready isomerisation of the kinetically controlled aM adducts to thermodynamically stable isomers when the former are stored was observed by NMR.[57,59] At a temperature below 0°C in the presence of $CaCO_3$, the ratio of the aM and M isomers remain unchanged. In the absence of $CaCO_3$, slow isomerisation took place (to give 90% of the M adduct) until equilibration. At room temperature the equilibrium was attained after 200 h, the isomerisation being accelerated by traces of acids. The isomerisation of the aM adduct of 2,4-disubstituted benzenesulphenyl chlorides with 4-methylpent-1-ene to the M adducts took place to the extent of 92–95% on heating in glacial acetic acid[102].

The substituents at the sulphur atom have a significant influence on the isomerisation of β-chloroalkyl sulphides. The adducts of methanesulphenyl chloride isomerise comparatively rapidly, while those of benzenesulphenyl chloride isomerise much more slowly[57,59]. The rate of isomerisation of the adducts of substituted arenesulphenyl chlorides is reduced to a particularly marked extent by the *o*-nitro-group, which can be explained either by steric hindrance or by the reaction of the nitro-group with the sulphur atom[112]. The isomerisation of adducts of olefins with acetylthio- and *OO*-dimethylphosphorylsulphenyl chlorides takes place to a very slight extent or does not occur at all[59,111]. Only a slight isomerisation of the adducts of olefins with dimethylaminosulphenyl chloride has been noted[110]. Increasing electronegativity of the substituent at the sulphur atom makes the latter less nucleophilic and weakens or eliminates the ability of sulphur to attack a β-carbon atom with formation of an episulphonium ion.

The rate of isomerisation depends also to some extent on the structure of the initial olefin. The M adduct formed in the reaction of methanesulphenyl or acetylthiosulphenyl chloride with styrene at room temperature does not isomerise. Slight isomerisation was achieved only on heating in the presence of acid catalysts[59,82].

β-Chloroalkyl sulphides isomerise with retention of configuration. Thus it has been shown by NMR that the aM *trans*-adducts of methanesulphenyl chloride with norbornene or acenaphthylene isomerise to the M adduct without change of the *trans*-configuration[57]. The *threo*- and *erythro*-configurations are retained in the isomerisation of the adducts of 4-chlorobenzenesulphenyl chloride with *cis*- and *trans*-1-phenylpropenes[35], which also confirms the hypothesis that the isomerisation proceeds via a three-membered episulphonium ion.

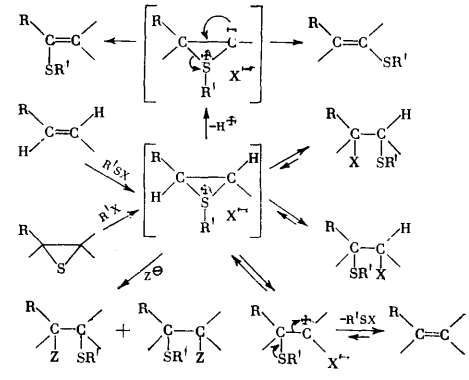
Acetolysis of diastereoisomeric pairs of adducts of arenesulphenyl chlorides with *trans*- or *cis*-but-2-ene gives rise to the diastereoisomeric pairs of the corresponding acetates[31]. The acetolysis of a mixture of the isomeric adducts of 2,4-dinitrobenzenesulphenyl chloride[31] and methanesulphenyl chloride[59] with propene led to identical mixtures of acetates, which is significant evidence for the existence of an intermediate episulphonium ion in the isomerisation of β-chloroalkyl sulphides:



## III. STABLE EPISULPHONIUM SALTS

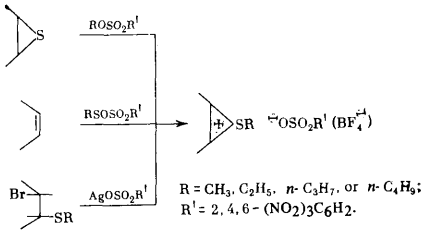
Thus experimental factors and kinetic evidence confirm indirectly that the addition of sulphenyl chlorides to olefins proceeds via the formation of an intermediate episulphonium ion. Subsequent nucleophilic attack by an anion on a ring carbon atom leads to the final reaction products with formation of the individual chloroalkyl sulphides or their mixture, consisting of the kinetically controlled aM adducts and the thermodynamically stable M isomers[23].

The initial ratio of the isomers is influenced both by steric and electronic factors in the initial olefin and by the nature of the substituents at the sulphur atom in the sulphenyl chloride, the solvent polarity, and the reaction temperature. At lower temperatures, the kinetically controlled aM adduct is formed preferentially, while at higher temperatures the M product is favoured:



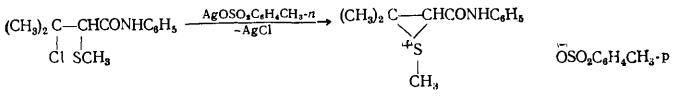
The concept of the formation of an intermediate episulphonium ion also proved important for the interpretation of a number of reactions of β-halogenalkyl sulphides. Thus it becomes clear from this point of view that the isomerisation of β-halogenalkyl sulphides (the conversion of the aM adducts into the M isomers) until equilibration proceeds via an intermediate episulphonium ion. The formation of a mixture of isomers in the nucleophilic substitution of the halogen atom in β-halogenalkyl sulphides occurs as a result of attack by the anion on one of the carbon atoms in the intermediate ion [120]. The elimination of the hydrogen halide from β-halogenalkyl sulphides with formation of isomeric vinyl sulphides evidently also proceeds with elimination of a proton from the episulphonium ion [2,59]. Finally the elimination of the sulphenyl halide from β-halogenalkyl sulphides with formation of an olefin on heating or on treatment with a nucleophile involves the same process [121] and the opening of the thiiran ring by electrophiles with formation of a mixture of isomeric compounds probably likewise proceeds via an episulphonium ion [122].

The episulphonium ion has not so far been isolated. The difficulty of its isolation is associated with its high reactivity and in most cases an equilibrium almost wholly displaced to the right is established under the usual conditions (see the scheme below). The stability of the episulphonium ion depends primarily on the nature of the nucleophile (on whether it is strong or weak), the electrophilic properties of the sulphur atom, and probably on steric factors.



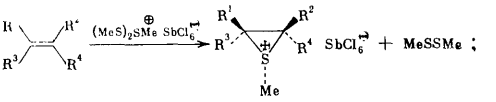

The formation of stable episulphonium salts was first confirmed in relation to two examples—the formation of *cis*-cyclo-octenyl-*S*-methylepisulphonium 2,4,6-trinitrobenzenesulphonate and a steroid *S*-phenylepisulphonium hexafluoroantimonate, where the thiiran ring was part of a complex condensed system [123–126]. The high stability of the episulphonium salt in the first instance enabled the authors to obtain it in three different ways, which confirms that the same episulphonium ion is a common intermediate in these reactions.

A stable episulphonium salt was obtained in this system (R = $CH_3$) also with the aid of silver tetrafluoroborate [125]. Stable episulphonium salts have been obtained recently for the acyclic series too. The anilide of β-chloro-α-methylthiovaleric acid reacts with silver toluene-*p*-sulphonate to form a stable salt, which is readily soluble in water and insoluble in ether [126]:



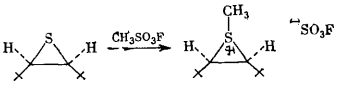

(m.p. 167–168°).

Stable episulphonium salts have been recently obtained also from alkenes [127]:




(a) R' = R² = R³ = R⁴ = Me;
(b) R' = R⁴ = Et; R² = R³ = H;
(c) R'R² = —(CH₂)₆—; R³ = R⁴ = H;
(d) R' = R³ = Me; R² = R⁴ = H;
(e) R' = R² = Me; R³ = R⁴ = H;
(f) R' = R⁴ = Me; R² = R³ = H;
(g) R' = R² = R³ = Me; R⁴ = H.

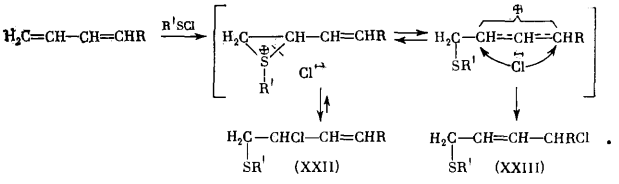
The first three salts were isolated in the form of analytically pure crystalline compounds, which are stable for a long time in the absence of moisture at temperatures below −10°C. The structure of the salts was also confirmed by NMR. It is noteworthy that analogous salts were obtained for selenium derivatives [128]. It was observed that, on methylation by methyl fluorosulphonate at 0°C in methylene chloride, *cis*-2,3-di-t-butylthiiran yields *cis*-2,3-di-t-butyl-*S*-methylepisulphonium fluorosulphonate in the form of crystals, which decompose at approximately 20°C: [129]




The geometrical parameters of the intermediate episulphonium ions have been calculated by the molecular orbital method for ethylene, propene, isobutene, and butadiene [130].

## IV. INTERACTION WITH CONJUGATED DIENES

It has been established by NMR that methane-, benzene-, and *p*-chlorobenzenesulphenyl chlorides add to 1,3-dienes with the initial formation of 1,2-adducts (XXII), mainly with the M structure, which isomerise to the 1,4-adducts (XXIII) (Table 2): [131–133]




The ratios of the aM and M isomers of the 1,2-adducts is influenced by the position of the alkyl substituents in the diene. Thus in the case of piperylene and 4-methylpenta-1,3-diene, where the methyl group is in the 4-position, steric factors promote the addition of the sulphenyl chloride to the unsubstituted double bond. In the isoprene molecule, having a methyl group in the 2-position, steric factors do not have a significant influence and virtually equal amounts of the aM and M isomers are formed. In the reaction involving chloroprene, the influence of electronic factors becomes significant, the more nucleophilic unsubstituted double bond being preferentially attacked with formation of the M adduct.

1,2-Adducts readily isomerise at room temperature to 1,4-adducts. The ease of isomerisation increases in the following sequence of dienes: buta-1,3-diene < isoprene < piperylene < 4-methylpenta-1,3-diene [132]. This isomerisation is also influenced by the nature of the substituent

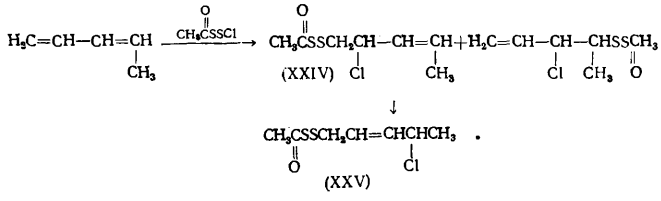
at the sulphur atom. The 1,2-adducts of benzenesulphenyl chloride with dienes do not isomerise, which has already been noted for the adducts with olefins. This also confirms that the intermediate episulphonium ion is involved in the isomerisation.

Table 2. The influence of the structure of the diene on the initial isomer ratio.

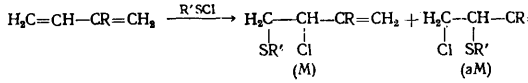
| Diene | Adducts | Ratio of adducts, % | |
|---|---|---|---|
| | | R=$CH_3$ | R=$C_6H_5$ |
| $H_2C{=}CHCH{=}CH_2$ | $RSCH_2CHClCH{=}CH_2$ | 95 | 98 |
| | $ClCH_2CHSRCH{=}CH_2$ | 5 | — |
| $H_2C{=}CHCH{=}CHCH_3$ | $RSCH_2CHClCH{=}CHCH_3$ | 86 | 82 |
| | $CH_3{=}CHCHClCHSRCH_3$ | 14 | 18 |
| $H_2C{=}CHCH{=}C(CH_3)_2$ | $RSCH_2CHClCH{=}C(CH_3)_2$ | 33 | — |
| | $RSCH_2CH{=}CHCl(CH_3)_2$ | 12* | — |
| $H_2C{=}C(CH_3)CH{=}CH_2$ | $RSCH_2CClCH_2CH{=}CH_2$ | 57 | 60 |
| | $CH_3{=}CCH_2CHClCH_2SR$ | 43 | 40 |
| $H_2C{=}CHCCl{=}CH_2$ | $RSCH_2CHClCCl{=}CH_2$ | 85 | — |
| | $ClCH_2CHSRCCl{=}CH_2$ | 15 | — |
|  |  | 85 | — |

*This result most probably represents postisomerisation.

The 1,2-adduct (XXIV) with the M structure, obtained from piperylene and acetylthiosulphenyl chloride, isomerises appreciably to the 1,4-adduct (XXV):[82]

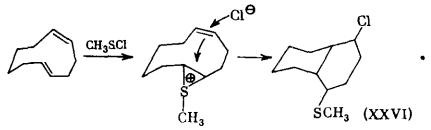


The M adduct predominates in mixtures of the M and aM isomers of the 1,2-adducts of *OO*-dimethylphosphorylsulphenyl chloride with butadiene and isoprene[99]. In an earlier study, where the structure of the adduct had been determined by a chemical method, only the presence of the M adduct was indicated[134];

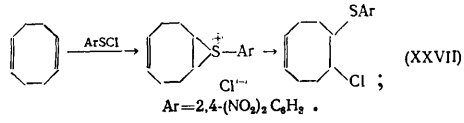


R=H (73% M and 27% aM); R=$CH_3$ (65% M and 35% aM); R'=$PO(OCH_3)_2$.

Methanesulphenyl chloride reacts with *cis,trans*-cyclodeca-1,5-diene to form the adduct (XXVI), whose structure has been demonstrated by NMR:[135]

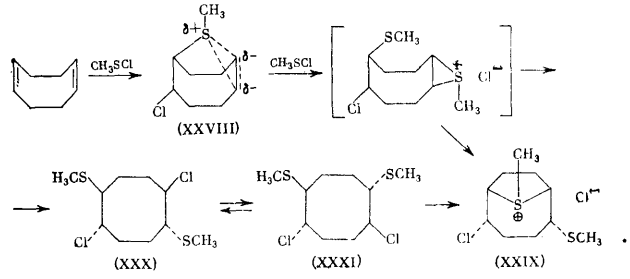


It has been shown that *cis,cis*-cyclo-octa-1,5-diene combines with 2,4-dinitrobenzenesulphenyl chloride to form the adduct (XXVII):[136,137]

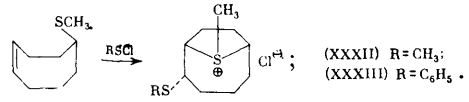


Ar=2,4-$(NO_2)_2C_6H_3$.

On the other hand, when methanesulphenyl chloride adds to *cis,trans*-cyclo-octa-1,5-diene, 80–90% of the diadducts (XXIX), (XXX), and (XXXI) and 8–13% of the monoadduct (XXVIII) are formed[127,138], although dienes usually combine with one equivalent of the sulphenyl chloride. This unusual behaviour can be explained by the transannular effect of the sulphur atom, which makes the double bond in the monoadduct more nucleophilic.



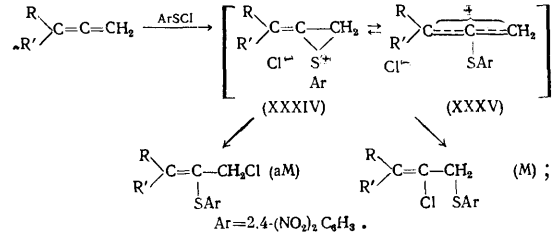
This mechanism is proved by the formation of the adducts (XXXII) and (XXXIII) together with adducts corresponding to (XXX) and (XXXI) when 5-methylthiocyclo-octene reacts with methane- and benzene-sulphenyl chlorides:



## V. REACTIONS WITH ALLENES

2,4-Dinitrobenzenesulphenyl chloride adds to allene with formation of two adducts: aM (87%) and M (13%).[139] The authors explained the observed proportions of the two adducts by the fact that the intermediate episulphonium ion (XXXIV) is attacked by the chloride anion at the terminal methylene carbon atom faster than at the vinyl carbon atom.

When the ring of the episulphonium ion is opened, the energetically more favoured carbonium ion (XXXV) is formed as an intermediate from the terminal carbon atom. The addition of $(CH_3O)_2POSCl$ to allene leads only to the aM adduct[58]:

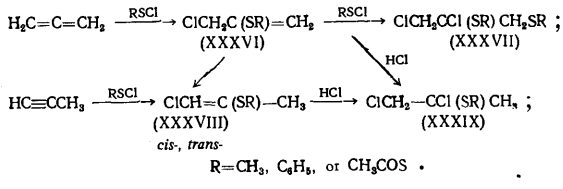


Ar=2,4-$(NO_2)_2C_6H_3$.

In the reactions with substituted allenes[140,141], steric factors direct the addition of sulphenyl chlorides to the unsubstituted double bond with formation of the aM adduct only. However, it was later shown that substituted allenes also form a mixture of adducts of types aM and M.[142]

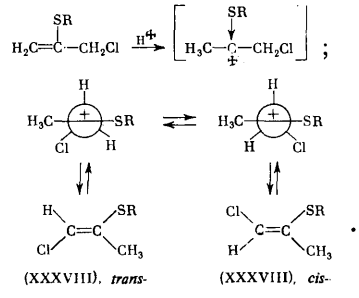
Methanesulphenyl, benzenesulphenyl, and acetylthiosulphenyl chlorides add to allenes with formation of a number of compounds, as shown by NMR and infrared spectroscopy[143]. Apart from the 1:1 adduct (XXXVI),

the 1 : 2 adduct (XXXVII) as well as the products of their subsequent reactions (XXXVIII) and (XXXIX) are formed:

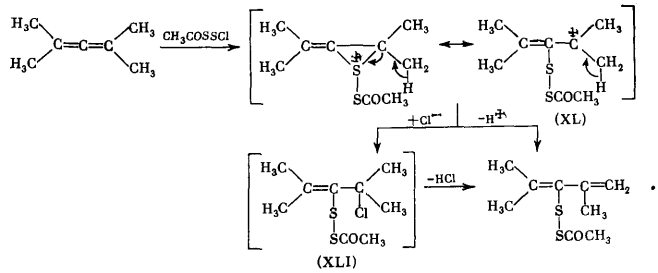


The stability of the adducts (XXXVI) and (XXXVII) depends on the nature of the substituent at the sulphur atom and decreases in the sequence R = $CH_3COS \gg C_6H_5 > CH_3$. Compound (XXXVII) decomposes with liberation of HCl and the amount of compound (XXXIX) in the reaction mixture increases.

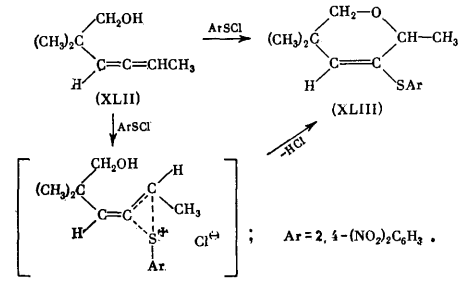
In the presence of acids, the monoadduct (XXXVI) isomerises to (XXXVIII). The authors postulate the possibility of the involvement in this isomerisation reaction of an intermediate carbonium ion, which is converted into the *cis*- or *trans*-isomer of compound (XXXVIII). The *cis*-isomer is kinetically controlled, being partly converted into the *trans*-isomer during the reaction. When the *trans*-isomer is acted upon by an acid, it may revert to the *cis*-isomer:



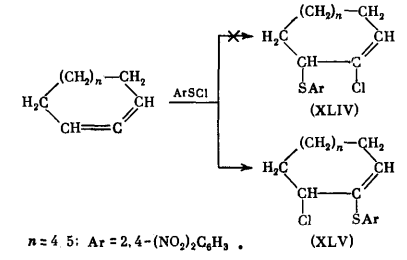
The addition of acetylthiosulphenyl chloride to tetramethylallene is accompanied by the subsequent elimination of HCl. The authors postulate the possibility of the formation of the allylcarbonium ion (XI), since additional signals due to the methylene groups in the postulated adduct (XLI) were detected in the NMR spectrum of the reaction mixture:



Sulphenyl chlorides add to allenes with rigorous stereospecificity. The optically active allene alcohol 2,2-dimethylhexa-3,4-dien-1-ol (XLII) combines with 2,4-dinitrobenzenesulphenyl chloride, forming the optically active adduct (XLIII). This indicates the absence of an intermediate carbonium ion in the addition reaction [144,145]:



The structure (XLIV) was initially adopted for the adduct of 2,4-dinitrobenzenesulphenyl chloride with the cyclic allenes cyclonona-1,2-diene and cyclododeca-1,2-diene [146]. However, it was later established by NMR that the adducts have the structure (XLV): [140]



## VI. ADDITION TO ACETYLENES

The addition of sulphenyl chlorides to acetylenes proceeds similarly to their addition to ethylene. However, the greater stability of the acetylenic $\pi$-bonds, in view of the reduced bond length compared with ethylene, and the greater degree of overlapping of $p$-orbitals require an elevated temperature in many instances of this reaction and sometimes also a catalyst. This is consistent with the addition of one mole of sulphenyl chloride exclusively to the double bond of vinylacetylene [147,148]. The rate of addition of 2,4-dinitrobenzenesulphenyl chloride to phenylacetylene is 0.01 of the rate of addition to styrene and the rate of addition to hex-3-yne is 0.1 of the rate of addition to cyclohexene [149].

The rate of addition of benzenesulphenyl chloride to the following olefin/acetylene pairs has been investigated: styrene/phenylacetylene, 1-phenylpropene/1-phenylpropyne, hex-1-ene/hex-1-yne, and hex-3-ene/hex-3-yne. The ratio of the rates in $Cl_2CHCHCl_2$ was 1 : 100, but it depends strongly on the solvent [150].

The rate of addition of various $p$-substituted arenesulphenyl chlorides to acetylene in ethyl acetate decreases in the following sequence of $p$-substituents: $OCH_3 > CH_3 > H > Cl > NO_2$. [151] The $o$-methyl and $o$-chloro-substituents have little influence on the rate of addition and only $o$-nitro- and 2,4-dinitro-benzenesulphenyl chlorides add to acetylenes 2000–3000 times more slowly than other benzenesulphenyl chlorides. This can be accounted by the strong interaction of the sulphur atom with the $o$-nitro-group [152].

The rate of addition of alkanesulphenyl chlorides to hex-1-yne increases with decrease of the degree of branching of the alkane from which the sulphenyl chloride

was derived and with increase of solvent polarity and temperature [153].

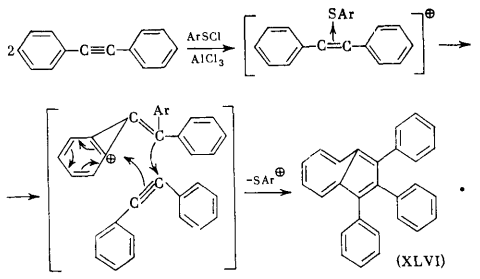
The addition of 2,4-dinitrobenzenesulphenyl chloride to acetylene in chloroethylene requires the presence of $AlCl_3$. Kharasch proposed the following mechanism for this reaction [154]:

$$ArSCl + AlCl_3 \rightleftarrows \overset{\oplus}{Ar}S\overset{\ominus}{AlCl_4}$$

$$\overset{\oplus}{Ar}S\overset{\ominus}{AlCl_4} + CH{\equiv}CH \rightleftarrows \left[\begin{matrix} CH{=}CH \\ | \\ ArS \end{matrix}\right]^{\oplus} AlCl_4^{\ominus} \rightarrow ClCH{=}CH{-}SAr + AlCl_3 ;$$

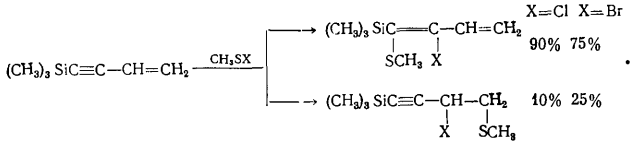
$$Ar = 2.4\text{-}(NO_2)_2C_6H_3 .$$

For the higher acetylenes but-2-yne, hex-3-yne, and diphenylacetylene, the presence of aluminium chloride is not obligatory. It has been shown that $AlCl_3$ complicates the addition of the arenesulphenyl chloride to phenylacetylene, since triphenylazulene (XLVI) is formed instead of the normal adduct [155]:



(XLVI)

Since electron-accepting groups deactivate the acetylenic bond towards attack by electrophiles, acetylenedicarboxylic acid and its diethyl ester do not react with 2,4-dinitrobenzenesulphenyl chloride [154]. However, methyl acetylenemonocarboxylate combines on heating with methane-, benzene-, and *p*-substituted arenesulphenyl chlorides [156]. Electron-donating substituents activate the triple bond in acetylenes. Thus methanesulphenyl halides add preferentially to the triple bond of 1-trimethylsilylbut-3-en-1-yne [157]:




Methanesulphenyl chloride adds to alkylthiovinylacetylenes at the acetylenic bond only [158]:

$$H_2C{=}CH{-}C{\equiv}C{-}SR \xrightarrow[CCl_4,\,-20^\circ]{CH_3SCl} H_2C{=}CHC(SCH_3){=}C\begin{matrix}SR\\Cl\end{matrix} ;$$

$$R = CH_3,\ C_2H_5,\ C_3H_7,\ \text{or}\ C_4H_9.$$

Various alkanesulphenyl chlorides add to acetylene with formation of both the monoadducts (XLVII) [43,47] and the diadducts (XLVIII). [105,159] The latter readily lose HCl on heating, undergoing conversion into the vinyl sulphides (XLIX), which tend to polymerise:

$$HC{\equiv}CH \xrightarrow{RSCl} \underset{(XLVII)}{RSCH{=}CHCl} \xrightarrow{RSCl} \underset{(XLVIII)}{RSCHClCHSR} \xrightarrow{-HCl} \underset{(XLIX)}{RSC(Cl){=}CHSR} ;$$

$$R = ClCH_2,\ ClCH_2CH_2,\ \text{or}\ CH_3CHCl .$$

The reaction of asymmetric acetylenes with sulphenyl chlorides can yield two isomeric adducts, M and aM, and their ratio is influenced both by the solvent and the temperature in the addition reaction [160]. But the addition of benzenesulphenyl chloride to phenylacetylene in benzene gave the adduct (L) with the aM structure, established by conversion into benzyl phenyl sulphone (LI): [161]

$$C_6H_5C{\equiv}CH \xrightarrow{C_6H_5SCl} \underset{\substack{|\\SC_6H_5\\(L)}}{C_6H_5C{=}CHCl} \xrightarrow{H_2O_2} \underset{|\\SO_2C_6H_5}{C_6H_5C{=}CHCl} \xrightarrow{KOH/H_2O} \rightarrow [C_6H_5CH(SO_2C_6H_5)CHO] \rightarrow \underset{(LI)}{C_6H_5CH_2SO_2C_6H_5} .$$

The adduct of phenylacetylene and 2,4-dinitrobenzenesulphenyl chloride, obtained in glacial acetic acid, has the M structure (LII), which was confirmed by specific synthesis from acetophenone [139]:

$$C_6H_5C{\equiv}CH \xrightarrow{\cdot ArSCl} \underset{\substack{|\\Cl\\(LII)}}{C_6H_5C{=}CHSAr} \xleftarrow[-HCl]{} C_6H_5CCl_2CH_2SAr \uparrow PCl_5$$

$$C_6H_5COCH_3 \xrightarrow[HCl]{ArSCl} C_6H_5COCH_2SAr ;$$

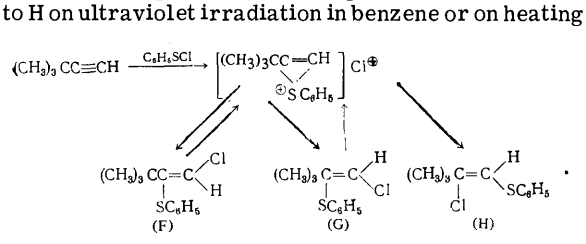
$$Ar = 2,4\text{-}(NO_2)_2C_6H_3 .$$

Studies by a group of Italian chemists helped to resolve the contradictions in the determination of the mode of addition of sulphenyl chlorides to acetylenes [142,143,162-169]. The reactions of *p*-methylbenzene-, *p*-nitrobenzene, and *o*-nitrobenzene-sulphenyl chlorides with but-1-yne, phenylacetylene, and other substituted acetylenes were investigated in various solvents: acetic acid, acetonitrile, and ethyl acetate in the presence of different amounts of trifluoroacetic or hydrochloric acid. The adducts were characterised either by the infrared spectra of the corresponding sulphones or chromatographically. It was shown that the nature of the *p*-substituents in the benzenesulphenyl chloride hardly influences the mode of addition and that aM adducts are formed preferentially. *o*-Nitrobenzenesulphenyl chloride gives rise to an approximately 1 : 1 mixture of the M and aM adducts under these conditions.

The influences of the solvent and the substituent at the acetylenic bond are mutually related. Thus the addition to but-1-yne or its homologues in any solvent gives rise to the aM adduct only, which has also been demonstrated by other investigations [170,171]. On the other hand, the mode of addition to phenylacetylene depends on the solvent: for example, more of the aM adduct is formed in ethylacetate and more of the M adduct is formed in acetic acid. Chloroform and acetonitrile occupy an intermediate position in this respect. As in the addition of sulphenyl chloride to olefins, this is associated with acid catalysis.

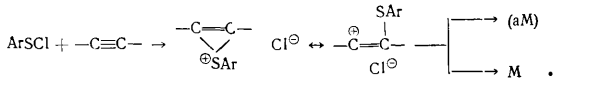
In the addition of sulphenyl chlorides to acetylenes in any solvent, the amount of the M adduct increases with increase of the concentration of acid. However, this effect was not noted for but-1-yne [169].

The addition of benzenesulphenyl chloride to isobutylacetylene gave three adducts (F, G, and H) in the proportions 75 : 17 : 8 respectively. Compounds F and G isomerised to H on ultraviolet irradiation in benzene or on heating [172]:




Kinetic studies on the addition of sulphenyl chlorides to acetylenes showed that this reaction is ionic and that its rate depends on the nucleophilic properties of the triple bond [149,153,164,166]. On the basis of these data, Calo et al. [152] proposed a reaction mechanism according to which the addition proceeds via a stage involving the formation

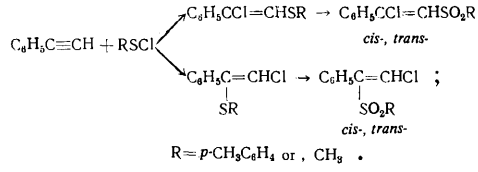
of an intermediate complex, consisting of the chloride ion and the organic cation. The degree of separation of this ion pair depends on the solvent and the structure of the cation determines the ratio of the aM and M adducts:



Later studies confirmed that the intermediate compound has the structure of an unsaturated episulphonium ion [127,128].

The addition of sulphenyl chlorides to acetylenes usually leads to the formation of *trans*-adducts, as shown by infrared [173] and NMR spectra [174] and by comparing the corresponding known *trans*- and *cis*-sulphones [152,153,170,175] as well as by studying the dipole moments [176-178].

*p*-Methylbenzene- and methane-sulphenyl chlorides interact with phenylacetylene in ethyl acetate in the presence of HCl to give a mixture of the *cis*- and *trans*-isomers, whose structure was determined by the NMR analysis of their sulphones and by specific synthesis [168,169]:

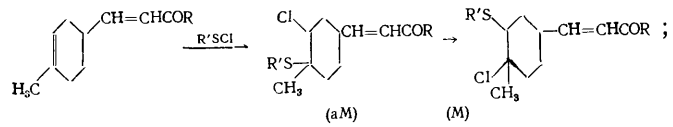


The formation of the *cis*-isomers in this reaction seemingly contradicts the results of other investigations showing the stereospecificity of the addition of sulphenyl chlorides, but the authors showed that the *cis*-isomers are formed owing to the isomerisation of the primary *trans*-adducts. The *trans*-adduct, obtained by the addition of *p*-methylbenzenesulphenyl chloride to phenylacetylene in acetic acid, is partly converted into the *cis*-isomer on storage in ethyl acetate containing 5% HCl.

## VII. REACTIONS WITH $\alpha\beta$-UNSATURATED ACIDS AND THEIR DERIVATIVES

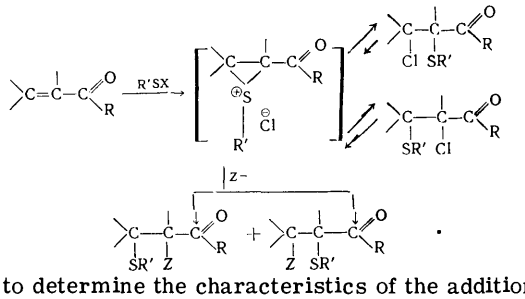
The double bond in $\alpha\beta$-unsaturated acids is little involved in electrophilic addition reactions owing to the electron-accepting properties of the carboxy- and related groups. The reactions of the $\alpha\beta$-unsaturated nitriles with sulphenyl chlorides are particularly difficult. Thus acrylonitrile and similar compounds do not react with 4-chloro-2-nitrobenzene- and 4-nitrobenzene-sulphenyl chlorides in chloroform [48]. 4-Substituted arene- and dichloromethane-sulphenyl chlorides add to acrylonitrile only on heating in glacial acetic acid [179-181]. In glacial acetic acid, the rate of addition of 2,4-dinitrobenzenesulphenyl chloride to vinylacetone, which also contains a powerful electron-accepting group, was 300 times lower than the rate of addition to styrene and 3000 times lower than the rate of addition to cyclohexene [182].

Alkanesulphenyl chlorides initially added in equimolar amounts to the ring double bonds of 3-(4′-methylcyclohex-3′-enyl)acrylic acid and its derivatives with formation of the aM adducts, which then readily isomerised to the M adducts [183]:



R=OH, OEt, $NH_2$, $NHC_6H_5$, or Cl; R′=$CH_3$, or $CH_2CH_2Cl$.

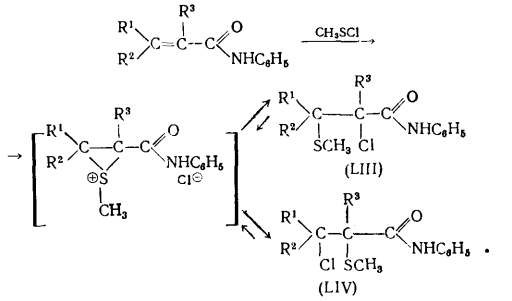
The interaction of sulphenyl halides with $\alpha\beta$-unsaturated acids may lead to a series of valuable polyfunctional compounds when specific addition and subsequent nucleophilic substitution are possible:



In order to determine the characteristics of the addition of sulphenyl halides to acrylic acids and their derivatives, a study was made of the influence of the position of the methyl groups and of the nature of the changes in the carboxy-group in homologues of $\alpha\beta$-unsaturated acids on the rate of addition of sulphenyl chlorides and also on the structures and stabilities of the adducts formed under these conditions.

The addition of various sulphenyl chlorides ($CH_3SCl$, $ClCH_2CH_2SCl$, $C_2H_5SCl$, $CH_3COSCl$, $CH_3COSSCl$, and $SCl_2$) to acrylic, methacrylic, crotonic, and dimethylacrylic acids and their derivatives (acid chlorides, esters, amides, substituted amides, and nitriles) was investigated. The studies elucidated the influence of the number and positions of the methyl groups in $\alpha\beta$-unsaturated acids, of the nature of the derivatives of $\alpha\beta$-unsaturated acids, and finally of the structure of the sulphenyl chloride on the rate of addition, the initial ratio of isomers, and the stability of the adducts formed. For this purpose, the reactions involving the addition of the same sulphenyl chloride to the same derivative of different $\alpha\beta$-unsaturated acids were compared. This was followed by a comparison of the additions of the same sulphenyl chloride to different derivatives of the same $\alpha\beta$-unsaturated acid and finally of the addition of different sulphenyl chlorides to the same derivative of the same $\alpha\beta$-unsaturated acid.

The studies on the influence of the position of methyl groups showed that, when methanesulphenyl chloride adds to the anilides of acrylic [184,185], crotonic [186], and dimethylacrylic acids [187], the kinetically controlled adducts of type (LIII) are formed preferentially in the initial stage:



Addition to methacrylic acid anilide [188] results in the initial preferential formation of the adduct (LIV), which is likewise unstable.

The addition of sulphenyl chlorides to $\alpha\beta$-unsaturated acids is also a process consisting of two consecutive steps: the initial formation of the intermediate episulphonium ion and further nucleophilic attack by the chloride ion on one of the carbon atoms in the ring with formation of a mixture of adducts (LIII) and (LIV). Evidently the preferred site of attack in acrylic, crotonic, and dimethyl-

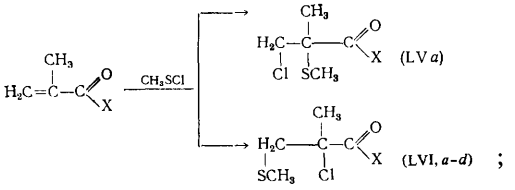
acrylic acids is the carbon atom in the $\alpha$-position relative to the carboxy-group, since the electron density at the $\alpha$-carbon atom in the intermediate episulphonium ion is relatively lower owing to the inductive effect of the carboxy-group. Steric factors, the presence of one and two methyl groups in the $\beta$-positions in crotonic and dimethylacrylic acids, also promote the attack by the chloride ion on the $\alpha$-carbon atom. The presence of the methyl group in the $\alpha$-position of methacrylic acid partly compensates the influence of the carboxy-group and creates an additional steric hindrance to attack on the $\alpha$-carbon atom. For this reason, the kinetically controlled adduct (LIV) is formed preferentially in this case.

It was established that in this instance the rate of addition of methanesulphenyl chloride decreases in the series of anilides of acids ranging from acrylic and methacrylic to crotonic and dimethylacrylic. The addition to both *cis*- and *trans*-derivatives of crotonic acid was studied[189,190]. The results obtained are inconsistent with the successive enhancement of the nucleophilic properties of the double bond. The decrease of the reactivity of the double bond is probably due to steric factors. Adducts with cinnamic acid could be obtained only in glacial acetic acid[191]. The rate of isomerisation of the kinetically controlled adducts formed initially to thermodynamically stable adducts increases in the inverse sequence: $\alpha$-chloro-$\beta$-methylthiopropionic acid anilide < butyric acid anilide < isovaleric acid anilide. The anilide of $\alpha$-alkylthio-$\beta$-chlorobutyric acid is an exception.

Changes in the carboxy-group of the $\alpha\beta$-unsaturated acid have a significant influence on the rate of addition of sulphenyl chlorides. In all cases, sulphenyl chlorides react most easily with amides, than with acids and esters, the reaction with acid chlorides and nitriles being more difficult. This is consistent with the decrease of electron density in the double bond of $\alpha\beta$-unsaturated acids as a function of the derivative employed. The nature of the changes in the carboxy-group has a significant influence on the initial ratio of the kinetically controlled and thermodynamically stable isomers. The amount of the kinetically controlled adduct decreases in the same sequence, from the amide to the nitrile, and the amount of the thermodynamically stable isomer naturally increases. Thus $^1$H NMR made it possible to observe the preferential formation in the mixture of products of the reactions of $\alpha\beta$-unsaturated acids and their amides and methyl esters of kinetically controlled unstable adducts, which can sometimes be isolated in a pure form[192].

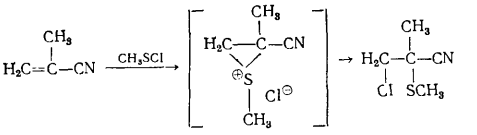
The addition of sulphenyl chloride to the chlorides and nitriles of $\alpha\beta$-unsaturated acids leads as a rule to the formation of a stable equilibrium mixture or of thermodynamically stable adducts.

The influence of the changes in the carboxy-group on the initial ratio of the isomers and on their stability has been demonstrated for the reaction of methanesulphenyl chloride with various derivatives of methacrylic acid. When methanesulphenyl chloride was allowed to add to methacrylic acid anilide, a single kinetically controlled isomer (LV*a*) was obtained:

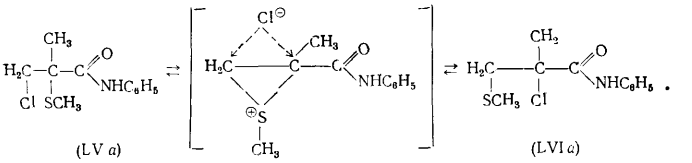


X=NHC$_6$H$_5$ (*a*); OH (*b*); OCH$_3$ (*c*) or Cl (*d*).

The reaction of methanesulphenyl chloride with methacrylic acid, its methyl ester, and chloride gives the following ratios of the isomers (LV, *b*–*d*) to the isomers (LVI, *b*–*d*): 89/11, 72/28, and 52/48 respectively. The addition of methanesulphenyl chloride to methacrylonitrile again leads to a single thermodynamically stable isomer: $\beta$-chloro-$\alpha$-methylthioisobutyronitrile (LV*e*):

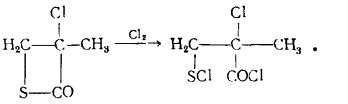


The unstable adducts usually isomerise to the stable adducts on storage or heating. The isomerisation is accelerated in the presence of catalytic amounts of acid. The stability of the adducts formed, which depends mainly on the nucleophilic properties of the sulphur atom, is clearly confirmed by the data obtained for the isomerisation reaction. Thus the unstable anilide (LV*a*) isomerises almost completely to the stable anilide of $\alpha$-chloro-$\beta$-methylthioisobutyric (LVI*a*):



In the addition to methyl methacrylate, the simultaneous formation of a mixture of the isomers (LV*c*) and (LVI*c*) is observed, with the kinetically controlled adduct (LV*c*) predominating. The ratio of isomers obtained is displaced towards the accumulation of the isomers (LVI*c*), equilibrium being attained when (LV*c*) : (LVI*c*) = 60 : 40.

$\beta$-Chloro-$\alpha$-methylthioisobutyronitrile (LV) is a stable isomer and remains unaltered under comparable conditions. The structure of methacrylic acid derivatives was confirmed, apart from $^1$H NMR data, by the cleavage of $\alpha$-chloro-$\alpha$-methyl-$\beta$-thiolactone by electrophilic agents, in which the position of the sulphur atom is rigorously specified[193]:

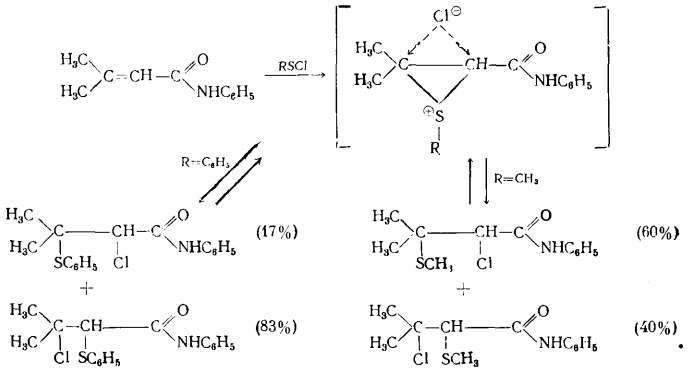


Thus the interconversions of the isomers, sometimes with formation of a single thermodynamically stable compound or an equilibrium mixture of isomers, can be explained by postulating an important role of the episulphonium ion in these processes. It follows from the above data that the outcome of the process is influenced significantly by changes in the carboxy-group and in the positions of the methyl groups, which affects in its turn the nucleophilic properties of the sulphur atom. The isomerisation of the adducts, based on the intermediate formation of the episulphonium ion, proceeds more readily as the sulphur atom of the adduct becomes more nucleophilic and the carbon atom subjected to nucleophilic attack by the sulphur atom becomes less effectively shielded in space.

Naturally, the nucleophilic properties of the sulphur atom decrease in the sequence $CON\langle$ > COOH > $COOCH_3$ > COCl > CN as a function of the substituent at the carboxy-group, which is consistent with the $-I$ and $-\epsilon$ effects of the substituents. This results in the complete absence of isomerisation of the nitriles.

The influence of the nature of the sulphenyl chloride on the rate of addition of methane-, β-chloroethane-, benzene-, acetyl-, and acetylthio-sulphenyl chlorides and of sulphur dichloride to αβ-unsaturated acids and their derivatives and on the ratio of the adducts showed that the ease of addition of sulphenyl chloride to the same derivative of the αβ-unsaturated acid decreases in the following sequence: $AlkSCl > ClCH_2CH_2SCl$ [194] $> C_6H_5SCl$ [195] $> ClSCl$ [196] $> CH_3COSCl$.[197] $CH_3COSSCL$ could not be added at all to αβ-unsaturated acids.

The ratio of the isomers in reactions involving addition to αβ-unsaturated acids changes significantly as a function of the nature of the substituent in the sulphenyl chloride. Thus, whereas in the addition of methanesulphenyl chloride to dimethylacrylic acid anilide the kinetically controlled α-chloro-β-methylthioisovaleric acid anilide is initially formed preferentially (60 : 40), in the addition of benzenesulphenyl chloride, the preferred product is the stable anilide of β-chloro-α-phenylthioisovaleric acid (83 : 17):[192]



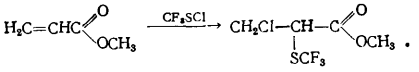

The results obtained were confirmed by kinetic data. The addition of benzenesulphenyl chloride to αβ- and βγ-unsaturated acids and their derivatives was investigated and it was shown that the rate of addition decreases in the sequence anilide > ester > acid > acid chloride as a function of the changes in the carboxy-group and in the sequence $H_2C{=}CH{-}CH_2COOCH_3 > H_2C{=}CHCOOCH_3 > H_2C{=}C(CH_3)COOCH_3 > CH_3CH{=}CHCOOCH_3 > (CH_3)_2C{=}CHCOOCH_3 > C_6H_5CH{=}CHCOOCH_3$ as a function of the changes in the molecular structure.

It was established that the addition of benzenesulphenyl chloride to unsaturated acids is a first-order reaction with respect to each reactant. The high negative activation entropy ($\sim -30$ cal mole$^{-1}$ K$^{-1}$) and energy are consistent with a polar mechanism of the addition reaction [198].

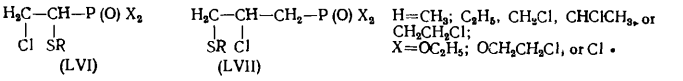
The above results, both for the addition of sulphenyl chlorides to αβ-unsaturated acids and their derivatives and for the isomerisation of the adducts, are consistent with the results of other workers [199-201].

When sulphenyl chlorides react with the nitriles of αβ-unsaturated acids, there is a possibility of addition not only to the C=C double bond but also to the nitrile group [200, 202].

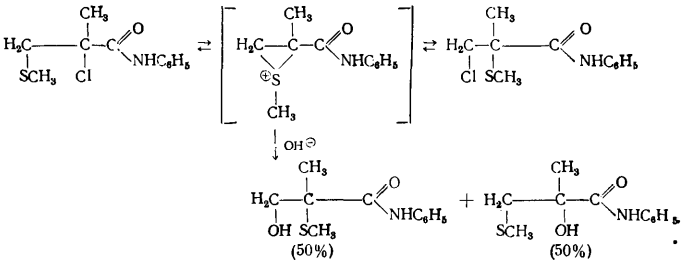
The free-radical addition of trifluoromethanesulphenyl chloride to methyl acrylate leads to the preferential formation (90%) of methyl β-chloro-α-trifluoromethylthiopropionate [202]:




Sulphenyl chloride add also to other αβ-unsaturated compounds containing electron-accepting groups: keten [202], α-chloroacrolein [204], trichloromethylethylene [205], alkenyl phosphites and phosphinates [204,205], and methyl vinyl sulphone [199]. The mode of addition being similar to that observed in the addition to carboxylic acid derivatives. The aM structure (LVI) and the M structure (LVII) were attributed to the adducts obtained in the reaction with vinyl- and allyl-phosphinates respectively:




Nucleophilic substitution of the chlorine atom in the isomeric derivatives of β-alkylthio-α-chloro- and α-alkylthio-β-chloro-carboxylic acids has so far been little studied. The kinetic investigations which have been carried out have shown that the rate of nucleophilic substitution depends significantly on the structure of the initial adduct [208]. The kinetically controlled adduct is always hydrolysed faster, approximately by an order of magnitude, than the thermodynamically stable isomer [209]. It has been observed that α-chloro-β-methylthio-isomers always react faster than the corresponding derivatives of the α-chloro-β-phenylthio-carboxylic acid. The rate of nucleophilic substitution is also influenced significantly by the changes in the carboxy-group: amides react more readily than the corresponding esters. The proportions of the isomers formed are independent of the position of the halogen in the molecule (the α- or β-position) and depend primarily on the substituents in the molecule and on the nature of the nucleophile. According to preliminary data, the solvent also affects the ratio of the isomers. For example, the hydrolysis of the anilides of both α-chloro-β-methylthio- and β-chloro-α-methylthio-isobutyric acids gives rise to a 1 : 1 mixture of the isomeric anilides of α-hydroxy-β-methylthio- and β-hydroxy-α-methylthio-isobutyric acids [209]:




The relative amount of the β-hydroxy-isomer in the hydrolysis of the anilides of β(α)-chloro-α(β)-methylthioalkanoic acids increases in the following sequence as a function of their structure: β(α)-chloro-α(β)-methylthiopropionic acid (1 : 1 : 5); corresponding derivatives of butyric acid (1 : 3); corresponding derivatives of isovaleric and hydrocinnamic acid—β-hydroxy-isomer only [210].

Thus the study of the addition of sulphenyl chlorides to αβ-unsaturated acids and their derivatives showed that kinetically controlled (unstable) adducts can be obtained in some instances, but stable isomers are produced as a rule. When nucleophiles act both on individual β-halogenosulphides and on their mixtures, the intermediate is the same episulphonium ion, the opening of the ring of which by the nucleophile may be made specific with the preferential formation of the α- or β-isomer by altering the structure and conditions.

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# The Synthesis of Heterocyclic Analogues of Prostaglandins

E.I.Levkoeva and L.N.Yakhontov

The available information about the methods of synthesis of prostaglandin analogues containing the oxygen, sulphur, and nitrogen heteroatoms in the cyclic part of the molecule is described.
The bibliography includes 101 references.

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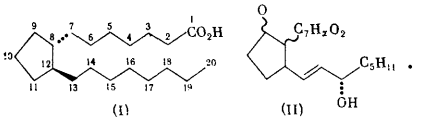
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## I. INTRODUCTION

Prostaglandins (PG) are a comparatively recently discovered class of naturally occurring physiologically active substances which have been the subject of continuous attention by biologists and chemists in the last 10–15 years. Pharmacological studies have shown that prostaglandins exhibit an extremely broad spectrum of activity; their influence on the smooth musculature of various organs, their mediating role in the central and peripheral nervous systems in inflammatory processes, and their hormone-like and antihormonal activities have been investigated in detail[1,2].

The need for large amounts of prostaglandins, which are required in experimental and clinical research, led to the vigorous development of methods for the extraction and purification of prostaglandins and stimulated the search for methods of synthesis of prostaglandins and their analogues. Biological research on prostaglandins began in 1930,[3] but it was not until 1962 that the structures of the first three compounds of this series were established[4]. Approximately twenty natural prostaglandins have now been isolated.

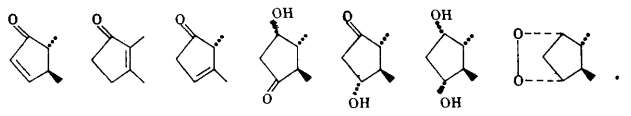
They are all derivatives of the hypothetical $C_{20}$ prostanoic acid (I), the $C_{(8)} - C_{(12)}$ atoms of which are part of the cyclopentane ring:



(I) (II)

The $C_{(1)} - C_{(7)}$ side chain, terminating in a carboxy-group, is designated by convention as the $\alpha$-chain and lies behind the plane of the cyclopentane ring. All prostaglandins have an oxygen-containing functional group attached to $C_{(9)}$ (OH or C=O), a hydroxy-group at $C_{(15)}$, and a *trans*-double bond (II) between $C_{(13)}$ and $C_{(14)}$.

Depending on the number and type of oxygen-containing functional groups, the degree of unsaturation of the cyclopentane ring, and the position of the double bond in the latter, prostaglandins are divided into groups designated by the letters A, B, C, D, E, F, G, and H:

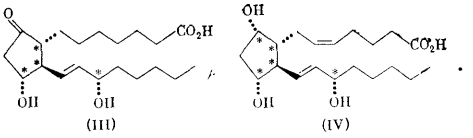


(A) (B) (C) (D) (E) ($F_\alpha$) (G, H)

Natural prostaglandins may contain in the side chains, one, two, or three double bonds (apart from the obligatory 13,14-*trans*-bond, there may also be the 5,6-*cis*- and 17,18-*cis*-bonds). On the basis of the number of double bonds, each group is subdivided into series (for example $PGE_1$, $PGE_2$, and $PGE_3$). Natural PGF prostaglandins in which the hydroxy-group at $C_{(19)}$ is in the *cis*-position relative to the $\alpha$-side chain have come to be designated as $PGF\alpha$, in contrast to the $PGF\beta$ compounds, epimeric with respect to $C_{(9)}$, which can only be obtained by synthesis.

## II. FUNDAMENTAL METHODS OF SYNTHESIS OF PROSTAGLANDINS

The complete synthesis of natural prostaglandins presents considerable difficulties because of the complexity of their chemical structure rather than their lability. Thus the distinctive features of the $PGE_1$ (III) are as follows: 4 chiral centres, the $\beta$-oxo-group in the cyclopentane ring, the *trans*-disposition of all three ring substituents, and the presence of the acyclic hydroxy-group at $C_{(15)}$:



(III) (IV)

The complete synthesis of $PGF_2\alpha$ (IV) is further complicated by the presence of an additional chiral centre at $C_{(9)}$ and the necessity for the introduction of a second double bond. For this reason, the stereospecific syntheses of natural prostaglandins consist of many stages (up to 21 stages) and the yields of the final products are comparatively low.

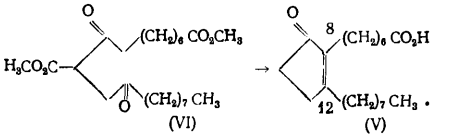
Analysis of the literature on the methods of synthesis of prostaglandins shows that all the methods can be divided into two groups:

1. Syntheses of prostaglandins based on long-chain compounds in which the cyclopentane ring is formed at one of the last stages of the synthesis.

2. Syntheses of prostaglandins based on cyclopentane derivatives.

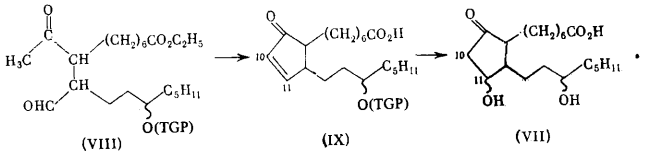
The synthetic methods of the first group can be conveniently regarded in their turn as a function of the C–C bond responsible for ring closure during the formation of the prostaglandin molecule. Thus one of the first attempts at the synthesis of prostaglandins was made in 1963 by

Samuelsson and Ställberg[5], who obtained 15-deoxy-13,14-dihydro-$PGB_1$ (V) by the intramolecular cyclisation of the diketone (VI) and the formation of the $C_{(8)} - C_{(12)}$ bond of the cyclopentane ring of $PGB_1$:



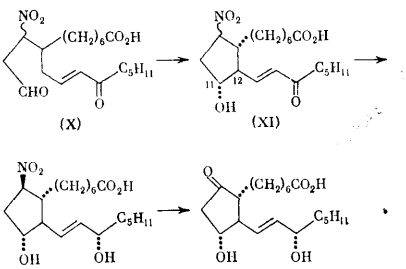
(VI) (V)

A stereoisomeric mixture of 13,14-dihydro-$PGE_1$ (VII) was obtained by Strike and Smith[6], who achieved during the synthesis the closure of the cyclopentane ring at the $C_{(10)} - C_{(11)}$ bond. For this purpose, they synthesised the aldehyde (VIII), which already contains both side chains of the prostaglandin molecule. The cyclisation of compound (VIII) led to the isolation of the enone (IX), which resulted in the formation of compound (VII) after epoxidation, hydrogenation, and the removal of the tetrahydropyranyl (TGP) protecting group:



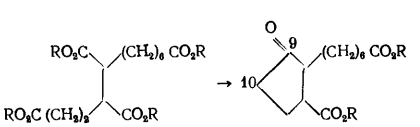
(VIII) (IX) (VII)

The methods for the formation of the $C_{(11)} - C_{(12)}$ bond in the prostaglandin molecule have been investigated in greatest detail. The study by Corey and coworkers[7,8] not only led to the preparation for the first time of pure crystalline prostaglandins, but also resulted in the development of methods which were subsequently used widely in prostaglandin chemistry; in particular, they employed the 9-nitrogroup as the precursor of the 9-oxo-group. The key compound in these syntheses was an aldehyde of type (X); it was subjected to aldol condensation to the enone (XI), which was shown to contain no 11-$\beta$-isomer whatsoever. Next, the 15-oxo-group was reduced with zinc tetrahydroborate, the nitro-group was transferred to the *trans*-position relative to the $\alpha$-chain with the aid of bases, the $C_{(15)}$ epimers were separated chromatographically, and the nitro-group was converted into the oxo-group via the amino- and *N*-bromoamino-groups:

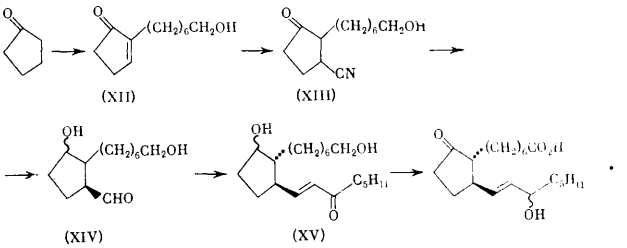


(X) (XI)

The closure of the cyclopentane ring at the $C_{(9)} - C_{(10)}$ bond by the Dieckmann reaction was achieved[9] in the course of the synthesis of (±)-11-deoxy-$PGE_1$:



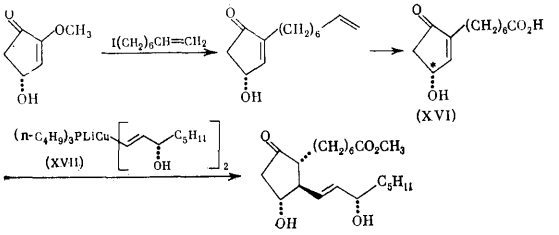
The second group of methods of synthesis of prostaglandins, from cyclopentane compounds, is based on both monocyclic and bicyclic systems containing the cyclopentane ring. An example of the synthesis achieved by the introduction of side chains into the molecule of a monocyclic cyclopentanone is provided by the scheme for the synthesis of 11-deoxy-$PGE_1$:[10]



(XII) (XIII) (XIV) (XV)

The enamine derived from cyclopentanone was alkylated by this method with $\omega$-hydroxyoenanthaldehyde. The alkylation product was dehydrated to the enone (XII), whose reaction with acetone cyanohydrin led to the nitrile (XIII). The reduction of the latter with di-isobutylaluminium hydride (DIBAL) involved the oxo- and cyano-groups simultaneously. The resulting hydroxyaldehyde (XIV) was converted by the Wittig reaction into compound (XV), in which both hydroxy-groups were subsequently oxidised with chromium trioxide and the 15-oxo-group was selectively reduced with sodium tetrahydroborate.

The syntheses of prostanoids from monocyclic cyclopentane derivatives, which also proceed via intermediates such as the aldehyde (XIV) or enones of type (XVI), are nowadays used on a fairly wide scale. This can be explained, on the one hand, by the availability of the initial cyclopentane and, on the other hand, by the comparative simplicity of the subsequent modification to give the prostaglandin molecule. Thus the enone (XVI) contains only one chiral centre, the required $\alpha$-chain is already present, and the stereospecific introduction of the second side chain can be successfully achieved[11] by means of the complex (XVII):



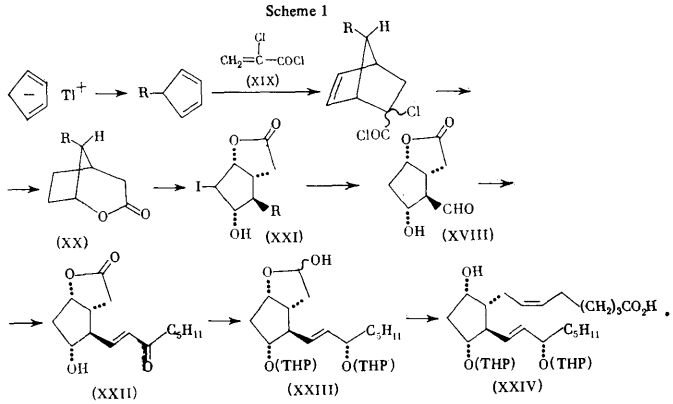
(XVI) (XVII)

Among the numerous methods for the synthesis of prostaglandins from bicyclic compounds, those developed by the Harvard group under the leadership of Corey, are of greatest interest. The key compound in these syntheses is the formyl-lactone (XVIII), which has come to be called in the literature the "Corey aldehyde". This compound is synthesised by Scheme 1[12,13] from pentadienylthallium. The product of the reaction of the latter with benzyl chloromethyl ether was then converted by condensation with the dienophile (XIX) into the corresponding bicyclic compound. The latter was converted by a series of reactions into 2-oxabicyclo[3,2,1]nonane, which formed the iodolactone (XXI) after hydrolysis and further reaction with potassium tri-iodide. This compound has the required configuration of all the nuclear centres. Its acylation, deiodination, and the conversion of the hydroxybenzyl group (R) into the formyl group led to the formyl-lactone (XVIII)—the "Corey aldehyde", which was subsequently made to undergo the Wittig condensation with the corresponding phosphorane to form compound (XXII). The 15-oxogroup in the latter was then reduced stereospecifically and the $\alpha$-chain was

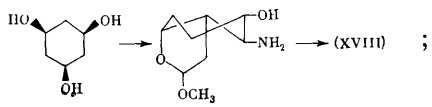
inserted (also by the Wittig reaction) after the conversion of the lactone into the lactol (**XXIII**).

Mild hydrolysis of the ether group led to the intermediate (**XXIV**) and then into $PGF_{2\alpha}$ after the removal of the THP protecting groups. Following the oxidation of the 9-hydroxy-group in compound (**XXIV**) and the removal of the THP protecting groups, $PGE_2$ was isolated. Compound (**XXIV**) was converted into a prostaglandin with a single double bond by hydrogenatoin over a palladium catalyst.

Scheme 1

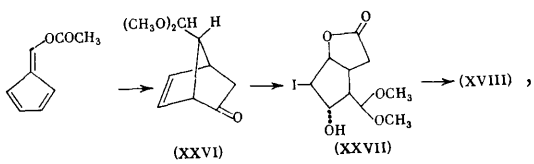


Corey's aldehyde (**XVIII**) became the key compound in various syntheses of prostaglandins. Several methods have been developed for its synthesis: from *cis*-cyclohexane-1,3,5-triol via the bicyclic aminoalcohol (**XXV**)[14]:



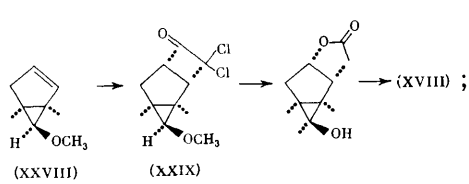
(**XXV**)

from acetoxyfulvene via bicyclo[2,2,1]heptene (**XXVI**) and the iodohydrin (**XXVII**):



(**XXVI**) (**XXVII**)

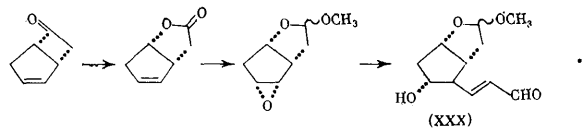
from the bicyclic ether (**XXVIII**) into which the elements of chloroketen are introduced stereospecifically with formation of the tricarbocyclic compound (**XXIX**)[16],



(**XXVIII**) (**XXIX**)

etc:

Another approach to the synthesis of prostaglandin structures involves the conversion of unsaturated bicyclic cyclopentanone derivatives into epoxides; the opening of the oxiran ring in the latter by specific reagents (for example[17], 1,3-bismethylthioallyl-lithium—the nucleophilic equivalent of the –CH=CH–CHO group) leads to an aldehyde of type (**XXX**):



(**XXX**)

A number of other novel methods for the synthesis of prostaglandins, which are outside the framework of the above schemes, have been described in special reviews, for example that of Mueller and Flanders[18].

## III. METHODS OF SYNTHESIS OF HETEROCYCLIC ANALOGUES OF PROSTAGLANDINS

Research on methods of synthesis of prostaglandin analogues, which are easier to synthesise than natural prostaglandins but have the same or comparable biological activity, has developed on a wide scale in recent years.

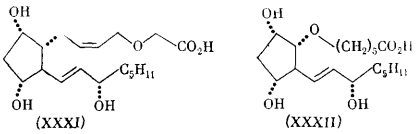
The search for synthetic analogues of prostaglandins is also dictated by other factors. In the study of the effect of prostaglandins on human organisms, undesirable side effects are frequently observed; a disadvantage of natural prostaglandins as medicinal substances is the short duration of their action, which necessitates their frequent administration. Furthermore, the wide variety of pharmacological effects creates major difficulties in their practical application. Preparations similar in structure to natural prostaglandins but acting more selectively on individual systems and functions of the organisms, are more stable, less toxic, and more easily administered to man than their natural prototypes are being sought for this reason. Finally, in many instances the structural analogues are synthesised in order to obtain prostaglandin antagonists and to elucidate the physiological role of natural prostaglandins.

A fairly large number of prostanoids, differing from natural prostaglandins by individual structural elements, have now been synthesised and their pharmacology investigated. In most instances, these are cyclopentane derivatives. They include active compounds with an alkyl chain longer than in prostaglandins[19] and prostanoids with shorter side chains[20] and with additional alkyl[21] or aryl[22] substituents. A wide variety of derivatives involving the functional groups of the prostaglandin molecule have been obtained, including oximes, thiosemicarbazides, semicarbazides[23], salts[24], and ethers[25]. Halogens[26,27] and heterocyclic residues[28,29] have been introduced into the side chain; the carboxy-group has been replaced by the sulpho-group[30], etc. The degree of unsaturation of the side chains[31,32] and the positions of the double bonds[33] have also been varied and oxo- and hydroxy-groups have been eliminated or additional ones have been introduced.

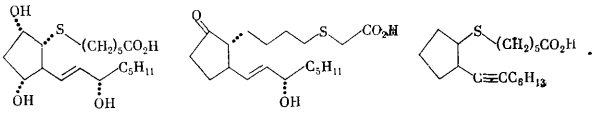
Such changes in the side chains led in most instances to a weakening of biological activity. On the other hand, many substances inhibiting the action of prostaglandins as well as a number of active preparations have been found.

The introduction of heteroatoms (sulphur or oxygen) into the $\alpha$-chain led to the formation of a series of prostanoids exhibiting both prostaglandin-like and antagonistic activity. Prostanoids containing oxygen atoms in the 3-, 4-, and 5-positions[34] and in the 7-position[35,36] of the prostaglandin

molecule [compounds (XXXI) and (XXXII)] as well as 7-thiaprostaglandin (XXXIII)[37] and 3-thiaprostaglandin (XXXIV)[38] have been obtained in recent years:



(XXXI) (XXXII)

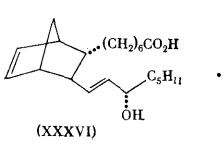


(XXXIII) (XXXIV) (XXXV)

The 7-thia-analogue (XXXV)[39], having a triple bond in the alkyl side chain and without an oxygen-containing functional group in the cyclopentane ring, showed a high activity in inhibiting PG-15-dehydrogenase. Analysis of compounds (XXXI)–(XXXIV) showed that a prostaglandin-like activity is shown only by the isomers in which all the chiral centres retain the absolute configuration characteristic of natural prostaglandins, while other isomers show little or no activity.

Various substituents, including halogen atoms[40,41] and alkoxy-[42], hydroxymethyl[44], alkyl[45], and other[46] groups, were introduced into the cyclic component of the prostaglandin molecule. The compounds synthesised, without an oxygen-containing functional group in the cyclopentane ring, for example[47], the 11-deoxy-analogue of PGE[32], 9-deoxyprostaglandin[48], etc. as well as prostaglandin analogues in which the cyclopentane ring was replaced by the benzene[49] or cyclohexane[50,51] rings, have also been synthesised.

Synthetic prostaglandin analogues having simpler structures in most cases did not show a distinctive effect on the smooth muscles in *in vitro* experiments, but interacted with the same receptors as prostaglandins, inhibiting their influence. Compound (XXXVI), which is a derivative of bicyclo[2,2,1]heptene, similar in structure to one of the postulated products of the biosynthesis of $PGE_1$, acts via a similar mechanism[52]. The authors[52] established that the compound inhibits selectively the isomerase responsible for the synthesis of $PGE_1$, but does not affect the reductase catalysing the formation of $PGF_{1\alpha}$.



(XXXVI)

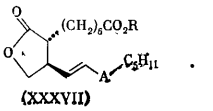
The introduction of a heteroatom into the cyclic part of the prostaglandin molecule was the next step in the modification of the structures of natural prostaglandins. The syntheses of heterocyclic prostanoids are based on the experience already gained with methods for the synthesis of natural prostaglandins. Both prostaglandins and their heteroanalogues are synthesised via two different schemes: either the side chains are attached to the complete cyclic fragment or ring closure is achieved in one of the last stages of the synthesis. The first pathway appears to have many advantages, since it makes it possible to vary the structures of the side chains and to attach them to a ring already containing the necessary stereochemical centres.

The syntheses of prostanoids containing oxygen, sulphur, and nitrogen atoms in the cyclic part of the molecule (oxa-, thia-, and aza-prostaglandins) have now been published.

## 1. Oxaprostaglandins

The majority of synthetic analogues of prostaglandins containing an oxygen atom in the cyclic part of the molecule are derivatives of tetrahydrofuran. In an attempt to obtain substances with potential antifertility activity, 9,10,11-mono-oxa- and 9,11-dioxa-prostaglandins were synthesised.

The first study on these lines involved the synthesis of 11-deoxy-10-oxaprostaglandin (XXXVII), carried out by Japanese workers in 1971[53]. The authors claimed that the compounds obtained exhibit a therapeutic activity similar to that of prostaglandins, and can be used in gastrointestinal disorders and in disturbances of blood pressure, as well as substances inducing natural birth and abortions.



(XXXVII)

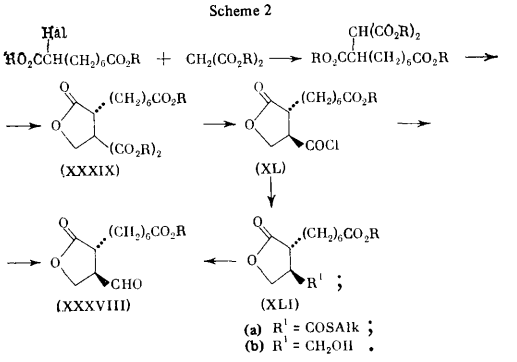
The key compound in the synthesis of a series of products (XXXVII) with R = H or alkyl and A = CO, CHOH, or CHOCOAlk is the aldehyde (XXXVIII), the synthesis of which is illustrated in Scheme 2.

The condensation of the diesters of $\alpha$-halogenoazelaic and malonic acids in the presence of bases (alkali metal hydrides and alkoxides) led to the formation of the corresponding 8,9,9-tricarboxy-derivative of pelargonic acid, the condensation of which with formaldehyde led to the trisubstituted tetrahydrofuranone (XXXIX). The latter was then partly decarboxylated at 150–170° and converted into the acid chloride (XL) by reaction with thionyl chloride. Compound (XL) was further converted into the aldehyde (XXXVIII) in different ways: by direct hydrogenation in the presence of a palladium catalyst, or via the thioester (XLIa), which was then reduced to compound (XXXVIII) over a deactivated nickel catalyst, or by oxidising with dicyclohexylcarbodiimide (DCC) the alcohol (XLIb) obtained as a result of the dehydrogenation of compound (XLIa) over active Raney nickel.

The second alkyl chain was attached to the aldehyde (XXXVIII) using dimethyl 2-oxoheptylphosphonate and the 15-oxo-group was reduced with various alkali metal tetrahydroborates. The mixture of epimeric alcohols formed in this process was separated chromatographically and the ester group was hydrolysed in a weakly acid or weakly alkaline medium.

*O*-Acyl derivatives [(XXXVII), R = H, A = CHOCOalk] were also obtained by acylating the 15-hydroxy-group.

Scheme 2



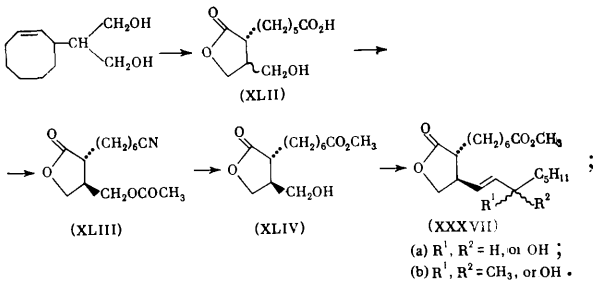
(XXXIX) (XL) (XXXVIII) (XLI)

(a) $R^1$ = COSAlk ;
(b) $R^1$ = $CH_2OH$ .

An alternative synthesis of 10-oxaprostaglandins was published in 1974 (Scheme 3).[54] The initial tetrahydrofuranone (XLII), obtained by oxidising 2-(3-cyclo-octenyl)-propane-1,3-diol, already contained the $\alpha$-chain, which was, however, shorter by one $CH_2$ group than in the prostaglandin. The $\alpha$-chain was lengthened in the following way; after protecting the 11-hydroxymethyl group, the carboxy-group was reduced with diborane to an alcoholic group and was then converted via the tosylate into a nitrile group [compound (XLIII)]. After the alkaline hydrolysis of compound (XLIII) and esterification, the ester (XLIV) was isolated and its hydroxymethyl group was oxidised to the formyl group.

The further conversion into the 10-oxaprostaglandin (XXXVII) was achieved by a series of reactions which had already been thoroughly tested previously in syntheses of prostaglandins: the interaction of the aldehyde with dimethyl 2-oxoheptylphosphonate resulted in the introduction of the alkyl side chain, in which the 15-oxo-group was then reduced with sodium tetrahydroborate to the hydroxy-group:

Scheme 3

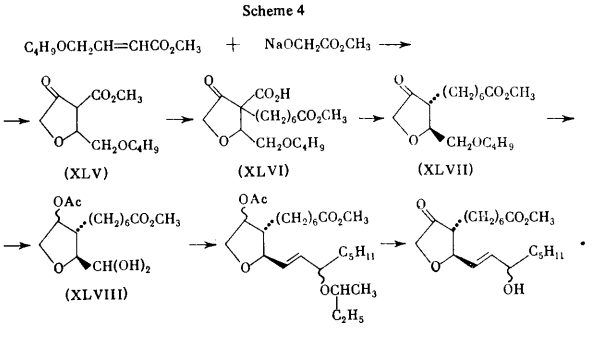


(XLII) (XLIII) (XLIV) (XXXVII)

(a) $R^1$, $R^2$ = H, or OH;
(b) $R^1$, $R^2$ = $CH_3$, or OH.

Fried and coworkers[55], who have been working for many years on the formation of prostanoids containing heteratoms in various parts of the molecule, achieved the synthesis of 11-oxaprostaglandin. The tetrahydrofuranone ring required to synthesise 11-oxaprostaglandin was formed by the condensation of 4-t-butoxybut-2-enoic acid with sodium methoxycarbonylmethoxide (Scheme 4). The resulting ketoester (XLV) was converted with alkali into the sodium salt, which was alkylated with methyl $\omega$-iodo-oenanthate. Analysis of the ketoester (XLVII) obtained as a result of decarboxylation of compound (XLVI), showed that both side chains are in the required more stable *trans*-configuration:

Scheme 4



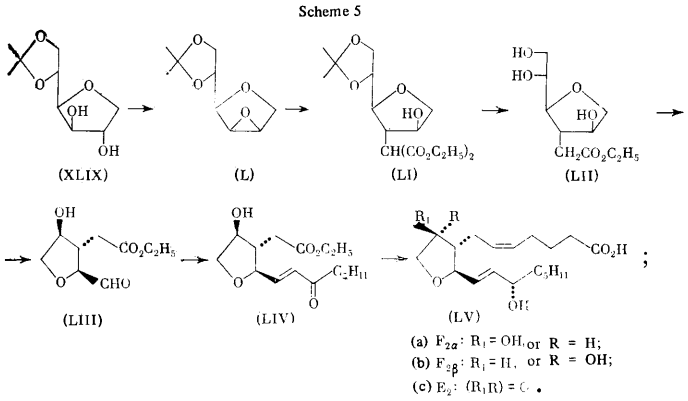
(XLV) (XLVI) (XLVII) (XLVIII)

The authors then reduced the t-butoxymethyl and 9-oxo-groups with zinc tetrahydroborate to alcoholic groups, selectively protected the 9-hydroxy-group, oxidised the 12-hydroxymethyl group with DCC to the aldehyde hydrate (XLVIII), and attached the alkyl chain via the Wittig reaction.

The 15-oxo-group was reduced with zinc tetrahydroborate; the resulting hydroxy-group was protected by ethyl vinyl ether, which permitted the oxidation of the 9-hydroxy-group to the carbonyl group with chromium trioxide after the removal of the 9-acetyl protecting group. The removal of the second protecting group in aqueous acetic acid led to a mixture of alcohols epimeric with respect to $C_{(15)}$, which were separated chromatographically. Both epimers exhibited a weak PGE-like activity in *in vitro* experiments (on the contraction of the smooth musculature of a section of the large intestine).

A novel stereospecific synthesis of 11-oxaprostaglandins containing a double bond in each side chain was developed by Canadian chemists[56] (Scheme 5). Starting with substituted 1,4-dihydrosorbitol (XLIX), the authors obtained via the monomethanesulphonate the epoxide (L), into which they subsequently introduced the malonic ester residue. After alkaline hydrolysis of compound (LI), partial decarboxylation, and esterification, the trisubstituted tetrahydrofuran (LII) was obtained, in which the ethylene glycol group was oxidised by sodium periodate to the formyl group. Treatment of the aldehyde (LIII) with dimethyl 2-oxoheptylphosphonate in the presence of sodium hydride gave an 80% yield of compound (LIV), which the authors regard as the key compound for the synthesis of 11-oxaprostanoids (LV):

Scheme 5



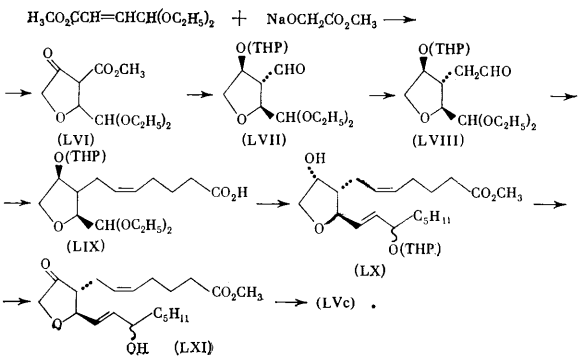
(XLIX) (L) (LI) (LII) (LIII) (LIV) (LV)

(a) $F_{2\alpha}$: $R_1$ = OH, or R = H;
(b) $F_{2\beta}$: $R_1$ = H, or R = OH;
(c) $E_2$: ($R_1$R) = O.

Vlattas and Lee[57] developed almost simultaneously with the Canadian workers[56] another version of the synthesis of the 11-oxa-analogue of $PGE_2$ [compound (LVc)] (Scheme 6). The disubstituted tetrahydrofuranone (LVI) was obtained by the condensation of methyl 4,4-diethoxycrotonate with sodium methoxycarbonylmethoxide. The reduction of compound (LVI) with sodium tetrahydroborate led to a mixture of epimeric alcohols. The main epimer was isolated chromatographically and, after protecting the hydroxy-group with THP, was converted into the aldehyde (LVII) by reaction with DIBAL. The following stage of the synthesis is of methodological interest: the formation of the homologous aldehyde (LVIII) via a vinyl sulphide. For this purpose, compound (LVII) was treated with triphenylphosphoranylidene(phenylthio)methane in dimethyl sulphoxide. The mixture of the *cis*- and *trans*-vinyl sulphides formed was converted by treatment with mercury acetate into an adduct, which was subjected to reductive cleavage with aluminium amalgam to the corresponding acetoxyphenylmercaptoacetal. Alkaline hydrolysis of the latter led to the aldehyde (LVIII), which was converted into compound (LIX) by reaction with sodium 5-triphenylphosphoranylidenepentanoate. The necessary alkyl chain was attached by the Wittig reaction with the corresponding phosphorane

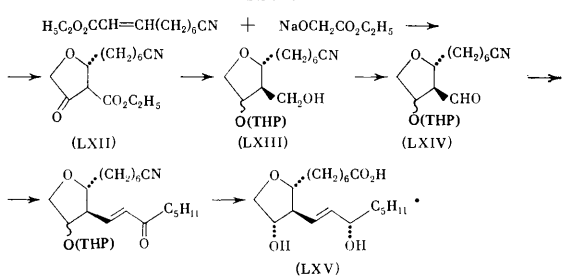
and the alcohol (LX) was converted into the ketone (LXI) by oxidation with thiocyanogen in dimethyl sulphide.

Scheme 6



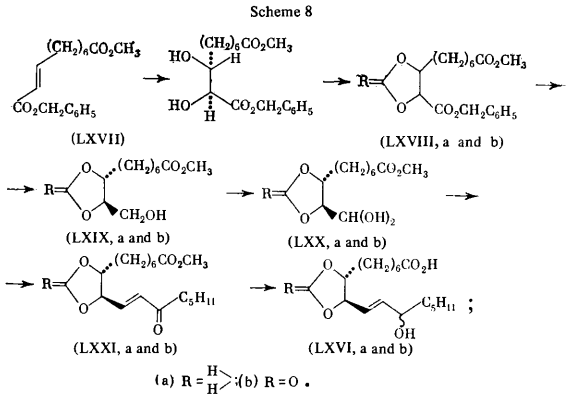
The synthesis of 9-oxaprostaglandin, published by Vlattas and Della Vecchia towards the end of 1974,[58] was achieved in accordance with one of the traditional schemes for the synthesis of $PGE_1$ and $PGF_{1\alpha}$ (see, for example, Caton[10]) (Scheme 7). The initial tetrahydrofuran derivative was obtained by condensing sodium ethoxycarbonylmethoxide with the corresponding substituted vinyl ether. The tetrahydrofuranone (LXII) synthesised already contained the required $\alpha$-chain. The second chain was introduced into the ring after the reduction of the oxo- and ethoxycarbonyl group to alcoholic groups (in succession with sodium tetrahydroborate and lithium tetrahydroaluminate) and the conversion of the alcohol (LXIII) into the aldehyde (LXIV) under the influence of chromium trioxide by the Wittig reaction of compound (LXIV) with the corresponding phosphorane. After the reduction of the 15-oxo-group with sodium tetrahydroborate, the mixture epimeric with respect to $C_{(15)}$ was separated on a column of silica gel. The nitrile group was hydrolysed with potassium-hydroxide in the last stage of the synthesis of the 9-oxa-analogue of $PGE_1$ [compound (LXV)]:

Scheme 7



Scheme 8 describes the synthesis of prostanoids in the five-membered ring of which two hydroxymethine groups have been replaced by oxygen atoms. The authors[59] state that they undertook the synthesis of compounds of type (LXVI) after the interesting biological properties of prostaglandin analogues in the side chains of which the methylene groups have been replaced by heteroatoms [compounds (XXXII) and (XXXIII)[35,37]] became known.

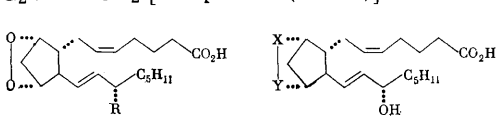
Scheme 8



Harrison et al. used as the initial compound the unsaturated *trans*-ester (XLVII), the synthesis of which they had developed previously for 9,11-bishydroxymethyl analogues of prostaglandins[44]. Hydroxylation of compound (LXVII) with osmium tetroxide in the presence of barium chlorate resulted in the formation of the corresponding diol, which was subsequently converted into the cyclic acetal (LXVIIIa) by heating with paraformaldehyde in benzene in the presence of perchloric acid. Hydrogenolysis of the benzyl group in compound (LXVIIIa) led to the corresponding acid which was converted into a mixed anhydride by a reaction with chlorocarbonic ester. The anhydride was reduced with sodium tetrahydroborate to the alcohol (LXIXa), whose oxidation with DCC led to the aldehyde hydrate (LXXa). The missing side chain was synthesised by the Wittig reaction and the 15-oxo-group was reduced with zinc tetrahydroborate. The mixture of epimers with respect to $C_{(15)}$ was separated chromatographically. The esters (LXXIa) were hydrolysed to the corresponding acids with a methanolic solution of sodium hydroxide.

In addition, the authors[59] developed the synthesis of a dioxaprostaglandin containing an oxo-group in the 10-position. In the synthesis of the heterocyclic nucleus, paraformaldehyde was replaced by phosgene, whose condensation with the diol was carried out in tetrahydrofuran in the presence of pyridine. The series of subsequent reactions, analogous to those employed in the synthesis of compound (LXVIa), led to compound (LXVIb). Both compounds exhibited a weak $PGE_2$ activity in *in vitro* experiments on their effect on the smooth muscles of a section of the large intestine.

Among the syntheses of oxaprostaglandins, mention must be made of the methods of synthesis of 2-oxabicyclo-[2,2,1]heptane analogues of the prostaglandin endoperoxides $PGG_2$ and $PGH_2$ [compounds (LXXII)]:

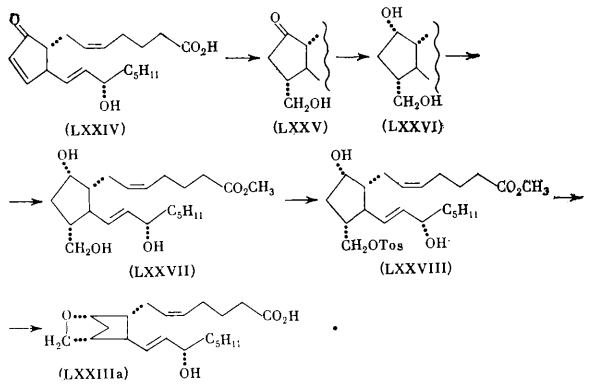


The compounds $PGG_2$ and $PGH_2$, which are intermediates in the biosynthesis of prostaglandins, have been obtained recently by biosynthesis; they were isolated and

characterised[60]. It was found that, despite their short half-life in an aqueous buffer, these compounds have an interesting spectrum of biological activity. This led Bundy[61] to synthesise the prostaglandin analogues (LXXIII) by replacing one of the peroxide oxygen atoms in the $PGH_2$ molecule by the methylene group.

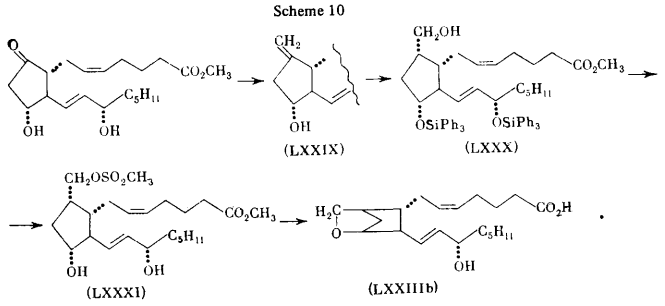
The 11-hydroxymethyl group was introduced (Scheme 9) into the carbon skeleton of $PGA_2$ [compound (LXXIV)], obtained from the coral *Plexaura Homomalla*, by irradiating a methanol solution of $PGA_2$ in the presence of benzoquinone. The resulting mixture of epimeric alcohols (LXXV), with the 11-$\alpha$-isomer predominating, was separated chromatographically. The oxo-group in the ring of the 11-$\alpha$-isomer isolated was reduced with lithium perhydro-9b-boraphenalyl hydride and the reaction was so stereospecific that the yield of the required 9-$\alpha$-isomer (LXXVI) reached 94%. After the esterification of the dihydroxy-acid (LXXVI) with diazomethane, the primary alcoholic group in compound (LXXVII) was selectively converted into the toluene-*p*-sulphonate ester (LXXVIII). Subsequent treatment of compound (LXXVIII) with potassium hydroxide in an aqueous methanol solution at room temperature made it possible to achieve both intramolecular substitution and hydrolysis of the ester group.

Scheme 9



The synthesis of compound (LXXIIIb), in which the oxygen atom attached to $C_{(9)}$ in the $PGH_2$ molecule has been replaced by a methylene group, is illustrated in Scheme 10.

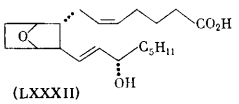
Scheme 10



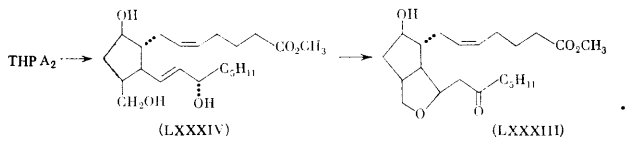
The methylene group was introduced in the 9-position of the methyl ester of $PGE_2$ by treating the latter with *N*-methylphenylimidoylmethylmagnesium chloride in tetrahydrofuran and subsequent reductive cleavage of the resulting adduct with aluminium amalgam. The yield of the 9-methylene derivative (LXXIX) was 75%.

The subsequent stages of the synthesis—the protection of the 11- and 15-hydroxy-groups with triphenylsilyl groups and selective hydroboration of the 9-methylene group with 9-borabicyclo[3,3,1]nonane (9-BBH)—led to the corresponding primary alcohol (LXXX). The stereochemistry of compound (LXXX) was determined by the preferred attack by 9-BBH from the less shielded side of the molecule and was confirmed by the ease of the subsequent cyclisation involving the 11-$\alpha$-hydroxy-group. For this purpose, the methanesulphonate was obtained initially by reaction with the primary alcoholic group, the silyl protecting group was removed, and the resulting monomethanesulphonate (LXXXI) was treated with an aqueous methanol solution of potassium hydroxide. Like $PGH_2$, the cyclic ethers (LXXXIII, a and b) manifested a bronchoconstricting activity in experiments on animals.

A report[62] of the synthesis of another series of endoperoxide analogues—derivatives of 7-oxabicyclo[2,2,1]-heptane (LXXXII)—was published recently. These compounds were obtained by the condensation of triethylphosphonosorbic acid esters and dimethyl 2-oxoheptylphosphonate with the corresponding derivatives of 7-oxabicyclo[2,2,1]heptane:

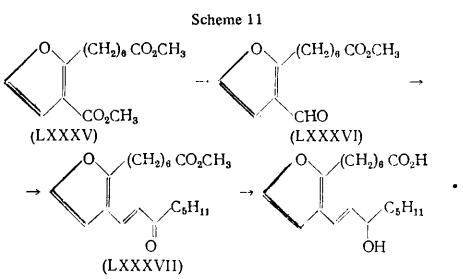


Yet another derivative of tetrahydrofuran, whose structure is similar to that of $PGE_2$, was obtained in the course of the synthesis of 9,11-bishydroxymethyl analogues of $PGE_2$.[63] Compound (LXXXIII) is formed when the triol (LXXXIV) is oxidised with 2,3-dichloro-5,6-dicyanobenzoquinone, which results in the conjugate addition of the *cis*-hydroxymethyl group to the intermediate enone:



The synthesis of oxygen-containing heteroaromatic prostanoids derived from furan and oxazole has also been described[64]. Scheme 11 was put forward for the synthesis of a furan analogue of prostaglandin. Dimethyl 3-oxosebacate was treated with chloroacetaldehyde; the resulting methyl 2-(6-methoxycarbonylhexyl)furan-3-carboxylate (LXXXV) was converted into the aldehyde (LXXXVI). The Wittig reaction of the latter with the corresponding phosphorane led to methyl 15-oxo-9-oxaprosta-8(12), 10,13-*trans*-trienoate (LXXXVII), in which the 15-oxo-group was then reduced and the ester group was hydrolysed:

Scheme 11



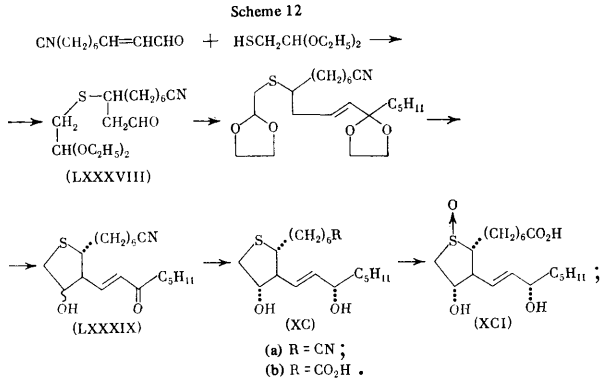
## 2-, 9-, and 11-Thiaprostaglandins

Literature data are available about the synthetic analogues of prostaglandins containing a sulphur atom in the 9- or 11-position in the molecule. They are all tetrahydrothiophen derivatives.

The synthetic scheme selected by Vlattas and Della-Vecchia[65] to obtain 9-thiaprostaglandins and their $C_{(11)}$ and $C_{(15)}$ epimers is fairly well known and is frequently used to synthesise natural prostaglandins (see, for example, Corey et al.[66]). A characteristic feature of the scheme is the closure of the cyclic components of the molecule (with formation of the $C_{(11)} - C_{(12)}$ bond) after both side chains have been synthesised (Scheme 12).

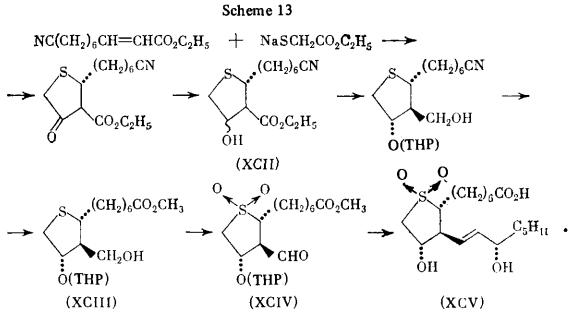
The condensation of 9-cyanononenal with the diethyl acetal of mercaptoacetaldehyde led to the adduct (**LXXXVIII**) which reacted under the conditions of the Wittig reaction with 1-tributylphosphoranylidene-2-heptanone to form the corresponding enone. After protecting both oxo-groups with ethylene glycol and subsequent intramolecular cyclisation of the dieketal (in the presence of toluene-*p*-sulphonic acid), a mixture of epimers of compound (**LXXXIX**) with respect to $C_{(11)}$ was obtained. Chromatographic separation of the isomers and subsequent reduction of the 15-oxo-group in the more polar isomer with zinc tetrahydroborate led to the formation of a new epimeric mixture with respect to $C_{(15)}$, from which the more polar isomer (**XCa**) was isolated on a column with silica gel. The isomer was then hydrolysed in an aqueous methanol solution of potassium hydroxide to (±)-9-thiaprostaglandin (**XCb**). In addition, a mixture of the isomeric sulphoxides (**XCI**) was obtained by oxidising compound (**XCb**) with sodium peroxide.

Scheme 12



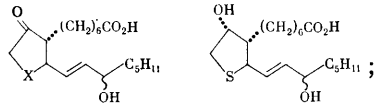
The same workers developed simultaneously an alternative scheme for the synthesis of 9-thiaprostaglandins[67] (Scheme 13). The tetrahydrothiophen ring was formed at the beginning of the synthesis. For this purpose, ethyl 9-cyanonon-2-enoate was condensed with the sodio-derivative of thioglycolic ester. The resulting substituted tetrahydrothiophenone was then reduced with sodium tetrahydroborate to a mixture of epimeric products (**XCII**) with respect to $C_{(11)}$, which was separated chromatographically. After protecting the 11-hydroxy-group in the more polar isomer (**XCII**) with THP, the ester group was reduced and the resulting hydroxynitrile was then converted into the corresponding hydroxyester (**XCIII**) by alkaline hydrolysis in methanol and esterification with diazomethane:

Scheme 13



The sulphide (**XCIII**) was then oxidised with *m*-chloroperbenzoic acid to a sulphone, which was in its turn converted into the aldehyde (**XCIV**) by treatment with chromium trioxide. Compound (**XCIV**) was converted into (±)-9-thia-$PGE_1$ dioxide (**XCV**) with the aid of reactions usually employed in this series of conversions: the introduction of the alkyl chain by the Wittig reaction, the reduction of the 15-oxo-group by sodium tetrahydroborate followed by the chromatographic separation of the epimeric alcohols, and the hydrolysis of the ester group in the 11-position with potassium carbonate in methanol. The enantiomeric form of compound (**XCV**) was obtained by esterifying the 11-hydroxy-group of *R*(-)-α-methoxyphenylacetyl chloride at the enone stage.

Derivatives of 11-thiaprostaglandin in which the sulphur atom replaces the hydroxymethine group in the 11-position of the $PGE_1$ [compounds (**XCVI**, a and b)] and $PGF_{1\alpha}$ [compound (**XCVII**)] molecules, have been recently synthesised in accordance with Scheme 14:[68]

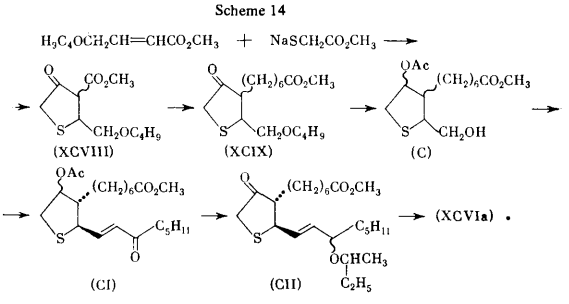


In this case the tetrahydrothiophen ring was formed from methyl 4-t-butoxybut-2-enoate and the sodio-derivative of thioglycolic ester. The resulting tetrahydrothiophenone (**XCVIII**) was alkylated with methyl 7-iodo-oenanthate and then the methoxycarbonyl group was eliminated by treatment with lithium hydride in boiling dimethylformamide. The 9-oxo-group in the resulting ketoester (**XCIX**) was reduced with sodium tetrahydroborate and the resulting hydroxy-group was protected by treatment with acetic anhydride, while the t-butyl group was eliminated by treatment with a mixture of 48% aqueous hydrofluoric acid and tetrahydrofuran.

The alcohol (**C**), isolated in this reaction, was subsequently converted into the corresponding aldehyde hydrate (as in Scheme 4) and then into the enone (**CI**). Analysis of the structure of compound (**CI**) enabled the authors to claim that the side chains in the compounds obtained are in the most stable *trans*-configuration. Next, compound (**CI**) was converted by treatment with zinc tetrahydroborate into a mixture of alcohols epimeric with respect to $C_{(15)}$ and the 15-hydroxy-group was protected with ethyl vinyl ether, after which the 9-hydroxy-group was oxidised with DCC in

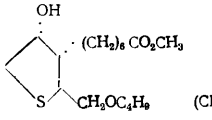
dimethyl sulphoxide to form the ketone (CII). Mild hydrolysis of the ester groups then led to the isolation of 15($\alpha$ + $\beta$)-hydroxy-9-oxo-11-thiaprost-13-enoic acid (XCVIa):

Scheme 14



In order to obtain the sulphoxide (XCVIb), the ketone (CII) was oxidised with *m*-chloroperbenzoic acid, which led to the formation of a mixture of the isomeric methyl esters of the sulphoxide.

Compound (XCVII), the thia-analogue of $PGF_1\alpha$, was synthesised by reducing the ketone (XCIX) with potassium tri-(s-butyl)hydroborate to the 8,9-*cis*-alcohol (CIII):



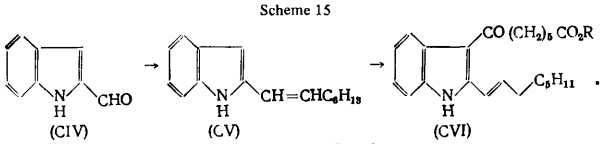
Using the methods described above, compound (CIII) was converted into the corresponding acetoxyalcohol and then into the aldehyde, the enone, and a mixture of alcohols epimeric with respect to $C_{(15)}$. Further hydrolysis yielded 9$\alpha$, 15($\alpha$ + $\beta$)-dihydroxy-11-thiaprost-13-enoic acid (XCVIII). 11-Thiaprostaglandins showed a weak $PGE_2$-like activity on the smooth muscles of a section of the large intestine in *in vitro* experiments.

### 3. Azaprostaglandins

The prostaglandin analogues in which the cyclopentane ring has been replaced by a nitrogen-containing heterocycle synthesised hitherto are indole, pyrrolidine, pyrazolidine, oxazole, and thiazole derivatives.

2-Oct-1-enylindole (CV) was obtained from indole-2-aldehyde (CIV) and heptylidenephosphorane[69,70] (Scheme 15). The authors selected the chloride of the half-ester of pimelic acid in order to introduce the side chain with a carboxy-group, simulating the $\alpha$-chain of prostaglandin molecules. Acylation of the organomagnesium derivative (CV) with this reagent took place with a high yield (80%) and led to ethyl 7-[2-(oct-1-enyl)-3-indolyl]-7-oxoheptanoate (CVIa) (the ratio of the *cis*- and *trans*-isomers was 45 : 55):

Scheme 15

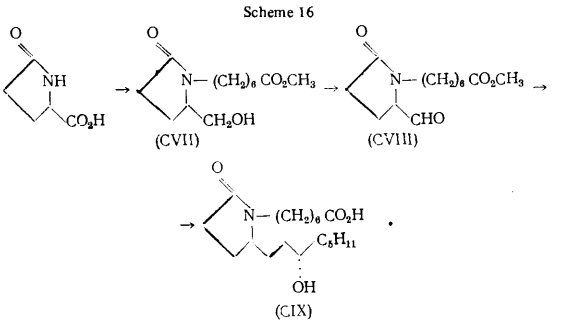


(a) R=$C_2H_5$; (b) R=H.

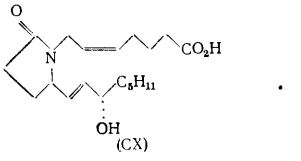
Alkaline hydrolysis of compound (CVIa) gave the *trans*-isomer of the corresponding acid (CVIb), whose structure was confirmed by $^1$H NMR.

The authors based the syntheses of (±)-11-deoxy-8-aza-prostaglandins, the pyrrolidine analogues of $PGE_1$ and $PGE_2$,[71,72] also on the "complete" cyclic component of the molecule (Scheme 16). 5-Hydroxymethyl-1-(6-methoxycarbonylhexyl)pyrrolidin-2-one (CVII) was obtained from the readily available (±)-pyroglutamic acid (five stages):

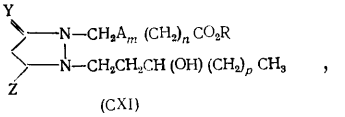
Scheme 16



The subsequent formation of the side chain, involving the oxidation of the alcoholic group to the aldehyde group, the condensation of the aldehyde (CVIII) with dimethyl 2-oxoheptylphosphonate, and the reduction of the resulting enone, presented no difficulties according to the authors' report and led to a mixture of alcohols epimeric with respect to the $C_{(15)}$ and separated chromatographically. The 8-aza-analogue of $PGE_2$ [compound (CX)] was also synthesised on the basis of a suitably modified scheme[71]:



A series of diazaprostaglandins—derivatives of pyrazolidine having the general formula (CXI)—have been synthesised by Scribner[73] in order to obtain prostaglandin inhibitors (Scheme 17):

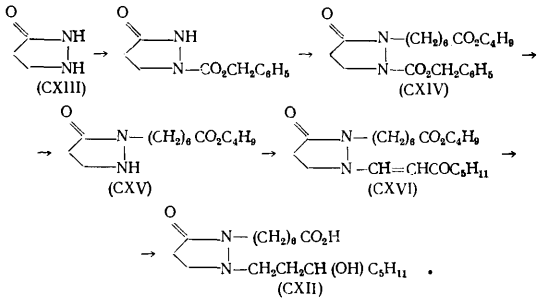


where A = CH = CH or C≡C, R = H, metal, amine salt, alkyl, or halogenoalkyl, $m$ = 0 or 1, $n$ = 0–6, $p$ = 0–6, and Y, Z = O or $H_2$.

According to the author[73], certain compounds of this class can be used as antipyretic, analgesic, and anti-inflammatory agents, and also in the treatment of certain forms of diarrhoea and shock. The synthesis of prostanoids of type (CXI) is facilitated relative to that of natural prostaglandin by the fact that compound (CXI) contains not more than one asymmetric carbon atom (in the side chain) and the asymmetric ring carbon atoms have been replaced by nitrogen atoms. As an example, Scheme 17 presents

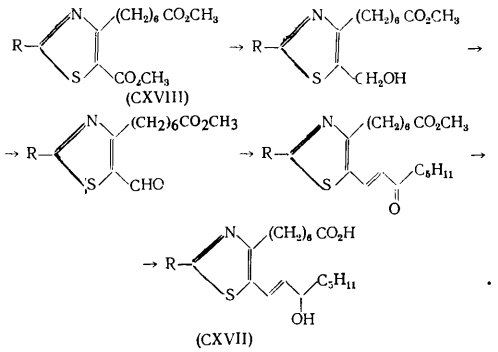
the synthesis of one representative of this series, namely (±)-15-hydroxy-9-oxo-8,12-diazaprostanoic acid (CXII):

Scheme 17



The more basic nitrogen atom was first protected in the initial pyrazolidinone (CXIII) with the aid of benzyl chloroformate, after which the compound was alkylated at the second nitrogen atom with t-butyl 7-bromo-oenanthate to form the ester (CXIV). Hydrogenation of compound (CXIV) over palladium made it possible to remove the protecting group from the basic nitrogen atom in the pyrazolidinone ring, after which the product (CXV) was converted by refluxing with oct-1-yn-3-one in alcohol into the enaminoketone (CXVI), which was subsequently reduced, without prior purification, with hydrogen in the presence of a platinum catalyst (the $C_{(13)} - C_{(14)}$ bond) and with sodium tetrahydroborate (the 15-oxo-group). The mixture of alcohols epimeric with respect to $C_{(15)}$ was separated chromatographically. It is noteworthy that 8,12-diazaprostanoids (CXII) are the first example of synthetic basic analogues of prostaglandins.

Prostanoids containing nitrogen and sulphur atoms in the cyclic part of the molecule have been synthesised by Hungarian chemists[64]. In the synthesis of thiazole analogues of prostaglandins [compound (CXVII)], the heterocyclic ring is formed as a result of the condensation of dimethyl 2-chloro-3-oxosebacate with various thioamides. The resulting methyl 4-(6-methoxycarbonylhexyl)thiazole-5-carboxylate (CXVIII) was converted into compound (CXVII) in accordance with the scheme



Like the furan and oxazole analogues of prostaglandins (see Section III, subsection 2), the thiazole analogue (CXVII) inhibits enzymes which catalyse the further conversion of prostaglandins (15-hydroxy-PG-dehydrogenase and PGA-isomerase) and exhibits a prostaglandin-like effect in certain biological tests.

After the preparation of the article for publication, a number of communications on the subject of the review were published[74-101].

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# Salting-out and Salting-in of Gaseous Non-electrolytes in Aqueous Solutions of Electrolytes

E.I.Konnik

Modern theories of salting-out and salting-in of gaseous non-electrolytes are reviewed and compared with experimental data. We conclude that a strict thermodynamic theory of salting-out and salting-in of non-electrolytes is not yet available. The use of salting-out and salting-in data to determine some physicochemical characteristics of solutions is described. 56 references.

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## I. INTRODUCTION

Salting-out and salting-in effects of non-electrolytes in aqueous solutions of electrolytes are of general interest in physical chemistry as well as being used in applied chemistry.

Salting-out and salting-in effects are widely used in extraction. Quantitative data on the salting out of gases such as hydrogen, carbon monoxide, and oxygen are highly relevant to the design of electrochemical generators (fuel cells). Electrochemical generators operate in the diffusion-controlled regime for the supply of gaseous reagents to the electrodes. In electrolyte solutions the concentration of these gases is decreased by salting out, and as a result the diffusional flow to the electrodes and the available current density both decrease. Salting-in and salting out are directly related to changes in the activity coefficients of the gaseous non-electrolytes. A knowledge of the activity coefficients of the non-electrolytes is essential to the calculation of electrode equilibria involving these non-electrolytes. The calculation of the activity coefficients of non-electrolytes in solutions of electrolytes will provide the main stimulus for the development of the theory of salting in and salting out of non-electrolytes.

Allowance for salting-out and salting-in effects is necessary also in the application of polarographic methods and apparatus to the analysis of gases in solutions. This is because some of these methods measure the activity rather than the concentration of the gas. Hence we need to know the activity coefficients of the gases in solution in order to calculate their concentrations.

The fund of experimental data on the salting out and salting in of non-electrolytes has grown very considerably during the last 25 years. Substantial progress has been made in developing the theory of the phenomenon. These achievements are due primarily to progress in the development of the theory of solutions.

## II. THE "HYDRATION" THEORY

The "hydration" theory of salting out—the first theory of the phenomenon—was proposed at the end of the 19th century. The first quantitative experimental results on the salting-out of gaseous non-electrolytes from aqueous solutions of electrolytes were published by Sechenov in 1875.[1,2] The result of this work was Sechenov's empirical equation, which is still one of the most successful expressions for describing quantitatively the salting out and salting in of non-electrolytes:

$$\lg \frac{s^0_{ne}}{s_{ne}} = Kc_e, \qquad (1)$$

where $s^0_{ne}$ and $s_{ne}$ are the solubilities of the non-electrolyte in water and in the electrolyte solution respectively, $c_e$ is the concentration of electrolyte, and $K$ is the salting-out coefficient (or constant).

Sechenov first put forward the suggestion that the decrease in solubility of the non-electrolyte is due to the hydration of the electrolyte. Most workers at the turn of the century explained the salting out of non-polar non-electrolytes in terms of hydration of the electrolyte: the non-electrolyte molecules are repelled from the ionic atmosphere of the electrolyte ion by the polar water molecules, and the volume of water available for dissolving the non-electrolyte is less than the total volume of water in the solution.

According to the hydration theory of salting out the quantity $s^0_{ne}/s_{ne}$ is equal to the ratio of the volumes of "free" water in the solution before and after addition of the electrolyte:

$$\frac{s^0_{ne}}{s_{ne}} = \frac{1}{1 - \Sigma c_e V^h_e}, \qquad (2)$$

where $V^h_e$ is the volume of one mole of hydrated molecules of electrolyte.

The hydration theory tried to explain salting-out and salting-in phenomena by considering only the hydration of the electrolyte, and it could not give a physical interpretation of the significance of the salting-out coefficient $K$ in Eqn. (1). More recently, Ruetschi and Amlie [3] obtained an expression for $\ln(s^0_{ne}/s_{ne})$ by a series expansion of the logarithm of the right-hand side of Eqn. (2):

$$\ln\frac{s^0_{ne}}{s_{ne}} = \Sigma c_e V^h_e + \frac{1}{2}(\Sigma c_e V^h_e)^2 + \frac{1}{3}(\Sigma c_e V^h_e)^3 + \ldots \quad (3)$$

For an electrolyte at infinite dilution they retained only the first term of the series to give the approximate linear equation

$$\ln\frac{s^0_{ne}}{s_{ne}} = \sum_{c_e\to 0} c_e V^h_e = \Sigma c_e V^0_e, \quad (4)$$

where $V^0_e$ is the intrinsic volume of one mole of the electrolyte at infinite dilution. For a fully dissociated electrolyte $c_e = \nu_e c^M_e$ (where $\nu_e$ is the number of ions produced by the dissociation of the electrolyte and $c^M_e$ is the molar concentration of the electrolyte), and therefore

$$\ln\frac{s^0_{ne}}{s_{ne}} = c^M_e \Sigma \nu_e V^0_e. \quad (5)$$

Thus the empirical Sechenov equation (1) can be interpreted theoretically. In particular, the salting-out coefficient in Sechenov's equation should be given, according to the hydration theory, by the sum of the products $\nu_e V^0_e$ for all the electrolytes present in the solution. In this way the hydration theory can account for the relative insensitivity of the $K$ value of an electrolyte to the nature of the non-polar non-electrolyte. It is also found that the neglect of the higher terms of the series in Eqn. (3) is compensated by the decrease of $V^h_e$ with increasing concentration of electrolyte, so that the parameter $K$ in Sechenov's equation remains constant up to relatively high concentrations of electrolyte. At the highest electrolyte concentrations, or if the electrolyte is not fully dissociated, the quantity $c_e$ is no longer proportional to $c^M_e$, and as a result the plot of $\lg(s^0_{ne}/s_{ne})$ against $c^M_e$ deviates from linearity.

The hydration theory cannot explain the salting-in effect occasionally observed with non-electrolytes; it follows that the constant $K$ in Sechenov's equation is not determined simply by the intrinsic volume of the electrolyte at infinite dilution and by the number of ions formed by the dissociation of the electrolyte. The difference between the $K$ values for hydrogen and oxygen (~25%) in both NaOH and KOH [4] is another fact which the hydration theory cannot explain.

Thus the hydration theory in its original form has only historical value as the first attempt at a theoretical interpretation of salting-out and salting-in effects of non-electrolytes. Further developments in the theory of this complicated phenomenon had to wait the appearance of the Debye–Hückel electrostatic theory of electrolyte solutions. Even more recently Ruetschi and Amlie [3] introduced the elements of electrostatic theory into the hydration theory, enabling it to take fuller account of all the factors which influence the salting out and salting in of non-electrolytes.

## III. ELECTROSTATIC THEORIES

A qualitatively new approach to the salting out and salting in of non-electrolytes in terms of electrostatic interactions in electrolyte solutions was developed in 1925 by Debye and McAuley [5]. Their electrostatic theory of salting out, which treats the electrolyte solution as an ideal solution, allows for the effect of the non-electrolyte on the dielectric constant of the solution. The electrostatic field of the electrolyte ions is altered by the change in the dielectric constant of the solvent from its initial value $\epsilon_0$ to a new value $\epsilon$ resulting from the presence of the non-electrolyte, and as a result the activity coefficient $f_{ne}$ of the non-electrolyte is also altered. The quantity $f_{ne}$ is given, according to the Debye–McAuley theory, by the equation [5]

$$\ln f_{ne} = \frac{N\delta_{ne}e^2}{\epsilon_0 bRT}\cdot\frac{\Sigma c_e z^2}{2}, \quad (6)$$

where $N$ is Avogadro's number, $\delta_{ne}$ is the decrement in the dielectric constant of the solution produced by dissolution of the non-electrolyte, $e$ and $z$ are the electronic charge and the valency of the electrolyte ion respectively, and $b$ is the ionic radius of the electrolyte.

Debye and McAuley calculated the quantity $\delta_{ne}$ in Eqn. (6) by a formula which includes the number of molecules of non-electrolyte per 1 ml of solution ($n_{ne}$):

$$\epsilon = \epsilon_0(1 - \delta_{ne}\eta_{ne}). \quad (7)$$

The $\delta_{ne}$ values for hydrogen and oxygen were determined by Scatchard [6] in 1927 (0.05 and 0.06 respectively). To calculate the ionic radius of the electrolyte Debye and McAuley proposed a formula involving the radii of the cation ($r_c$) and of the anion ($r_a$), and $\nu_e$:

$$\frac{1}{b} = \frac{1}{\nu_e}\left(\frac{1}{r_c} + \frac{1}{r_a}\right). \quad (8)$$

The effect of hydration of the electrolyte on salting out is accounted for by the term $\Sigma c_e z^2/2$ in the Debye–McAuley equation. (This term appears also in the Born equation for the hydration energy of the electrolyte.)

Eqn. (6) has the same form as the empirical equation

$$\lg f_{ne} = K\mu, \quad (9)$$

where $\mu$ is the ionic strength of the solution. Eqn. (9) is also called the Debye–McAuley equation. In the electrostatic theory the salting-out coefficient is given by the expression

$$K = \frac{N\delta_{ne}e^2}{\epsilon_0 bRT}. \quad (10)$$

Debye and McAuley assumed that the electrolyte solution was ideal, and therefore confined the application of their electrostatic theory to the case of very dilute solutions.

Randall and Failey [7] showed that simple linear expressions such as Eqns. (6), (9), and (10) cannot be strictly correct. In particular, using Eqn. (9) to interpret experimental data on the salting out of hydrogen, oxygen, and other gases, they obtained varying values of $K$ for these gases in the same electrolyte at different concentrations, which is inconsistent with the definition of a salting-out constant.

The salting-out theory of Debye and McAuley correctly predicts an increase in $K$ with increasing charge and decreasing radius of the electrolyte ions. This theory allows for the decrease in the dielectric constant of the solvent caused by the presence of the non-electrolyte. However Debye and McAuley made no allowance for the decrease in the dielectric constant of the solvent caused by the presence of the electrolyte, which can be substantial [8]. The Debye–McAuley theory also fails to allow for specific interactions between the non-electrolyte and the solvent, and therefore it is powerless to explain the

salting-in effect of non-electrolytes. Experimental verification of the Debye–McAuley equation is not easy because the equation applies to very dilute solutions of electrolytes. The effect of non-electrolytes on the activity coefficient of electrolytes was first considered by Born[9]. Somewhat later Debye improved the Debye–McAuley theory[10] by treating the mixture of water and non-electrolyte as a heterogeneous medium. Assuming that the dielectric constant of the solution varies with distance $r$ from the ion in such a way that the overall free energy of the system is a minimum, he showed that

$$f_{ne} = \left(1 - \frac{4\pi N}{1000}\sum_i I_i c_i\right)^{-1}, \qquad (11)$$

where $c_i$ is the molar concentration of the solute. From the spherical structure of the ionic atmosphere he obtained the equation

$$I_i = \int_{r_i}^{\infty}\left[1 - \exp\left(-\frac{\bar{R}}{r}\right)^4\right] r^2\,dr, \qquad (12)$$

where $r_i$ is the radius of the ion of solute $i$.

Debye's improved electrostatic theory introduces, in addition to the quantity $\delta_{ne}$, also the change in the dielectric constant of the solution caused by the presence of the electrolyte. This leads to the equation

$$\bar{R}^4 = \frac{(ze)^2\,[v_{ne}(\partial\varepsilon/\partial c_w)\,c_{ne} - v_w(\partial\varepsilon/\partial c_{ne})\,c_w]}{8\pi RT\varepsilon^2 v_w}, \qquad (13)$$

where $c_w$ is the molar concentration of water, $v_{ne} = V_{ne}/N$, $V_{ne}$ is the molar volume of the non-electrolyte in the solution, $v_w = V_w/N$, $V_w$ is the molar volume of water. The difference in the numerator of Eqn. (13) determines whether salting out or salting in of the non-electrolyte will take place.

The integration of Eqn. (12) is not taken to infinity. As shown by Ruetschi and Amlie[3], the effect of the electric field of the ion on the dielectric constant of the solution extends over the layer of solution lying between the radius of the hydrated ion ($r_h$) and the radius of the ionic atmosphere ($r_n$). Hence the integration of Eqn. (12) can be taken from $r_h$ to $r_n$. The same workers[3] used the ideas of the improved Debye–McAuley electrostatic theory to develop the hydration theory, and obtained a more accurate form of Eqn. (2):

$$\frac{s^0_{ne}}{s_{ne}} = 1 - \Sigma c_e V^0_e - \Sigma I_i c_i. \qquad (14)$$

For the integral [see Eqn. (12)] which appears in Eqn. (14) Ruetschi and Amlie chose the limits $r_h$ and $r_n$. At low concentrations of electrolyte they obtained

$$\ln\frac{s^0_{ne}}{s_{ne}} = c^M_e \Sigma v_e V^0_e + \Sigma I_i c_i\ . \qquad (15)$$

The parameter $r_n$ can be calculated by the expression

$$r_n = \left(\frac{3}{4\pi n_e}\right)^{1/3}, \qquad (16)$$

where $n_e$ is the number of ions of electrolyte in 1 ml of solution.

Eqn. (15) combines the concepts of the hydration theory and of the Debye–McAuley electrostatic theory. It is only one of the many salting-out equations.

An equation similar to Eqn. (15) was put forward by Long and McDevit[4] on the basis of an equation given in Ref. 11. For solutions of intermediate concentration, without chemical interaction between the non-electrolyte and the solution and at not too high concentrations of non-electrolyte (the solubility of gaseous non-electrolytes being usually small), Long and McDevit obtained the equation

$$\lg f_{ne} = K_e c^M_e + K_{ne} s_{ne}. \qquad (17)$$

The authors point out[4] that most theories of salting out concentrate the attention on $K_e$, whereas we also need to know $K_{ne}$ to calculate $\lg f_{ne}$. Since the chemical potentials of the non-electrolyte in solution in equilibrium with the pure non-electrolyte or with the non-electrolyte in the gas phase are the same, we can write

$$f_{ne} s_{ne} = f^0_{ne} s^0_{ne}. \qquad (A)$$

It follows that

$$\lg\frac{f_{ne}}{f^0_{ne}} = \lg\frac{s^0_{ne}}{s_{ne}}, \qquad (B)$$

and

$$\lg f^0_{ne} = K_{ne} s^0_{ne}, \qquad (C)$$

and therefore Eqn. (17) can be re-written[4]

$$\lg\frac{f_{ne}}{f^0_{ne}} = K_e c^M_e + K_{ne}(s_{ne} - s^0_{ne})\ . \qquad (18)$$

The parameter $K_{ne}$ according to Long and McDevit is determined only by internal interactions of the non-electrolyte molecules. If the difference between $s^0_{ne}$ and $s_{ne}$ is not large Eqn. (18) becomes identical to Sechenov's Eqn. (1). The Sechenov equation is often obeyed also when the last term of Eqn. (18) is relatively large. The empirical coefficient $K$ of Eqn. (1) is not equal to the theoretical coefficient $K_e$ of Eqn. (18). Experimental studies of the solubility of non-electrolytes give $K_e$ values. However we need to know also $K_{ne}$ in order to calculate the activity coefficients of non-electrolytes having intermediate or high solubility. Eqn. (15) makes fuller allowance than Eqn. (18) for the effects of various factors on the salting-out process.

Givon and coworkers[12] further developed the ideas of Debye and McAuley. They obtained, by a series expansion, an approximate value of the integral in Eqn. (12) between the limits 0 and the radius of the hydrated electrolyte ion. Assuming that $K = \lim_{c_e \to 0}\dfrac{d\lg f_{ne}}{dc_e}$, and that the solubility of the non-electrolyte is much greater than the concentration of electrolyte (in order to simplify the calculation of the effect of the non-electrolyte on the $\epsilon$ value of the solution), they obtained the following equation as a first approximation (for 25 °C):

$$K = 0.025 z^{5/3} V^{5/6}_{ne}\left(\frac{\delta_e}{V^0_e + 18h^0_e} + \frac{\varepsilon_0 - \varepsilon_{ne}}{1000}\right)^{5/6}, \qquad (19)$$

where $\delta_e$ is the decrement in the dielectric constant of the solvent due to the presence of the electrolyte, $h^0_e$ is the hydration number of the electrolyte at infinite dilution, and $\epsilon_{ne}$ is the dielectric constant of the non-electrolyte.

Eqn. (19) is one of the most accurate equations of the electrostatic theory of salting-out effects of non-electrolytes. All the parameters in the equation can be determined. The $\delta_e$ values for many electrolytes are known,[7,13] and $V^0_e$ and $h^0_e$ values are also available[14,15].

Eqn. (19) correctly predicts an increase of $K$ with increasing charge on the electrolyte ion, with the molar volume of the non-electrolyte, and with the decrement $\epsilon_0 - \epsilon_{ne}$. This equation takes account of the hydration of the electrolyte and also (unlike the Debye–McAuley theory) of the correction $\delta_e$ due to the electrolyte. As a result Eqn. (19) predicts an increase of $K$ with the

decrement in the dielectric constant of the solvent due to the presence of the electrolyte. This prediction agrees with experimental results. Eqn. (19) also allows the possibility of salting in of the non-electrolyte, which occurs when $(\epsilon_0 - \epsilon)/1000$ is negative and greater than $\delta_e/(V_e^0 + 18h_e^0)$ in absolute value. However Eqn. (19) was obtained from an approximate solution of Eqn. (12). Furthermore, several values, differing by 50–70%, have been reported[14,15] for $V_e^0$ and $h_e^0$, suggesting that available data on the hydration of electrolytes have a low precision. A more exact solution of Eqn. (12) and more accurate numerical values of the parameters of Eqn. (19) can be expected to result from a better understanding of the structure of solutions of electrolytes and non-electrolytes.

Frank[16] described a derivation of the basic equation of the electrostatic theory of salting out which is stricter than Debye and McAuley's but equivalent to it. He envisaged the role of the ion as merely to generate an electrostatic field, and he assumed that the non-electrolyte forms an ideal solution. He also assumed that local fluctuations in the concentration of water are negligibly small in comparison to changes in the concentration of the non-electrolyte during salting out, and that the chemical potentials of the electrolyte and of the water are constant. Conway and coworkers[17] calculated the dielectric decrement $\partial\epsilon/\partial c_{ne}$ in Frank's equation in terms of Kirkwood's theory[18] of the polarisation of non-electrolytes in polar liquids:

$$\left(\frac{\partial\varepsilon}{\partial c_{ne}}\right)_{T,p,n_w} = \frac{9}{2}P_{ne} - V_{ne}\varepsilon_0, \qquad (20)$$

where $n_w$ is the number of water molecules in 1 ml of solution, and $P_{ne}$ is the total molecular polarisation of the non-electrolyte.

The integral form of the Frank–Conway equation is

$$K = \frac{V_e^h}{1000} + \frac{(ze)^2}{2000\varepsilon_0 kT}\left(V_{ne}\varepsilon_0 - \frac{9}{2}P_{ne}\right)\left(\frac{1}{r_h} - \frac{1}{r_n}\right), \qquad (21)$$

where $k$ is Boltzmann's constant.

In the case of non-polar non-electrolytes the quantity $\frac{9}{2}P_{ne}$ can be ignored in comparison to $V_{ne}\epsilon_0$.[16] We then have

$$K = \frac{V_e^h}{1000} + \frac{(ze)^2 V_{ne}}{2000\varepsilon_0 kT}\left(\frac{1}{r_h} - \frac{1}{r_n}\right). \qquad (22)$$

$V_e^h$ can be evaluated by the equation[19]

$$V_e^h = V_e + hv_s^h. \qquad (23)$$

Where $V_e$ is the intrinsic molar volume of the electrolyte, $h$ is the hydration number of the ion pair, and $v_s^h$ is the molar volume of the solvent in the hydration shell of the electrolyte. Formulae for the calculation and for the experimental determination of $V_e$, $h$, and $v_s^h$ are given in Ref. 19.

However Conway and coworkers[17] in their derivation of the integral equation for $K$ failed to take account of the dielectric decrement of the electrolyte. They also carried out the integration in two steps (from the crystal-chemical radius $r$ to $r_h$, and from $r_h$ to $r_n$) because of the difference in dielectric saturation between these two regions. However the maximum of the integrand was not always found at a distance $r_h$ from the centre of the ion: its position is a function of the nature of the electrolyte and of the non-electrolyte. Because of these simplifications the $K$ values calculated by Eqn. (21) differ significantly from experimental values: for example the discrepancy for the noble gases is at least 50%.[17]

According to Kirkwood's theory[18] the parameter $P_{ne}$ in Eqn. (21) is

$$P_{ne} = \frac{4}{3}\pi N[\alpha_0 + (n^2+2)\mu_0^2/27kT], \qquad (24)$$

where $\mu_0$ is the dipole moment of the non-electrolyte in the gaseous state, $\alpha_0$ is its polarisability, and $n$ is the refractive index. The value of the parameter $P_{ne}$ in the quantitative treatment of salting-in and salting-out phenomena is demonstrated by the good correlation between the $K$ and $\mu_0$ values of different types of non-electrolyte (Table 1).

**Table 1.** Dipole moments and salting-out coefficients of various non-electrolytes in KCl.[4]

| Non-electrolyte | $K$, litre mole$^{-1}$ | $\mu_0$, D | Non-electrolyte | $K$, litre mole$^{-1}$ | $\mu_0$, D |
|---|---|---|---|---|---|
| $O_2$ | 0.132 | 0.0 | $NH_3$ | 0.057 | 1.4 |
| $H_2$ | 0.102 | 0.0 | HCN | 0.006 | 2.7 |
| $N_2O$ | 0.099 | 0.1 | $SO_2$ | −0.022 | 1.7 |
| $CO_2$ | 0.072 | 0 0 | $NH_4NO_3$ | −0.070 | 3.6 |
| $H_2S$ | 0.067 | 1.0 | | | |

Conway and coworkers[17] have proposed and experimentally confirmed an expression for the quantity $V_e^h$ in Eqns. (21) and (22). The expression was derived from "free-water" considerations adopted from the hydration theory: it can be written

$$V_e^h = \frac{18h_e^n}{1000d - mM}, \qquad (25)$$

where $h_e^p$ is the primary hydration number of the electrolyte, $m$ is the molarity and $d$ is the density of the electrolyte solution, and $M$ is the molecular weight of the electrolyte.

Cohn and Edsell[11] obtained an expression for $P_{ne}$ different from Eqn. (24):

$$P_{ne} = 4\pi N\mu_0^2/9kT. \qquad (26)$$

Using Eqn. (26) they arrived at the following expression for the dielectric decrement of the non-electrolyte:

$$\delta_{ne} = \frac{V_{ne}(\varepsilon_1 - j)}{\varepsilon_0} - \frac{hP_{ne}}{1000\varepsilon_0}. \qquad (27)$$

Cohn and Edsell combined Eqn. (27) with the Debye–McAuley equation (6) in order to facilitate the application of the latter in practical calculations.

Kirkwood's electrostatic theory of the salting-out effect[20,21] is based on the polarisation of the non-electrolyte in solutions of electrolytes. Using his theory[18] of the polarisation of non-electrolytes in polar liquids, Kirkwood calculated the total electrostatic energy of a spherical ion and a neutral molecule, and obtained the following expression for the activity coefficient of the non-electrolyte in an electrolyte solution:

$$\ln f_{ne} = \Sigma K_e z^2 c_e. \qquad (28)$$

The quantity $K_e$ in Eqn. (28) is defined by the expression

$$K_e = \frac{2\pi Ne^2}{2.303\varepsilon_0 kT}\left[\frac{3\mu_0^2}{2\varepsilon akT} - \frac{r_{ne}^3\Gamma(\rho)}{a}\right], \qquad (29)$$

where

$$\Gamma(\rho) = \frac{1}{3\rho^4}[(\rho^3-2)\lg(1+\rho) - (\rho^3-2)\lg(1-\rho) - 2\rho^2], \qquad (D)$$

$$\rho = r_{ne}/a,$$

$a$ is the distance of closest approach between the non-electrolyte molecule and the electrolyte ion, and $r_{ne}$ is the radius of the non-electrolyte molecule.

The salting-out coefficients calculated by Kirkwood's equation (29) agree better with experiment than those calculated by either the Debye–McAuley or the Debye theory. However even the $K$ values given by the Kirkwood equation differ from the experimental values by much more than the experimental error.

Long and McDevit, in an attempt to allow for the Van der Waals forces in the salting-out effect, obtained the equation[4]

$$\lg f_{ne} = A\Sigma z^2 c_e - B\Sigma\alpha_e c_e, \qquad (30)$$

where $A$ and $B$ are parameters depending on the non-electrolyte and (to a lesser extent) on the electrolyte, and constant to a first approximation for a series of similar electrolytes (e.g. halides); $\alpha_e$ is the polarisability of the electrolyte ion. The first term of Eqn.(30) depends on the ion–molecule interaction, the second term depends on the Van der Waals' forces between water molecules opposing the replacement of water molecules by electrolyte ions. The constancy of $A$ and $B$ implies that the distance of closest approach between ions and molecules must be similar to the distance of closest approach between ions.

Bockris and coworkers[22] allowed for the effect of dispersion forces by using the London formula[23] for the dispersion potential, and obtained the equation

$$\frac{\Delta s_{ne}}{s^0_{ne}} = \left(P_{ne} - P_w\frac{V_{ne}}{V_w}\right)\frac{2\pi Ne^2}{1000\varepsilon^2 kT}\sum\frac{z^2c_e^2}{r_i} + \left(\frac{\alpha_{ne}\nu_{ne}}{\nu_{e\pm}+\nu_{ne}} - \frac{\alpha_w\nu_w}{\nu_{e\pm}+\nu_{ne}}\cdot\frac{V_{ne}}{V_w}\right)\frac{2\pi N\hbar}{1000\varepsilon kT}\sum\frac{\alpha_e\nu_{e\pm}c_e}{r_i^3}, \qquad (31)$$

where $\nu_{ne}$ and $\nu_e^{\pm}$ are the characteristic frequencies of the non-electrolyte and of the electrolyte respectively, $\alpha_{ne}$ is the polarisability of the non-electrolyte, $\hbar$ is Planck's constant, and $P_W$ is the molar polarisation of water. Eqn.(31) is generally similar to Eqn.(30), but in Eqn.(31) the second term, which determines the salting-in effect, is much less sensitive to the nature of the electrolyte and of the non-electrolyte than is found in practice. This is because of the approximation used in Eqn.(31) for the distance of nearest approach (taken as the ionic radius $r_i$ rather than the sum of the radii of the ion and of the neutral molecule). In practice the factor $r_i^3$ nullifies the attempt to allow for the change in polarisability of the ions, and as a result the theory predicts far less specificity in the effect of various ions on salting out and salting in than is found in practice. However the theory does predict the experimentally observed salting in of non-electrolytes by large ions such as tetra-alkyl-ammonium ions.

Neither the Kirkwood theory[20,21] nor the equations of Long and McDevit[4] [Eqn.(30)] and of Bockris and coworkers[22] [Eqn.(31)] can explain the anomalously small salting out observed in the presence of electrolytes containing $H^+$ or $Li^+$ cations. Because of these shortcomings, and of their theoretical limitations pointed out above, Eqns.(28)–(31) cannot be said to give an adequate representation of the role of dispersion forces in the salting out and salting in of non-electrolytes.

Danckwerts[24] has suggested the use of salting-out coefficients in conjunction with the Henry constants of the non-electrolytes in water ($He^0$) to calculate the Henry constants of gaseous non-electrolytes in solutions. He obtained an equation similar in form to the Sechenov equation (1) and to the empirical Debye–McAuley equation (9):

$$\lg\frac{He}{He^0} = K\mu. \qquad (32)$$

The salting-out coefficient in Eqn.(32) is defined as

$$K = h_+ + h_- + h_g, \qquad (33)$$

where $h_+$ and $h_-$ are constants relating to the cation and the anion of the electrolyte (litre g-ion$^{-1}$), and $h_g$ is a constant relating to the gaseous non-electrolyte (litre mole$^{-1}$).

Danckwerts considers that the change in $K$ with temperature is due entirely to the change in $h_g$ with temperature. Values of $h_g$ for hydrogen, oxygen, carbon dioxide, hydrogen sulphide, ammonia, and sulphur dioxide are given in Ref. 24 together with $h_+$ and $h_-$ values for a large number of ions. However Danckwerts does not give any theoretical justification of Eqn.(33), which is merely a sum of empirical constants for the electrolyte and the non-electrolyte and therefore cannot be reconciled with any of the theories of salting out and salting in. Furthermore Danckwerts does not state the considerations used in selecting values for the $h_+$, $h_-$, and $h_g$ constants for different ions and non-electrolytes.

## IV. THE "EFFECTIVE PRESSURE" THEORY

As its name implies, this theory treats the salting out and salting in of non-electrolytes as a consequence of the internal pressure generated in solutions of electrolytes by the electrostatic interaction between electrolyte and solvent.

Geffcken[25], and later Tammann[26], established a correlation between salt effects in solutions and the relative effects of salts on the compressibility of solutions. On the basis of this work McDevit and Long[27] developed the "effective pressure" theory of salting out and salting in of non-electrolytes. They derived an expression for $K$ by considering the electro-striction effect resulting from the interaction between electrolyte and solvent following the addition of an electrolyte to a solution of a non-polar non-electrolyte. This effect gives rise to an effective pressure $p_e$ within the solution which tends to eject the non-electrolyte molecules from the solution because they are non-polar and they oppose the electrolyte–solvent interaction. Thus according to the "effective pressure" theory the salting in or salting out of a non-electrolyte is determined by the extent to which the solution is compressed or dilated by the addition of the electrolyte.

McDevit and Long based their quantitative conclusions on a calculation of the change in free energy attending the transfer of the non-polar non-electrolyte from water to the electrolyte solution. They found that the change in free energy of the non-electrolyte due to this process is $p_e V_{ne}$, and they obtained the following theoretical equation for $K$ [27]:

$$K = \lim_{c_e\to 0}\frac{V^0_{ne}}{2{,}3RT}\cdot\frac{dp_e}{dc_e} = \frac{V^0_{ne}(V^g_e - V^0_e)}{2.3\beta_w RT}, \qquad (34)$$

where $V^0_{ne}$ is the partial molar volume of the non-electrolyte at infinite dilution in the solution, $V^g_e$ is the hypothetical molar volume of the pure supercooled electrolyte in the liquid state, and $\beta_W$ is the compressibility of water.

The McDevit–Long equation (34) predicts an increase of $K$ with increasing molar volume of the non-electrolyte at infinite dilution. The main advantage of the "effective pressure" theory is its ability to account for

salting in in terms of the properties of the electrolyte only, in keeping with experimental results. According to Eqn. (34) salting in of non-electrolytes occurs when the difference ( $V_e^g - V_e^0$) for the electrolyte is negative.

The $K$ values for a range of structurally different non-electrolytes (hydrogen, oxygen, nitrogen dioxide, benzene) in the same electrolytes are very similar [4]. Hence we may conclude that salting-out and salting-in effects are far more sensitive to the properties of the electrolyte in solution than to the nature of the non-electrolyte or its interaction with the solution. This conclusion is implicit in Eqn. (34), according to which the salting in and salting out of the non-electrolyte is determined mainly by the ion–solvent interaction and by the effect of this interaction on the volume difference $V_e^g - V_e^0$. Values of $V_e^g$ for various electrolytes are given in Ref. 28.

When the electrolyte is added to the water the primary effect is the attraction of the water dipoles towards the electrostatic field of the ions. At ordinary temperatures most of the water molecules are in a quasi-crystalline state with an open structure, and when the water dipoles are attracted towards the field of the ions the rearrangement of this open structure to give a more closely packed structure around the ions is primarily responsible for the compression effect. If the size of the ions added to the solution is increased the electro-striction of the solution decreases for two reasons. Firstly, the electrostatic field of the ion decreases with increase in the ionic radius, and its effect on the breakdown of the water structure is less marked (decrease in the structure factor). Secondly, water molecules are replaced by ions (replacement factor). If the electrolyte ions had been uncharged spheres the replacement would have led to a decrease in the breakdown energy of the system accompanied by an increase in volume. Both the structure factor and the replacement factor make a large contribution to the decrease in the difference $V_e^g - V_e^0$ with increasing size of the electrolyte ion. The "effective pressure" theory indicates that the difference $V_e^g - V_e^0$ may become negative as the influence of both these factors increases, leading to salting in of the non-electrolyte.

The salting-out effects of the very small hydrogen and lithium ions are not quantitatively consistent with the small size of these ions, suggesting that the quasi-crystalline structure of water is stabilised rather than broken down by hydrogen and lithium ions [4]. One possible explanation is that these ions are incorporated in the water structure in sites normally occcupied by hydrogen atoms. The result is the formation of electrostatic bridges between the oxygen atoms of the water molecules, with an energy comparable to the energy of the hydrogen bond [4].

The electrostatic theories of salting in and salting out ignore the structure factor and the replacement factor, which depend on the size of the electrolyte ion. Hence these theories give best results when these terms are small (e.g. in solutions of sodium or potassium chloride [4]).

Gibson showed [29] that the linear plots of $p_e$ against $c_e$ and of lg ($s_{ne}^0/s_{ne}$) against $c_e$ lie in the same relative sequwnce, indicating a common underlying cause. This observation confirms that the "effective pressure" theory offers, on the whole, a correct description of the main features of the salting out and salting in of non-electrolytes.

One weakness of this theory is its failure to allow for the non-electrolyte–solution interaction of a given non-electrolyte in different electrolytes. Furthermore, the value of Eqn. (34) for calculating $K$ is doubtful as long as published values of $V_e^g$ remain scarce and inaccurate.

## V. EFFECT OF TEMPERATURE ON SALTING OUT AND SALTING IN OF NON-ELECTROLYTES

Experimental and theoretical studies of the effect of temperature on the salting out and salting in of non-electrolytes began in 1907. [30] Changes in temperature affect the state of all three components of the non-electrolyte–electrolyte–solvent system. Ion hydration decreases as the temperature increases. At the same time the energy needed to break down the structure of pure water decreases, and exothermic effects in concentrated solutions (formation of ion pairs and of undissociated molecules of electrolyte) also decrease. It was pointed out [31] that the enhanced translational motion of the water and mobility of the electrolyte ions at elevated temperatures may even convert the positive hydration of the ions into negative hydration. Simultaneously, the solubility of the non-electrolyte decreases, both in water and in the electrolyte solution.

Because so many parameters of the three-component system are affected by temperature changes, the theoretical interpretation of the effect of temperature on the salting out and salting in of non-electrolytes is a complex problem. The temperature coefficient of the quantity $\ln (f_{ne}/f_{ne}^0)$ can be obtained (as first pointed out by Rothmund [30]) by differentiating the Gibbs–Helmholtz equation:

$$\Delta G_{ne}^0 = \Delta H_{ne} - T\Delta S_{ne} = RT \ln \frac{f_{ne}}{f_{ne}^0}, \qquad (35)$$

where $\Delta G_{ne}^0$ is the change in standard free energy of the non-electrolyte attending the transfer of one mole of non-electrolyte dissolved in water into the electrolyte solution. From Eqn. (35) Rothmund obtained [30] the following expression for the temperature coefficient of $\ln (f_{ne}/f_{ne}^0)$:

$$\frac{d\left(\ln \frac{f_{ne}}{f_{ne}^0}\right)}{dT} = -\frac{\Delta H_{ne}^0}{RT^2}. \qquad (36)$$

He also derived the equation

$$\frac{d\left(T \ln \frac{f_{ne}}{f_{ne}^0}\right)}{dT} = -\frac{\Delta S_{ne}^0}{R}. \qquad (37)$$

In Eqns. (36) and (37) $\Delta H_{ne}^0$ and $\Delta S_{ne}^0$ are the changes in standard enthalpy and entropy of the non-electrolyte when 1 mole (dissolved in water) is transferred to the electrolyte solution at the same temperature.

Frank and Evans [32] obtained an expression for $\Delta S_{ne}^0$ during the transfer of the non-electrolyte from water into the solution of electrolyte:

$$\Delta S_{ne}^0 = -\left(\frac{\partial \Delta G_{ne}^0}{\partial T}\right)_{p_{ne} m_{ne}} = R \ln f_{ne} + RT \left(\frac{\partial \ln f_{ne}}{\partial T}\right)_{p_{ne} m_{ne}}, \qquad (38)$$

where $p_{ne}$ is the partial pressure of the gaseous non-electrolyte (atm) and $m_{ne}$ is the molar concentration of the non-electrolyte.

Using the Debye–McAuley electrostatic theory Frank and Evans derived the expression [32]

$$\Delta S_{ne}^0 = -RT \ln f_{ne} \left(\frac{\partial \ln \varepsilon_0}{\partial T} - \frac{\partial \ln \delta_{ne}}{\partial T} + \frac{\partial \ln b}{\partial T} + \frac{\partial \ln V}{\partial T}\right), \qquad (39)$$

where $V$ is the volume of the solution.

If the internal interactions of the non-electrolyte molecules are negligibly small, or if the solubility of the

non-electrolyte is very low, Eqn.(18) becomes similar to Eqn.(1) and we can write

$$\lg \frac{s^0_{ne}}{s_{ne}} = \lg \frac{f_{ne}}{f^0_{ne}} = Kc_e. \quad (40)$$

Combining Eqns.(36), (37), and (40) we can evaluate $dK/dT$ from the known quantities $\Delta H^\circ_{ne}$ and $\Delta S^\circ_{ne}$. This is because the difference between $s^0_{ne}$ and $s_{ne}$ is small and the internal interactions of the gaseous non-electrolyte molecules can be ignored.

The heat of dissolution of the non-electrolyte in a given solution of electrolyte can be calculated from solubility data at different temperatures. We use an equation analogous to the Clapeyron–Clausius equation

$$\frac{d \ln s_{ne}}{d(1/T)} = -\frac{\Delta H_{ne}}{R}, \quad (41)$$

where $\Delta H_{ne}$ is the heat of dissolution of the non-electrolyte. $\Delta H_{ne}$ is given by the slope of a plot of ln $s_{ne}$ against $1/T$.

On general grounds we would expect $dK/dT$ to be negative, since the properties of solutions tends towards ideality on raising the temperature, and ideal solutions do not exhibit salting-out effects. Negative temperature coefficients of $K$ were indeed obtained by Long and McDevit[4] for nitric oxide in various electrolytes, and by Yatskovskii [33] and by David and coworkers [34] for oxygen in KOH solutions. Knaster [35] found that in KOH solutions the temperature coefficient of $K$ is negative for oxygen and positive for hydrogen, but this discrepancy is neither discussed nor explained by Knaster [35].

Morrison has pointed out [36] that the Debye–McAuley equation (10) cannot give a negative value of $dK/dT$, since the product $\epsilon_0 T$ in Eqn.(10) decreases as the temperature increases. However the parameter $\delta_{ne}$ in the same equation should also change with temperature, but there are no data on the sign and magnitude of this change.

An expression for $dK/dT$ for non-polar, gaseous non-electrolytes (oxygen, hydrogen, methane, ethane, etc.) was obtained[4] by differentiating the McDevit–Long equation (34):

$$\frac{dK}{dT} = -\frac{V^0_{ne}}{2.3\beta_\infty RT^2} \cdot \frac{dV^0_e}{dT}. \quad (42)$$

Values of $dV^0_e/dT$ for various gases and electrolytes are given in Refs. 37 and 38. However no experimental test of Eqn.(42) has yet been reported.

Knaster [35] combined the Sechenov equation with the thermodynamic equation for the temperature dependence of the solubility of gases in water and in electrolyte solutions, and obtained the expression

$$K = A' + \frac{B'}{T}, \quad (43)$$

where $A'$ and $B'$ are temperature-independent constants:

$$A' = \frac{\Delta S^1_{ne} - \Delta S^2_{ne}}{2.303 c_e R}, \quad (44)$$

$$B' = \frac{\Delta H^1_{ne} - \Delta H^2_{ne}}{2.303 c_e R}. \quad (45)$$

In these equations $\Delta S^1_{ne}$ and $\Delta S^2_{ne}$ are the entropy changes of the non-electrolyte when dissolved in water and in the electrolyte respectively for the same activity of non-electrolyte in the gas phase; $\Delta H^1_{ne}$ and $\Delta H^2_{ne}$ are the corresponding enthalpy changes of the non-electrolyte.

Eqn.(43) is obeyed up to 7 $N$ concentration of KOH in the salting out of hydrogen from KOH solutions [35]. The constants $A'$ and $B'$ in this equation are determined (for a given electrolyte and non-electrolyte) by using two known values of $K$ for a non-electrolyte in the electrolyte of interest.

Thus both Eqns.(36), (37) and Eqn.(43) for $dK/dT$ require a separate experimental determination of the relevant thermodynamic quantities (the enthalpy and entropy of dissolution of the non-electrolyte). This is because of the inadequacy of the existing theory of solutions, which does not provide an analytic expression for calculating the change in entropy and enthalpy of gases dissolved in water and in electrolyte solutions.

The $K$ values of highly soluble non-electrolytes are much more sensitive to temperature than those of sparingly soluble non-electrolytes such as non-polar gases [4]. $K$ usually changes in the same sense as the solubility of non-electrolytes in water [36]. For readily soluble non-electrolytes the quantity $K_{ne}(s_{ne} - s^0_{ne})$ in Eqn.(18) changes significantly with temperature even if $K$ is practically temperature-independent, because of the strong temperature dependence of the solubility of the non-electrolyte. As a result $K_{ne}(s_{ne} - s^0_{ne})$ can change sign, and salting in of the non-electrolyte occurs instead of salting out.[36].

Experimental information on the effect of temperature on the salting-in and salting-out behaviour of non-electrolytes is still scarce, and the development of a theory of this effect is shown by our review to be only in its initial stages.

## VI. EXPERIMENTAL DATA. COMPARISON OF THEORY AND EXPERIMENT

A large body of experimental information on the salting out and salting in of gaseous non-electrolytes in aqueous solutions of electrolytes is available in the published literature. The data appear either as salting-out coefficients or, more often, as tabulations of the solubility of the non-electrolyte for different concentrations of electrolyte.

Salting-out coefficients and solubilities in various electrolytes have been reported for oxygen[4,25,33,34,37,39-45], hydrogen [4,33,41-43,45], carbon dioxide [45,46], hydrogen sulphide [47], and ethylene [45]. Some of the other published data on the salting out of gaseous non-electrolytes are fragmentary and unsystematic, and their reliability is doubtful. The salting-out coefficients for oxygen, hydrogen, carbon dioxide, hydrogen sulphide, and ethylene quoted in the above references or calculated from the published data on the solubility of these gases are listed in Tables 2 and 2'.

The salting-out and salting-in effects of oxygen and hydrogen in solutions of acids, salts, and bases with cations from Group Ia of the Periodic Table have been investigated most fully. In some cases there are discrepancies between the $K$ values reported by different workers or calculated from the published solubilities of the gaseous non-electrolytes. Occasionally the discrepancy between $K$ values from different sources reaches 50–60%.

The solubility of non-electrolytes at different concentrations of electrolytes has been measured[4,25,33,34,37,39-47] by different methods, but the precision of the concentration measurements (2–5%) is quoted in only five of the fourteen papers [33,34,40,41,44]. Only three of these [34,41,44] include evidence that the equilibrium concentration (solubility)

**Table 2.** Salting-out coefficient of oxygen in aqueous solutions of various electrolytes at 25°C.

| Anion | H+ | Li+ | Na+ | K+ | Rb+ | Cs+ | $Mg^{2+}$ | $Ca^{2+}$ | $Ba^{2+}$ | $NH_4^+$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Oxygen | | | | | | |
| $F^-$ | — | from 0.725 to −0.385[44] | 0.284[44] | 0.203[44] | 0.146[44] | 0.114[44] | — | | | |
| $Cl^-$ | 0.030[43]<br>0.034[39]<br>0.029[25]<br>0.031[4]<br>0.022[45] | 0.096[43]<br>0.100[4]<br>0.137 (20°)[37]<br>from 0.112 to 0.070[44] | 0.140[37]<br>0.141[39]<br>0.145[42]<br>0.137[43]<br>0.127[25]<br>0.141[4]<br>0.136[44]<br>0.101[45] | 0.142 (20°)[37]<br>0.132[39]<br>0.128[43]<br>0.129[44] | 0.120[44] | 0.098[44] | 0.428[43]<br>0.516 (20°)[37]<br>0.456[39] | 0.397[43] | 0.528[4]<br>0.520[43] | 2.792[39]<br>2.950[43] |
| $Br^-$ | — | from 0.252 to 0.084[44] | 0.110[4]<br>0.115[43]<br>0.131[44] | 0.123[43]<br>0.117[44] | 0.104[44] | 0.078[44] | — | — | — | — |
| $I^-$ | — | 0.163[44] | 0.120[44] | 0.090[4]<br>0.092[43]<br>0.093[44] | 0.086[44] | 0.062[44] | — | — | — | — |
| $NO_3^-$ | 0.019[4]<br>0.016[25]<br>0.018[26]<br>0.019[42] | from 0.196 to −0.040[44] | 0.124[44] | 0.100[4]<br>0.098[39]<br>0.100[43]<br>0.105[44] | 0.096[44] | 0.066[44] | — | — | — | — |
| | — | from 0.218 to 0.066[44] | 0.160[44] | 0.150[44] | 0.138[44] | — | — | — | — | — |
| $OH^-$ | — | from 0.332 to 0.091[44] | 0.179[4]<br>0.178[25]<br>0.183[39]<br>0.188[43]<br>0.179[43]<br>0.180[44] | 0.175[44]<br>0.172[25]<br>0.183[39] | 0.168[44] | 0.158[44] | — | — | — | — |
| | — | — | — | 0.152[40]<br>0.170[41]<br>0.176[42]<br>0.175[24]<br>0.168[38]<br>0.176[44] | — | — | | | | |
| $SO_4^{2-}$ | 0.104[4]<br>0.086[25]<br>0.089[39]<br>0.152[43]<br>0.091[42]<br>0.081[43] | 0.244[44] | 0.306[43]<br>0.323[39]<br>0.376[44] | 0.344[4]<br>0.334[25]<br>0.346[42]<br>0.304[43]<br>0.323[39]<br>0.297[44] | 0.290[44] | 0.255[44] | — | — | — | — |
| $CO_3^{2-}$ | — | 0.254[44] | 0.464[44] | 0.379[44] | — | — | — | — | — | — |
| $PO_4^{3-}$ | 0.053[38]<br>0.046[47] | — | 0.652[44] | 0.507[44] | — | — | — | — | — | — |

**Table 2′.** Salting-out coefficients of hydrogen, carbon dioxide, hydrogen sulphide, and ethylene in aqueous solutions of various electrolytes at 25°C.

| Anion | H+ | Li+ | Na+ | K+ | $Mg^{2+}$ | $Ca^{2+}$ | $Ba^{2+}$ | $Zn^{2+}$ | $Al^{3+}$ | $NH_4^+$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Hydrogen | | | | | | |
| $Cl^-$ | 0.030[4]<br>0.027[42]<br>0.020[45] | 0.076[4]<br>0.075 (15°)[42]<br>0.095 (15°)[43]<br>0.066[45] | 0.114[4]<br>0.107 (15°)[42]<br>0.088[43]<br>0.094[45] | 0.102 (20°)[4]<br>0.087 (15°)[42]<br>0.078[45] | — | 0.217 (15°)[42]<br>0.065[45] | 0.190[43] | — | 0.270 (15°)[42]<br>0.028[45] | — |
| $NO_3^-$ | 0.022[4]<br>0.020[42]<br>0.022[43] | —<br>—<br>— | 0.100 (20°)[4]<br>0.091 (15°)[42]<br>0.080[45] | 0.070 (20°)[4]<br>0.061[45] | — | — | — | — | — | 0.035 (20°)[43]<br>0.038 (20°)[47] |
| $OH^-$ | — | — | 0.140[4]<br>0.142[43] | 0.130[4]<br>0.126[42]<br>0.146[43]<br>0.123 (21°)[41]<br>0.127 (21°)[33] | — | — | — | — | — | — |
| $SO_4^{2-}$ | 0.076[43] | — | 0.278 (15°)[4]<br>0.278 (15°)[42] | — | 0.302 (15°)[43]<br>0.057[45] | — | — | 0.211 (15°)[42] | — | — |
| $CO^{2-}$ | — | — | 0.293 (15°)[42] | 0.273 (15°)[42] | — | — | — | — | — | — |
| $PO_4^{3-}$ | 0.034 (21°)[38] | — | — | — | — | — | — | — | — | — |
| | | | | Carbon dioxide | | | | | | |
| $Cl^-$ | 0.006[45] | — | — | 0.059[45] | — | — | 0.060[45] | −0.008[46] | — | — |
| $Br^-$ | — | — | — | 0.045[45] | — | — | — | — | — | — |
| $I^-$ | — | — | — | 0.032[45] | — | — | — | — | — | — |
| $NO_3^-$ | — | — | 0.053[45] | 0.025[45] | — | — | — | — | — | — |
| $SO_4^{2-}$ | — | — | 0.100[45] | — | — | — | — | — | — | — |
| | | | | Hydrogen sulphide | | | | | | |
| $Cl^-$ | −0.013[47] | — | — | — | — | — | — | −0.005±0.002[47] | — | — |
| | | | | Ethylene | | | | | | |
| $Cl^-$ | — | — | 0.093[45] | 0.062[45] | 0.055[45] | 0.058[45] | 0.067[45] | — | 0.044[45] | — |
| $NO_3^-$ | — | — | 0.050[45] | 0.030[45] | — | 0.028[45] | — | — | — | — |
| $SO_4^{2-}$ | — | — | 0.098[45] | — | 0,064[45] | — | — | — | 0.043[45] | — |
| $Br^-$ | — | — | 0.077[45] | 0.049[45] | — | — | — | — | — | — |

of the non-electrolyte was measured, i.e. that the non-electrolyte had come to equilibrium with the electrolyte solution.

Table 2 shows that the agreement between the salting-out coefficients reported by different workers for oxygen and hydrogen in solutions of electrolytes with cations from Group Ia is usually better than 5%. We may conclude that the published $K$ values for oxygen and hydrogen in these electrolytes are reliable.

Differences between experimental $K$ values for hydrogen in excess of 100% (see Tables 2 and 2′) are found only in solutions of $CaCl_2$, $AlCl_3$,[42,45] and $MgSO_4$.[43,45] These results are unacceptable, particularly since neither the experimental method of measuring the solubility of hydrogen nor the magnitude of the measurement error is mentioned in those papers[42,43,45].

Because of the small number of publications on the salting-out and salting-in behaviour of carbon dioxide, hydrogen sulphide, and ethylene, a discussion of the consistence and reliability of the data (Tables 2 and 2′) is not justified.

The theories of salting out and salting in of non-electrolytes discussed above differ very substantially in their treatment of the phenomenon. Hence a comparison of the theoretical $K$ values for oxygen and hydrogen with experimental data should provide a reliable criterion of the relative success of the various theoretical treatments.

Table 3. Comparison of experimental mean values of $K$ for oxygen at 25°C with values calculated by different theoretical equations.

| Electrolyte | $K_{exper}$ | $10^8 b$, cm | $K$ (10) | $K$ (19) | $K$ (33) | $K$ (34) |
|---|---|---|---|---|---|---|
| HCl | 0.031 | 4.54 | 0.095 | 0.205 | 0.043 | 0.030 |
| $HNO_3$ | 0.018 | 4.47 | 0.097 | 0.225 | 0.021 | — |
| $H_2SO_4$ | 0.100 | 3.55 | 0.123 | 0.428 | 0.044 | — |
| LiF | from 0.725 to −0.385 | 3.03 | 0.143 | 0.216 | — | — |
| LiCl | from 0.112 to 0.070 | 3.51 | 0.124 | 0.198 | — | 0.109 |
| LiBr | from 0.252 to 0.084 | 3.63 | 0.120 | 0.160 | — | — |
| LiI | 0.163 | 3.88 | 0.112 | 0.158 | — | — |
| $LiNO_3$ | from 0.196 to −0.040 | 3.44 | 0.126 | 0.198 | — | — |
| $LiClO_4$ | from 0.218 to 0.066 | 3.72 | 0.117 | 0.154 | — | — |
| LiOH | from 0.332 to 0.091 | 3.87 | 0.112 | 0.237 | — | — |
| $Li_2SO_4$ | 0.244 | 2.61 | 0.166 | 0.470 | — | — |
| $Li_2CO_3$ | 0.254 | 2.40 | 0.181 | — | — | — |
| NaF | 0.284 | 3.34 | 0.130 | 0.254 | — | 0.235 |
| NaCl | 0.131 | 3.82 | 0.114 | 0.162 | 0.134 | 0.131 |
| NaBr | 0.119 | 3.94 | 0.110 | 0.173 | 0.125 | 0.126 |
| NaI | 0.120 | 4.19 | 0.104 | 0.185 | 0.118 | 0.097 |
| $NaNO_3$ | 0.124 | 3.75 | 0.116 | 0.175 | 0.112 | 0.109 |
| $NaClO_4$ | 0.160 | 4.03 | 0.108 | 0.173 | — | 0.091 |
| NaOH | 0.180 | 4.18 | 0.104 | 0.249 | 0.179 | 0.205 |
| $Na_2SO_4$ | 0.335 | 2.95 | 0.147 | 0.485 | 0.226 | 0.471 |
| $Na_2CO_3$ | 0.464 | 2.67 | 0.163 | — | 0.225 | — |
| KF | 0.203 | 3.82 | 0.114 | 0.283 | — | — |

It is evident from our view of the existing theories that a strict thermodynamic theory of the salting in and salting out of non-electrolytes is not available at present. Hence we cannot expect full agreement between theory and experiment. Furthermore, some of the physicochemical quantities which appear in the theoretical equations are not known with high precision, and therefore any observed discrepancy between theory and experiment cannot be ascribed wholly to inadequacies of the theory.

The salting-out coefficients for oxygen in electrolyte solutions calculated by various theoretical equations are listed in Table 3. The ionic radius $b$ which appears in formula (10) was calculated (for a 1–1 electrolyte) by the expression

$$b = r_a + r_c,$$

where $r_a$ and $r_c$ are the radii of the hydrated anion and cation.

For polyvalent electrolytes the ionic radius was determined as suggested by Debye and McAuley[5] by formula (8); the hydrated ion radii for $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $F^-$, $Cl^-$, $Br^-$, and $I^-$ were taken from Ref. 48, those for $H^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $OH^-$, $NO_3^-$, $ClO_4^-$, and $SO_4^{2-}$ from Ref. 15. The $r_1^h$ value for the $CO_3^{2-}$ ion was taken from Ref. 49.

In the calculation of $K$ by formula (19) we took $V_{ne}$ from Ref. 50, $\delta_e$ from Refs. 8 and 12, $V_e^0$ from Refs. 14, 15, and 51, $h_e^0$ from Refs. 14, 15, 52, and 53, and $\epsilon_{ne}$ from Ref. 54. In the calculation of $K$ by formula (34) $V_{ne}^0$ was taken from Ref. 50 and $(V_e^g - V_e^0)$ from Ref. 27. The $K$ values for hydrogen in electrolyte solutions (Table 4) were calculated with constants taken from the same sources as those for oxygen.

Table 4. Comparison of experimental mean values of $K$ for hydrogen at 25°C with values calculated by formulae (10), (19), (22), and (32), and from Ref. 24.

| Electrolyte | $K_{exper}$ | $10^8 b$, cm | $K$ (10) | $K$ (19) | $K$ (33) | $K$ (34) |
|---|---|---|---|---|---|---|
| HCl | 0.026 | 4.54 | 0.080 | 0.176 | 0.019 | 0.025 |
| $HNO_3$ | 0.021 | 4.47 | 0.081 | 0.198 | −0.003 | — |
| $H_2SO_4$ | 0.076 | 3.55 | 0.103 | 0.270 | 0.020 | — |
| LiCl | 0.071 | 3.51 | 0.104 | 0.171 | — | 0.091 |
| NaCl | 0.098 | 3.82 | 0.095 | 0.139 | 0.110 | 0.126 |
| $NaNO_3$ | 0.080 | 3.75 | 0.097 | 0.152 | 0.088 | 0.091 |
| NaOH | 0.141 | 4.18 | 0.087 | 0.196 | 0.155 | 0.248 |
| $Na_2SO_4$ | 0.278 (15°) | 2.95 | 0.128 (15°) | 0.263 | 0.196 (15°) | 0.394 (15°) |
| $Na_2SO_3$ | 0.293 (15°) | 2.67 | 0.141 (15°) | — | 0.195 (15°) | — |
| KCl | 0.078 | 4.30 | 0.085 | 0.123 | 0.093 | 0.101 |
| $KNO_3$ | 0.061 | 4.23 | 0.086 | 0.121 | 0.071 | — |
| KOH | 0.134 | 4.66 | 0.078 | 0.224 | 0.138 | — |
| $K_2CO_3$ | 0.273 (15°) | 3.01 | 0.125 (15°) | — | 0.161 (15°) | — |
| $MgSO_4$ | 0.302 (15°) | 3.88 | 0.097 (15°) | 0.312 | 0.065 (15°) | — |
| $CaCl_2$ | 0.217 (15°) | 3.56 | 0.106 (15°) | 0.248 | 0.087 (15°) | — |
| $BaCl_2$ | 0.190 | 3.40 | 0.107 | 0.266 | 0.100 | 0.298 |
| $ZnSO_4$ | 0.211 (15°) | 5.36 | 0.070 (15°) | — | 0.062 (15°) | — |
| $NH_4NO_3$ | 0.036 (15°) | 3.91 | 0.096 (15°) | — | 0.019 (15°) | — |
| KCl | 0.132 | 4.30 | 0.101 | 0.152 | 0.117 | 0.121 |
| KBr | 0.120 | 4.42 | 0.098 | 0.154 | 0.108 | — |
| KI | 0.092 | 4.67 | 0.093 | 0.193 | 0.101 | — |
| $KNO_3$ | 0.101 | 4.23 | 0.103 | 0.207 | 0.095 | — |
| $KClO_4$ | 0.150 | 4.51 | 0.096 | 0.184 | — | — |
| KOH | 0.172 | 4.66 | 0.093 | 0.259 | 0.162 | — |
| $K_2SO_4$ | 0.324 | 3.38 | 0.128 | 0.462 | 0.192 | — |
| $K_2CO_3$ | 0.379 | 3.01 | 0.144 | — | 0.191 | — |
| RbF | 0.146 | 3.96 | 0.110 | — | — | — |
| RbCl | 0.120 | 4.44 | 0.098 | 0.236 | — | 0.109 |
| RbBr | 0.104 | 4.56 | 0.095 | — | — | — |
| RbI | 0.086 | 4.81 | 0.090 | — | — | — |
| $RbNO_3$ | 0.096 | 4.37 | 0.099 | — | — | — |
| $RbClO_4$ | 0.138 | 4.65 | 0.093 | — | — | — |
| RbOH | 0.168 | 4.80 | 0.090 | — | — | — |
| $Rb_2SO_4$ | 0.290 | 3.48 | 0.125 | — | — | — |
| CsF | 0.114 | 4.18 | 0.104 | — | — | — |
| CsCl | 0.098 | 4.66 | 0.093 | — | — | 0.091 |
| CsBr | 0.078 | 4.78 | 0.091 | — | — | — |
| CsI | 0.062 | 5.03 | 0.086 | — | — | — |
| $CsNO_3$ | 0.066 | 4.59 | 0.095 | — | — | — |
| CsOH | 0.158 | 5.02 | 0.086 | — | — | — |
| $Cs_2SO_4$ | 0.255 | 3.64 | 0.119 | — | — | — |
| $MgCl_2$ | 0.442 | 3.69 | 0.118 | 0.230 | 0.115 | — |
| $CaCl_2$ | 0.397 | 3.56 | 0.122 | 0.249 | 0.117 | — |
| $BaCl_2$ | 0.524 | 3.40 | 0.128 | 0.269 | 0.124 | 0.356 |

Inspection of Tables 3 and 4 shows that the agreement between calculated and experimental values of $K$ is best when Eqn. (33) is used to calculate $K$. However, as we have already pointed out, this equation is merely the sum of empirical constants for the electrolyte ions and for the

non-electrolyte which allow the salting-out coefficient to be calculated to some approximation. In the case of 1–1 electrolytes this approximation is adequate both for hydrogen and for oxygen (see Tables 3 and 4). With polyvalent electrolyte solutions Eqn. (33) gives an error approaching 100% in some cases.

Eqn. (34), obtained by the "effective pressure" theory, is the next most succesful. This suggests that the electrostriction of non-electrolyte solutions produced by the addition of electrolytes can adequately account for all the phenomena involved in the salting out and salting in of non-electrolytes in solutions of electrolytes. However the range of application of this equation is limited by the lack of published values of $(V_e^g - V_e^0)$ for many electrolytes, and for the same reason the equation cannot be tested against a comprehensive range of experimental data. The agreement with experimental data is again unsatisfactory when $K$ values are calculated by Eqn. (34) for polyvalent electrolytes.

In all cases, agreement to within 10% between theoretical and experimental values of $K$ was considered satisfactory.

It is interesting to note from Tables 3 and 4 that the fairly complicated equation (19), proposed[12] as an improved expression of the Debye–McAuley electrostatic theory, produces $K$ values for hydrogen and oxygen less consistent with experimental data than the simpler equation (10) of the electrostatic theory. This is because the parameters which appear in Eqn. (19) are not accurately known, published values differing by as much as 50–70%. Under these conditions even the mean of the published values, used in the calculations of $K$ by Eqn. (19), could be seriously in error.

Table 5. Values of $V_e^h/1000$ in Eqn. (22) for different electrolytes.

| Electrolyte | $V_e^h/1000$, litre mole$^{-1}$ | Electrolyte | $V_e^h/1000$, litre mole$^{-1}$ |
|---|---|---|---|
| LiCl | 0.107 | KBr | 0.109 |
| LiBr | 0.097 | KI | 0.096 |
| LiI | 0.089 | RbCl | 0.096 |
| NaF | 0.148 | RbBr | 0.095 |
| NaCl | 0.125 | RbI | 0.090 |
| NaBr | 0.118 | CsCl | 0.094 |
| NaI | 0.110 | CsBr | 0.099 |
| KF | 0.135 | CsI | 0.093 |
| KCl | 0.112 | | |

Eqn. (22), derived from the Frank–Conway electrostatic theory, is difficult to test against experimental data for purely mathematical reasons: the second term of Eqn. (22) depends on the concentration of the electrolyte through the concentration dependence of the radius of the co-ordination sphere $r_n = (3/4\pi n_e)^{1/3}$. Thus the salting-out coefficient given by Eqn. (22) will have different values, according to the concentration of the electrolyte. This is incompatible with the definition of the salting-out coefficient as a constant for a given non-electrolyte in a given electrolyte. But if we assume that the $K$ value given by Eqn. (22) is dominated by the term $V_e^h/1000$, and we calculate $V_e^h/1000$ by formula (23), we arrive at $K$ values for hydrogen and oxygen fairly close to the experimental values. However there can be no doubt that the equation should take account of the specific aspects of the salting-out behaviour of the non-electrolyte, and in this respect Eqn. (22) is practically useless. Calculated values of $V_e^h/1000$ are given in Table 5.

The values of $V_e$, $h$, and $v_s^h$ which appear in Eqn. (23) were taken from Ref. 19. The following approximation is suggested[19] for $v_s^h$:

$$v_s^h = v_s + 2 \text{ ml mole}^{-1},$$

where $v_s$ is the molar volume of the solvent. If the solvent is water $v_s^h = 20$ ml mole$^{-1}$.

The effect of temperature on the salting-out coefficient has been studied only for hydrogen and oxygen in KOH solutions[34,41]. Only the "effective pressure" theory gives an analytic expression for $dK/dT$ [see Eqn. (42)]. However there are no published data on $dV_e^0/dT$ for hydrogen and oxygen in KOH solutions, and without such data the temperature coefficient of $K$ cannot be calculated by Eqn. (42).

We must conclude from this attempt at comparing the various theories of salting out and salting in of non-electrolytes with experiment that none of the present theories gives acceptable agreement with the experimental values for hydrogen and oxygen in all electrolytes. This conclusion is not unexpected, since none of the theories takes account of all the factors which have a bearing on salting out and salting in. However the three main theoretical approaches described in this review have laid the foundations for a generalised thermodynamic treatment of the salting out and salting in of non-electrolytes in solutions of electrolytes. Eqn. (15) is a good example of the adoption by one theory of some aspects of a different theory which approaches the theoretical interpretation of the phenomenon from an entirely different direction[3]: this equation combines the best features of the hydration theory and of the improved Debye–McAuley electrostatic theory.

## VII. USE OF EXPERIMENTAL DATA ON SALTING OUT AND SALTING IN TO DETERMINE SOME PHYSICO-CHEMICAL CHARACTERISTICS OF SOLUTIONS

The activity coefficient is one of the most important characteristics of dissolved substances. The $f_e$ values for electrolytes have been fully investigated up to quite high concentrations. On the other hand, until recently the $f_{ne}$ values could be determined experimentally only by complex laboratory methods requiring high-precision equipment as well as being very time-consuming.

By using the salting-out coefficient of the non-electrolyte in conjunction with Eqn. (40) the $f_{ne}$ values for the non-electrolyte at various electrolyte concentrations can readily be calculated. The use of this equation is justified because the solubility of gaseous non-electrolytes in water and in electrolyte solutions is usually small (~$10^{-3}$ to $10^{-5}$ mole litre$^{-1}$). Since $f_{ne}^0 = 1$ Eqn. (40) can be re-written

$$\lg f_{ne} = Kc_e. \qquad (46)$$

A new electrochemical method has been developed in our laboratory[55] to measure $f_{ne}$ and other physico-chemical properties of three-component solutions (water–electrolyte–gaseous non-electrolyte) by using salting out data for the non-electrolyte. The method is based on the measurement of the limiting diffusion currents for the electrolytic reduction or oxidation of the dissolved non-electrolyte at an electrode separated from the solution by a polyethylene, polypropylene, or Teflon-4 membrane 10–40 μm thick. We have shown[55] that the limiting diffusion current $I_d$ for a dissolved gas on such an electrode is

proportional to the activity rather than to the concentration of the gas in solution:

$$I_d = k_1 a_{ne} = k_1 f_{ne} c_{ne}. \quad (47)$$

If $I_d$ is measured at saturation of the electrolyte solution by the gaseous non-electrolyte we have

$$I_d = k_1 f_{ne} s_{ne}. \quad (48)$$

Since according to Eqn. (1) $s_{ne} = s^0_{ne} - 10^{Kc_e}$, by substituting this expression into Eqn. (48) we obtain

$$f_{ne} = \frac{I_d}{k_1 (s^0_{ne} - 10^{Kc_e})}. \quad (49)$$

The coefficient $k_1$ in Eqn. (49) is determined by measuring $I^I_d$ for a saturated solution of the non-electrolyte in water, for which $s_{ne} = s^0_{ne}$, so that $k_1$ becomes

$$k_1 = I^I_d / s^0_{ne}.$$

From measurements of $I_d$ in non-electrolyte–water–electrolyte solutions we can determine the volume of 1 mole of hydrated electrolyte molecules $V^h_e$. It has been shown[56] that

$$\lg f_{ne} = -\lg (1 - c_e V^h_e). \quad (50)$$

Thus we can calculate the volume of 1 mole of hydrated molecules of the electrolyte in solution by using Eqn. (50) together with the $f_{ne}$ value calculated by Eqn. (49).

By measuring limiting diffusion currents of non-electrolytes in water and in electrolyte solutions saturated with one of the non-electrolytes we can determine the hydration numbers of the electrolytes at different electrolyte concentrations. The method relies on the observation[55] that the $I_d$ values of non-electrolytes at an electrode covered by a membrane are the same in water and in electrolyte solutions of different concentrations if the solvent is saturated with the non-electrolyte. This shows that the $I_d$ value for an electrode of this type is proportional to the activity rather than to the concentration of the non-electrolyte. The activity of the non-electrolyte in the liquid phase is proportional to the partial pressure of the non-electrolyte over the saturated water or electrolyte solution of the non-electrolyte. But since both the water and the electrolyte solutions are saturated with the non-electrolyte at the same partial pressure, the activity of the non-electrolyte is constant.

The number of free water molecules per non-electrolyte molecule ($n^I_w$) in water saturated with the non-electrolyte is given by

$$n^I_w = \frac{c^I_w}{s^0_{ne}} = \frac{c^I_w k_1}{I^I_d}, \quad (51)$$

where $c^I_w$ is the molar concentration of water in the solution of non-electrolyte in water. This quantity is given by

$$c^I_w = c_w - V_{ne}. \quad (52)$$

If we add electrolyte to water saturated with the non-electrolyte to a molar concentration $c_e$ of the electrolyte the number of free water molecules per molecule of the non-electrolyte ($n^{II}_w$) decreases as a result of the hydration of the electrolyte and becomes

$$n^{II}_w = \frac{c^{II}_w - c^h_w}{s^{II}_{ne}} = \frac{(c^{II}_w - c^I_w) k_2}{I^{II}_d}, \quad (53)$$

where $c^{II}_w$ is the molar concentration of water in the water–electrolyte–non-electrolyte solution, $c^h_w$ is the number of moles of water in 1 litre of this solution taken up by the hydration shells of the dissolved electrolyte, $s^{II}_{ne}$ is the solubility of the non-electrolyte in a solution of electrolyte of concentration $c_e$ expressed in mole litre$^{-1}$. Eqn. (53) was obtained by using the expression

$$s^{II}_{ne} = \frac{I^{II}_d}{k_2}.$$

The quantity $c^{II}_w$ in Eqn. (53) is given by

$$c^{II}_w = c_w - V_{ne} - V_e, \quad (54)$$

where $V_e$ is the intrinsic volume of 1 mole of electrolyte.

Since $I^I_d = I^{II}_d$, we obtain from Eqns. (51) and (53)

$$c^I_w k_1 = (c^{II}_w - c^h_w) k_2, \quad (E)$$

or in other words

$$c^h_w = (c^{II}_w k_2 - c^I_w k_1)/k_2. \quad (55)$$

By using Eqn. (55) the hydration number $h_e$ of the electrolyte at the given concentration $c_e$ can easily be determined:

$$h_e = \frac{c^h_w}{c_e} = \frac{c^{II}_w k_2 - c^I_w k_1}{c_e k_2}. \quad (56)$$

The quantities $k_1$ and $k_2$ are calculated from the measured values of $I^I_d$ and $I^I_d$ in water saturated with the non-electrolyte and in the water–electrolyte–non-electrolyte solution. The required values of $s^{II}_{ne}$ are determined from Eqn. (1) using the known salting-out coefficient of the non-electrolyte in the solution of interest.

Ruetschi and Amlie[3] suggested the use of Eqn. (2) of the hydration theory together with their Eqn. (5) to calculate the volume of a mole of hydrated electrolyte molecules ($V^h_e$) and the intrinsic volume of a mole of the electrolyte at infinite dilution. They inserted $s^0_{ne}/s_{ne}$ from Eqn. (5) into Eqn. (2) and, knowing $V^h_e$, they calculated $\nu_e V^0_e$ for KOH. Hence they arrived at the radius $r_h$ of the hydrated KOH molecule, and they obtained a value in good agreement with those reported by other workers. By the same procedure Ruetschi and Amlie calculated $V^0_e$ for HCl, LiCl, NaCl, KCl, NaOH, and KOH. However Eqns. (2) and (5) of the hydration theory of salting out and salting in are only approximate, as was pointed out above, and therefore Ruetschi and Amlie's calculations must also be treated as approximate.

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# Computational Procedures for the Determination of the Physical Characteristics of Polymers

A.A.Askadskii

Methods are described for the calculation of the principal physical characteristics of polymers from data for the chemical structure of the repeating polymer unit. These characteristics include the density, coefficient of thermal expansion, glass point, melting point, refractive index, coefficient of optical sensitivity to stress, and the solubility parameters of low-molecular-weight liquids and polymers. A consistent relation between these characteristics and the chemical structure of polymers has been traced.
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## I. INTRODUCTION

As a consequence of the extension of the range of chemical substances involved in polymerisation and polycondensation processes, the problem of the synthesis of polymers with specified properties has now become even more acute. Such properties include the glass point, the density, the coefficient of volume expansion, the refractive index, etc. The solution of the problem associated with the solubility of the polymer in a particular solvent is particularly important. The above properties of polymers are the most important ones and in many respects they determine the many other properties. It is shown in the present review that all the parameters enumerated above can be determined even before synthesising the polymer solely on the basis of the chemical structure of the repeating unit.

We shall examine primarily problems associated with the packing of macromolecules in monolithic polymeric materials and with the calculation of their densities.

## II. THE PACKING OF MACROMOLECULES AND THE DENSITIES OF POLYMERS

The packing coefficient $k$, which is defined as the ratio of the van der Waals volume of atoms and groups of atoms in the molecule to the true volume determined from experimental data, serves as a measure of the packing density of the macromolecules[1-3]. The calculation of the packing coefficients of molecules is usually based on the molar volumes of the repeating units. Then

$$k = \frac{N_A \sum_i \Delta V_i}{M/d}, \qquad (1)$$

where $\Delta V_i$ are the increments of the van der Waals volumes of the atoms in the repeating unit of the polymer, $m$ the molecular weight of the repeating unit, $d$ the density of the polymer, and $N_A$ the Avogadro number. In order to evaluate the packing coefficients $k$, the volume increments $\Delta V_i$ for a large number of atoms, linked by valence bonds with a wide variety of other atoms, have been calculated in a number of studies[1-8]. Since the values of $\Delta V_i$ will be convenient subsequently for the calculation not only of the densities but also of other properties of polymers, a detailed table of their values is included (Table 1).

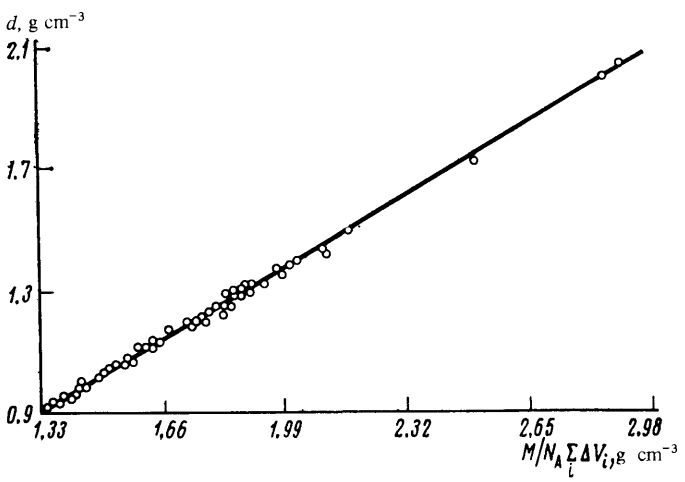



Figure 1. Variation of the densities of amorphous and amorphous-crystalline polymers with the ratio $M/N_A \sum_i \Delta V_i$.

In the calculation of the packing coefficients of amorphous monolithic polymers, it was found[2] that, regardless of the chemical structure of the polymers, their packing coefficients are approximately the same and amount to 0.681 at 20°C. In order to demonstrate this experimental finding, Table 2 lists the values of $k$ for a number of amorphous polymers and Fig. 1 illustrates the variation of the densities of polymers having different chemical structures with the ratio $M/N_A \sum_i \Delta V_i$. Evidently this relation is described by a straight line on which the experimental

values of $d$ fit satisfactorily. Its slope is equal to the packing coefficients $k = 0.681$. Since $k$ is to a first approximation a constant for amorphous monolithic bodies, the density of the polymer may be calculated solely from the chemical structure of the repeating unit by the equation

$$d = \frac{k_{av} M}{N_A \sum_i \Delta V_i}, \qquad (2)$$

where $k_{av} = 0.681$.

Table 1. The van der Waals volumes of atoms and atomic groups.

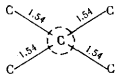
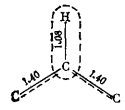
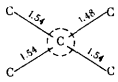
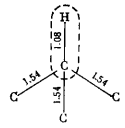
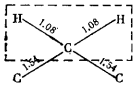
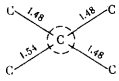
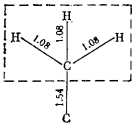
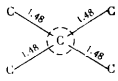
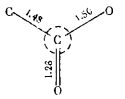
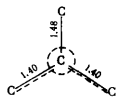
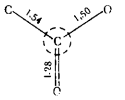
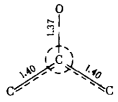
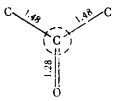
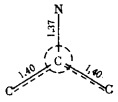
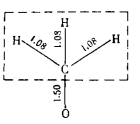
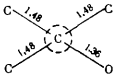
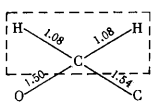
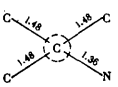
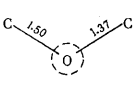
| Group | $\Delta V_i$, Å³ | Group | $\Delta V_i$, Å³ |
|---|---|---|---|
|  | 5.0 |  | 14.7 |
|  | 4.7 |  | 11.1 |
|  | 4.5 |  | 17.1 |
|  | 4.2 |  | 23.5 |
|  | 4.0 |  | 15.7 |
|  | 8.4 |  | 15.9 |
|  | 11.65 |  | 12.3 |
|  | 10.2 |  | 26.3 |
|  | 7.25 |  | 20.2 |
|  | 5.8 |  | 2.7 |
|  | 5.85 | | |

Table 1 (continued).

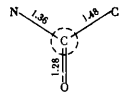
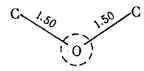
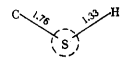
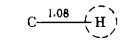
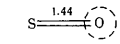
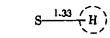
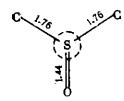
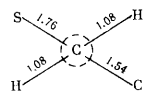
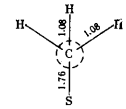
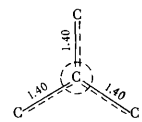
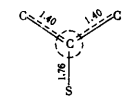
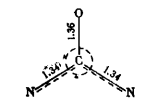
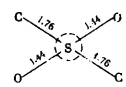
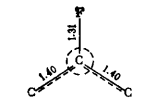
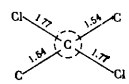
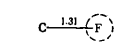
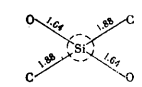
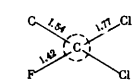
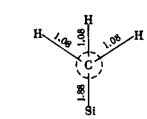
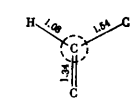
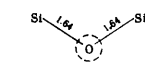
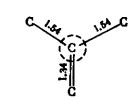
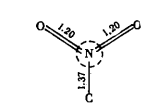
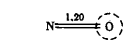
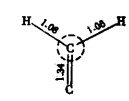
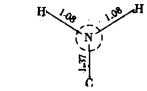
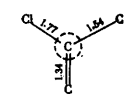
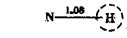
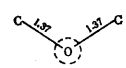
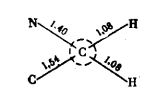
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|---|---|---|---|
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|  | 19.5 |  | 2.0 |
| | |  | 6.6 |
|  | 3.2 | | |
|  | 14.7 |  | 14.3 |
|  | 18.4 |  | 8.1 |
| | |  | 5.8 |
|  | 9.6 | | |
| | |  | 15.8 |
|  | 12.9 | | |
| | |  | 10.65 |
|  | 7.1 |  | 9.0 |
| | |  | 27.6 |
|  | 8.2 |  | 16.0 |
|  | 13.1 |  | 0.49 |
|  | 9.0 |  | 7.00 |
| | |  | 7.2 |
|  | 17.1 |  | 9.1 |
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|  | 2.1 |  | 14.7 |

**Table 1** (continued).

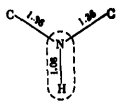
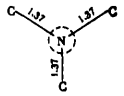
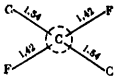
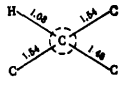
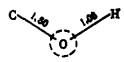
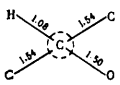
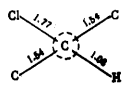
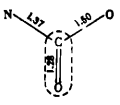
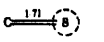
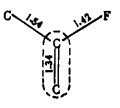
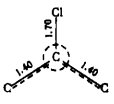
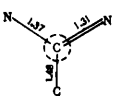
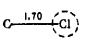
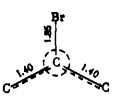
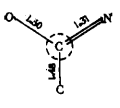
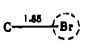
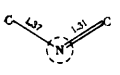
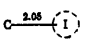
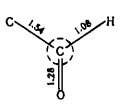
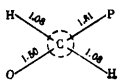
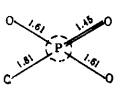
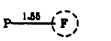
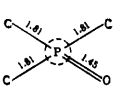
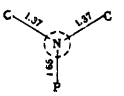
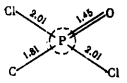
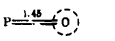
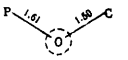
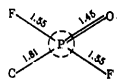
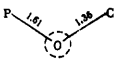
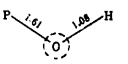
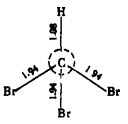
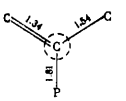
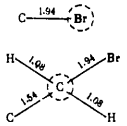
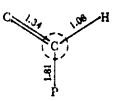
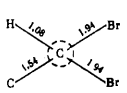
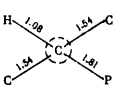
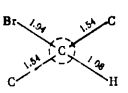
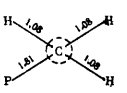
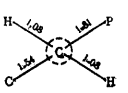
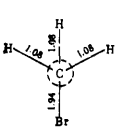
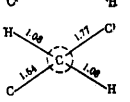
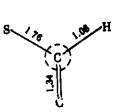
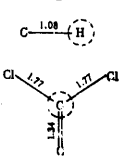
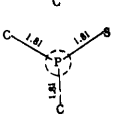
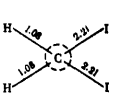
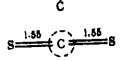
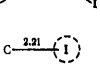
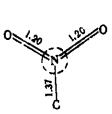
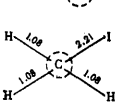
| Group | $\Delta v_i$, Å³ | Group | $\Delta v_i$, Å³ |
|---|---|---|---|
|  | 8.3 |  | 15.9 |
| | |  | 10.0 |
|  | 0.9 | | |
| | |  | 9.4 |
|  | 8.6 |  | 9.6 |
|  | 5.6 | | |
|  | 12.2 |  | 10.1 |
|  | 4.7 |  | 19.85 |
|  | 23.3 |  | 20.2 |
| | |  | 14.8 |
|  | 20.7 |  | 10.5 |
|  | 12.6 |  | 19.5 |
| | |  | 9.9 |
|  | 14.1 |  | 27.1 |
|  | 6.1 |  | 10.5 |
| | |  | 37.9 |
|  | 16.9 |  | 17.4 |
|  | 16.4 | | |
|  | 19.6 |  | 9.3 |
|  | 14 8 |  | 1.55 |

**Table 1** (continued).

| Group | $\Delta v_i$, Å³ | Group | $\Delta v_i$, Å³ |
|---|---|---|---|
|  | 16.5 |  | 6.0 |
| | |  | 3.15 |
|  | 17.9 |  | 2.4 |
|  | 20.0 |  | 5.4 |
|  | 10.5 |  | 9.25 |
|  | 27.3 | | |
|  | 13.6 |  | 13.3 |
|  | 10.0 |  | 9.3 |
|  | 9.6 |  | 17.4 |
| | |  | 13.3 |
|  | 17.7 |  | 14.1 |
|  | 2.0 |  | 14.2 |
|  | 11.0 |  | 14.7 |
|  | 13.5 |  | 14.9 |
|  | 38.4 |  | 7.0 |
|  | 17.3 | | |

The calculations[2] have shown that the density of an amorphous polymer may be calculated as a rule to within 0.01 g cm$^{-3}$. Table 3 presents as an example the experimental and calculated densities $d$ at 20°C for representatives of various classes of polymers in the amorphous monolithic state. It can be seen that these agree with adequate accuracy. We may note immediately that the

packing coefficients for crystalline polymers depend significantly on the chemical structure of the polymers and their values lie within very broad limits. It should also be noted that calculations of the densities of polymers have been performed in a study[9] where the increments of the van der Waals volumes obtained by different workers were used.

Table 2. The packing coefficients $k$ for amorphous monolithic polymers.

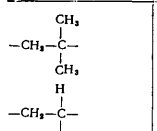
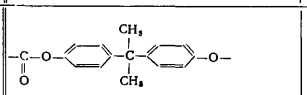
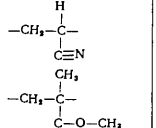
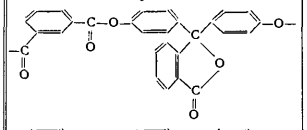
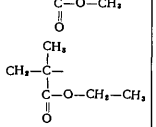
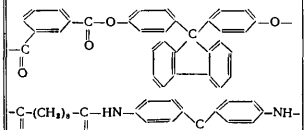
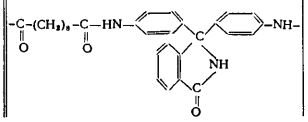
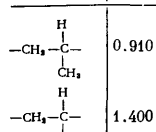
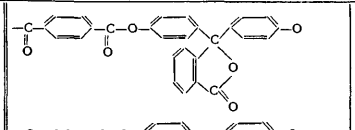
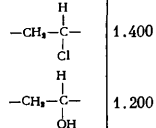
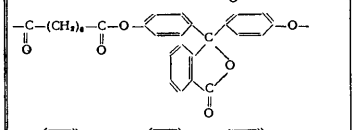
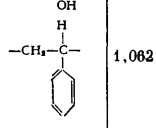
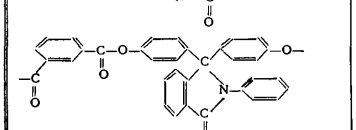
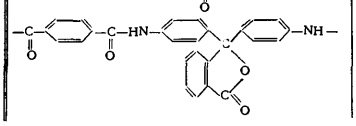
| Polymer unit | Volume of unit, Å$^3$ | $k$ | Polymer unit | Volume of unit, Å$^3$ | $k$ |
|---|---|---|---|---|---|
|  | 41.6 | 0.678 |  | 144.3 | 0.679 |
|  | 32.6 | 0.682 |  | 234.7 | 0.679 |
|  | 58.5 | 0.684 | | | |
|  | 69.1 | 0.680 |  | 263.1 | 0.680 |
| | | |  | 277.5 | 0.688 |

Table 3. The calculated and experimental densities of amorphous monolithic polymers.

| Polymer unit | $d_{exp}$, g cm$^{-3}$ | $d_{calc}$, g cm$^{-3}$ | Polymer unit | $d_{exp}$, g cm$^{-3}$ | $d_{calc}$, g cm$^{-3}$ |
|---|---|---|---|---|---|
|  | 0.910 | 0.905 |  | 1 307 | 1.301 |
|  | 1.400 | 1.380 |  | 1,213 | 1 213 |
|  | 1.200 | 1.201 | | | |
|  | 1.062 | 1.051 |  | 1 253 | 1.256 |
| | | |  | 1.302 | 1.280 |

The packing coefficients of crystalline polymers have been calculated[4] from the crystallographic densities evaluated from the results of X-ray diffraction analysis, namely the unit cell volumes and the masses of the atoms in the unit cell. Calculations were performed for 80 polymeric systems with a wide variety of chemical structures. It was found as a result that crystalline polymers have a very broad distribution curve with regard to the packing coefficients, which depend on the chemical structure of the polymer (Table 4). The distribution curve with respect to the packing coefficients is illustrated in Fig. 2, which also shows an analogous curve for amorphous polymers. It can be seen that the distribution curve with respect to the values of $k$ for amorphous systems is extremely narrow.

Table 4. The packing coefficients $k$ for crystalline polymers.

| Polymer | Type of unit cell | $d$, g cm$^{-3}$ | $N_A \sum_i \Delta V_i$, cm$^3$ mole$^{-1}$ | $M$ | $k$ |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| Polyethylene | orthorhombic | 1.0 | 20.6 | 28 | 0.736 |
| | | 1.014 | 20.6 | 28 | 0.746 |
| | pseudomonoclinic | 0.965 | 20.6 | 28 | 0.710 |
| | triclinic | 1.013 | 20.6 | 28 | 0.745 |
| Polypropylene | | | | | |
| isotactic | monoclinic | 0.936 | 31.1 | 42 | 0.693 |
| syndiotactic | monoclinic | 0.910 | 31.1 | 42 | 0.674 |
| Polystyrene | rhombohedral | 1.12 | 66.0 | 104 | 0.711 |
| Polybut-1-ene | rhombohedral | 0.95 | 41.2 | 56 | 0.699 |
| Polyisobutylene | orthorhombic | 0.937 | 41.6 | 56 | 0.696 |
| Polybuta-1,2-di-ene | | | | | |
| syndiotactic | orthorhombic | 0.963 | 38.8 | 54 | 0.692 |
| isotactic | rhombohedral | 0.960 | 38.8 | 54 | 0.690 |
| *trans*-Polybuta-1,4-diene | pseudohexagonal | 1.02 | 38.8 | 54 | 0.733 |
| *cis*-Polybuta-1,4-diene | monoclinic | 1.01 | 38.8 | 54 | 0.726 |
| *cis*-Poly-1,4-isoprene | monoclinic | 1.00 | 49.3 | 68 | 0.725 |
| *trans*-β-Poly-1,4-isoprene | orthorhombic | 1.11 | 49.3 | 68 | 0.805 |
| *trans*-Penta-1,4-diene | pseudohexagonal | 0.98 | 49.3 | 68 | 0.710 |
| Poly-3-methylbut-1-ene | monoclinic | 0.93 | 51.5 | 70 | 0.684 |
| Poly-4-methylpent-1-ene | tetragonal | 0.813 | 61.8 | 84 | 0.598 |
| Polyvinylcyclopentane | triclinic | 0.986 | 64.9 | 96 | 0.666 |
| Polyvinylcyclohexane | tetragonal | 0.95 | 75.2 | 110 | 0.649 |
| | triclinic | 0.982 | 75.2 | 110 | 0.671 |
| Poly-o-methylstyrene | tetragonal | 1.071 | 76.1 | 118 | 0.691 |
| Poly-*m*-methylstyrene | tetragonal | 1.010 | 76.1 | 118 | 0.651 |
| Poly-α-vinylnaphthalene | tetragonal | 1.124 | 93.6 | 154 | 0.683 |
| Poly(vinyl chloride) | orthorhombic | 1.44 | 29.5 | 62.5 | 0.680 |
| | orthorhombic | 1.522 | 29.5 | 62.5 | 0.718 |
| | monoclinic | 1.455 | 29.5 | 62.5 | 0.687 |
| Poly(vinylidene chloride) | monoclinic | 1.949 | 38.5 | 97 | 0.773 |
| | monoclinic | 1.959 | 38.5 | 97 | 0.777 |
| Polytetrafluoroethylene | pseudohexagonal | 2.40 | 33.1 | 100 | 0.794 |
| | hexagonal | 2.36 | 33.1 | 100 | 0.781 |
| Polychlorotrifluoroethylene | hexagonal | 2.10 | 39.6 | 116.5 | 0.714 |
| Poly(vinyl alcohol) | monoclinic | 1.35 | 25.1 | 44 | 0.770 |
| Poly(methyl methacrylate) | | | | | |
| isotactic | pseudo-orthorhombic | 1.23 | 58.5 | 100 | 0.719 |
| Poly(vinyl fluoride) | hexagonal | 1.44 | 23.7 | 46 | 0.742 |
| Polyacrylonitrile | orthorhombic | 1.11 | 32.6 | 53 | 0.677 |
| Polychloroprene | orthorhombic | 1.657 | 47.7 | 88.5 | 0.893 |
| Poly-o-fluorostyrene | rhombohedral | 1.526 | 63.2 | 122 | 0.790 |
| Poly(*NN*-dibutylacryl-amide) | hexagonal | 1.06 | 121.7 | 183 | 0.705 |
| Poly(ethylene terephthalate) | triclinic | 1.455 | 102.4 | 192 | 0.776 |
| Poly(hexamethylene terephthalate) | triclinic | 1.131 | 143.6 | 249 | 0.652 |
| Poly(decamethylene terephthalate) | triclinic | 1.012 | 184.8 | 304 | 0.615 |
| Poly(ethylene isophthalate) | triclinic | 1.358 | 102.4 | 192 | 0.724 |
| Poly(tetramethylene isophthalate) | triclinic | 1.309 | 123 | 220 | 0.732 |
| Poly(ethylene succinate) | triclinic | 1.175 | 75.2 | 128 | 0.690 |
| Poly(ethylene adipate) | triclinic | 1.274 | 95.8 | 156 | 0.782 |
| Poly(ethylene sebacate) | monoclinic | 1.187 | 137 | 212 | 0.767 |
| | triclinic | 1.120 | 137 | 212 | 0.724 |
| Poly(trimethylene sebacate) | tetragonal | 1.090 | 147.3 | 226 | 0.710 |
| Nylon 6,6 | | | | | |
| α | triclinic | 1.240 | 139.2 | 226 | 0.764 |
| β | triclinic | 1.248 | 139.2 | 226 | 0.769 |
| Nylon 6, 10 | triclinic | 1.157 | 180.4 | 282 | 0.740 |
| | triclinic | 1.196 | 180.4 | 282 | 0.765 |
| Nylon 7,7 | pseudohexagonal | 1.108 | 159.8 | 254 | 0.693 |
| Nylon 6 | monoclinic | 1.23 | 69.9 | 113 | 0.758 |
| | monoclinic | 1.23 | 69.9 | 113 | 0.745 |
| Nylon 7 | triclinic | 1.211 | 79.9 | 127 | 0.762 |
| Nylon 8 | hexagonal | 1.038 | 90.2 | 141 | 0.664 |
| Nylon 10 | hexagonal | 0.019 | 110.8 | 169 | 0.668 |
| Nylon 11 | triclinic | 1.192 | 121.1 | 183 | 0.789 |
| | triclinic | 1.228 | 121.1 | 183 | 0.813 |
| Poly(isobutyl vinyl ether) | orthorhombic | 0.940 | 68.1 | 100 | 0.640 |
| Cellulose | | | | | |
| I | monoclinic | 1.592 | 79.5 | 162 | 0.781 |
| II | monoclinic | 1.625 | 79.5 | 162 | 0.797 |
| Cellulose triacetate | pseudo-orthorhombic | 1.30 | 148.8 | 288 | 0.672 |
| Polyoxymethylene | hexagonal | 1.506 | 16.1 | 30 | 0.808 |
| Poly(ethylene oxide) | hexagonal | 1.205 | 26.4 | 44 | 0.723 |
| Poly(propylene oxide) | orthorhombic | 1.096 | 34.9 | 58 | 0.659 |
| | orthorhombic | 1.102 | 34.9 | 58 | 0.663 |
| | orthorhombic | 1.154 | 34.9 | 58 | 0.694 |

Table 4 (continued).

| Polymer | Type of unit cell | $d$, g cm$^{-3}$ | $N_A \sum \Delta V_i$, cm$^3$ mole$^{-1}$ | $M$ | $k$ |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| Polyacetaldehyde | tetragonal | 1.14 | 26.6 | 44 | 0.689 |
| Polypropionaldehyde | tetragonal | 1.05 | 36.9 | 58 | 0.668 |
| Poly-n-butyraldehyde | tetragonal | 1.00 | 47.2 | 72 | 0.655 |
| Polybisphenol | orthorhombic | 1.30 | 144.3 | 254 | 0.738 |
| Poly(hexamethylene sulphone) | monoclinic | 2.77 | 78.7 | 148 | 0.736 |
| Poly(hexamethylene pentaethylene sulphone) | monoclinic | 2.83 | 116.1 | 282 | 0.583 |
| Poly(hexamethylene tetramethylene sulphone) | monoclinic | 2.92 | 136.7 | 268 | 0.745 |
| Poly(pentamethylene sulphone) | monoclinic | 2.95 | 68.4 | 134 | 0.753 |
| Poly(pentamethylene tetramethylene sulphone) | monoclinic | 3.06 | 126.4 | 254 | 0.761 |

*In the crystallographic data [3] for polymers containing the sulphone group, an error was made in the calculation of the density, which is too high by a factor of two.

We shall now consider the temperature variation of the packing coefficient. It was calculated [10] by Eqns. (3) and (4), which follow directly from Eqn. (1):

$$k(T) = \frac{N_A \sum_i \Delta V_i}{MV_g[1 + \alpha_G (T - T_g)]}; \quad T < T_g, \tag{3}$$

and

$$k(T) = \frac{N_A \sum_i \Delta V_i}{MV_g[1 + \alpha_L (T - T_g)]}; \quad T > T_g, \tag{4}$$

where $V_g$ is the specific volume of the polymer at the glass point $T_g$ and $\alpha_G$ and $\alpha_L$ are the coefficients of volume expansion of the polymer below and above the glass point respectively. The calculations carried out using Eqns. (3) and (4) have shown [10] that the temperature variation of the packing coefficients of a number of polymers is of the form shown in Fig. 3. A remarkable properties of these temperature variations is that the packing coefficients are the same to a first approximation for all polymers at any selected temperature below their glass points. To a second, more accurate approximation, the packing coefficient is the same for each polymer at its glass point and amounts to $k_g = 0.667$.

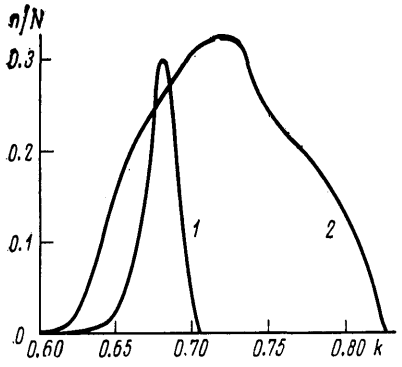



Figure 2. Distribution curves with respect to packing coefficients for amorphous (curve *1*) and crystalline (curve *2*) polymers.

At low temperatures ($T_0 \simeq 6$ K), the packing coefficients of polymers, determined by the extrapolation of the temperature variations of $k$ to $T \to 0$, are also approximately the same and calculations have shown [10] that they can be estimated as $k_0 = 0.731$.

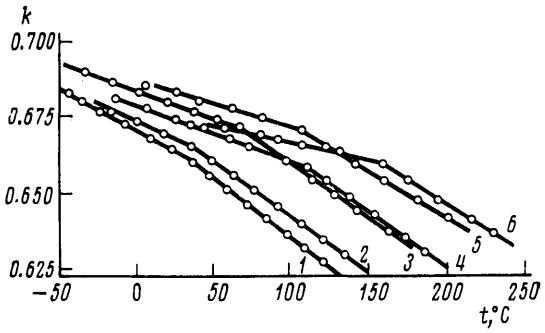



Figure 3. Temperature variation of the packing coefficients of polymers: 1) poly(n-butyl methacrylate); 2) poly(n-propyl methacrylate); 3) poly(ethyl methacrylate); 4) polystyrene; 5) poly(methyl methacrylate); 6) polycarbonate of di-(4-hydroxyphenyl)propane.

## III. CALCULATION OF THE GLASS POINTS, COEFFICIENTS OF THERMAL EXPANSION, AND MELTING POINTS OF POLYMERS

An empirical relation has been proposed [11] whereby one can calculate the glass points $T_g$ of polymers from the chemical structure of the repeating unit of the macromolecule and the density of the polymer:

$$\lg T_g = \frac{d}{M} \sum_i K_i' + A, \tag{5}$$

where $M$ is the molecular weight of the repeating unit, $d$ the density of the polymer, and $\sum_i K_i'$ the effective volume of the repeating unit, which consists of the effective volumes of the atoms and groups of atoms in this unit, and the parameter $A$ is constant for a given class of polymers. Eqn. (5) holds satisfactorily for several classes of polymers (aromatic polyesters and polyamides, polymethacrylates).

Subsequently a more accurate universal computational scheme was proposed [12], which is valid for polymers of different classes. According to this scheme, the glass point is determined from the relation

$$\lg T_g = \frac{\sum_i K_i^*}{N_A \sum_i \Delta V_i} + A^*, \tag{6}$$

where $A^* = 1.435$ for any polymer and $\sum_i K_i^*$ is the effective volume of the repeating unit, differing from $\sum_i K_i'$ in Eqn. (5) by the fact that the values of $K_i^*$ are determined by solving the excess system of equations based on Eqn. (6), which includes the van der Waals volume, while the $K_i'$ are determined by the same procedure on the basis of Eqn. (5), which includes the molar volume.

In order to calculate the glass points of polymers, it is necessary to know the parameters $K_i^*$ characterising the contributions of each atom and type of intermolecular interaction to the glass point. These quantities are listed in Table 5. Knowing them, it is easy to calculate the glass points of many polymers using Eqn.(6).

Table 5. The increments $K_i^*$ for various atoms and types of intermolecular interaction.

| Element or type of interaction | Designation | Value |
|---|---|---|
| Carbon | $K_C^*$ | 10.739 |
| Oxygen in side group | $K_{O,s}^*$ | 3.925 |
| Oxygen in main chain | $K_{O,m}^*$ | −5.244 |
| Hydrogen | $K_H^*$ | −1.248 |
| Hydrogen in side group | $K_{N,s}^*$ | 9.520 |
| Hydrogen in main chain | $K_{N,m}^*$ | 2.185 |
| Chlorine | $K_{Cl}^*$ | 7.242 |
| Silicon | $K_{Si}^*$ | 19.570 |
| Hydrogen bond | $K_h^*$ | 7.333 |
| Dipole-dipole interaction | $K_d^*$ | 7.333 |
| Symmetry coefficient | $K_p^*$ | 10.500 |

Note. The coefficient $K_d^*$ is introduced in all cases when a hydrogen atom is replaced by a group of any type other than phenyl. This rule does not extent to polyisoprene and polychloroprene. When two hydrogen atoms are replaced by identical groups, the quantity $0.5K_d^*$ is introduced. The coefficient $K_p^*$ is introduced when all the aromatic rings in the main chain are substituted in the *p*-position.

Table 6. The increments $a_i$, $b_i$, $\alpha_i$, and $D_i$ for various atoms and types of intermolecular interaction.

| Atom or type of interaction | Designation | $a_i \cdot 10^3$ ($b_i \cdot 10^3$), K$^{-1}$ | $\alpha_i \cdot 10^4$, K$^{-1}$ | $D_i$, kcal mole$^{-1}$ |
|---|---|---|---|---|
| Carbon* | $a_C$ | 0.021 | — | — |
| Hydrogen | $a_H$ | 10.98 | 1.92 | 0.45 |
| Oxygen in main chain | $a_{O,m}$ | 22.95 | 2.21 | 0.39 |
| Oxygen in side chain | $a_{O,s}$ | 7.03 | 0.68 | 1.28 |
| Nitrogen in main chain | $a_{N,m}$ | 8.62 | 0.83 | 1.04 |
| Nitrogen in side chain | $a_{N,s}$ | 6.35 | 0.61 | 1.43 |
| Chlorine | $a_{Cl}$ | 4.01 | 0.39 | 2.25 |
| Sulphur in main chain | $a_{S,m}$ | 3.53 | 0.34 | 2.56 |
| Dipole-Dipole interaction | $b_d$ | −55.37 | — | — |
| Hydrogen bond** | $b_h'$ | −206.78 | — | — |
| Symmetry coefficient*** | $b_h$ | −139.60 | | |
| Coefficient for polydienes taking into account the greater freedom of rotation in the presence of double bonds in the main chain | $b_C$ $b_{=}$ | −90.50 92.22 | | |

*$\alpha_i$ and $1/D_i$ are negligibly small.
**$b_h'$ is introduced for aliphatic polyamides.
***$b_h$ is introduced in all other instances when the polymer contains hydrogen bonds.

Eqn.(6) makes it possible to estimate with adequate accuracy the glass points of polymers, but the physical significance of its parameters has not been established. An attempt was therefore made[10] to construct a computational scheme based on the previously proposed[12] principle of the additivity of the contributions of the individual atoms to the glass point, taking into account the physical ideas concerning volume expansion.

We shall now consider this scheme. According to Eqn. (1), $k_g/k_0 = V_0/V_g$, where $V_0$ is the specific volume of the polymer at the temperature $T_0$. Taking into account this equation, it was found[10] that

$$T_g = \frac{k_0/k_g - 1}{\alpha_G}. \tag{7}$$

The coefficient of volume expansion $\alpha_G$ can be expressed[10] in terms of the equation

$$\alpha_G = \frac{\sum_i a_i \Delta V_i}{\sum_i \Delta V_i} + \frac{\sum_i \beta_i}{\sum_i \Delta V_i}, \tag{8}$$

where $\alpha_i$ is the partial coefficient of volume expansion of the $i$th atom or groups of atoms in the repeating unit of the polymer, $\Delta V_i$ the volume increment of the $i$th atom or atomic group, and $\beta_i$ are increments taking into account the contribution of strong intermolecular interactions to the coefficient of volume expansion (hydrogen bonds, dipole−dipole interaction, etc.; see Table 6).

The initial expression establishing the relation between $T_g$ and the structure of the repeating unit has been obtained[10] by substituting Eqn.(8) in Eqn.(7):

$$T_g = \frac{\sum_i \Delta V_i}{\sum_i a_i \Delta V_i + \sum_i b_i}. \tag{9}$$

where

$$a_i = \alpha_i/(k_0/k_g - 1); \quad b_i = \beta_i/(k_0/k_g - 1). \tag{10}$$

The numerical values of $a_i$ and $b_i$ characteristic of each atom and of each type of intermolecular interaction have been determined[10] by a statistical treatment of the experimental data using the method of least squares. These results are presented in Table 6.

We shall now trace the relation between the coefficient $\alpha_i$ in Eqn.(10) and the intermolecular interaction parameters (the intermolecular bond energy and the distance between the interacting atoms). It is known[13] that the coefficient of volume expansion is described by the expression

$$\alpha_i = 3R\beta_i'/\gamma_i^2 r_{0i}, \tag{11}$$

where $\beta_i' = -\frac{1}{2}\partial^3\varphi/\partial r^3|_{r_{0i}}$ is the anharmonic coefficient, $\gamma_i = \partial^2\varphi/\partial r^2|_{r_{0i}}$ the harmonic force constant, $r_{0i}$ the distance between the given $i$th and neighbouring atoms, $\varphi$ the potential of the interaction of the $i$th atom with a neighbouring atom, and $R$ the gas constant.

When the Lennard-Jones potential is used in the form for the determination of $\beta_i'$ and $\gamma_i$ [14]

$$\varphi(r) = D\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^6\right],$$

where $D$ is the bond energy (the depth of the potential well) and $r_0$ the equilibrium distance between the atoms, then

$$\gamma_i = 72D_i/r_{0i}^2, \quad \beta_i' = 666D_i/r_{0i}^3;$$

or

$$\alpha_i = \frac{7}{16}\cdot\frac{R}{D_i}, \quad D_i = \frac{7}{16}\cdot\frac{R}{\alpha_i}. \tag{12}$$

Estimates of the values of $D_i$ for bonds of different types have shown [10] that the bond energies derived from experimental data correspond to the intermolecular interaction energies (and not to chemical bonds).

Calculations carried out by Eqn.(12) demonstrated [10] that the average bond energies $D_i$ assume the values listed in Table 6. Since, according to the literature [15,16] the bond energies $D_i^0$ for different atoms, included in Table 6, are several times smaller than the observed values of $D_i$, it follows that [10]

$$D_i = zD_i^0, \qquad (13)$$

where $z$ is the coordination number.

Table 7. The calculated and experimental glass points of polymers.

| Polymer | $\sum_i \Delta V_i$, Å³ | $T_g$, K (calc.) | $T_g$, K (expt.) |
|---|---|---|---|
| Polyisoprene | 81.8 | 198 | 200 |
| Polychloroprene | 79.15 | 213 | 225 |
| Polydimethylsiloxane | 72.1 | 150 | 150 |
| Polypropylene | 51.7 | 278 | 258, 293 |
| Polyisobutylene | 69.1 | 215 | 199 |
| Polybutene | 68.8 | 259 | 248 |
| Poly(methyl vinyl ether) | 61.0 | 292 | 258 |
| Poly(ethyl vinyl ether) | 78.4 | 270 | 248 |
| Poly(n-butyl vinyl ether) | 112.6 | 250 | 221 |
| Poly(vinyl propionate) | 97.1 | 260 | 266 |
| Poly(vinyl acetate) | 79.65 | 318 | 298 |
| Poly(vinyl chloride) | 49.05 | 340 | 355 |
| Poly(vinylidene chloride) | 69.3 | 267 | 256 |
| Poly(methyl methacrylate) | 97.0 | 353 | 378 |
| Poly(ethyl methacrylate) | 114.45 | 322 | 338 |
| Poly(n-propyl methacrylate) | 131.55 | 302 | 308 |
| Poly(n-butyl methacrylate) | 148.65 | 288 | 293 |
| Poly(n-hexyl methacrylate) | 182.85 | 270 | 268 |
| Poly(n-octyl methacrylate) | 217.05 | 259 | 253 |
| Poly(methyl acrylate) | 79.65 | 318 | 293 |
| Poly(ethyl acrylate) | 97.1 | 293 | 261 |
| Poly(n-butyl acrylate) | 131.7 | 267 | 233 |
| Polystyrene | 109.9 | 413 | 378 |
| Poly-α-methylstyrene | 127.2 | 437 | 435 |
| Poly(vinyl alcohol) | 41.6 | 366 | 358 |
| Poly(ethylene terephthalate) | 165.9 | 369 | 353 |
| Polyacrylonitrile | 54.1 | 420 | 418 |
| Nylon 6,6 | 232.3 | 332 | 325 |
| Nylon 6 | 116.15 | 332 | 335 |
| Polyacrylamide | 64.05 | 428 | 426 |
| Polyacrylic acid | 60.25 | 388 | 379; 439 |
| Polycarbonate based on 2,2-di-(4-hydroxyphenyl)propane | 239.25 | 422 | 411 |
| Polyarylate of sebacic acid and phenolphthalein | 450.5 | 367 | 363 |
| Polyarylate of isophthalic acid and phenolphthalein | 388.9 | 522 | 543 |
| Polyarylate of terephthalic acid and phenolphthalein | 388.9 | 594 | 583 |
| Polyarylate of isophthalic acid and phenolphthalein anilide | 470.9 | 532 | 563 |
| Polyarylate of terephthalic acid and phenolphthalein anilide | 470.9 | 593 | 593 |
| Polyarylate of diphenylphthalide-4,4'-dicarboxylic acid phenolphthalein | 571.6 | 581 | 598 |
| Polyarylate of biphenyl-4,4'-dicarboxylic-acid and phenolphthalein | 464.5 | 569 | 603 |
| Polyarylate of isophthalic acid and phenolfluorene | 436.8 | 516 | 543 |
| Polyarylate of biphenyl-4,4'-dicarboxylic acid and phenolfluorene | 512.5 | 558 | 587 |
| Polyarylate of diphenylphthalidedicarboxylic acid and 4,4'-dihydroxybiphenyl | 465.2 | 569 | 585 |
| Polyarylate of oxydi(4-carboxybenzene) and phenolphthalein | 473.8 | 547 | 573 |
| Polyarylate of terephthalic acid and dimethyldian | 367.8 | 412 | 423 |
| Polyamide of terephthalic acid and anilinephthalein imide | 399.6 | 590 | 618 |
| Polyamide of sebacic acid and anilinephthalein imide | 460,7 | 458 | 451 |
| Polyamide of diphenylphthalidedicarboxylic acid and anilinephthalein imide | 582,9 | 637 | 641 |
| Polyimide of the dianhydride of oxydi(3,4-dicarboxybenzene) and anilinefluorene | 537.9 | 640 | 670 |
| Polyimide of the dianhydride of oxydi(3,4-dicarboxybenzene) and anilinephthalein | 490.6 | 658 | 664 |
| Polyimide of the dianhydride of 3,3',4,4'-tetracarboxybiphenyl and anilinefluorene | 530.1 | 669 | 687 |
| Polypyromellitimide of anilinephthalein | 407.2 | 766 | 789 |

The initial Eqn.(9) can then be written in the form

$$1/T_g = 4.55R\left\langle \frac{1}{zD_0} \right\rangle, \qquad (14)$$

where

$$\left\langle \frac{1}{zD_0} \right\rangle = \sum_i \frac{1}{z_i D_i^0} \Delta V_i \Big/ \sum_i \Delta V_i.$$

Eqn.(9) can be used conveniently for the calculation of the glass points of polymers. A test of the applicability of Eqn.(9) has shown [10] that, for many polymers with a wide variety of chemical structures, the calculated and experimental values of $T_g$ agree satisfactorily. These data are compiled in Table 7. Fig.4 illustrates the variation of $T_g$ with $\sum_i \Delta V_i/(\sum_i a_i \Delta V_i + \sum_i b_i)$ for a number of polymers. The figure also includes the theoretical straight line based on Eqn.(9), the points corresponding to the experimental values of $T_g$. Fig.4 shows that Eqn.(9) holds over a very wide range of temperatures. Thus there is a possibility, in principle, of calculating the glass point of a polymer before its synthesis, regardless of the class to which it belongs. It is possible to calculate at the same time the coefficient of volume expansion $\alpha_G$ of the solid amorphous polymer from Eqn.(8). Calculations for a number of polymers showed a satisfactory agreement between the calculated and experimental data (Table 8).

Table 8. The volume expansion coefficients of polymers.

| Polymer | $\sum_i \Delta V_i$, Å³ | $\sum \alpha_i \Delta V_i \cdot 10^4$, Å³K⁻¹ | $\alpha_G \cdot 10^4$, K⁻¹ | |
|---|---|---|---|---|
| | | | calc. | expt. |
| Poly(methyl methacrylate) | 97.0 | 208.5 | 2.15 | 2.73 |
| Poly(ethyl methacrylate) | 114.4 | 314.6 | 2.75 | 2.99 |
| Poly(n-propyl methacrylate) | 131.5 | 414.2 | 3.15 | 3.19 |
| Poly(n-butyl methacrylate) | 148.6 | 564.7 | 3.80 | 3.34 |
| Poly(methyl acrylate) | 79.6 | 214.9 | 2.70 | 3.03 |
| Polystyrene | 109.9 | 274.7 | 2.50 | 2.34 |

We shall now consider how the change in the packing density of the macromolecules on passing from the amorphous to the crystalline state of the polymer affects its melting point. We note first that, according to Beaman's data [17], the ratio of the glass point $T_g$ to the melting point $T_m$ is approximately constant for many polymeric systems and can be estimated as $\gamma = T_g/T_m \simeq 0.67$. However, a detailed analysis [18] showed that this relation does not always hold. The ratio $\gamma = T_g/T_m$ can assume a wide variety of values (ranging from 0.25 to 0.97).

Calculations have shown [4] that $\gamma$ depends on the ratio of the packing coefficients of the fully amorphous and fully crystalline polymers ($k_{am}/k_{cr}$). This dependence is illustrated in Fig.5, from which it follows that $\gamma$ increases approximately linearly with increase of $k_{am}/k_{cr}$. Consequently $\gamma$ depends on the difference between the packing densities of the macromolecules in the amorphous and crystalline states. The greater the increase of packing density on crystallisation of the polymer, the greater the difference between the melting and glass points.

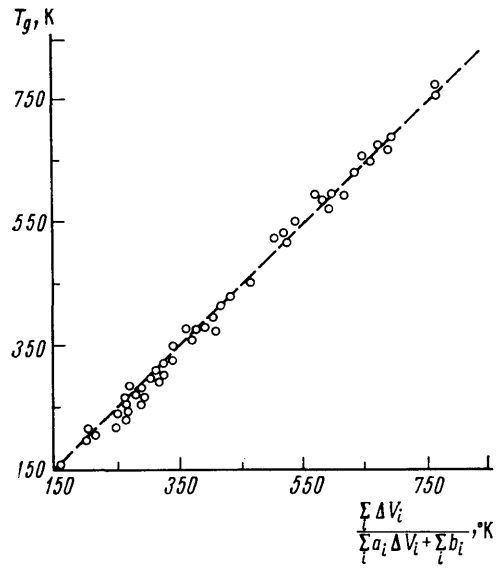



Figure 4. Variation of $T_g$ with the ratio $\sum_i \Delta V_i / (\sum_i a_i \Delta V_i + \sum_i b_i)$.

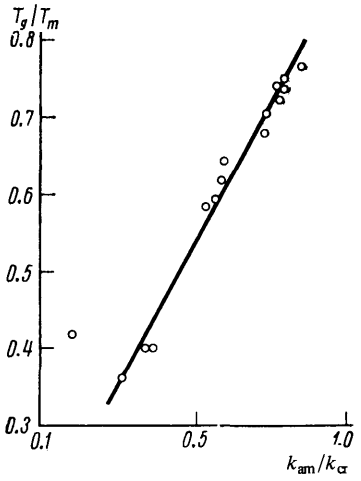



Figure 5. Variation of $T_g/T_m$ with $k_{am}/k_{cr}$.

An attempt has been made [19] to establish a relation between $\gamma$ and the parameters of the chemical structure of the repeating units of the polymer. The approach developed by Askadskii et al. [10] in devising a computational scheme for the estimation of the glass points of polymers was used. The initial relation for the determination of the melting point $T_m$ can be written in the form [19]

$$V_m = V_0[1 + \alpha_{cr}(T_m - T_0)] \approx V_0(1 + \alpha_{cr} T_m), \quad (15)$$

where $V_m$ is the specific volume of the polymer at the melting point, determined by the extrapolation of the dilatometric relation from temperatures $T < T_m$ to $T_m$, $V_0$ the specific volume of the crystalline polymer at the characteristic temperature $T_0$, which is approximately 6 K according to Askadskii et al. [10], and $\alpha_{cr}$ the coefficient of volume expansion of the crystalline polymer in the range of temperatures below the melting point.

Bearing in mind that $V_m/V_0 = k_{0,cr}/k_{m,cr}$, where $k_{0,cr}$ and $k_{m,cr}$ are the coefficients of molecular packing of the crystalline polymer at the temperatures $T_0$ and $T_m$ respectively, we find from Eqn. (15)

$$\frac{T_g}{T_m} = \frac{k_{0,a} - k_{g,a}}{k_{0,cr} - k_{g,a}}. \quad (16)$$

Eqn. (16) was obtained [19] from the familiar experimental observation that the coefficients of volume expansion of amorphous and crystalline polymers having the same structure are virtually identical. The quantities $k_{0,a} = 0.731$ and $k_{g,a} = 0.667$ in Eqn. (16) are constant [10].

Taking into account the additivity of the volume, the packing coefficients of crystalline polymers can be expressed in the form [19]

$$k_{0,cr} = \sum_i \Delta V_i / V = \sum_i \Delta V_i / \sum_i \frac{1}{k_i} \Delta V_i, \quad (17)$$

where $k_i$ is the partial packing coefficient of the $i$th atom, $\Delta V_i$ the increment of the van der Waals volume of the $i$th atom, and $V$ the total volume of the given body.

When account is taken of Eqn. (8), Eqn. (16) becomes

$$\frac{T_g}{T_m} = \left[ \frac{\sum_i \Delta V_i}{\sum_i \delta_i \Delta V_i} - A \right]^{-1}, \quad (18)$$

where

$$A = k_{g,a}/(k_{0,a} - k_{g,a}) = \text{const}, \quad (19)$$

$$\delta_i = (k_{0,a} - k_{g,a})/k_i. \quad (20)$$

Table 9. The parameters $\delta_i$ and $\gamma_i$ for various atoms and types of intermolecular interaction.

| Atom or type of interaction | Designation | $\delta_i$ | $\gamma_i$, Å³ |
|---|---|---|---|
| Silicon | $\delta_{Si}$ | 0.0840 | — |
| Carbon | $\delta_C$ | 0.08685 | — |
| Hydrogen | $\delta_H$ | 0.0740 | — |
| Oxygen in main chain | $\delta_{O,m}$ | 0.0621 | — |
| Oxygen in side chain | $\delta_{O,s}$ | 0.0963 | — |
| Nitrogen in main chain | $\delta_{N,m}$ | −0.0212 | — |
| Dipole-dipole interaction | $\gamma_d$ | — | −0.0727 |
| Hydrogen bond | $\gamma_h$ | — | −0.0188 |

It follows from the computational scheme described that fusion of a crystalline polymer and the transition from the vitreous state to the viscoelastic state occur when the same molecular packing coefficient $k_{g,a} = k_{m,a}$, which is equal to 2/3 for all polymers, is attained. Consequently, the fusion of crystalline and the softening of amorphous polymers of any chemical structure require a definite fraction of the free volume, equal to 0.333. The difference between $T_g$ and $T_m$ (or their ratio $T_g/T_m$) will then be determined by the difference between (or the ratio) of the packing coefficients of the amorphous ($k_{am}$) and crystalline ($k_{cr}$) polymers, which has been demonstrated independently in another study [4].

In order to determine the parameters $\delta_i$,[19] the excess system of equations derived from Eqn.(18) was solved by least squares. The results showed that a satisfactory calculation of $T_g/T_m$ (or $T_m$) requires the introduction of the parameters listed in Table 9. These parameters take into account the influence of the type of atom on the melting point. Knowing the parameters $\delta_i$, it is possible to calculate $T_g/T_m$ (or $T_m$) for a large number of polymers. The results of the analysis showed that the calculated and experimental values of $T_m$ agree as a rule to within 2–3% and that the error reaches a higher value only in a few instances (see Table 10).

Table 10. The melting points $T_m$ of polymers ($T_g$ obtained from dilatometric data).

| Polymer | $\sum_i \Delta V_i$, Å³ | $T_g$, K | $T_m$, K | |
|---|---|---|---|---|
| | | | calc. | expt. |
| Polypropylene | 51.7 | 263 | 449 | 449 |
| Polystyrene | 109.9 | 378 | 544 | 513; 523 |
| Polybut-1-ene | 68.8 | 249 | 412 | 405; 398 |
| Poly-4-methylpent-1-ene | 103.4 | 302 | 515 | 523; 508 |
| Poly-α-vinylnaphthalene | 155.4 | 453 | 626 | 633 |
| Poly(ethylene adipate) | 159.1 | 223 | 342 | 323 |
| Nylon 6,6 | 232.3 | 351 | 541 | 539 |
| Nylon 6,10 | 300.7 | 323 | 495 | 499; 488 |
| Nylon 6 | 116.15 | 323; 348 | 498 | 488; 499 |
| Nylon 11 | 201.65 | 319 | 467 | 467; 455; 448 |
| Poly(isobutyl vinyl ether) | 113 | 246 | 396 | 438 |
| Poly(ethylene oxide) | 43.8 | 206 | 348 | 339 |
| Poly(propylene oxide) | 61.3 | 198 | 323 | 340; 348 |
| Poly(styrene oxide) | 119.5 | 310 | 442 | 422 |
| Poly(tetramethylene oxide) | 77.8 | 194 | 312 | 309 |
| Poly(methyl methacrylate) | 97.05 | 318 | 466 | 433 |
| Poly(tetramethylene adipate) | 193.3 | 205 | 314 | 332 |
| Poly(trimethylene adipate) | 176.2 | 214 | 315 | 311 |
| Poly(ethyl vinyl ether) | 78.4 | 254 | 387 | 359 |
| Poly(methyl vinyl ether) | 61.0 | 260 | 399 | 417 |
| Polydimethylsiloxane | 72.09 | 150 | 234 | 234 |

## IV. OPTICAL PROPERTIES

Among the parameters of the optical properties of polymers, the refractive index $n$ is most important. The relation

$$\frac{n^2-1}{n^2+2}\cdot\frac{N_A\sum_i \Delta V_i}{k_{av}} = R = \sum_i m_i A_i r_i, \qquad (21)$$

where $k_{av}$ is the average molecular packing coefficient (for monolithic block materials, $k_{av} = 0.681$ and for films, $k_{av} = 0.695$), $R$ the molar refraction, $m_i$ the number of atoms of the $i$th kind in the repeating unit, $r_i$ the specific refraction of atoms of the $i$th kind, and $A_i$ the atomic weight, was derived[20]. It is based on the Lorenz–Lorentz equation and Eqn.(2). The relevant investigation[21] demonstrated a satisfactory agreement between the calculated and experimental refractive indices for aromatic systems (Table 11).

Another important parameter is the coefficient of optical sensitivity to stress $C_\sigma$, which is defined as the proportionality coefficient between the double refraction $\Delta n$ and the stress $\sigma$ responsible for it:

$$\Delta n = C_\sigma \sigma . \qquad (22)$$

The coefficient $C_\sigma$ is extremely sensitive to the chemical structure of the polymer. Heat resistant card polymers are particularly interesting in this respect. It was found[21] that the optical sensitivity of such systems is an order of magnitude higher than the optical sensitivity of all the polymers investigated previously. Table 12 lists the optico-mechanical properties of many polymers.

Table 11. The refractive indices of certain aromatic polymers.

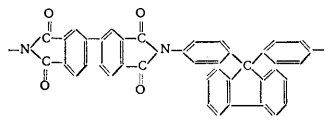
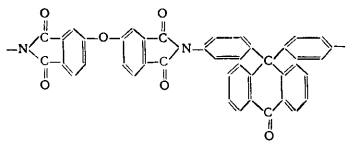
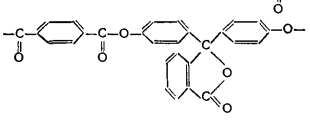
| Structure of repeating unit | Density (calc.), g cm⁻³ | $n$ | |
|---|---|---|---|
| | | calc. | expt. |
|  | 1.314 | 1.491 | 1.493 |
|  | 1.346 | 1.553 | 1.552 |
|  | 1.326 | 1.516 | 1.512 |

Table 12. The optico-mechanical properties of polymers ($E$ is the modulus of elasticity and $T_s$ the softening temperature).

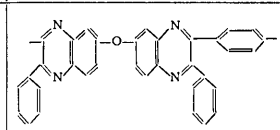
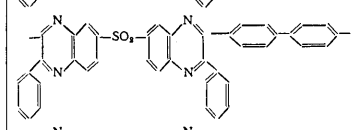
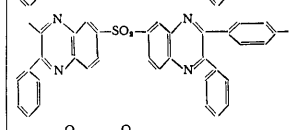
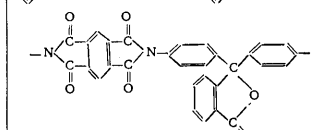
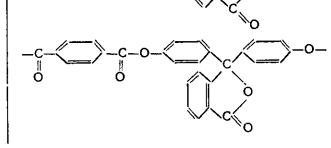
| No. | Structure of repeating unit | $T_p$, °C | $10^{-4}E$, kgf cm⁻² | $10^7 C_\sigma$, cm² kgf⁻¹ | | $N_A \cdot \sum_i \Delta V_i$, cm³ mole⁻¹ |
|---|---|---|---|---|---|---|
| | | | | expt. | calc. | |
| 1 |  | — | 1.9 | 161.1 | 156.9 | 276 |
| 2 |  | — | 1.45 | 152.0 | 142.8 | 334 |
| 3 |  | — | 1.1 | 150.1 | 150.8 | 288 |
| 4 |  | 515 | 3.1 | 111.2 | 110.7 | 245 |
| 5 |  | 320 | 2.9 | 92.7 | 85.5 | 234 |

**Table 12** (continued).

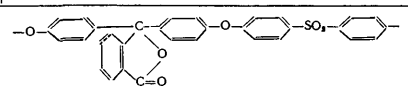
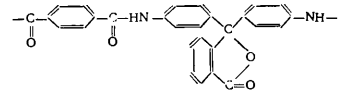
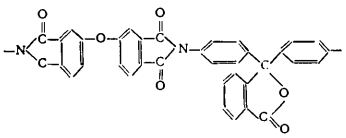
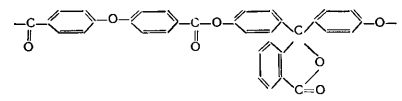
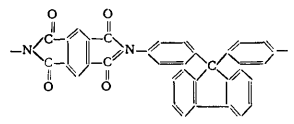
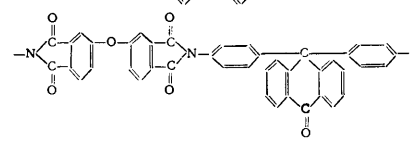
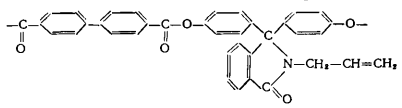
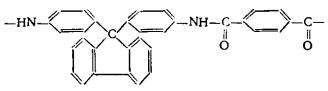
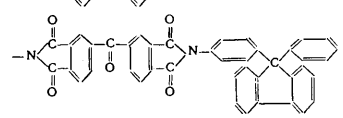
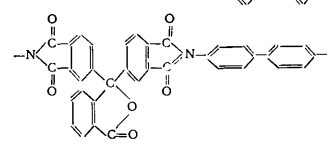
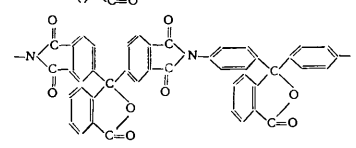
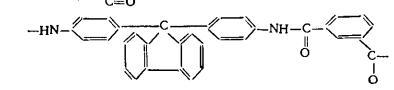
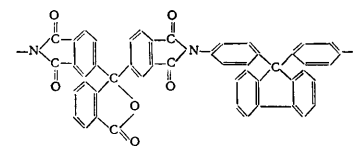
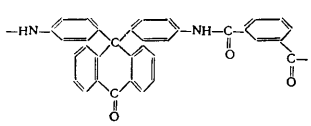
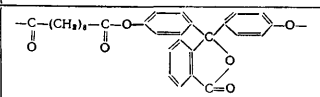
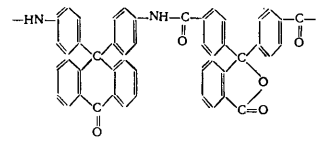
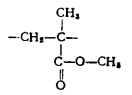
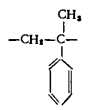
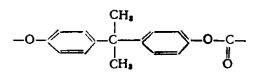
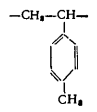
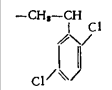
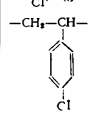
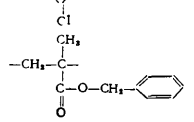
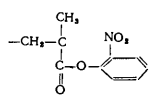
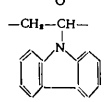
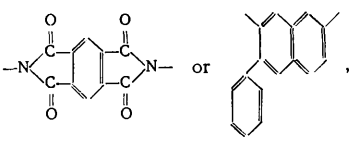
| No. | Structure of repeating unit | $T_p$, °C | $10^{-4}E$, kgf cm$^{-2}$ | $10^7 C_\sigma$, cm$^2$ kgf$^{-1}$ expt. | $10^7 C_\sigma$, cm$^2$ kgf$^{-1}$ calc. | $N_A \cdot \sum \Delta V_i$, cm$^3$ mole$^{-1}$ |
|---|---|---|---|---|---|---|
| 6 |  | — | 1.63 | 72.8 | 72.0 | 262 |
| 7 |  | — | 1.25 | 90.4 | 87.0 | 237 |
| 8 |  | 350 | 2.4 | 88.9 | 91.8 | 296 |
| 9 |  | 320 | 2.45 | 89.4 | 94.0 | 285.4 |
| 10 |  | 450 | 3.67 | 86.6 | 75.0 | 319.3 |
| 11 |  | 350—400 | 4.3 | 82.5 | 82.1 | 335.4 |
| 12 |  | 250—280 | 1.57 | 82.1 | 73.6 | 310.0 |
| 13 |  | — | 1.26 | 77.4 | 84.0 | 266.4 |
| 14 |  | 350—400 | 3.75 | 75.3 | 75.6 | 330.1 |
| 15 |  | 500 | 2.7 | 73.0 | 76.2 | 290.8 |
| 16 |  | 450 | 3.52 | 67.2 | 63.6 | 355.7 |
| 17 |  | — | 1.25 | 62.0 | 59.0 | 266.4 |
| 18 |  | 520 | 1.93 | 56.2 | 63.6 | 384,2 |
| 19 |  | — | 1.28 | 61.5 | 51,0 | 277,3 |

**Table 12** (continued).

| No. | Structure of repeating unit | $T_p$, °C | $10^{-4}E$, kgf cm$^{-2}$ | $10^7 C_\sigma$, cm$^2$ kgf$^{-1}$ expt. | $10^7 C_\sigma$, cm$^2$ kgf$^{-1}$ calc. | $N_A \cdot \sum \Delta V_i$, cm$^3$ mole$^{-1}$ |
|---|---|---|---|---|---|---|
| 20 |  | 100 | 1.50 | 55.8 | 58,7 | 271.5 |
| 21 |  | — | 1.40 | 53.0 | 60,0 | 387,6 |
| 22 |  | 80—90 | — | 10,7 | 16.9 | 66.0 |
| 23 |  | 135 | 2.10 | —3.27 | —3,99 | 58.5 |
| 24 |  | — | 3.50 | —2.04 | —9.6 | 76.6 |
| 25 |  | 150 | 1.40 | 111.0 | 115.5 | 144.3 |
| 26 |  | — | — | 15.7 | 21.5 | 76.2 |
| 27 |  | — | 3.52 | 7,3 | 13.2 | 82.6 |
| 28 |  | — | 2.65 | 22,9 | 15.3 | 74.4 |
| 29 |  | — | — | 24.5 | 22.0 | 103.9 |
| 30 |  | — | — | 22.4 | 20.0 | 104.6 |
| 31 |  | — | — | 57.5 | 57.8 | 111.7 |

The elastic mechanical behaviour of vitreous polymers, characterised by the modulus of elasticity $E$ and the glass point $T_g$, can be influenced by two factors—the rigidity of the chains and the intermolecular interaction energy. If the polymer includes groups of the type



which lead to an increase of the skeletal and kinetic rigidity, it has as a rule a high modulus of elasticity.

The high optical sensitivity of these polymers is due to their structure—the presence of a large number of condensed rings, which are characterised by a considerable anisotropy of polarisability. Compounds saturated by nitrogen and sulphur atoms and aromatic rings have the highest values of $C_\sigma$, as can be seen from Table 12.

The optical sensitivity can also be greatly influenced by the type of substitution in the aromatic ring contained in the main chain. Thus a polymer where the aromatic ring in the main chain is substituted in the *p*-position has a higher optical sensitivity than a polymer where the ring is substituted in the *m*-position (see polymers 13 and 17 in Table 12).

The presence of a large number of polar groups leads to a decrease of optical sensitivity. For a given series of polymers, this behaviour is observed in relation to the C=O group. Having a high negative anisotropy of polarisability, it reduces the overall positive effect. The fact that the C=O group is a carrier of the negative effect has also been noted by Bazhenov et al.[21]

The data compiled in Table 12 show that there is a clearly defined relation between the structure of polymers and their optico-mechanical properties, which can be expressed in quantitative terms[21]. It has been shown[21] that the variation of $C_\sigma$ with the parameters of the structure of the polymer chain can be determined by means of an additive scheme analogous to that used previously[11] to estimate the glass points.

Table 13. The increment $C_i$ for various atoms and types of intermolecular interactions.

| Atom or type of interaction | Designation | Value |
|---|---|---|
| Carbon | $C_C$ | −2.0492 |
| Hydrogen | $C_H$ | −0.5227 |
| Oxygen in main chain | $C_{O,\,m}$ | 3.198 |
| Oxygen in side group | $C_{O,\,s}$ | −0.7568 |
| Nitrogen in main chain | $C_{N,\,m}$ | 7.175 |
| Nitrogen in side group | $C_{N,\,s}$ | 1.303 |
| Chlorine | $C_{Cl}$ | −3.476 |
| Sulphur | $C_S$ | −0.790 |
| Dipole-dipole interaction* | $C_d$ | −2.512 |
| Hydrogen bond in aromatic polyamides | $C_h$ | −6.21 |
| Symmetry coefficient** | $C_n$ | 6.791 |
| Universal parameter | Π | 0.3544 |

*The coefficient $C_d$ is introduced for each polar group of any type; if there are two identical polar groups attached to the same atom, they are counted as one group. When the benzene ring is present in the substituent, the increment $C_{Ph} = -1.70$ is introduced instead of $C_d$.
**The symmetry coefficient is introduced if all the aromatic rings in the main chain are substituted in the *p*-position.

Interpretation of a large amount of experimental data led[21] to a relation between $C_\sigma$ and the parameters of the chemical structure of the repeating unit of the polymer:

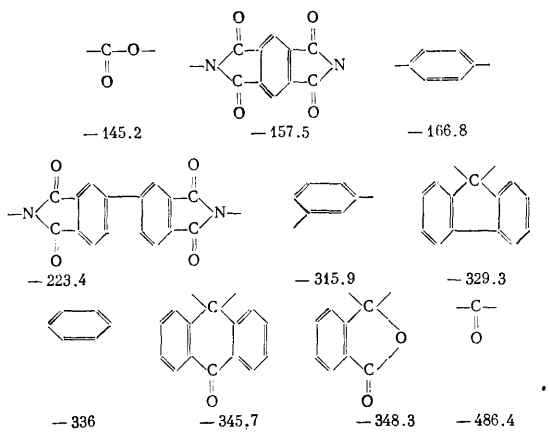
$$C_\sigma = \frac{\sum_i C_i}{N_A \sum_i \Delta V_i} + \Pi, \qquad (23)$$

where $C_i$ are increments characterising the contribution of each atom and type of intermolecular interaction to the coefficient of optical sensitivity (see Table 13).

$\Sigma V_i$ is the van der Waals volume of the repeating unit, consisting of the volumes of all the atoms in this unit, and $\Pi = 0.3544 \times 10^{-4}$ cm$^2$ kg$^{-1}$ is a universal parameter.

In order to determine the increments $C_i$, an excess system of equations, derived on the basis of Eqn.(23) for the polymers listed in Table 12, was solved[21] by the method of least squares using the matrix theory. The calculation showed[21] that, for an adequate assessment of the influence of various atoms on $C_\sigma$, it is necessary to know at least 11 increments, which are listed in Table 13.

A test of the validity of Eqn.(23) showed that the calculated values of $C_\sigma$ agree fairly satisfactorily with experimental data (Table 12). A separate calculation demonstrated that $C_{ph} = -1.700 \times 10^{-4}$ for a benzene ring in the side chain. Knowing the numerical values of $C_i$, which are listed in Table 13, it is possible to calculate the values of $C_\sigma$ for polymers incorporating the corresponding atoms. A quantitative estimate of the contribution of each group of atoms to the coefficient of optical sensitivity is also possible on the basis of Eqn.(23). This contribution is characterised by the quantity $\sum_i C_i / N_A \sum_i \Delta V_i$, and, since this ratio is negative, the highest value of $C_\sigma$ corresponds to the smallest absolute value of $\sum_i C_i / N_A \sum_i \Delta V_i$. Individual groups can be arranged in the following sequence in terms of the contribution of the ratio $\sum_i C_i / N_A \sum_i \Delta V_i$ to the coefficient of optical sensitivity (the ratios have been multiplied by $10^7$):




Thus the computational scheme described for the determination of the coefficient of optical sensitivity makes it possible to estimate the expected optical sensitivity of the polymer and has a definite practical value for the synthesis of polymers with specified properties. It is also noteworthy that the high optical sensitivity of thermostable polymers can be of great practical value when the latter are used as models in a polarisation-optical study on stresses. The disadvantages of the usual polymeric materials are, on the one hand, the occurrence of distinct relaxation processes following the application of a mechanical load, and, on the other hand, a low optical sensitivity. In order to obtain a distinct pattern of the distribution of stresses in a given structure, it is necessary to employ fairly high stresses, which are undesirable owing to the intense relaxation processes (creep and relaxation of the stress). The availability of materials with an extremely high coefficient of optical sensitivity

permits their use with comparatively small loads, for which the relaxation processes are weak and Hooke's law virtually holds.

## V. INTERMOLECULAR INTERACTION ENERGY AND SOLUBILITY

One of the principal parameters of the extent of intermolecular interaction in liquids is the density of cohesion energy, which is numerically equal to the potential energy $E/V$ of 1 $cm^3$ of the substance. For a liquid, this parameter is usually estimated from its heat of evaporation $\Delta H_v$ and is calculated by the formula

$$\delta^2 = E/V = (\Delta H_v - RT)/V \ , \qquad (24)$$

where $\delta$ is the Hildebrand solubility parameter and $V$ the molar volume of the liquid.

$\Delta H_v$ can be determined experimentally only for low-molecular-weight substances capable of evaporating without decomposition; naturally, this cannot be done for polymers. For this reason, many investigators [22-25] have attempted to calculate $\delta$ by resolving $E$ and $V$ into their constituent increments; other methods have also been proposed. However, evidently such resolution is not legitimate, since the volumes occupied by the same atom in different molecules are different owing to the differences between the molecular packing coefficients of liquids. This applies also to the cohesion energy $E$.

It has been shown [26] that the calculation of the increments of the cohesion energy density, when the latter is referred to the van der Waals (intrinsic) volume of the atoms and not to the molar volume, is physically justified in this case. For this purpose, Eqn. (24) is written [26] in the form

$$\delta^2 = \frac{Ek}{N_A \sum_i \Delta V_i} = \frac{E^*}{N_A \sum_i \Delta V_i} \ , \qquad (25)$$

where $k$ is the molecular packing coefficient of the liquid and $\sum_i \Delta V_i$ the van der Waals volume of the molecule, consisting of the van der Waals volumes of the atoms $\Delta V_i$.

Table 14. The values of $\Delta E_i^*$ for each atom and type of intermolecular interaction.

| Atom | Designation | $\Delta E_i^*$ kcal/mole | Interaction | Designation | $\Delta E_i^*$ kcal/mole |
|---|---|---|---|---|---|
| Carbon | $\Delta E_C^*$ | 550.67 | dipole-dipole | $\Delta E_d^*$ | 1623 |
| Hydrogen | $\Delta E_H^*$ | 47.71 | dipole-dipole in dipolar aprotic solvents of the amide type | $\Delta E_{a,N}^*$ | 1623 |
| Oxygen | $\Delta E_O^*$ | 142.6 | dipole-dipole in solvents of the dimethyl sulphoxide type | $\Delta E_{a,S}^*$ | 2600 |
| Nitrogen | $\Delta E_N^*$ | 1205 | hydrogen bond | $\Delta E_h^*$ | 3929 |
| Fluorine | $\Delta E_F^*$ | 24.2 | aromatic ring (skeleton) | $\Delta E_{Ph}^*$ | 713 |
| Sulphur | $\Delta E_S^*$ | 1750 | double bond | $\Delta E_{\neq}^*$ | −323 |

The quantity $E^* = Ek$ is in essence the molar cohesion energy of the liquid decreased by a factor equal to the factor by which the intrinsic molar volume of the molecule is smaller than the true molar volume. The quantity $E^*$, called the effective molar cohesion energy, has been expressed [26] as $E^* = \sum_i \Delta E_i^*$, where $\Delta E_i^*$ is the contribution of each atom and type of intermolecular interaction to $E^*$. Then

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \ . \qquad (26)$$

In order to calculate the values of $\Delta E_i^*$, an excess system of equations was derived [26] on the basis of Eqn. (26) and was solved by least squares. The results show that a sufficiently accurate calculation of the solubility parameters $\delta$ requires the introduction of the increments $\Delta E_i^*$ listed in Table 14. Knowing $\Delta E_i^*$ and $\Delta V_i$, it is possible to calculate the values of $\delta$ for organic liquids having different chemical structures. Table 15 presents as an example the calculated and experimental values of $\delta$ for many organic liquids, which are the same to a high degree of accuracy.

Table 15. The solubility parameters for solvents and polymers.

| Name | $\sum_i \Delta E_i^*$, cal mole$^{-1}$ | $N_A \sum_i \Delta V_i$, cm$^3$ mole$^{-1}$ | $\delta$, cal$^{1/2}$ cm$^{-3/2}$ | |
|---|---|---|---|---|
| | | | calc. | expt. |
| Cyclohexane | 3876 | 61.8 | 7.92 | 8.2 |
| n-Octane | 5264 | 90.1 | 7.6 | 7.55 |
| Benzene | 4303 | 53.1 | 9.0 | 9.15 |
| Toluene | 4949 | 63.3 | 8.8 | 8.9 |
| Styrene | 5177 | 69.8 | 8.61 | 8.66 |
| Perfluoro-n-pentane | 3044 | 96.4 | 5.6 | 5.5 |
| Perfluorocyclohexane | 3578 | 99.4 | 6.01 | 6.0 |
| Glycol | 9532 | 36.7 | 16.1 | 15.7 |
| Methanol | 4814 | 22.0 | 14.8 | 14.5 |
| 1-Propanol | 6106 | 42.8 | 11.9 | 11.9 |
| Acetic acid | 5307 | 33.5 | 12.6 | 12.6 |
| Ethyl formate | 3847 | 45.1 | 9.2 | 9.4 |
| Ethyl acetate | 4493 | 55.6 | 9.0 | 9.1 |
| Ethyl propionate | 5139 | 65.9 | 8.8 | 8.9 |
| Methyl acrylate | 4074 | 52.8 | 8.8 | 8.9 |
| Methyl methacrylate | 4720 | 63.3 | 8.6 | 8.7 |
| Acetone | 3704 | 39.5 | 9.7 | 10.0 |
| Acetamide | 9984 | 35.8 | 16.6 | 16.7 |
| Dimethylformamide | 6808 | 46.5 | 11.9 | 12.1 |
| Acrylonitrile | 4084 | 37.4 | 10.7 | 10.45 |
| Dimethyl sulphide | 3183 | 39.3 | 8.9 | 9.0 |
| Diethyl sulphone | 10266 | 65.7 | 12.7 | 12.5 |
| Poly(methyl methacrylate) | 5043 | 58.5 | 9.3 | 9.1; 9.5 9.4 |
| Poly(ethyl methacrylate) | 5689 | 69.0 | 9.1 | 8.95 |
| Poly(n-propyl methacrylate) | 6335 | 79.3 | 8.9 | — |
| Poly(n-butyl methacrylate) | 6981 | 89.6 | 8.8 | — |
| Poly(methyl methacrylate) | 4397 | 48.2 | 9.55 | 10.1 |
| Poly(ethyl acrylate) | 5043 | 58.5 | 9.3 | 9.4 |
| Polystyrene | 5500 | 66.0 | 9.1 | 9.1; 8.6 8.7 |
| Polyisobutylene | 2584 | 41.6 | 7.9 | 7.85; 7.8 8.05 |
| Polyacrylonitrile | 4623 | 32.6 | 11.9 | — |
| Poly(ethylene terephthalate) | 10418 | 102.4 | 10.1 | — |
| Nylon 6,6 | 18210 | 139.2 | 11.4 | — |

Fig. 6 illustrates the theoretical variation of $\delta$ with the [square root of the] ratio $\sum_i \Delta E_i^* / N_A \sum_i \Delta V_i$, on which the experimental points fit satisfactorily.

All the considerations described above permit the application of this method to the calculation of the cohesion energy density of polymers. Table 15 shows that the calculated [26] values of $\delta$ for many polymers agree with the available experimental data [27]. However, one should note that the experimental methods employed are not sufficiently accurate and the calculated values of $\delta$ may therefore prove to be more reliable.

Since the increments $\Delta E_i^*$ and $\Delta V_i$ have been determined (see above) for almost all atoms and groups in polymers of all structures, the proposed method can be used to calculate the values of $\delta$ for virtually any polymer, which is very important for the estimation of their solubilities and compatibilities with plasticisers and with one another.

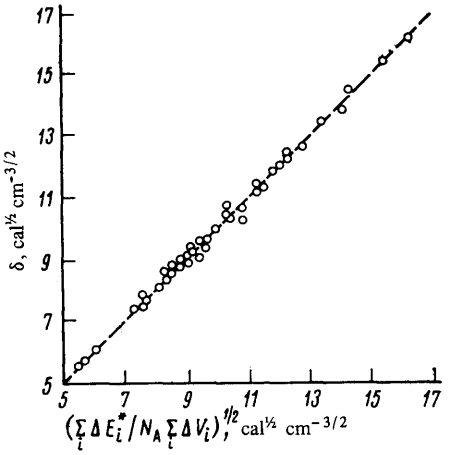



**Figure 6.** Variation of $\delta$ with [the square root of] the ratio $\sum_i \Delta E_i^* / N_A \sum_i \Delta V_i$ for low-molecular-weight liquids.

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# The Application of the Spectroscopy of Light Scattering Media in Physicochemical Research

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The theoretical and applied aspects of the spectroscopy of light scattering media are examined and approximate methods for the solution of the radiative transfer equation are described. The data obtained with the aid of certain approximations are compared with the results of accurate calculations and certain experimental light scattering data are analysed. The bibliography includes 123 references.

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## I. INTRODUCTION

In order to follow and investigate the mechanisms of a wide variety of chemical processes, optical spectroscopy is frequently used. However, its scope is most completely realised only for transparent (non-scattering) systems. On the other hand, many important chemical processes, for example catalytic, photochemical, polymerisation, etc. reactions, proceed in light-scattering media, where optical spectroscopy in its usual version developed for transparent media is inapplicable.

In a study of such processes, the optical spectroscopy of scattering media is a very important and sometimes the only physical method which can yield the required information about the course of the chemical reaction. However, despite the probable utility of the spectroscopy of light scattering media (SLM) in the solution of many physicochemical problems, it has not been adequately developed, particularly compared with the spectroscopy of transparent media. This is due to the following causes: firstly, the complexity of the mathematical description of the processes involving light transmission through scattering systems and the difficulties associated with the solution of the corresponding equations (thus the spectroscopy of transparent media involves only two parameters—optical density and the optical path length, while a light-scattering

layer is characterised, together with these parameters, also by the scattering coefficient, the angular distribution of the scattered light, and the refractive index of the layer. In real systems, the scattering coefficient and the angular structure of the scattered light may also depend on the direction of propagation of light); secondly, the lack of simple, reliable, and well founded experimental methods, which is related directly to the foregoing considerations.

In the spectroscopy of transparent media, one usually measures the optical density, which is related to the extinction coefficient and the concentration of the test substance by a simple linear expression. In SLM, the measured quantities are usually the integral reflectance ($R$) or transmittance ($T$) defined as the ratios of the amount of reflected radiation or radiation which has passed through the layer to the incident light flux. Furthermore, one can measure the angular dependence of the reflected and transmitted light as well as the angular dependence of the radiation within the medium.

Unfortunately, none of the experimentally measured quantities is linked by simple relations to the system parameters. In the general case, the measured quantity depends on the characteristics of the medium in a fairly complex manner, and this relation frequently cannot be expressed in an analytical form. Nevertheless, in terms of certain approximations, it is possible to put forward analytical relations whereby one can derive information from the experimental data about the characteristics of the medium and ultimately about the concentrations and extinction coefficients of the chemical compounds present in the scattering specimen.

There have been a number of extensive reviews and books on the theory of light scattering and its practical applications[1-13]. Some of these[1,2,11-13] are devoted mainly to the consideration of the theoretical problems of light scattering using a complex mathematical procedure. Other studies also deal with the analysis of the experimental data. However, we may note that, among these studies, only two[5,7] are specifically concerned with the application of SLM to physicochemical research, although some results of physicochemical experiments are given in the other investigations.

Analysis of the available studies[1-13] shows that there is a significant gap between the work of theoreticians and experimental chemists. Also the conditions under which particular approximate expression used in the interpretation of the experimental data are applicable are frequently not clearly defined in chemical literature.

The aim of the present review is, on the one hand, to give an account of various methods for the approximate description of light scattering processes, to indicate the limits of their applicability, and to compare the different approximate methods with one another, and, on the other hand, to demonstrate the possibility of applying these approximations to the solution of practical chemical problems.

## II. EQUATION OF RADIATIVE TRANSFER. NOTATION

Processes involving the transmission of light through scattering media are described by the integrodifferential equation of the transmission of radiation[1-3,8,9]:

$$\mu \frac{\partial I(z, \mu, \varphi)}{\partial z} = -(\alpha+\sigma) I(z, \mu, \varphi) + \frac{\sigma}{4\pi} \int_{(4\pi)} I(z, \mu', \varphi') \chi(\mu, \varphi, \mu', \varphi') \, d\mu' \, d\varphi' + Q(z, \mu, \varphi), \quad (1)$$

where $I(z, \mu, \varphi)$ is the intensity of the light beam, $z$ the coordinate, $\theta = \arccos\mu$ and $\varphi$ are the polar and azimuth angles respectively, $\alpha$ and $\sigma$ are the absorption and scattering coefficients of the volume element of the medium, the function $\chi$ specifies the angular distribution of the scattered light (the scattering indicatrix for the volume element), and the function $Q$ characterises the internal sources of photons.

The equation of radiative transfer [Eqn.(1)] reflects the change in the intensity of the light beam during its passage through a volume element of the scattering medium[2,8]. The first term on the right-hand side of the equation takes into account the weakening of the intensity owing to absorption and scattering and the second represents the contribution of the light beams incident on the volume element from all sides (these beams are characterised by variable angular coordinates $\mu'$ and $\varphi'$) and scattered with particular scattering indicatrix in the direction of the beam under consideration ($\mu$ and $\varphi$). Finally, the third term $Q(z, \mu, \varphi)$ takes into account the contribution of the internal sources of photons in the direction considered.

In the solution of practical problems, it is very important to determine from the known light fluxes the parameters of the medium: $\alpha$, $\sigma$, and $\chi$. Among all the parameters of the scattering medium, the absorption coefficient is of greatest interest in chemical research, since it is related to the concentration of the light absorbing substance $c$ by the usual expression

$$\alpha = 2.3 \varepsilon c,$$

where $\epsilon$ is the molar extinction coefficient on the decadic scale.

In view of the complexity of Eqn.(1), the procedures used for its solution involve either certain simplifying assumptions or specific experimental conditions. In particular, a generally accepted method involves the consideration of a plane-parallel layer illuminated with monochromatic light at right angles to the layer ($\mu_0 = 1$ is the cosine of the angle of incidence of the light) or with diffuse light (diffuse light is light whose intensity is independent of angular variables[14]).

In view of the planar symmetry of the problem and the selected illumination conditions (light incident at right angles or diffuse light), the intensity depends only on two variables: the coordinate $z$ at right angles to the bulk of the layer and reckoned from the upper boundary of the layer and the cosine of the angle $\mu$ between the direction of the light beam and the normal. With these assumptions, Eqn.(1) becomes[9,12]

$$\mu \frac{\partial I(z, \mu)}{\partial z} = -(\alpha+\sigma) I(z, \mu) + \frac{\sigma}{2} \int_{-1}^{1} I(z, \mu') \chi(\mu, \mu') \, d\mu' + Q(z, \mu). \quad (2)$$

A number of simplifying assumptions are usually introduced. In order to eliminate the edge effects, the dimensions of the layer and of the light source are assumed to be infinite in the $z$ = const. plane. Next, it is postulated that the layer is uniform, i.e. the parameters $\alpha$, $\sigma$, and $\chi$ are independent of the coordinates. To simplify the notation, we also assume that the layer is illuminated with a light flux having a single intensity both for light at normal incidence and for diffuse light. Finally we exclude from consideration polarisation effects, luminescence, and departure from steady-state conditions.

Although the media considered do not contain internal sources of radiation, in directional illumination one must regard the direct light quanta, i.e. quanta which penetrate

to a depth $z$ without scattering, as such sources. In this case, the function $Q$ is [1,9]

$$Q(z, \mu) = \frac{\sigma}{2} \chi(\mu) \exp[-(\alpha+\sigma)z]. \quad (3)$$

In diffuse illumination, the function $Q$ is assumed to be zero and the incident radiation is taken into account in the boundary conditions. We may note that in Eqn. (2) the quantity $I(z, \mu)$ should be understood as the intensity of scattered light only.

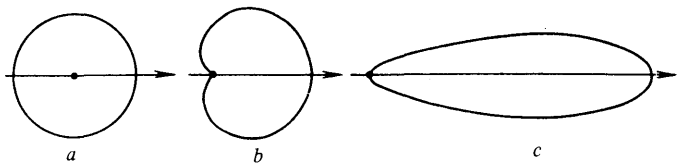



Figure 1. The scattering indicatrices of a volume element. The arrow indicates the direction of the light beam incident on the volume element (point): *a*) $\chi_1$; *b*) $\chi_2$; *c*) $\chi_3$.

Fig. 1 illustrates certain scattering indicatrices of the volume element described by the following expressions:

$$\chi_1 = 1, \ \chi_2 = 1+\mu, \ \chi_3 = 0.21/(1.1-\mu)^2. \quad (4)$$

We may note that the scattering indicatrices are normalised:

$$\frac{1}{2}\int_{-1}^{1} \chi(\mu) \, d\mu = 1.$$

For the practical analysis of data obtained with the aid of SLM, it is necessary to define the relation between the experimental quantities $R$ and $T$ and the characteristics of the layer. The coefficients $R$ and $T$ are related to the light fluxes directed along the $z$ axis $[F_1(z)]$ and in the opposite direction $[F_2(z)]$:

$$R = F_2(0), \ T = F_1(l), \quad (5)$$

where $l$ is the thickness of the layer and the fluxes are defined as follows:

$$F_1(z) = \int_0^1 I(z, \mu) \mu \, d\mu, \quad F_2(z) = -\int_{-1}^0 I(z, \mu) \mu \, d\mu. \quad (6)$$

The minus sign of $F_2$ was chosen so that the flux should be positive. We may point out that Eqn. (5) for the coefficient $T$ is valid only for diffuse illumination, while in directed illumination it must be supplemented by the term $\exp[-(\alpha+\sigma)z]$ taking into account the direct light which has passed through the layer. Thus, in order to relate the coefficients $R$ and $T$ to the parameters of the layer, it is necessary to know the light fluxes emerging from the layer, which may be found by solving Eqn. (2). However, this problem is mathematically very difficult and algorithms for its solution have been developed only in relatively simple cases and largely in a numerical form [1-3,8-12].

Approximate methods for the solution of the radiative transfer equation therefore play an important role and an advantage of some of them is the possibility of obtaining a solution in an analytical form. Physically reasonable postulates and agreement with the results of the accurate numerical solution of the radiative transfer equation should serve as the criteria of the accuracy of the approximate methods.

In conclusion, we may point out that the characteristics of the medium are sometimes formulated in the form of the following relations: the attenuation factor:

$$k = \alpha + \sigma,$$

the probability of the survival of a quantum in a single scattering step or the albedo of a single scattering step:

$$\Lambda = \sigma/(\alpha+\sigma),$$

the coefficient of the specific absorption of the layer:

$$\beta = \alpha/\sigma,$$

and the optical thickness of the layer

$$\tau_0 = \int_0^l (\alpha+\sigma) \, dz = k l.$$

In considering the instances of the illumination of the layer by diffuse light, we shall henceforth use the superscript (or subscript) $d$ in all the expressions and the coefficients for layers with a refractive index $N$ differing from unity will be formulated thus: $R(N)$ and $T(N)$.

## III. THE TWO-FLUX APPROXIMATION METHOD

The two-flux approximation method is one of the simplest and most widely used approximation procedures, the main idea of which is as follows. One considers the light fluxes $F_1$ and $F_2$ [see Eqn. (6)], whereupon the radiative transfer equation is replaced by a system of differential equations, which is solved with certain additional postulates. We shall consider the principal features of the two-flux approximation method.

### 1. Diffuse Illumination of the Layer

Suppose that the layer is illuminated by diffuse light and $Q(z, \mu) = 0$. We integrate Eqn. (2) with respect to the upper and lower hemispheres, i.e. the integral is evaluated with respect to $d\mu$ from $-1$ to 0 and from 0 to 1. We obtain as a result a system of equations for the fluxes $F_1$ and $F_2$: [8,9]

$$\frac{dF_1(z)}{dz} = -\frac{\alpha+\sigma\psi_1(z)}{\nu_1(z)} F_1(z) + \frac{\sigma\psi_2(z)}{\nu_2(z)} F_2(z),$$
$$\frac{dF_2(z)}{dz} = \frac{\alpha+\sigma\psi_2(z)}{\nu_2(z)} F_2(z) - \frac{\sigma\psi_1(z)}{\nu_1(z)} F_1(z). \quad (7)$$

$$\nu_1(z) = \frac{\int_0^1 I(z, \mu) \mu \, d\mu}{\int_0^1 I(z, \mu) \, d\mu}, \quad \nu_2(z) = -\frac{\int_{-1}^0 I(z, \mu) \mu \, d\mu}{\int_{-1}^0 I(z, \mu) \, d\mu}. \quad (8)$$

The following notation has been introduced here: the average cosines of the angles of inclination of the light beams (the minus sign of $\nu_2$ was chosen so that $\nu_2$ is positive)

$$\psi_1(z) = \frac{1}{2} \frac{\int_0^1 I(z, \mu') \, d\mu' \int_{-1}^0 \chi(\mu, \mu') \, d\mu}{\int_0^1 I(z, \mu') \, d\mu'}, \quad (9)$$

$$\psi_2(z) = \frac{1}{2}\frac{\int_{-1}^{0} I(z,\mu')\,d\mu' \int_{0}^{1} \chi(\mu,\mu')\,d\mu}{\int_{-1}^{0} I(z,\mu')\,d\mu'}$$

are the components of the light flux scattered by an infinitessimal layer (for its illumination from above and below respectively) backwards in relation to the entire scattered light. We may note that, when the light intensity in the layer is diffuse, then $\nu_1 = \nu_2 = 0.5$ and $\psi_1(z) = \psi_2(z)$.

All the numerous versions of the two-flux approximation reduce to the different selections of the functions $\nu_i(z)$ and $\psi_i(z)$ ($i$ = 1 or 2) and the solution of Eqns.(7) with the corresponding boundary conditions. This problem has already been discussed in detail [9]. However, in most cases in the interpretation of the experimental data one uses the two-parameter equation of the two-flux approximation (TFA) in which it is assumed *a priori* that the following conditions hold: $\nu_1 = \nu_2 = \nu$ and $\psi_1 = \psi_2 = \psi$. [3,9] We may note that such averaging of the quantities defined by Eqns.(8) and (9) with respect to the thickness of the layer is justified only when the bulk-phase conditions obtain and only far from the boundaries of the layer [9].

The boundary conditions for Eqn.(7) in TFA are chosen in the form [9] ($N$ = 1)

$$F_1(0) = 1,\ F_2(l) = 0. \tag{10}$$

The solution of Eqns.(7) with the boundary conditions (10) makes it possible to find the coefficients $R$ and $T$ [Eqns. (5)] [8,9]

$$R_d = \frac{[1-\exp(-2al)]\,R_\infty^d}{1-(R_\infty^d)^2\cdot\exp(-2al)},$$
$$T_d = \frac{[1-(R_\infty^d)^2]\exp(-al)}{1-(R_\infty^d)^2\exp(-2al)}, \tag{11}$$
$$R_\infty^d = 1+\frac{\alpha}{\sigma\psi}-\left[\left(\frac{\alpha}{\sigma\psi}\right)^2+2\frac{\alpha}{\sigma\psi}\right]^{1/2}.$$

Here $R_\infty^d$ is the reflectance of an infinitely thick layer and $a$ is the attenuation coefficient under bulk-phase conditions defined by

$$a = \frac{1}{\nu}[\alpha(\alpha+2\sigma\psi)]^{1/2}.$$

Similar expressions have been obtained by Gurevic [15].

Eqns.(11) are known in the literature as the Gurevic–Kubelka–Munk (G–K–M) relations [5,9]. The Kubelka–Munk (K–M) function can be readily obtained from them:

$$f(R_\infty^d) = (1-R_\infty^d)^2/(2R_\infty^d) = \alpha/(\sigma\psi). \tag{12}$$

The TFA formulae (11) and (12) are widely used in the interpretation of the experimental data. However, unfortunately many workers ignore the multiplier $1/\psi$ and use the G–K–M relations for directed illumination of the layer, although the relations can be obtained only for the layer illuminated with diffuse light.

Zege [9] examined in detail the possibility of applying the TFA formulae to the description of the light-scattering properties of a planar layer and arrived at the following conclusion as a result of comparison with data derived by the numerical solution of Eqn.(2) and also as a result of extrapolation to the bulk-phase light conditions in weakly absorbing media. When the parameters $\nu$ and $\psi$ were chosen in the form

$$\nu = 0.5,\quad \psi = \frac{3}{8}(1-\bar{\mu}), \tag{13}$$

where $\bar{\mu}$, defined by the expression

$$\bar{\mu} = \frac{1}{2}\int_{-1}^{1}\chi(\mu)\,\mu\,d\mu, \tag{14}$$

is the cosine of the scattering angle averaged with respect to the scattering indicatrix of the volume element, calculation by the TFA formulae (12) agrees with the results of the accurate calculation with an accuracy sufficient for practical purposes (the relative error is less than 10%). We may note that, for isotropic scattering ($\chi_1$), $\psi \simeq 3/8$ was also obtained in other investigations [16,17]. Henceforth in calculations employing TFA formulae we shall likewise select the parameters $\nu$ and $\psi$ defined by Eqns. (13).

Mention should also be made of the criterion imposed on the degree of extension of the scattering indicatrix of the volume element for which the TFA relations are valid [9]:

$$\frac{(8\psi_d q-1)^2}{8\psi_d q} \ll 1, \tag{15}$$

where

$$\psi_d = \frac{1}{2}\int_{0}^{1}\int_{-1}^{0}\chi(\mu,\mu')\,d\mu\,d\mu',\quad q = \frac{1}{3(1-\bar{\mu})}. \tag{16}$$

Evaluation of the left-hand side of inequality (15) for the scattering indicatrices of the volume elements $\chi_1$, $\chi_2$, and $\chi_3$ yields 0.08, 0.17, and 0.64 respectively. Thus, for layers with the indicatrix $\chi_3$, one may expect a less satisfactory agreement of the results of approximate calculations with accurate data compared with the calculations for the layers with $\chi_1$ and $\chi_2$ for which the criterion defined by formula (15) may be regarded as valid.

We shall now consider a scattering layer the refractive index of which is different from that of the surrounding medium. To simplify the treatment, we shall assume that the layer has optically smooth interfaces. The deviation of the refractive index of the layer from unity must be taken into account in the boundary conditions, since in this case the light flux supplied to the boundary no longer emerges from the layer in its entirety. This is due to the reflection of the light from the boundaries of the layer, the main contribution arising from the effect of the total internal reflection. In addition, we shall introduce yet another simplification, namely we shall assume that the light approaching the boundary from within the layer is diffuse.

We introduce the following notations for a layer with optically smooth boundaries: the coefficient $\rho$ of reflection from the boundary of the diffuse light incident on the layer from outside and the reflectance $r$ of the light incident on the boundary and directed outward from the layer. Explicit expressions for the coefficient $\rho$ and the relation between $\rho$ and $r$ have been given, for example, by Gershun [14].

When account is taken of the refractive index, the boundary conditions become [14]

$$F_1(0) = 1-\rho+rF_2(0),\ F_2(l) = r\cdot F_1(l).$$

The reflectance and transmittance are defined as follows:

$$R_d(N) = \rho+(1-r)F_2(0),\quad T_d(N) = (1-r)F_1(l). \tag{17}$$

Eqns.(17) have been published in an explicit form [14,18,19] and we shall merely formulate the coefficient of reflection for a semi-infinite layer:

$$R_\infty^d(N) = 1-(1-\rho)(1-R_\infty^d)/(1-rR_\infty^d),$$

where $R_\infty^d$ is described by Eqn.(11).

For weakly absorbing layers, the asymptotic relation between $1/T_d(N)$ and the thickness of the layer may be found from the TFA formulae. The intercept which this straight line makes on the ordinate axis is $(1+r)/(1-\rho)$. This is qualitatively consistent with Gurevic's data [14] for the transmission of light through weakly absorbing milky glasses (Fig. 2).

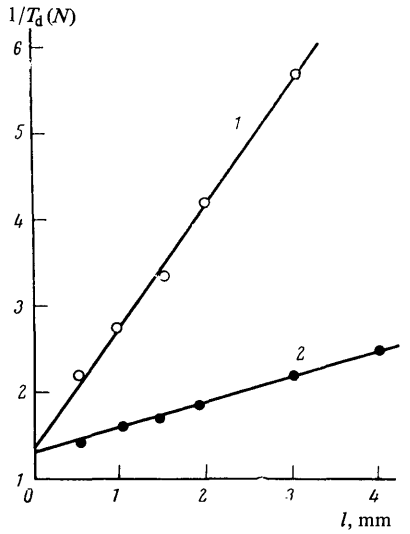



Figure 2. Dependence of $1/T_d(N)$ on the thickness of the layer (diffuse illumination): 1) highly opalescent (dense) milky glass [14]; 2) weakly opalescent milky glass [14].

## 2. Layers Illuminated with a Light Flux at Right Angles

The problem of the transmission of a directed light beam through a scattering layer is of practical importance. In this case Eqns. (7) are supplemented by terms taking into account the internal sources of photons [Eqn. (3)]. The solution of such equations for a layer with $N = 1$ and the boundary conditions

$$F_1(0)=0,\ F_2(l)=0$$

leads to the following expressions for the coefficients defined by Eqns. (5): [9]

$$\begin{aligned} T &= c_1 T_d + (1-c_1+c_2R_d)\exp(-(\alpha+\sigma)l), \\ R &= c_1R_d + c_2T_d\exp(-(\alpha+\sigma)l) - c_2, \\ R_\infty &= c_1R_\infty^d - c_2, \end{aligned} \qquad (18)$$

where the coefficients $R_d$, $T_d$, and $R_\infty^d$ are defined by Eqns. (11) and the parameters $C_1$ and $C_2$ satisfy the following equations when account is taken of Eqn. (13):

$$c_1=\frac{(1-\omega)(3\beta+1)+2\psi}{1+2\beta(1-4\psi)-3\beta^2},\quad c_2=\frac{\omega(\beta-1)+2\psi}{1+2\beta(1-4\psi)-3\beta^2}; \qquad (19)$$

the quantity $\omega$ is defined by the expression

$$\omega=\frac{1}{2}\int_{-1}^{0}\chi(\mu)\,d\mu.$$

Zege [9] suggests that, as for diffuse illumination, the quantities $\nu$ and $\psi$ should be defined by Eqns. (13). Calculations carried out on this assumption within the framework of TFA are presented in Tables 1–5, which show that the proposed TFA version gives rise to a satisfactory accuracy of the calculation of the coefficients $R$ and $T$ for different scattering indicatrices over a wide range of variation of $\beta$.

Table 1. The coefficients $R$ and $T$ for a planar layer ($\chi_1 = 1$, $\mu_0 = 1$, $N = 1$).

| $\tau_s$ | Exact calculation | | TFA [Eqn.(18)] | | $P_1$ [Eqn.(30)] | |
|---|---|---|---|---|---|---|
| | $R$ | $T$ | $R$ | $T$ | $R$ | $T$ |
| | | | $\Lambda=0.95$ | | | |
| 0.5 | 0.185 | 0.781 | 0.186 | 0.784 | 0.186 | 0.784 |
| 2 | 0.429 | 0.409 | 0.433 | 0.418 | 0.433 | 0.419 |
| 5 | 0.525 | 0.128 | 0.533 | 0.130 | 0.533 | 0.131 |
| | | | $\Lambda=0.9$ | | | |
| 0.5 | 0.169 | 0.765 | 0.172 | 0.770 | 0.172 | 0.770 |
| 2 | 0.362 | 0.357 | 0.371 | 0.366 | 0.371 | 0.368 |
| 5 | 0.413 | 0.077 | 0.423 | 0.077 | 0.424 | 0.078 |
| | | | $\Lambda=0.7$ | | | |
| 0.5 | 0.115 | 0.714 | 0.121 | 0.721 | 0.121 | 0.721 |
| 2 | 0.197 | 0.241 | 0.211 | 0.247 | 0.212 | 0.250 |
| 5 | 0.209 | 0.023 | 0.219 | 0.021 | 0.220 | 0.023 |

Table 2. The coefficients $R_\infty$ for a planar layer ($\chi_1 = 1$, $\mu_0 = 1$, $N = 1$).

| $\Lambda$ | Exact calculation (Ref.31) | TFA [Eqn.(18)] | $P_1$ [Eqn.(31)] | $\Lambda$ | Exact calculation (Ref.31) | TFA [Eqn.(18)] | $P_1$ [Eqn.(31)] |
|---|---|---|---|---|---|---|---|
| 0.9999 | 0.972 | 0.972 | 0.972 | 0.8 | 0.285 | 0.296 | 0.297 |
| 0.999 | 0.913 | 0.913 | 0.914 | 0.7 | 0.209 | 0.219 | 0.220 |
| 0.9975 | 0.866 | 0.866 | 0.868 | 0.6 | 0.055 | 0.164 | 0.165 |
| 0.995 | 0.817 | 0.817 | 0.819 | 0.5 | 0.115 | 0.123 | 0.124 |
| 0.99 | 0.753 | 0.756 | 0.756 | 0.4 | 0.083 | 0.089 | 0.090 |
| 0.975 | 0.641 | 0.647 | 0.647 | 0.3 | 0.057 | 0.061 | 0.062 |
| 0.95 | 0.536 | 0.544 | 0.544 | 0.2 | 0.035 | 0.038 | 0.039 |
| 0.9 | 0.415 | 0.425 | 0.425 | 0.1 | 0.016 | 0.018 | 0.018 |

Table 3. The coefficients $R_\infty$ for a planar layer with $\chi_2 = 1+\mu$, $\mu_0 = 1$, and $N = 1$.

| $\Lambda$ | Exact calculation (Ref.31) | TFA [Eqn.(21)] | $P_1$ [Eqn.(36)] | TA with $m = 1.8$ [Eqn.(38)] | |
|---|---|---|---|---|---|
| | | | | TFA [Eqn.(21)] | $P_1$ [Eqn.(32)] |
| 0.999 | 0.894 | 0.895 | 0.895 | 0.886 | 0.886 |
| 0.995 | 0.779 | 0.781 | 0.781 | 0.767 | 0.767 |
| 0.99 | 0.703 | 0.706 | 0.706 | 0.691 | 0.691 |
| 0.975 | 0.573 | 0.579 | 0.579 | 0.564 | 0.564 |
| 0.95 | 0.455 | 0.464 | 0.463 | 0.451 | 0.452 |
| 0.9 | 0.327 | 0.338 | 0.336 | 0.331 | 0.332 |
| 0.8 | 0.200 | 0.213 | 0.210 | 0.212 | 0.214 |
| 0.7 | 0.133 | 0.146 | 0.142 | 0.148 | 0.149 |
| 0.6 | 0.091 | 0.103 | 0.099 | 0.170 | 0.108 |
| 0.5 | 0.062 | 0.073 | 0.069 | 0.077 | 0.078 |
| 0.4 | 0.041 | 0.051 | 0.047 | 0.054 | 0.055 |
| 0.2 | 0.015 | 0.020 | 0.018 | 0.022 | 0.023 |

We shall now turn to the consideration of a scattering layer with optically smooth interfaces and $N \neq 1$. We introduce the following notation: the coefficient of the specular reflection of the beam illuminating the layer

$\rho_{sp} = (N-1)^2/(N+1)^2$ and the coefficient of reflection of the light directed from the layer to the outside $r$. As before, $r$ may be calculated from Gershun's formulae[14] on the assumption that the light incident on the boundary from inside is diffuse.

Table 4. The coefficients $R$ and $T$ for a planar layer ($\chi_2 = 1 + \mu$, $\mu_0 = 1$, $N = 1$).

| $\tau_0$ | Exact calcn. (Ref.9) | | TFA [Eqn.(18)] | | TA with $m$ = 1.8 [Eqn.(38)] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | TFA [Eqn.(18)] | | $P_1$ [Eqn.(30)] | |
| | $R$ | $T$ | $R$ | $T$ | $R$ | $T$ | $R$ | $T$ |
| | | | | $\Lambda=0.95$ | | | | |
| 0.5 | 0.092 | 0.835 | 0.111 | 0.859 | 0.113 | 0.859 | 0.113 | 0.860 |
| 2 | 0.309 | 0.505 | 0.323 | 0.527 | 0.304 | 0.565 | 0.304 | 0.565 |
| | | | | $\Lambda=0.9$ | | | | |
| 0.5 | 0.084 | 0.817 | 0.102 | 0.840 | 0.103 | 0.842 | 0.103 | 0.842 |
| 2 | 0.252 | 0.444 | 0.269 | 0.462 | 0.257 | 0.506 | 0.257 | 0.506 |
| | | | | $\Lambda=0.7$ | | | | |
| 0.5 | 0.055 | 0.759 | 0.069 | 0.773 | 0.072 | 0.778 | 0.072 | 0.778 |
| 2 | 0.121 | 0.298 | 0.137 | 0.301 | 0.138 | 0.346 | 0.139 | 0.349 |

Table 5. The coefficients $R$ and $T$ for a planar layer [$\chi_3 = 0.21/(1.1-\mu)^2$, $\mu_0 = 1$, $N = 1$].

| $\tau$ | Exact calcn. | | TFA [Eqn.(18)] | | TA with $m$ = 6.86 [Eqn.(38)] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | TFA [Eqn.(18)] | | $P_1$ [Eqn.(30)] | |
| | $R$ | $T$ | $R$ | $T$ | $R$ | $T$ | $R$ | $T$ |
| | | | | $\Lambda=0.95$ | | | | |
| 2 | 0.101 | 0.766 | 0.133 | 0.709 | 0.106 | 0.788 | 0.106 | 0.788 |
| 5 | 0.197 | 0.453 | 0.248 | 0.383 | 0.185 | 0.546 | 0.185 | 0.547 |
| 10 | 0.240 | 0.177 | 0.282 | 0.136 | 0.230 | 0.284 | 0.230 | 0.287 |
| | 0.244 | | 0.291 | | 0.242 | | 0.243 | |
| | | | | $\Lambda=0.9$ | | | | |
| 2 | 0.077 | 0.683 | 0.108 | 0.642 | 0.088 | 0.714 | 0.088 | 0.714 |
| 5 | 0.127 | 0.325 | 0.169 | 0.247 | 0.134 | 0.418 | 0.134 | 0.418 |
| 10 | — | — | 0.179 | 0.051 | 0.148 | 0.158 | 0.149 | 0.161 |
| ∞ | — | — | 0.182 | | 0.150 | | 0.151 | |
| | | | | $\Lambda=0.7$ | | | | |
| 2 | 0.038 | 0.452 | 0.044 | 0.381 | 0.044 | 0.484 | 0.044 | 0.485 |
| 5 | 0.036 | 0.103 | 0.049 | 0.058 | 0.050 | 0.154 | 0.051 | 0.151 |
| 10 | 0.036 | 0.009 | 0.052 | — | 0.050 | 0.021 | 0.051 | 0.022 |
| ∞ | 0.036 | | 0.053 | | 0.050 | | 0.051 | |

The boundary conditions for the equations describing the fluxes for directional illumination are as follows:

$$F_1(0) = rF_2(0), \quad F_2(l) = rF_1(l). \tag{20}$$

Reflectance and transmittance can be formulated by analogy with Eqns.(17), but in the expression for the coefficient $T(N)$ account must be taken of the direct light quanta which have passed through the layer. In particular, the coefficient $R_\infty(N)$ assumes the following form in this case:

$$R_\infty(N) = \rho_{sp} + (1-\rho_{sp})(1-r)\left[\frac{(c_1 - rc_2)R_\infty^d}{1 - rR_\infty^d} - c_2\right]. \tag{21}$$

All the quantities in this formula were defined above [see Eqns.(11) and (19)]. Some of the values of $R_\infty(N)$ calculated from Eqn.(21) are listed in Tables 6 and 7 and their comparison with the results of the numerical solution of Eqn.(2) demonstrates a satisfactory agreement.

Table 6. The coefficients $R_\infty(N)$ for a planar layer with an optically smooth surface ($\chi_1 = 1$, $\mu_0 = 1$, $N = 1.5$).

| $\Lambda$ | Exact calculation (Ref.31) | TFA [Eqn.(21)] | $P_1$ [Eqn.(32)] | $\Lambda$ | Exact calculation (Ref.31) | TFA [Eqn.(21)] | $P_1$ [Eqn.(32)] |
|---|---|---|---|---|---|---|---|
| 0.999 | 0.841 | 0.846 | 0.846 | 0.7 | 0.129 | 0.148 | 0.147 |
| 0.995 | 0.691 | 0.702 | 0.702 | 0.6 | 0.102 | 0.118 | 0.117 |
| 0.99 | 0.602 | 0.617 | 0.617 | 0.5 | 0.084 | 0.097 | 0.096 |
| 0.975 | 0.469 | 0.489 | 0.488 | 0.4 | 0.071 | 0.080 | 0.080 |
| 0.95 | 0.361 | 0.386 | 0.385 | 0.3 | 0.061 | 0.067 | 0.067 |
| 0.9 | 0.260 | 0.286 | 0.285 | 0.2 | 0.052 | 0.057 | 0.056 |
| 0.8 | 0.172 | 0.195 | 0.194 | 0.1 | 0.046 | 0.048 | 0.047 |

Table 7. The coefficients $R_\infty(N)$ for planar layer with an optically smooth surface ($\chi_2 = 1 + \mu$, $\mu_0 = 1$, $N = 1.5$).

| $\Lambda$ | Exact calculation (Ref.31) | TFA [Eqn.(21)] | $P_1$ [Eqn.(36)] | TA with $m$ = 1.8 [Eqn.(38)] | |
|---|---|---|---|---|---|
| | | | | TFA [Eqn.(21)] | $P_1$ [Eqn.(32)] |
| 0.999 | 0.811 | 0.816 | 0.816 | 0.802 | 0.802 |
| 0.995 | 0.639 | 0.651 | 0.651 | 0.631 | 0.631 |
| 0.99 | 0.542 | 0.558 | 0.558 | 0.537 | 0.537 |
| 0.975 | 0.400 | 0.423 | 0.422 | 0.404 | 0.404 |
| 0.95 | 0.294 | 0.320 | 0.318 | 0.306 | 0.305 |
| 0.9 | 0.197 | 0.226 | 0.223 | 0.218 | 0.217 |
| 0.8 | 0.121 | 0.147 | 0.144 | 0.145 | 0.144 |
| 0.7 | 0.087 | 0.110 | 0.106 | 0.110 | 0.109 |
| 0.5 | 0.057 | 0.073 | 0.070 | 0.074 | 0.074 |

In concluding this Section, we shall formulate the expression defining the coefficients $R(N)$ and $T(N)$ for a non-absorbing layer ($\alpha = 0$):

$$R(N) = 1 - T(N) = \rho_{sp} + (1-\rho_{sp})\left(1 - \frac{2p + (8\psi - 4\omega - p + 2)(1 - \exp(-\sigma l))}{8\sigma\psi l + 2p}\right), \tag{22}$$

where

$$p = 2(1+r)/(1-r). \tag{23}$$

## IV. THE DIFFUSION APPROXIMATION

The diffusion approximation method is also widely used in practical calculations[12,20-27]. It is a special case of the $P_n$ approximation, the essential feature of which is as follows. The functions $I$, $\chi$, and $Q$ at each point in the scattering medium are expanded in series in Legendre polynomials, the expansions being limited to the $n$th term. They are then substituted in the radiative transfer equation and, having multiplied the latter in succession by the Legendre polynomials ranging from $P_0$ to $P_n$, we carry out the integration with respect to the angular variable $\mu$ from $-1$ to 1. We obtain as a result a system of $n+1$ first-order differential equations, which may be solved with the appropriate boundary conditions.

The diffusion approximation is the lowest-order approximation ($P_1$). It has been used successfully in the description of the diffusion of neutrons[20-24] and of light scattering[25-28]. We shall now consider certain specific instances.

1. Isotropic Scattering; $\mu_0 = 1$, $N = 1$

The light intensity is represented by an expansion in terms of the first two Legendre polynomials ($P_0 = 1$, $P_1 = \mu$):

$$I(z, \mu) = \frac{1}{2}[n(z)c + 3\mu F(z)]. \quad (24)$$

The coefficients of the expansion have a simple physical significance[25]: $n(z)$ is the concentration of the diffusing quanta, $F(z)$ is their overall flux, and $c$ is the velocity of light.

The applicability of the $P_1$ approximation depends on how well the intensity can be represented by a linear function of $\mu$; this condition is equivalent to the inequality $n(z)c \gg F(z)$. In particular, this should hold for a virtually isotropic light intensity distribution (a non-absorbing medium with isotropic scattering)[3].

In conformity with the above procedure, we obtain the following system of equations:

$$\frac{dF}{dz} + \alpha cn - \sigma \exp(-(\alpha+\sigma)z) = 0$$
$$F = -\frac{c}{3(\alpha+\sigma)}\frac{dn}{dz}. \quad (25)$$

The second equation (25) resembles the form of Fick's law for diffusion in a gas and relates the light flux to the density gradient (this is the reason for the term diffusion approximation). The diffusion coefficient $D$ in isotropic scattering is

$$D = c/3(\alpha+\sigma),$$

in agreement with the ideas of the gas-kinetic theory[29] on the assumption that the mean free path in the transport process is $1/(\alpha + \sigma)$. Clearly, the consideration of the diffusion of photons is significant only for weakly absorbing media ($\beta \ll 1$).

After eliminating the function $F(z)$ from Eqn.(25) we pass to the steady-state diffusion equation for diffusing quanta:

$$D\frac{d^2n}{dz^2} - \alpha cn + \sigma \exp(-(\alpha+\sigma)z) = 0. \quad (26)$$

We may note that Eqn.(26) may be obtained directly from general considerations when light scattering processes are treated as the diffusion of photons within the framework of the gas diffusion theory. In this case, the second term of Eqn.(26) describes the disappearance of quanta with a rate constant $\alpha c$, and the third term describes the generation of the diffusing quanta from the direct beam as a result of scattering.

According to Eqns.(6) and (24), the expressions for the fluxes are

$$F_1 = \frac{nc}{4} - \frac{D}{2}\frac{dn}{dz}, \quad F_2 = \frac{nc}{4} + \frac{D}{2}\frac{dn}{dz}, \quad (27)$$

and the boundary conditions (17) become

$$\frac{nc}{2}\Big|_{z=\begin{cases}0\\l\end{cases}} = \pm D\frac{dn}{dz}\Big|_{z=\begin{cases}0\\l\end{cases}}. \quad (28)$$

The solution of Eqn.(26) can be formulated thus:

$$n = A\exp(-az) + B\exp(az) + E\exp(-(\alpha+\sigma)z), \quad (29)$$

where

$$A = \frac{E}{3\Delta}[-5(1+b)\exp(al) + (1-b)\exp(-(\alpha+\sigma)l)],$$
$$B = \frac{E}{3\Delta}[5(1-b)\exp(-al) - (1+b)\exp(-(\alpha+\sigma)l)],$$
$$a = [3\alpha(\alpha+\sigma)]^{1/2}, \quad b = 2[\alpha/3(\alpha+\sigma)]^{1/2},$$
$$E = -3\sigma/c(\sigma-2\alpha),$$
$$\Delta = (1+b)^2\exp(al) - (1-b)^2\exp(-al).$$

The coefficients $R$ and $T$ are defined on the basis of Eqns. (5) and (27):

$$R = \frac{c}{2}[A+B+E],$$
$$T = \frac{c}{2}\left[A\exp(-al) + B\exp(al) + \left(E + \frac{2}{c}\right)\exp(-(\alpha+\sigma)l)\right], \quad (30)$$

and the expression for the coefficient $R_\infty$ is fairly simple:

$$R_\infty = \left[1 + 3\beta + \frac{5}{3}(3\beta(1+\beta))^{1/2}\right]^{-1}. \quad (31)$$

It is of interest to compare results of the calculation using the $P_1$ approximation with the results of the exact calculation. This is done in Tables 1 and 2, which show that the coefficients $R$ and $T$, calculated in terms of the $P_1$ approximation with the boundary conditions (28), agree satisfactorily with the results of the exact solution of the radiative transfer equation and virtually agree with the TFA version.

2. Allowance for the Refractive Index. Isotropic Scattering ($\mu_0 = 1$)

We shall consider a scattering layer with optically smooth interfaces and $N \neq 1$. As before, the influence of the refractive index will be taken into account in the boundary conditions (20). Retaining the notation introduced in the previous section, the boundary conditions (20) will be reformulated as follows by simple transformations taking into account Eqn.(27):

$$\frac{nc}{p}\Big|_{z=\begin{cases}0\\l\end{cases}} = \pm D\frac{dn}{dz}\Big|_{z=\begin{cases}0\\l\end{cases}},$$

where $p$ is defined by Eqn.(23). The expression for $R_\infty(N)$ then assumes the following form:

$$R_\infty(N) = \rho_{sp} + (1-\rho_{sp})/[1 + (1+p)\beta + (1+p/3)(3\beta(1+\beta))^{1/2}]. \quad (32)$$

The main contribution to the coefficient $r$ comes from the effect of the total internal reflection. Taking only this into account and assuming that the light incident on the layer boundary from the inside is diffuse, it is easy to find[30]

$$r = 1 - 1/N^2. \quad (33)$$

The exact expression for the reflectance of diffuse light with allowance for Frenel's formulae is[14,31,32]

$$r = 1 - \frac{1}{N^2}\left[1 - \frac{3N^8 - 10N^7 - 6N^6 - 4N^5 + 16N^4 - 10N^3 + 2N^2 + 1}{3(N^4-1)^2} - \right.$$
$$\left. - \frac{N^2(N^2-1)^2}{(N^2+1)^3}\ln\frac{N+1}{N-1} + \frac{8N^4(N^4+1)}{(N^2-1)^2(N^2+1)}\ln N\right]. \quad (34)$$

However, the numerical difference between Eqns.(34) and (33) is small; for example, $r = 0.6$ and 0.56 respectively when $N = 1.5$. In approximate calculations, it is therefore fully justifiable to use the simpler formula (33).

When account is taken of Eqns.(33) and (23), the parameter $p$ can be expressed thus:

$$p = 2(2N^2 - 1). \quad (35)$$

The coefficients $R_\infty(N)$ for a layer with an optically smooth boundary have been calculated[31] by the numerical

solution of the radiative transfer equation. These data are compiled in Table 6 for $N = 1.5$ and compared with the values calculated by Eqn.(32) taking into account Eqn. (35). The discrepancy does not exceed 3% (absolute deviation), which demonstrates the possibility of the practical application of the formulae based on the $P_1$ approximation. Similar results were obtained in calculations by the TFA Eqn.(21) taking into account Eqn.(35) [see Eqn.(6)].

### 3. Non-Isotropic Scattering ($\mu_0 = 1$)

For a layer with an optically smooth interface, the coefficient $R_\infty(N)$ is described by the formula

$$R_\infty(N) = \rho_3 + \frac{(1-\rho_3)\,[y - \bar{\mu}\,(3\beta y)^{1/2}]}{y[1+\beta\,(1+p)] + \left[y + \frac{p}{3}\,(1+\beta)(3\beta y)^{1/2}\right]}, \qquad (36)$$

where $\bar{\mu}$ is the cosine of the scattering angle [Eqn.(14)] averaged with respect to the scattering indicatrix of the volume element and $y = 1 + \beta - \bar{\mu}$.

Tables 3 and 7 present the results of the study by Giovanelli [31] and the calculations based on Eqns.(36), (18), and (21) for layers with a scattering indicatrix $\chi_2$ [see Eqn.(4)]. The agreement between these results is quite satisfactory.

Analysis of Eqn.(36) makes it possible to determine readily the limitations imposed on the degree of anisotropy of the scattering indicatrix of the volume element in the $P_1$ approximation. Thus, when $\mu > 1/\sqrt{3}$, the coefficient $R_\infty(N)$ becomes negative starting from a certain value of $\beta$, which has no physical significance for the given problem. The application of the $P_1$ approximation is therefore limited to the range $0 \leq \bar{\mu} \leq 1/\sqrt{3}$. This postulate is satisfactorily consistent with the fact that the light intensity in the medium should differ only slightly from the isotropic intensity.

Finally, we have the formula for the coefficients of the non-absorbing layer:

$$R(N) = 1 - T(N) = \rho_{sp} + (1-\rho_{sp})\left[1 - \frac{(3+p) - (3-p)\exp(-\sigma l)}{2p + 3\sigma l\,(1-\bar{\mu})}\right]. \qquad (37)$$

For the scattering indicatrices $\chi_1$ and $\chi_2$ [Eqn.(4)], Eqn. (37) agrees with the TFA formula (22).

## V. THE TRANSPORT APPROXIMATION

It is seen from the above considerations that the $P_1$ approximation can be used only for the scattering indicatrices of the volume element, which are not unduly extended in the forward direction ($\bar{\mu} < 1/\sqrt{3}$). On the other hand, in real systems $\bar{\mu}$ can probably be greater [33,34]. In order to apply the formulae of the $P_1$ approximation to systems with the scattering indicatrices of the volume element extended forward, use is made of the so called transport approximation (TA). In this case, the true scattering coefficient is replaced in the approximate solution of the problem for isotropic scattering by the effective coefficient $\sigma_{eff}$, which takes into account both $\sigma$ and the form of the indicatrix [12,30,35] (the coefficient $\alpha$ then remains unchanged):

$$\sigma_{eff} = \sigma/m, \qquad (38)$$

where $m$ is the parameter taking into account the anisotropy of the scattering.

The physical significance of the transport approximation consists in the replacement of, for example, a scattering indicatrix extended forward by a spherical indicatrix with a larger number of direct light quanta for compensation of the preferential forward scattering. In practice the choice of $m$ makes it possible to bring into fairly good agreement with the exact calculation either the coefficient $R$ or $T$. The transport approximation can be applied also to other approximate methods for the solution of the radiative transfer equation, for example to the TFA version. We may note that the transport approximation is empirical, since the exact TFA Eqn.(21) and the $P_1$ equation (36) contain both $\sigma$ and $\sigma_{eff} = \sigma(1 - \bar{\mu})$.

The exact $R_\infty(\beta)$ relations for layers with the scattering indicatrices $\chi_1$, $\chi_2$, and $\chi_3$ [Eqn.(4)] have the form of monotonically decreasing functions. By selecting the parameter $m$, it is possible to bring these curves into satisfactory agreement with the relation for isotropic scattering. The possibility of achieving the compatibility of the $R_\infty$ curves for the $\chi = 1 + P_i(\mu)$ indicatrices, where $i = 0$, 1, 2, or 3 and $P_i$ is the $i$th Legendre polynomial, has been demonstrated [36] by means of a similar operation. This factor also supports the validity of the transport approximation. As an example, Table 3 presents the values of $R_\infty$ for a layer with the scattering indicatrix $\chi_2$ [Eqn. (4)] calculated in the terms of the transport $P_1$ approximation and TFA for $m = 1.8$. They evidently agree satisfactorily with the results of the exact calculation over a wide range of variation of $\beta$. The principal feature of the transport approximation is that in this case the theory involves only two parameters: $\alpha$ and $\sigma_{eff}$. It is therefore very convenient to use it in the analysis of experimental data.

For a layer with an optically smooth interface ($N = 1.5$) and the indicatrix $\chi_2$, the values of $R_\infty(N)$ were calculated in terms of the $P_1$ approximation and TFA as well as the transport approximation with $m = 1.8$ and compared with Giovanelli's results [31] (Table 7). The extent of the agreement of all the results is quite satisfactory and the TA data differ little from those obtained from the exact $P_1$ and TFA formulae.

Table 4 presents the results of the calculation of the coefficients $R$ and $T$ ($P_1$ and TFA) for all layers of final thickness with the indicatrix $\chi_2$. As before, the extent of the agreement with the transport approximation is quite acceptable, although the difference between the $T$ coefficients is greater. This is because the choice of the parameter $m$ [Eqn.(38)] is determined by the best agreement between the coefficients $R_\infty$. Similar calculations for layers with the scattering indicatrix $\chi_3$ [Eqn.(4)] are presented in Table 5. The parameter $m$, found from the condition for best agreement between the coefficients $R_\infty$ ($m = 6.86$), differs from $1/(1 - \bar{\mu}) = 4.55$. Table 5 shows that the agreement between the coefficients $R$ is fairly good, but that between the coefficients $T$ is only qualitative, which is also consistent with the method of selection of $m$.

The above data suggest that the transport approximation can yield satisfactory results when it is applied to real systems with anisotropic scattering.

Finally, we may note an important fact. The calculations of the coefficients $R$ and $T$ within the framework of the transport, TFA, and $P_1$ approximations reveals a discrepancy between the results, which does not exceed three units in the third decimal place. The range of the values covered was very wide:

$$0.01 \leqslant \beta \leqslant 3;\ 0.2 \leqslant (\alpha+\sigma)\,l \leqslant 15;\ 1 \leqslant m \leqslant 10.$$

This permits the conclusion that the transport, TFA, and $P_1$ approximations yield quantitatively concordant integral values of $R$ and $T$, i.e. they are virtually equivalent.

## VI. OTHER METHODS FOR THE DESCRIPTION OF LIGHT SCATTERING PROCESSES

These include in the first place the layer model where the scattering layer is regarded as an assembly of plane-parallel layers with a thickness equal to the average size of the scattering centre [37-40]. In this approach, the expressions for the coefficients $R$ and $T$ are analogous to the TFA formulae [Eqn.(11)].[37]

A novel approach to the solution of the radiative transfer equation was proposed by Rozenberg, who expanded the solution in series in terms of a small parameter $\gamma$ equal to the ratio of the decay coefficient under bulk-phase conditions ($a$) to the attenuation coefficient of the medium [4,6,41,42]. For the diffuse illumination of weakly absorbing media, Rozenberg obtained the following expression ($N = 1$) with an accuracy to within a quantity of the order of magnitude of $\gamma^3$:

$$T_d = \frac{\sinh y}{\sinh(x+y)}, \quad R_d = \frac{\sinh x}{\sinh(x+y)}, \quad R_\infty^d = e^{-y}, \tag{39}$$

where $x = al$ and $y = 4q\gamma$. When the illumination is directional, the coefficients are expressed as follows:

$$T = gT_d, \quad R = R_\infty - T_d \exp(-x-y), \quad R_\infty = \exp(-Sy).$$

Here $T_d$ and $R_d$ are described by Eqns.(39) and $g$, $q$, and $S$ are so called Rozenberg parameters, whose detailed investigation has already been carried out [8]. It is noteworthy that the unambiguous relation between the reflectance and transmittance, on the one hand, and the parameters $x$ and $y$, on the other, makes it possible to obtain a simple expression for the absorption coefficient [6]:

$$\alpha = xy/4l.$$

We may also point out that Eqns.(39) are equivalent to the TFA formulae (11).[43] Rozenberg used a similar approach also for strongly absorbing media [44,45].

Yet another approach to the consideration of light scattering processes in powders was proposed by Melamed [46], assuming that a semi-infinite layer consists of spherical particles and, using a soundly based treatment of the light passing through the upper monolayer (similarly to the layer model), he obtained [46] the following expression:

$$R_\infty = 2x\rho + \frac{(1-2x\rho)(1-\rho R_\infty)xt}{(1-\rho R_\infty) - (1-x)(1-\rho)tR_\infty},$$

where $x$ is the fraction of light emerging from the particle in the upward direction, $t$ the transmission coefficient of the particle, and $\rho$ a quantity having the same significance as in subsection 1 of Section III. Melamed has published these expressions in an explicit form [46].

The problem of the reflectances of a semi-infinite layer with $N \neq 1$ was dealt with by Giovanelli [31], who considered two types of interfaces of the layer: optically smooth and diffuse. We shall assume that the diffuse interface has a hypothetical property such that the radiation which has passed through it or which has been reflected from it is diffuse regardless of the type of incident radiation [31]. In order to find the reflectance of the layer, the author [31] separated the processes involving the passage of light through the surface of the layer from the reflection processes. Then, considering the radiation fluxes immediately at the boundary, directed inwards and outwards, Giovanelli obtained the following expression:

$$R_\infty(N) = \rho + \frac{(1-\rho)^2 R_\infty^d}{N^2(1-rR_\infty^d)}.$$

Either the exact function [1,2,11] or approximate expressions, for example Eqn.(11), may be used as the coefficient $R_\infty^d$.

A similar approach was also used for a layer with an optically smooth interface. Assuming that the light intensity is independent of the angle, an approximate expression is obtained [31]:

$$R_\infty(N) = \rho_{sp} + (1-\rho_{sp})\frac{(1-\rho)R_\infty}{N^2(1-2J)},$$

where

$$J = \int_0^1 r(\mu) R_\infty(\mu)\mu\, d\mu;$$

$r(\mu)$ is the Fresnel reflectance for the light incident on the interface from within and the coefficients $r$, $\rho$, and $\rho_{sp}$ have the previous significance. Giovanelli evaluated by numerical integration the coefficients $R_\infty(N)$ also taking into account the angular structure of the light [31]. Some of these data are presented in Tables 6 and 7.

An attempt at a description of photochemical reactions in powdered substances made by Simmons and Wendlandt [47,48] is noteworthy. Assuming that the powder consists of spherical particles which are capable of ideal scattering of radiation, the authors [48] obtained the following relation for the reaction $A \xrightarrow{h\nu} B$ within the framework of the one-dimensional layer model:

$$g(R_\infty) - g(R_\infty(A)) = \varphi\varepsilon N^2 I_0 t, \tag{40}$$

where $R_\infty$ is the reflectance at time $t$ from the start of the photochemical reaction, $R_\infty(A)$ refers to the pure substance A, $\varphi$ is the quantum yield, $\epsilon$ the molar extinction coefficient of the substance A, $I_0$ the intensity of the incident light, and $g(R_\infty)$ a function whose explicit form has been published [48], Thus the plot of $g(R_\infty)$ against $t$ should be linear and the quantum yield of the photochemical reaction can be estimated from the slope. In conclusion, we may indicate approximate methods for the solution of the radiative transfer equation analogous to the $P_n$ approximation. In contrast to the usual method of spherical harmonics, an expansion in different series is carried for the upper ($\mu < 0$) and lower ($\mu > 0$) half-planes [the so called double $P_n$ method $(DP)_n$] [12,49] or for four regions (with additional subdivision of the half-planes) [50]. In this approach, the light intensity can have a discontinuity at $\mu = 0$. However, as a result of the double expansion, the accuracy of the $DP_1$ method is higher than that of the $P_3$ approximation for the same complexity of the mathematical expressions [12]. In particular, one can formulate an expression for the coefficient $R_\infty$ for an isotropically scattering layer obtained in the $DP_0$ approximation with the usual boundary conditions ($\mu_0 = 1$, $N = 1$):

$$R_\infty = [1 + 3\beta + 3(\beta(1+\beta))^{1/2}]^{-1}.$$

This formula resembles Eqn.(31), but agrees better with the results of the exact calculation, which probably also indicates a higher accuracy of the $DP_0$ method compared with the $P_1$ approximation.

## VII. THE APPLICATION OF THE SPECTROSCOPY OF LIGHT SCATTERING MEDIA TO THE INTERPRETATION OF EXPERIMENTAL DATA

This section is devoted to the practical applications of the SLM. Naturally since not all the studies in this field can be described, we shall confine ourselves to the most typical investigations. These include in the first place the determinations of the absorption band maxima in the diffuse reflection spectra [51-58]. Studies designed to elucidate the coordination and valence states of transition metal ions on the surfaces of different carriers are related to these. By comparing the energies of the electronic transitions of the ions on the surface with the analogous transitions in solutions, it is possible to reach a conclusion, within the framework of the crystal field theory, about the coordination of valence states of the ion investigated. The study of the state of molybdenum [59] and cobalt [60] ions on the surfaces of magnesium and aluminium oxides, of cobalt and chromium ions on silica gel [61-63], and of copper [64], nickel [65], and neodymium [66] ions, as well as the study of the properties of nickel catalysts [67-69], the acid properties of catalysts [70,71], and the interaction of certain organic compounds with the surface of the catalyst [72,73] are typical investigations of this kind.

In practice, one encounters fairly frequently the problem of the determination of the optical characteristics of substances from diffuse reflection or transmission spectra and hence the problems of the determination of the structures of compounds and their concentrations. Most of the approximate models for the description of light scattering systems were described in previous sections. Among these, the TFA model, yielding relatively simple G–K–M relations [Eqns. (11)], is most widely used. We may recall that Eqns. (11) were obtained for homogeneous layers illuminated with diffuse light. Outwardly similar formulae are obtained when a one-dimensional scattering medium [2] or a layer model [37] are considered.

Numerous studies on the application of the spectroscopy of light scattering media in chemistry have been carried out by Kortüm and his coworkers [74-85]. Using the K–M functions [Eqn. (12)], the authors determined the form of the absorption spectra of molecular compounds of trinitrobenzene as a function of concentration, adsorbent, temperature, and degree of adsorption, and also estimated the dissociation constants of these compounds [76,77]. Kortüm and Vogel [78] described the dependence of the absorption spectra of powdered $K_3Fe(CN)_6$ and $KMnO_4$ on particle size taking into account certain refinements of the G–K–M theory [78,79]. Using polarised light, an attempt was made to separate the diffuse and specular components of the reflected radiation, and the influence of the particle size on the reflection spectra of the powders was demonstrated [80]. The luminescence characteristics of powdered substances were calculated [81] within the framework of the G–K–M model. Using the K–M function [Eqn. (12)], the photochemical reactions of adsorbed substances (anthracene, anthraquinone, substituted pyridines, and spiropyrans) were studied qualitatively [82-84]. However, all the studies enumerated above are only qualitative, owing to the use of a simplified model for the description of the properties of real systems (we may note that the K–M formula does not take into account the refractive index of the medium and, in addition, diffuse light was sometimes replaced by directed light in the experiments).

Ivanov et al. [86] determined the concentrations of dyes adsorbed on fibres. Several types of dyes and fibres were investigated, the results were interpreted with the aid of the K–M function, and the layer was illuminated at normal incidence. Satisfactorily linear relations between $f(R_\infty)$ and the dye concentration are quoted for the individual dyes and it was shown experimentally that the absorption coefficients for a mixture of dyes are additive quantities [86]. A method for the determination of microamounts of mercury from the coefficient of reflection from paper dyed with a mercury complex of diphenylcarbazone was described in a similar study [87]. As in the usual photometry, mercury was determined by comparing the experimental data with a calibration curve obtained by plotting $f(R_\infty)$ against [Hg].

Oelkrug [88] investigated the structure of copper complexes on the basis of reflection spectra with the aid of the K–M function and Gavrilova et al. [89] described the correlation between $f(R_\infty)$ for cellulose and the degree of its acetylation. Toporets [90] studied the light scattering processes in pigments and obtained a linear relation between $f(R_\infty)$ and the concentrations of various pigments in magnesium, zinc, and titanium oxides.

The light scattering processes in weakly absorbing milky glasses have been investigated within the framework of the TFA version [18,19,91]. Voishvillo [91] interpreted the results in terms of the G–K–M formulae, although light at normal incidence had been used in the experiments. The attenuation coefficient under bulk-phase conditions [the parameter $a$ in Eqns. (11)] was estimated from the dependence of the coefficients $R$ and $T$ on the thickness of the layer, the error in the determination of this parameter was analysed, and the absorption coefficient of the glass was determined. The average cosines of the angles of inclination of the light beams [$\nu_1$ and $\nu_2$ in Eqn. (8)] were estimated by measuring the indicatrix of the radiation emerging from the layer [91]. They were found to be [virtually] equal, but their average (0.63) differs from the value (0.5) proposed by Zege [9]. This may be due both to the elongation of the scattering indicatrix and to the use of radiation emerging from the layer rather than the radiation within the layer. Voishvillo [18,19] interpreted experimental data in terms of the TFA formulae, taking into account the refractive index of the glass.

The limits of applicability of the G–K–M relations have been determined by Rozenberg et al. [92], who claim that the absorption coefficients of weakly absorbing media can be determined correctly with the aid of the K–M function by introducing an effective scattering coefficient. This postulate was confirmed experimentally for magnesium oxide and zinc oxide layers [92-95]. The region where the two-flux approximation is applicable has also been considered by Sakhnovskii and Kotik [96].

The experimental data have been interpreted within the framework of the layer model in a number of investigations [37-40], where the reflection spectra of powdered phosphors [39] and ground coloured glasses [37,38,40,97] were studied.

The absorption coefficients of powdered didymium glasses and GaP have been obtained [46] with the aid of Melamed's theory from reflection spectra. The results agree well with the true absorption coefficients of transparent specimens. Pool and Itzel [98] used the reflection spectra of chromium and aluminium oxides to determine the structures of the electronic transitions and the state of ions. The results were interpreted and, in particular, the extinction coefficients were determined on the basis of Melamed's theory [46].

The photochemical decomposition of powdered $K_3[Mn.(C_2O_4)_3].3H_2O$ was investigated by Simmons and Wendlandt [48]. The plot of $g(R_\infty)$ against $t$ [Eqn. (40)] was indeed

linear for different wavelengths and light intensities and the observed quantum yields were 0.41 ($\lambda$ = 400 nm) and 0.13 ($\lambda$ = 350 nm).[48]

The $P_1$ approximation for the description of light scattering processes has been examined in a study[28] whose authors investigated the scattering properties of layers consisting of spherical methyl methacrylate particles. The extinction coefficient of methyl methacrylate was found within the framework of the diffusion model and the optical characteristics of such layers were predicted. In a subsequent study[99], the authors estimated theoretically the parameters of the scattering layers in dispersed radiation detectors and confirmed experimentally the calculated results.

The diffusion model for the description of radiative transfer processes from point sources in weakly absorbing media was used by Brinkworth[100]. The solution of the diffusion equation in the spherical coordinate system, taking into account the influence of the reflecting walls surrounding the given space, agreed satisfactorily with experimental data for the passage of light through aqueous solutions of poly(methyl methacrylate) and poly(vinyl chloride) [100]. The diffusion approximation method has been used successfully by Gribakin and Istomin to determine the optical behaviour in photographic emulsions and to find certain parameters of such emulsions[10,101]. The scattering properties of photographic emulsions have also been described in other studies[102,103].

The diffusion theory of neutron scattering has been used to describe the light scattering processes[104]. The specimens (blue and green glasses) were used to determine the absorption spectra from the reflection spectra of ground glasses with the aid of the $P_1$ approximation. A satisfactory agreement was achieved between the absorption spectra observed for the transparent glasses and the absorption spectra calculated from the reflection spectra. The $P_1$ approximation has been examined for diffuse illumination without taking into account the refractive index of the glass[104]. A similar approach has been used in another study[105] to determine the scattering cross-sections in dense suspensions of spherical particles (polystyrene latex).

The transport $P_1$ approximation has been used[30] to describe the scattering properties of pure and coloured filter paper. It follows from Eqn.(37) of the $P_1$ approximation that the following relation holds for weakly absorbing media with a fairly considerable optical thickness of the layer

$$\frac{1}{T(N)} = \frac{1}{(1-\rho_{sp})}\left[\frac{2p}{(3+p)} + \frac{3\sigma_{eff}}{(3+p)}l\right]. \qquad (41)$$

$\sigma$eff can be found from the dependence of the coefficient $T(N)$ on the thickness of the paper (the number of filter papers) by Eqn.(41), since the paper absorbs only slightly in the visible part of the spectrum. Fig. 3 illustrates the variation of $1/T(N)$ with $l$ for the filter paper ($\lambda$ = 600 nm) from whose slope and the intercept on the ordinate axis it is possible to estimate $\alpha$ and $\sigma$eff.[30] Using the characteristics of the medium found from the experiments on light transmission, it is possible to calculate $R_\infty(N)$ in terms of the $P_1$ approximation (Table 8). Table 8 shows that these data agree satisfactorily with experiment.

The reflectivity of coloured filter paper was also investigated. Nitratohexamminecobaltate(III), potassium hexacyanoferrate(III), and anthraquinone-2-sulphonate were used as dyes. This choice was dictated by the fact that the above substances show no tendency towards specific adsorption on the paper and it is therefore easy to determine their concentration on the paper. By measuring the reflection coefficient of the coloured paper and knowing the characteristics of the layer ($\alpha$ and $\sigma$eff), it is possible to find from the Eqn.(32) of the $P_1$ approximation, taking into account the relation $\alpha = 2.3\epsilon c$, the concentration of the dye or its optical characteristics when the concentration is known.

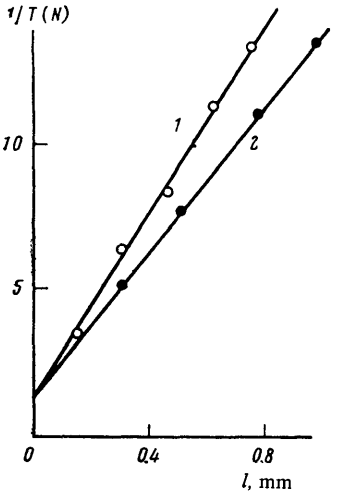



**Figure 3.** Dependence of $1/T(N)$ on the thickness of the layer ($\mu_0$ = 1): 1) filter paper; 2) MS-14 milky glass[33].

As an example, Figs. 4 and 5 present the variation of the coefficients of specific absorption of the paper with the concentrations of the dyes and also the absorption spectra calculated from the diffuse reflection spectra[30], obtained on the assumption that the introduction of the dye does not alter $\sigma$eff and that the dye is uniformly distributed throughout the paper.

Table 8. The coefficients $R_\infty(N)$ of filter paper [Eqn.(32)] ($\beta$ determined from data for the transmission of light through the paper[30]).

| $\lambda$, nm | 400 | 420 | 450 | 480 | 500 | 600 |
|---|---|---|---|---|---|---|
| $R_\infty(N)$, (calc.) | 0.837 | 0.856 | 0.882 | 0.897 | 0.905 | 0.940 |
| $R_\infty(N) \pm 0.02$, (expt.) | 0.834 | 0.851 | 0.875 | 0.906 | 0.922 | 0.950 |

We shall now consider certain literature data which we interpreted in terms of the $P_1$ approximation. Fischer and Vratny[106] published the coefficients $R_\infty(N)$ for magnesium carbonate as a function of the amount of the light absorbing additive. We shall assume that the absorption coefficients are proportional to the weight fraction of the substance whereupon

$$\frac{1}{\beta} = \frac{m\sigma_d + \sigma_{MgCO_3}}{m\alpha'_d + \alpha'_{MgCO_3}}, \qquad (42)$$

where $m$ is the weight fraction of the additive (subscript $d$) and $\alpha'$ are quantities proportional to the true parameters $\alpha$. Since $R_\infty(N) \simeq 0.97$ in the visible part of the $MgCO_3$ spectrum[107], we neglect the term $\alpha'_{MgCO_3}$. In this case, the plot of $1/\beta$ against $1/m$ should be linear. Indeed, measurements of the reflection of light from a mixture of $MgCO_3$ and Congo Red[106], interpreted in terms of Eqn. (42) ($N = 1.515$),[107] fit satisfactorily on a straight line (Fig. 6).

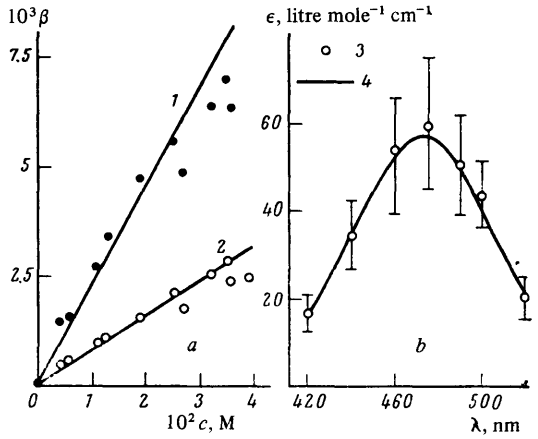



Figure 4. Nitratohexamminecobaltate(III) in filter paper[30]: *a*) dependence of $\beta$ on concentration [1) $\lambda$ = 475 nm; 2) $\lambda$ = 520 nm]; *b*) [3) extinction coefficient calculated from reflection spectra; 4) ditto for an aqueous solution].

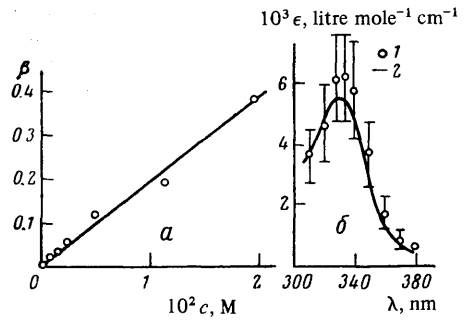



Figure 5. Anthraquinone-2-sulphonate in filter paper[30]: *a*) dependence of $\beta$ on concentration ($\lambda$ = 330 nm); *b*) [1) extinction coefficient calculated from reflection spectra; 2) ditto for aqueous solution].

A linear relation between the specific absorption coefficient and the concentration of the light absorbing additive (carbon black), analogous to the Beer–Lambert law, has been observed for aqueous suspensions of $BaSO_4$, ZnO, and $TiO_2$ ($N = 1.33$). The values of $R_\infty(N)$ for such systems, quoted by Blevin and Brown[108], have been interpreted in terms of Eqn. (32) (Fig. 7). We obtained a similar straight line from data[109] for eosin adsorbed on alumina.

We shall now consider the reflection spectra of coloured glass powders[97,110] ($N = 1.5$). General considerations suggest that $1/\sigma$ should be proportional to the average particle size in the layer. Indeed, knowing the absorption coefficients of ZhZS-1, NS-3, and ZS-6 coloured glasses and having calculated $1/\sigma$ in terms of the $P_1$ approximation, we obtain satisfactorily linear relations between $1/\sigma$ and the average particle size in the powder ($\bar{a}$), which are almost unaffected by the absorption coefficient (see, for example, Fig. 8).

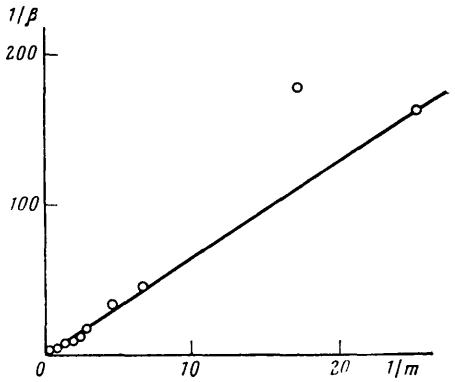



Figure 6. Dependence of $1/\beta$ on $1/m$ for a mixture of $MgCO_3$ and Congo Red powders. Data[106] interpreted in terms of the $P_1$ approximation.

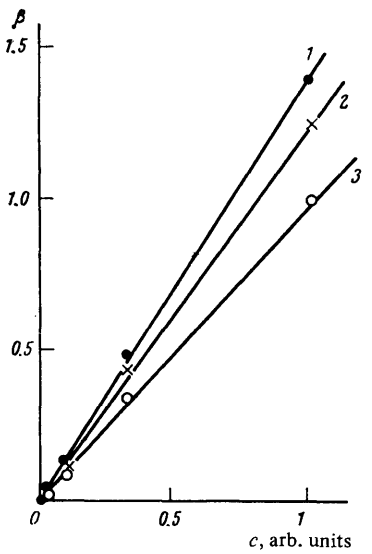



Figure 7. Dependence of $\beta$ for an aqueous suspension of ZnO on the concentration of carbon black $c$. Data[108] interpreted in terms of the $P_1$ approximation; $\lambda$ (nm): 1) 400; 2) 500; 3) 700.

The reflection and transmission coefficients of the MS-14 glass have been published[33] as a function of the layer thickness ($\mu = 1$, $N = 1.5$). Fig. 3 illustrates the variation of $1/T(N)$ with $l$ ($\lambda$ = 550 nm) based on these

data, which is linear, in agreement with Eqn. (41). The intercept on the ordinate axis is approximately 1.3, which is close to the values predicted by Eqn. (41). We may recall that a similar straight line for milky glasses has been found [14] to make an intercept greater than unity (Fig. 2). These findings apparently indicate the necessity for taking into account the refractive index of the scattering medium. The effective scattering coefficient of the MS-14 glass can be estimated from the slope of its straight line (Fig. 3) and $\alpha$ can then be found from the value of $R_\infty(N)$. Using the values of $\alpha$ and $\sigma_{eff}$ obtained in this way, we calculated in terms of the $P_1$ approximation $R(N)$ and $T(N)$ for the MS-14 glass as a function of the layer thickness, the results agreeing with experimental data within the limits of the accuracy of the latter [33].

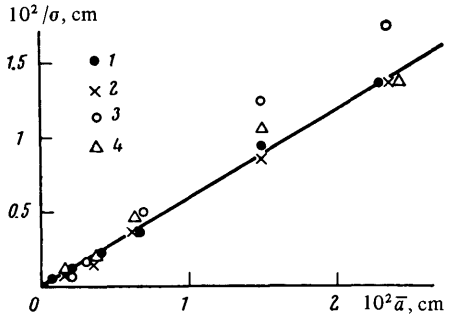



Figure 8. Dependence of $1/\sigma$ on $\bar{a}$ for ZS-6 glass powder ($\bar{a}$ is the average particle size). Data [97] interpreted in terms of the $P_1$ approximation; $\alpha$ ($cm^{-1}$): 1) 11; 2) 55; 3) 21.2; 4) 47.

Bearing in mind that the sum $[A] + [AH_2]$ is constant, it is possible to obtain the following expression for the initial section of the kinetic curve for the photolytic reaction [111]:

$$\varphi = -\frac{(d\beta/dt)_e \cdot \sigma_e/\sigma_p}{2.3(\varepsilon_A - \varepsilon_{AH_2})_e \cdot (\beta - \beta_0)_p c n_p}, \quad (43)$$

where the subscript $e$ refers to the quantities corresponding to the experimental wavelength, $p$ refers to photolysis, $\beta_0$ corresponds to pure paper, and $n_p$ is the density of the quanta in the layer taking into account its illumination from both sides. A similar expression for $\varphi$ is obtained also when it is assumed that the light which has entered the layer is fully absorbed by compound A.

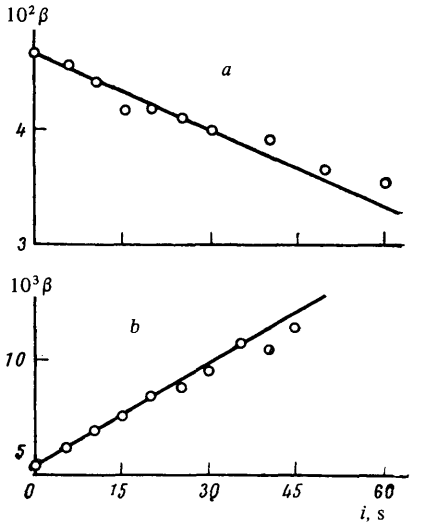



Figure 9. Initial sections of the kinetic curves for the photolysis of compound A in paper [111]; $\lambda_p$ = 335 nm, $\lambda_e$ = 335 nm (*a*); $\lambda_e$ = 385 nm (*b*).

We estimated with the aid of SLS the quantum yield $\varphi$ in the photochemical hydrogenation of anthraquinone-2-sulphonate (A) in filter paper [111]. A is reduced under the action of light to anthrahydroquinone-2-sulphonate ($AH_2$). The absorption band maxima for compounds A (335 nm) and $AH_2$ (385 nm) are well separated so that it is convenient to follow the photochemical reaction from the change in $R_\infty$ (and hence also $\beta$) at the absorption band maxima. The methods described above, in particular the $P_1$ approximation, presuppose the homogeneity of the absorption coefficients throughout the layer, while the light profile has the form of a sharply decreasing function [Eqn. (29)]. As a result, the concentrations of A and $AH_2$ are significantly different throughout the layer. To a rough approximation, the light profile can be regarded as constant if thin sheets of paper are illuminated from both sides and then stacked to form a thick pile in order to measure $R_\infty$.

Thus, assuming that the intensity of the photochemically active light is constant along the layer, we have at a certain instant $t$

$$\beta_e = \frac{2.3}{\sigma_e}(\varepsilon_A [A] + \varepsilon_{AH_2} [AH_2])_e + (\beta_0)_e.$$

The quantum yield of the photochemical hydrogenation of A, estimated by Eqn. (43), proved to be 0.12 ± 0.07, which agrees satisfactorily with the value obtained by an indirect chemical method. As an example, Fig. 9 presents the initial sections of the photolysis curves calculated by Eqn. (32) from the measured coefficients $R_\infty(N)$ for $[A] = 1.7 \times 10^{-3}$ M and $I_0 = 6 \times 10^{-14}$ quanta $cm^{-2}$ $s^{-1}$, where $I_0$ is the intensity of the light incident on the layer.

The propagation of light in a medium having the shape of an infinitely long cylinder has been described with the aid of the diffusion theory [112], the description agreeing well with data for light scattering in polystyrene latices [113,114].

## VIII. CONCLUSION

Approximate methods. The transport, two-flux, and diffusion approximations are most suitable for the analysis of experimental data and, when the specimen is illuminated with diffuse light, it is best to use the two-flux approximation. For directional illumination, both

approaches can be employed. However, we give preference to the transport diffusion approximation, since it can be used without resorting directly to the radiative transfer equation with which it is possible to take into account readily a wide variety of conditions within the specimen and on its surface. On the other hand, the diffusion equation is very frequently used to solve various chemical problems and for this reason physical chemists are much more accustomed to it than to the radiative transfer equation.

The Kubelka – Munk formula. The Kubelka–Munk formula [Eqn.(12)] is widely used in the analysis of experimental data even for directed illumination of the specimen. If the experimenter is satisfied with deducing a relation of the type $\alpha \propto c$, the application of the K–M formula does not lead to qualitatively incorrect results. However, in quantitative analysis it is best to employ the formulae of the transport, diffusion, or two-flux approximations, since the application of the K–M function for directed irradiation of the specimen is theoretically unjustified.

The radiative transfer equation. In the analysis of experimental data obtained for physicochemical systems such as powders, papers, fabrics, etc., the direct use of the radiative transfer equation can hardly be regarded as useful not only owing to mathematical difficulties, but because of certain fundamental considerations. The point is that it is not altogether clear how to formulate the radiative transfer equation for polydisperse systems such as powders or paper[115]. Furthermore, in complex polydisperse systems the coefficients $\alpha$, $\sigma$, and $\chi$ depend not only on the coordinates but also on the direction of the incident beam. Consequently quantities averaged in some way must be substituted in the radiative transfer equation. However, the usefulness of employing average quantities within the framework of the exact radiative transfer equation is far from evident. The approach within the framework of the various approximations, some of which have been discussed above, appears more justified. Nevertheless, the rigorous solution of the problem of radiative transfer for different conditions should be the starting point for testing approximate methods.

There is apparently no great risk in extrapolating the solutions obtained to the region of strong absorption, provided that the treatment is restricted to the analysis of the coefficient $R_\infty$ only, since the formal application of approximate theories to the region of strong absorption yields the following qualitative relation: $R_\infty \propto \beta^{-1} \propto c^{-1}$. We may note that the analogous relation $R_\infty \propto c^{-1}$ follows from Rozenberg's theory[4,6]. The proportionality coefficient between $R_\infty$ and $c^{-1}$ may be found experimentally.

The possibility of the quantitative measurement of the absorption coefficient. The spectroscopy of light scattering media is nowadays used inadequately in chemical research. With a few exceptions, no attempts have been made to determine the absorption coefficients. We may note that, in order to determine the absorption maximum of a substance in a scattering medium, no theories are required, since it is sufficient for this purpose to have, for example, the $R_\infty - \lambda$ or $(1 - R_\infty) - \lambda$ curves.

One of the ways of determining absorption coefficients quantitatively may be as follows. One may hope that in certain cases light scattering will be determined mainly by the light scattering matrix and not the admixtures introduced into it. This can be demonstrated by introducing into the matrix different substances which do not interact with it assuming at the same time that the absorption coefficient of the added substance does not change and is equal to that for the same substance in solution. The problem now is to what extent this assumption can be justified. One may note that the introduction of a substance into a light scattering matrix does not differ in principle in any way from dissolution. For this reason, the change in the extinction coefficient should be close to the change in the extinction coefficient when the compound is dissolved in various solvents. According to Stern and Dammons[116], in most cases it does not exceed 5–10%. The data quoted in their book[116] for the extinction coefficients of the $n - \pi^*$ transition of the acetone molecule in various solvents, show that it does not change by more than 25% on either side of the average value. We may note that the $n - \pi^*$ transitions are most sensitive to the environment. On the other hand, when molecules with internal transitions of the type $\pi - \pi^*$ or $a - d$, for example $Co(NH_3)_6^{3+}$, are used, one may hope that their extinction coefficients do not vary markedly when they are introduced into a light scattering matrix. By using several specially selected compounds, it is possible to determine the dependence of the scattering coefficient on the wavelength. This would make it possible to determine subsequently the absorption coefficient of any other compound introduced into the matrix. Naturally the objection arises that this procedure is not very accurate; however, the accuracy of the above approach is not lower than that of the ESR method, widely used in physicochemical research, for which the accuracy of the quantitative determination of free radicals is usually assumed to be approximately 40%.

Thus the present state of SLM permits the quantitative determination of the absorption coefficient. The absence of the relevant reports from the literature is incomprehensible.

The problem of the separation of $\epsilon$ and $c$. The knowledge of the absorption coefficient $\alpha$ does not of course permit the separate determination of $\epsilon$ and $c$. It is therefore necessary to employ other methods whereby the concentration can be measured directly, for example, the ESR method. Such combinations of ESR and SLM methods appears to be fairly promising, particularly in catalytic research.

Procedures involving the transition of the given substance from one form to another under the influence of some agent, for example chemical or radiation-chemical, are very important for the problem of the resolution of the two parameters. This factor also appears to have been overlooked by experimenters.

The size of light beams. In the approximate methods considered, light beams of infinite extent are postulated. On the other hand, in practice light beams of finite dimensions are used. However, they satisfy the problem formulated if their size is significantly greater than the characteristic parameter of the specimen: $1/(\alpha + \sigma\text{eff})$. The existence of halos, for example in the case of milk, indicates the unsuitability for research of beams approximately 1 cm long, since the characteristic size of the halos is of the same order of magnitude. Beams whose size is significantly greater than the geometrical dimensions of the powder particles are probably suitable for powders.

The specular component in the diffuse reflection spectra. For layers with an optically smooth surface, the specular component may be readily taken into account [31]. For powdered specimens, whose boundary cannot be clearly determined, the allowance for the specular component in the measurement of the reflection spectra is much more difficult. It apparently depends on the packing density of the powder particles [75]. On the other hand, in view of the uneveness of the boundary of the powdered medium, the specular component may be actually smaller than for an optically smooth surface. The problem has not been finally solved and is by no means always taken into account in experimental research.

Allowance for the effect of total internal reflection. The existence of total internal reflection must be taken into account for specimens with an optically smooth surface, for example solutions. The necessity for this in the case of powdered specimens is less clear. The elucidation of the above problem requires further experiments, although one can adduce arguments in support of allowance for total internal reflection in these media too.

Illumination of specimens at an angle. It is sometimes suggested that specimens be illuminated at an angle, for example 45°, since in this case the values of $R_\infty$ obtained from the exact solution of the radiative transfer equation for a spherical scattering indicatrix and calculated from the Kubelka–Munk equation are approximately the same [2,31]. However, this approach has no appreciable advantages compared with the usual illumination of specimens at right angles ($\mu_0 = 1$) and may actually suffer from disadvantages. The point is that it is not clear how to proceed when the scattering indicatrix deviates from the spherical shape and in practice this situation does in fact occur. On the other hand, in the study of systems with an optically smooth surface one must take into account the refraction of the light beam and the angle must be varied in order that the light should enter the medium at an angle of 45°. Furthermore, for illumination at an angle the coefficient $R_\infty$ increases and the method becomes less sensitive to small amounts of impurities.

The reference specimen. By analogy with the spectroscopy of transparent media, diffuse reflection spectra are sometimes measured relative to the light-scattering matrix assuming thereby that the absorption in the initial matrix, for example owing to impurities, is taken into account. However, as a result of the absence of a linear relation between $R_\infty(\lambda)$ and $\alpha(\lambda)$, this method of taking absorption into account is incorrect. $R_\infty(\alpha)$ can of course be measured relative to the initial light-scattering material, but in quantitative calculations the data obtained ($R_\infty^{exp}$) must be converted into the true reflectance ($R_\infty^{true}$) by means of the formula

$$R_\infty^{true} = R_\infty^{org} R_\infty^{ref},$$

where $R_\infty^{ref}$ is the reflection coefficient relative to a specimen giving 100% reflection. Either milky glasses [117–119] or white powders, for example MgO, ZnO, and $BaSO_4$ with known reflectances [120,121], are normally used as reference specimens with 100% reflection.

The apparatus. All types of apparatus for measurement of the integral coefficients $R$ and $T$ can be divided into two classes: devices with an integrating sphere [122] (SF-10 and SF-14 apparatus) and devices with elliptical or parabolic mirrors [4,8] (the PDO-1 and PDO-2 attachments). In both systems, light is directed in succession to the experimental and reference specimens. We may note that the PDO-1 attachment does not measure the entire reflected radiation but only its component reflected within conical angles of 10–80° relative to the normal. In the measurement of the true coefficient $R_\infty$, it is therefore necessary that the angular characteristics of the radiation reflected from the test and reference specimens should be similar. Simpler devices can also be used to measure $\alpha_{max}$ for reflection spectra [123].

Prospects. The present state of SLM is such that it permits quantitative measurements with an accuracy close to that of the ESR method (approximately 40%). One may hope that SLM will find much wider applications in studies on photochemical, radiation-chemical, and, particularly, catalytic processes.

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# The Reactions of Mono-olefins in the Presence of Alkali Metals and Their Derivatives

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Studies devoted to reactions of mono-olefins in the presence of alkali metals and their derivatives—mainly metallation, dimerisation, codimerisation, and isomerisation reactions—are reviewed. The catalysts, the reaction conditions, the product composition, and the problems of the reaction mechanisms are considered. It is shown that the specificity of the action of alkali metal catalysts is associated with the common features of the formation and reactions of organic derivatives of the alkali metals and that the reactions in the presence of such catalysts may serve as a basis for the development of promising procedures for the processing of mono-olefins.
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## I. INTRODUCTION

Mono-olefins are the main raw material in modern petrochemical industry; their world-wide manufacture runs into many millions of tonnes per year. For this reason, studies on the reactions of these hydrocarbons are as a rule of great practical importance.

Mono-olefins are known to have a dual nature: they are regarded as weak acids and bases, since they are capable of exchanging hydrogen for a metal, of combining with a proton, or of behaving as an electron donor. The dimerisation, codimerisation, metallation, alkylation, and isomerisation reactions of mono-olefins in the presence of basic catalysts give rise to extensive possibilities for the synthesis of individual hydrocarbon monomers and intermediates in petrochemical synthesis. The high selectivity of these reactions makes it possible to obtain in useful amounts such relatively thermodynamically unstable olefins as 4-methylpent-1-ene, 3-methylpent-1-ene, 3-ethylpent-1-ene, etc. The content of these $\alpha$-alkenes in the petroleum processing products (cracking or pyrolysis products) is negligible and their isolation is hindered by the similarity of the physicochemical properties of the isomers.

The isomerisation of mono-olefins and certain diolefins in the presence of alkali metal catalysts makes it possible to shift the double bond to the required position under mild conditions without affecting the carbon skeleton. The alkylation of alkylbenzenes [by olefins] in the presence of these catalysts results in the selective addition of the olefins to the side chain only, so that subsequent dealkylation can yield also chain olefins with a specific structure, for example isopentenes.

The first attempt at a broad survey of the reactions catalysed by bases was made in 1962 by Pines and Schaap [1]. Pis'man's monograph was devoted to the industrial synthesis of 4-methylpent-1-ene [2]. Two reviews [3,4] dealt mainly with the dimerisation and codimerisation of olefins in the presence of transition metal complexes, the problems of the reactions on basic catalysts being only partly considered.

The present review is concerned with the extensive data published in recent years and also with certain early studies on the reactions of unsaturated compounds, mainly mono-olefins, in the presence of alkali metals and their derivatives in the light of modern ideas about the nature and mechanism of acid–base catalysis.

## II. REACTIONS OF OLEFINS WITH ALKALI METALS AND THEIR COMPOUNDS

The hydrogen in many hydrocarbons can be replaced by an alkali metal, which is characteristic of acids, and an organometallic compound may be obtained. The substitution can occur both on direct treatment with the metal and on treatment with another organometallic compound containing the alkali metal. With increase of the atomic weight of the alkali metal, the rate of metallation as a rule increases. The rate can also increase when the metal in the fused or finally comminuted state, solutions in liquid ammonia, and the sodium–potassium eutectic mixture are used [5]. The rate of metallation depends on the mobility of the hydrogen in the molecule of the organic compound too. Olefins exhibit a comparatively weak acidity and are only slowly metallated directly by alkali metals [6]. The transmetallation reaction, described for the first time by Shorygin [7], proceeds much more readily:

$$HR + R' - M \rightleftarrows R - M + R'H ,$$

where M = Li, Na, K, Cs, or Rb and R and R' are hydrocarbon groups.

Kocheskov and Talalaeva [8] formulated the rules for metallation: (a) the yield of the organometallic compound increases with acidity when the same metallating agent acts on different hydrocarbons; (b) under identical conditions, the hydrocarbon with greater acidity is metallated faster; (c) in the presence of a deficiency of the metallating agent, the compound which is a stronger acid is also metallated preferentially.

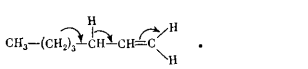
The presence of multiple bonds or rings in the molecule of the organic substance greatly alters the energy required to abstract a proton. Thus it amounts to 95

kcal mole$^{-1}$ in propane and 98 kcal mole$^{-1}$ in ethane, while in toluene it is only 77.5 kcal mole$^{-1}$ and the abstraction of the allyl hydrogen atom in propene requires 77 kcal mole$^{-1}$.[9] Alkylbenzenes are alkylated at a high rate at the $\alpha$-carbon atom of the aliphatic substituent[10-12]. The substitution of hydrogen in naphthalene by a metal is much faster than in benzene[13-15]. The acidity of alkynes is still higher, increasing in the sequence[14] $HC{\equiv}CH < HC{\equiv}C-C_5H_{11} < {\equiv}C-C_6H_5$.

Ethylene is a much weaker acid than acetylene; it is metallated only by strong bases, for example by pentylsodium[11]. The substitution of protons in ethylene by alkyl groups increases the acidity of the olefin, because the vinyl group activates the hydrogen atoms at the carbon atom nearest to it. For this reason, propene is metallated more readily than ethylene, the hydrogen in the methyl group being preferentially substituted by the metal[5,6,17,18]. Its dimetallation leads to the formation of $NaCH_2-CH{=}CHNa$.[19] Mono- and di-substituted products were also obtained in the metallation of isobutene[17]: $CH_2{=}C(CH_3)CH_2Na$ and $CH_2{=}C(CH_2Na)_2$.

The metallation of but-1-ene by pentylsodium and subsequent carbonation yield mainly $CH_2{=}CHCH(CH_3)COOH$ and smaller amounts of $CH_3CH{=}CHCH_2COOH$, $CH_3CH_2CH{=}CHCOOH$, and dimetallation products[17]. Pent-1-ene is metallated[17] mainly with formation of $CH_2{=}CHCHNaCH_2CH_3$ and $NaCH{=}CH(CH_2)_2CH_3$. Under the influence of pentylsodium, hex-1-ene also gives rise to two compounds[16]: the first corresponds to the metallation of the methylene group in the $\alpha$-position relative to the multiple bond and the second is formed, as in the case of but-1-ene, as a result of the migration of the double bond: $CH_3(CH_2)_2CH{=}CHCH_2Na$. Such isomerisation with migration of the double bond to the centre of the chain has been described for reactions with phenyl-, benzyl-, and pentylsodium[20]. The metallation of hexenes with a branched chain also involves mainly the substitution of the allyl hydrogen atom; for example 2,3-dimethylbut-1-ene is converted, after metallation and carbonation, into $CH_2{=}C(i\text{-}C_3H_7)CH_2.COOH$. When there is no allyl hydrogen atom, as in 3,3-dimethylbut-1-ene, the terminal carbon atom in the vinyl group is metallated[16].

Studies on the metallation of $C_7$ and higher $\alpha$-olefins[21-28] have shown that, with increase of the carbon chain length in olefins, their acidic properties are weakened[5] and the nature of their reactions changes somewhat. For example, it has been established experimentally[25,26] that already in the case of hept-1-ene vinyl substitution products predominate in the reaction mixture at the beginning of the reaction. It appears that in $\alpha$-olefins with more than six carbon atoms the double bond not only withdraws electrons from the C–H bond in the allyl position but is also responsible for the successively decreasing inductive shift of electron pairs in the same direction[26]:



This shift compensates to some extent the decrease of electron density in the C–H allyl bond, which leads to the predominance of vinyl substitution products. This phenomenon has not been observed in low-molecular-weight $\alpha$- and $\beta$-olefins and their acidity changes in the following sequence[5]: $(CH_3)_2C{=}CH_2 > CH_3-CH{=}CH_2 > CH_3CH{=}CHCH_3 > CH_3CH_2CH{=}CH_2 > (CH_3)_2C{=}CHCH_3 > (CH_3)_2C{=}C(CH_3)_2$.

Conant and Wheland[30] estimated the acidity by a calorimetric method and by carboxylating organosodium or organopotassium compounds; McEwen[31] and Shatenshtein[32] used in addition the polarimetric method. Streitwieser and coworkers[33,34] measured the equilibrium constant in the reactions of lithium or caesium cyclohexylamide with C–H acids. Cram[35] attempted to establish a universal acidity scale for all classes of hydrocarbons using the above data and the results obtained in other studies[36-38]. In an extensive review, Reutov et al.[39] examined the available methods for the determination of the equilibrium acidity and concluded that it is so far possible to determine the acidity of hydrocarbons in aprotic solvents only up to $pK_a \simeq 30$. The acidity of weaker acids (alkenes, arenes, alkanes, etc.), which is estimated by indirect methods, is lower than the value predicted by Cram's scale. This somewhat limited information about the relative acidities and basicities of hydrocarbons, enabled Shatenshtein[5,40,41] and Cram[35] to correlate the above properties of organic compounds with their behaviour in different chemical reactions.

Isotope exchange of hydrogen with strong bases[40] makes it possible not only to estimate the acidities of individual C–H bonds but also to characterise simultaneously the base functioning as the nucleophile[42]. For example, examination of the rate of exchange of hydrogen in propene showed that at 25 °C three hydrogen atoms are already exchanged after 15 min. The exchange of five atoms takes place comparatively rapidly (up to 1.5 h), while the last hydrogen atom exchanges at a much lower rate[32]. The rate of exchange of six hydrogen atoms in the two methyl groups of isobutene is approximately an order of magnitude lower than in the $CH_3$ group of propene but an order of magnitude higher than the rate of exchange of the last two atoms. When isobutene is compared with tetramethylethylene (whose molecule has the same group of atoms but its structure is symmetrical and for this reason it has no dipole moment), the rate of reaction is seen to decrease by almost two orders of magnitude[5].

Thus the acidity of individual hydrogen atoms varies significantly as a function of the structure of the olefin molecule and in metallation one must expect the formation of an organometallic compound in which the most acidic hydrogen atom has been replaced by the metal. However, according to Morton and Holden's data[17], the structure and proportions of straight-chain butene metallation product are independent of the position of the double bond in the initial olefin. It has been shown for crotyl-lithium[43] that the ratio of different forms of organometallic compounds of the allyl type is determined by the reaction conditions, in particular by the temperature and the nature of the solvent. It has been established by NMR methods[44] that the first and third hydrogen atoms are equivalent in allyllithium $CH_2{=}CH-CH_2Li$, which indicates either the possibility of a rapid reversible migration of lithium between these atoms or the formation of a compound in which the lithium atom is delocalised[45]. It has been shown similarly[46] that the following species coexist in ethereal solutions of crotyl-lithium: $CH_3-CH{=}CH-CH_2Li$ and $CH_3-CH(Li)-CH{=}CH_2$.

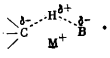
A number of workers[42,47-49] explained the nature of such organometallic compounds in terms of the concept of "polar" quantum-mechanical resonance, for the description of which the ground state of the anionic component is represented by a set of classical structural formulae for all possible electronic isomers, each of which is characterised by a definite contribution to this state[42]. The delocalisation of bonds, lone electron pairs, charges, and spins is energetically favourable and leads to resonance stabilisation of the molecule[42]. Delocalisation of the

negative charge facilitates the formation of a carbanion, but lowers the reactivity of the given compound[50].

Lefebvre and Chauvin[4] quote stability and reactivity series for carbanions:

| | | |
|---|---|---|
| Increasing reactivity ↓ | $R-CH-\bar{C}H-\bar{C}H-\bar{C}H_2$ | Increasing stability ↑ |
| | $R-CH=\bar{C}H$ | |
| | $R-\bar{C}H_2$ | |
| | $R_1-\bar{C}H-R_2$ | |
| | $R_1-\bar{C}(R_3)-R_2$ | |

In the metallation and isotope exchange reaction under consideration, which proceeds via the mechanism of an acid–base interaction, one must expect the formation in the limit of ions with a tervalent negatively charged carbon atom (free carbanions). In practice, polarised transition complexes with more or less stable hydrogen bonds are probably formed[5,32]. Their structure can be represented by the scheme[51,52]

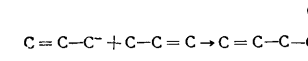


The organic derivatives of alkali metals, formed as a result of metallation, can be highly reactive intermediates in many chemical reactions which are discussed below. This is explained by the greater ionic character of the C–M bond in these compounds compared with other organoelement compounds[53]. Alkenylsodium compounds can also be used to synthesise various unsaturated derivatives with functional groups and also unsaturated carboxylic acids, unsaturated sulphonic acids, unsaturated alcohols, etc.[54]

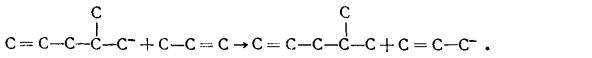
## III. REACTIONS OF OLEFINS CATALYSED BY DISPERSED ALKALI METALS AND THEIR COMPOUNDS

The first reports about the catalytic reactions of olefins in the presence of alkali metals were published as early as 1936.[55] Thirteen years later Freed took out patents for the dimerisation and codimerisation of alkenes in the presence of these catalysts[56,57]. The liquid products of the codimerisation of ethylene and propene, catalysed by metallic sodium, contained hydrocarbons with less than 10 carbon atoms, mainly pentenes and heptenes. The process was carried out under fairly severe conditions at temperatures and pressures in the range 275–400°C and 250–1000 atm respectively[56]. Under the same conditions, mainly hexenes were obtained from ethylene and isobutene and heptenes from propene and isobutene. The use of promoting agents (anthracene and naphthalene) made it possible to reduce the reaction temperature to 125–250°C.[57] The individual compositions of the olefins obtained were not determined.

Having investigated the dimerisation and codimerisation reactions of olefins in the presence of the "sodium with anthracene" catalyst, Mark and Pines[58] concluded that this reaction proceeds via the intermediate formation of resonance-stabilised carbanions, which determine the position where the olefin molecule adds. In the dimerisation of propene via the mechanism



the resulting isohexenyl carbanion, which is not stabilised by resonance, is rapidly involved in an acid–base reaction with the excess olefin. This leads to the regeneration of the allyl carbanion and the formation of 4-methylpent-1-ene:



The codimerisation of cyclohexene with ethylene, propene, and isobutene yielded mainly the products of the addition of olefins to cyclohexenyl carbanion, which confirms the postulated mechanism. 2,4,4-Trimethylpent-1-ene was obtained on dimerisation of isobutene[58].

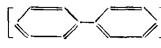
The low content of the thermodynamically least stable hexene, namely 4-methylpent-1-ene, in the products of the dimerisation of propene in the presence of the "sodium with anthracene" catalyst can be explained by its isomerisation with migration of the olefinic double bond to more stable methylpentenes with the double bond in the inner part of the molecule, in consequence of the high reaction temperature and the presence of the aromatic promoting agent. Indeed, subsequent studies[59–61] showed that propene can be successively dimerised to 4-methylpent-1-ene in the presence of dispersions of potassium, rubidium, and caesium in hydrocarbon solvents (such as alkanes, mineral oil, naphthenes, and aromatic hydrocarbons) as well as ethers and ammonia. The highest rates were achieved in benzene, but in this case a much greater amount of propane and solid condensation products is formed[61].

In the absence of aromatic promoting agents, dispersions of sodium and lithium are as a rule ineffective. However, their mixtures with "heavier" alkali metals (potassium and caesium) as well as mixtures of these metals are much more effective in the oligomerisation of olefins than potassium and caesium individually[62]. The dispersion of lithium obtained by the exchange reaction between an organolithium compound LiR (where R is an alkyl group) and a free alkali metal (as a rule potassium) is highly active[63–65]. Possibly in this case the high activity is associated with the fact that the catalytic complex incorporates a mixture of potassium and lithium. It has been shown[66] that preliminary heating of the catalyst to temperatures preceding codimerisation and its maintenance at these temperatures in the presence of olefins (for example, but-2-ene) greatly increases the rate of codimerisation of this olefin with ethylene and increases the yield of 3-methylpent-1-ene from 38 to 55 wt.%. It is suggested that the alkali metal catalyst be regenerated by heating it to 200–400°C in an inert solvent[67], but it has been stated[68] that such regeneration is ineffective.

A detailes study of the dimerisation of propene in the presence of dispersions of alkali metals[69] led to the conclusion that the yield of 4-methylpent-1-ene depends on the experimental conditions and the nature of the alkali metal used. A higher content of 4-methylpent-1-ene (up to 86 wt.%) in the reaction products was achieved in the presence of potassium dispersions without aromatic promoting agents at a reaction temperature not exceeding 150°C and an alkali metal concentration not exceeding 50 g litre$^{-1}$;[70–72] admittedly, under these conditions the degree of conversion fell appreciably (to 10–15%). Simultaneous experiments on the isomerisation of 4-methylpent-1-ene and 4-methylpent-2-ene in the presence of a dispersion of sodium containing anthracene and a dispersion of potassium without aromatic additives[69] showed that, under the conditions of the dimerisation of propene, the double

bond of 4-methylpent-1-ene migrates. The use of dispersions of heavy alkali metals without aromatic promoting agents in inert alkane solvents complicates somewhat the formation of the organometallic initiator derived from the alkali metal. It is most likely that it proceeds via unstable intermediates, formed as a result of electron transfer from the alkali metal to the olefin $\pi$-bond (radical-anions) [69].

When the dimerisation and codimerisation reactions of olefins are carried out in the presence of alkali metals in aromatic hydrocarbons [60] or using aromatic promoting agents such as biphenyl, naphthalene, and anthracene [73,74], the induction period decreases and (under the conditions of periodic experiments) the degree of conversion rises owing to the high acidity of the aromatic hydrocarbons. The highest degree of conversion and selectivity were achieved in the presence of the "potassium with biphenyl" catalyst [73]. The authors state that this is due to the higher rate of metallation of this aromatic hydrocarbon with formation of the "complex"



The modification of alkali metal catalysts by aliphatic or aromatic ethers and ketones [75] did not lead to a significant increase of the rate of reaction and process selectivity. It is recommended that catalysts consisting of a mixture of alkali metals with their oxides, hydroxides, or fluorides be used [76-78]. Catalysts having the general formula $A(MR^1, R^2, R^3)$, where A is the alkali metal, M is zinc, mercury, cadmium, or tin, and $R^1$, $R^2$, and $R^3$ are hydrocarbon groups or hydrogen, have been described [79,80]. The selectivity of the formation of 4-methylpent-1-ene in the presence of these catalysts is not more than 80%.

Promotion of catalysts based on alkali metals by alkyl halides [81-83], alkylphenols [84,85], allyl or aryl ethers [86], alkylamines [87], and other organic compounds [88-92] did not increase significantly their activity and selectivity in the formation of $\alpha$-olefins in the dimerisation and codimerisation reactions of low-molecular-weight alkenes.

The formation mainly of 3-ethyl-substituted products in the codimerisation of ethylene with but-2-ene and pent-2-ene [66,68] instead of the straight-chain olefins expected from the relative acidity, can be accounted for in terms of the characteristics of the metallation reaction. These results can probably be explained by the formation from both $\alpha$- and $\beta$-olefins of the same organometallic compounds, the carbanionic component of which can be described by the resonance involving the following structures:

$$R-\bar{C}H-CH=CH_2 \longleftrightarrow R-CH=CH-\bar{C}H_2 .$$

The authors [68] represent the intermediate in combination with the alkali metal cation and not in the form of an individual kinetic species, as was suggested previously [58], but the influence of the cation on the reaction is not discussed.

Wilkes [70,74,93-97] attempted to reproduce the laboratory data [56,57] on a larger scale in a pilot apparatus (reactor volume 38 litres) and to test the schemes for industrial processes developed by the authors of these investigations [62,67]. He concluded [74] that a dispersion of potassium is appreciably reactive only for a particle size in the range 1–10 $\mu$m. With increase of particle size, the access of the starting material to lower layers of the metal is hindered, which leads to reactions between organopotassium compounds with formation of condensation products which hinder access to the catalyst surface. Potassium is in the fused state at the reaction temperature (120–170°C) and the maintenance of suspensions with such fine particles is difficult, since they combine into larger aggregates on collision. In order to avoid the coagulation of the liquid metal particles, it is suggested [74] that oleic acid be added and that potassium be deposited on 50 $\mu$m talc particles. The use of such a stabilised dispersion, or the "precipitation catalyst" in Wilkes' terminology, ensures more satisfactory results. However, they are not quite as good [74] as in the gas-phase process in the presence of catalysts consisting of "alkali metals on inorganic carriers", which will be described below.

Analysis of studies on the codimerisation of olefins [68] led Wilkes to the conclusion that the reactivity of olefins with respect to metallic potassium decreases in the sequence ethylene > propene > isobutene and that a radical-anion is not formed as an intermediate. On the basis of these data as well as the results of the alcoholysis of the catalysts—metallic potassium and potassium hydride in a dispersed form and on a carrier ($K_2CO_3$), Wilkes suggested that the catalyst is formed on two centres, the hydride and a vinyl substitution product being generated [98]:

$$R-\underset{R_1'}{\overset{}{C}}=CH_2 + 2K \rightleftarrows \underbrace{\left[R-\overset{R'}{\overset{|}{C}}=CH\right]^-}_{(I)} K^+ + KH ,$$

where R, R′, and $R_1'$ are hydrogen or alkyl groups.

In the subsequent reaction with propene, the vinyl carbanion (I) gives rise to the thermodynamically more stable allylpotassium and the initial olefin is regenerated. The reaction of potassium hydride with propene yields propane and allylpotassium.

This mechanism is inconsistent with later experimental data [68]. Preferential vinyl metallation would be expected to result in the formation of a product of the addition of propene to vinylsodium (3-methylbut-1-ene) in the codimerisation reactions between ethylene and propene and in vigorous dimerisation of ethylene with formation of but-1-ene. However, appreciable amounts of 3-methylbut-1-ene were not detected under these conditions [68,97], while the dimerisation of ethylene proceeds at a rate approximately two orders of magnitude lower than the dimerisation of butenes [100]. It is interesting to note that even insignificant amounts of but-1-ene, formed in the dimerisation of ethylene, rapidly combine with another ethylene molecule, and up to 27.0 wt.% of the ethylene trimer 3-methylpent-1-ene was detected in the reaction product [100].

All these findings permit the conclusion that the metallation of ethylene (vinyl metallation) proceeds, as shown previously [6,16,17], at a much lower rate than the allyl metallation (for example, the metallation of propene). The stage involving the formation of the catalyst, where the metallation takes place in the presence of a relatively inactive metallating agent (alkali metal), therefore proceeds via a stage in which a radical-anion is formed and not the product of the vinyl metallation of the olefin. The cause of the high rate of codimerisation of ethylene with propene or straight-chain butenes is probably the greater ease of addition of ethylene to anions compared with other olefins [58].

The dimerisation and codimerisation reactions of olefins are regarded not only as the addition of alkenes to carbanions but also as a specific instance of limited (degenerate) anionic homopolymerisation or copolymerisation of olefins [4,102]. This approach makes it possible to explain certain features of these reactions, for example the

dependence of the yield of oligomerisation products on the monomer ratio and the degree of conversion [102,103].

Having examined the possible pathways to the formation of dimerisation and codimerisation products of monoolefins in the presence of alkali metal catalysts, we shall now proceed to the prototropic shifts induced by the isomerisation of unsaturated hydrocarbons which is catalysed by bases as well as other substances. It has been established [104] that in an anhydrous medium KOH causes the stereospecific isomerisation of straight-chain butenes at 320°C to *cis*-but-2-ene. But-1-ene has been obtained from *cis*- or *trans*-but-2-ene. Sodium hydroxide catalyses this reaction at 400°C, while LiOH, which is a weaker base, catalyses it at 440°C. The isomerisation of high-molecular-weight $\alpha$-olefins with migration of the double bond in the presence of sodium isopropoxide [105] and potassium butoxide [106] has been described.

A number of workers [107-113] investigated the isomerisation of olefins under the influence of potassium amide at the boiling points of the hydrocarbons. They put forward for the first time the idea that the first stage of this reaction is the partial dissociation of hydrogen from the C–H bond in the allyl position relative to the double bond [108]:

$$R{-}CH_2{-}CH{=}CH_2 + MNH_2 \rightarrow [R{-}\overline{C}H{-}CH{=}CH_2]\,M^+NH_3 .$$

The negative charge in the resulting carbanion can shift in the direction of the double bond with formation of the carbanion (III):

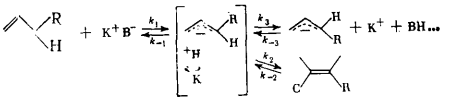
$$\underset{(II)}{[R{-}\overline{C}H{-}CH{=}CH_2]\,M^+NH_3} \rightarrow \underset{(III)}{[R{-}CH{=}CH{-}\overline{C}H_2]\,M^+NH_3} .$$

After the addition of a proton, the carbanion gives rise to an olefin with the double bond in a new position. As was to be expected on the basis of the proposed mechanism, the hexenes where the allyl position contains the maximum number of hydrogen atoms isomerise faster [109], since substitution of hydrogen by electron-donating alkyl groups entails a decrease of the mobility of the remaining hydrogen atoms.

Shatenshtein and coworkers [5,114,115] showed that not only calcium amide but also potassium amide in liquid ammonia cause the isomerisation of alkenes. Later it was noted that the reactions catalysed by these amides involve the isotope exchange of hydrogen [32] together with the migration of the double bond, which constitutes a clear confirmation of the views of Gostunskaya et al. [108]

The participation of the carbanion in the isomerisation process in the presence of basic catalysts has also been demonstrated by Astaf'ev and Shatenshtein [116]. The C–H bonds in allylbenzene $C_6H_5{-}\overset{*}{C}H_2{-}CH{=}CH_2$ located at the position marked with as asterisk are involved in conjugation with the electronic system of the aromatic ring and with the multiple bond. The hydrogen in this position therefore ionises in an ammonia solution of potassium amide and a carbanion is formed with the characteristic absorption spectrum [5]. When the amide is neutralised with an ammonium salt, mainly propenylbenzene $C_6H_5CH{=}C{-}CH_3$ is formed, i.e. the double bond migrates [117]. However, a free carbanion is by no means always formed during isomerisation. According to Shatenshtein [5], in most cases partial dissociation of hydrogen in the form of a proton is most likely to occur with its simultaneous migration, for example in the trimolecular complex in the transition state.

Certain observations confirming these views have been described [118-121]. It has been established that the isomerising activity of potassium t-butoxide depends on the nature of the solvent [119]. At a temperature as low as 40–60°C, albeit for a comparatively long contact time (24 h for linear and up to 500 h for branched olefins), it was possible to achieve thermodynamic equilibrium in butene, pentene, and 2-methylpentene isomers. The use of labelled olefins showed that the isomerisation occurring in the potassium t-butoxide–dimethylsulphoxide system proceeds within the complex of the olefin and the catalyst [118-121]. Hydrogen transfer from one molecule to another was not observed; there is only an intense isotope exchange between the olefin and the solvent–dimethyl sulphoxide. These results were interpreted on the basis of a model with a chemically bound ion pair [120]:



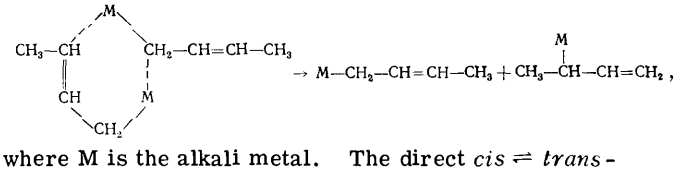
$k_3 < k_1$; $k_2$

$B^- = O^-$-Bu-t .

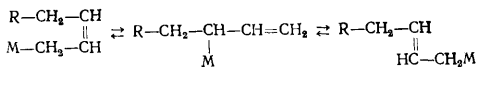
The rate of isomerisation of hydrocarbons depends both on the strength of the base and on the acidity of the allyl hydrogen atom in the olefin. For example, penta-1,4-diene, which has very acidic hydrogen atoms, isomerises under the influence of potassium t-butoxide in dimethyl sulphoxide approximately $10^8$ times faster than does pent-1-ene [121]. It has been noted [118,120] that 2-methylpent-1-ene isomerises to 2-methylpent-2-ene faster than 2-methylpent-2-ene isomerises to 4-methylpent-2-ene. The authors [118,120] explained the kinetic observations by the relative stability of the carbanions formed as intermediates.

The migration of the multiple bond is also catalysed by organosodium compounds formed as a result of the reaction of sodium with the promoting agent, for example *o*-chlorotoluene or anthracene [122-125]. The possibility of using the product of the reaction of lithium with ethylenediamine as a homogeneous catalyst of this reaction has been reported [126,127]; the replacement of lithium by sodium in this instance lowers the activity of the catalyst.

Wittig [128] established that organolithium compounds are dimerised in solution. On this basis, Kropachev et al. [43] suggested that this facilitates the isomerisation step, as a result of which one of the molecules isomerises, while the other remains unchanged:



where M is the alkali metal. The direct *cis* $\rightleftharpoons$ *trans*-transition is known to require an appreciable activation energy, so that the reaction may proceed via the mechanism [43]



All the studies of the isomerisation reactions of olefins in the presence of basic catalysts have shown that the catalysts examined accelerate only the migration of the double bond in the molecule and do not affect the carbon skeleton. The alkylation of alkylbenzenes by monoolefins, catalysed by alkali metals and some of their compounds, exhibits a remarkable selectivity: olefins add only to the side chain of the alkylbenzene. A detailed

examination of these reactions suggested[1] that the characteristic features of these transformations are associated with the formation of intermediates—alkylbenzene carbanions.

Thus the investigators who studied both the hydrogen isotope exchange in hydrocarbons in the presence of bases and the base-catalysed dimerisation, codimerisation, isomerisation, and alkylation reactions of olefins concluded that all these reactions proceed via a stage involving the formation of carbanions. However, free carbanions are not as a rule produced. Only an electron shift in the direction of the formation of $\equiv C^-$ may occur in the transition state[5].

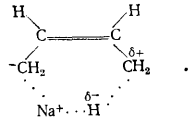
## IV. REACTIONS OF OLEFINS UNDER THE INFLUENCE OF ALKALI METALS ON CARRIERS

Alkali metals on solid inorganic carriers are more effective catalysts of the isomerisation, dimerisation, codimerisation, oligomerisation, and hydrogenation reactions of olefins than dispersions of alkali metals or solutions of their compounds in hydrocarbon solvents. Thus, in their early studies of the isomerisation of olefins in the presence of basic catalysts, Pines and coworkers[129,130] already investigated a whole series of catalysts consisting of sodium or lithium on inorganic carriers and showed that alkali metals "with a large surface area as a result of their deposition on activated alumina"[1] are the most active catalysts. According to the authors, they are capable of abstracting protons from olefin molecules with formation of intermediates, stabilised as a result of the resonance involving the following structures:[130]

$$\underset{\text{(IV)}}{R-\overset{Na^+}{\overline{C}H}-CH=CH_2} \leftrightarrow \underset{\text{(V)}}{R-CH=CH-\overset{Na^+}{\overline{C}H_2}}\ .$$

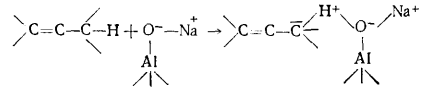
In the presence of an excess of the olefin, the metal is exchanged for an allyl proton, which leads to the formation of the isomerised olefin with structure (V) and the regeneration of the intermediate (IV). This reaction may be interrupted as a result of the formation of a compound which is insufficiently basic to metallate the olefin, for example a polyene, when a hydride ion is split off[1].

Study of the isomerisation kinetics[130] showed that, after a short contact time, but-1-ene is converted preferentially into *cis*-but-2-ene and not into the thermodynamically more stable *trans*-isomer. The stereospecificity of the catalyst may be accounted for either by the fact that but-1-ene reacts faster with the *cis*-butenyl carbanion or by the fact that the *cis*-butenyl carbanion is present in the reaction mixture at higher concentrations. The latter interpretation is more probable[130], which may be accounted for by the additional resonance stabilisation of the structure[1]



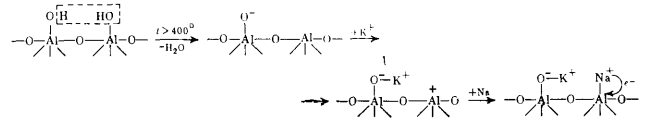
It has been shown[123] that a dispersion of lithium on $\gamma$-$Al_2O_3$ is not as active as the corresponding sodium catalyst. The authors[130] believe that one of the causes of the high activity of the latter catalyst may be the formation of organosodium compounds from the alkali metal and reactive impurities in the olefin. This view is based on data[122,123,129,131-134] showing that sodium isomerises olefins much more readily in the presence of such an organic compound, for example chlorobenzene and chlorotoluene.

Another cause may be the replacement of the protons of the hydroxy-groups on the surface of alumina by sodium, which leads to the suppression of the Brønsted acidity with the simultaneous appreciable enhancement of the basicity of the oxygen anions[130,135]. The formation of carbanions can be explained in this case by the mechanism[135]



This hypothesis makes it possible to explain also the increased activity of the "Na on $\gamma$-$Al_2O_3$" catalyst in reactions involving the migration of the multiple bond in hexenes and vinylnorbornene {5-vinylbicyclo[2,2,1]hept-2-ene} when alumina is modified by solutions of potassium carbonate[136-140]. Preliminary vacuum heat treatment or treatment in a stream of inert gas is known to entail the dehydration of the surface of this oxide and the formation of Lewis acid or basic centres[141,142]. The $K^+$ ions in the potassium carbonate solution deactivate the Lewis basic centres and the residual Brønsted acid centres[143,144], while sodium apparently forms an ion linked by a one-electron bond to the $Al_2O_3$ surface[102]. The ionisation of sodium is clearly demonstrated by the appearance of a blue colour when it is deposited[102]. A similar pattern of colour changes is observed when alkali metals are dissolved in ammonia. The formation of ions under these conditions is known and has been confirmed by many methods, in particular by the high electrical conductivity of the solution[145].

The increase of the activity of the "Na on $\gamma$-$Al_2O_3$" catalyst when the carrier has been thermally activated at 400–500°C is probably associated with the fact that the sodium atom forms with a surface-unsaturated aluminium atom (a Lewis acid centre) an active catalytic complex, for example of the kind represented schematically below[102]:



Other workers[146], who investigated the isomerisation of $\alpha$-butene on potassium deposited on $\gamma$-, $\eta$-, and $\alpha$-$Al_2O_3$ and quartz, reached similar conclusions.

The use of not only the "sodium on $\gamma$-alumina" catalysts[147-151] or others where sodium is deposited on molecular sieves[152,153] but also catalysts of a similar type, namely potassium or potassium amide on $\gamma$-$Al_2O_3$[154-156] and a complex of graphite with an alkali metal[157], has been recommended for the isomerisation of butenes, pentenes, and hexenes[157]. The enhancement of the isomerising capacity of the "Na on $\gamma$-$Al_2O_3$" catalyst has been observed when the latter is flushed with air[151]. The kinetics of the isomerisation of vinylnorbornene on potassium amide in liquid ammonia have been described[158]. In contrast to the thermal isomerisation of this hydrocarbon[159], which leads to the formation of tetrahydroindene {bicyclo[4,3,0]-nonadiene}, the base-catalysed reaction leads only to the migration of the multiple bond without affecting the ring.

As a rule, in the processes described alkenes with the double bond in an internal position are obtained from $\alpha$-olefins. However it has been suggested[160,161] that

$\alpha$-alkenes be obtained from their $\beta$- and $\gamma$-isomers using the shift of thermodynamic equilibrium, by distilling from the reaction zone the required $\alpha$-olefins, which are as a rule more volatile than their isomers. Although this idea arouses no objections in principle, when it is applied one encounters the difficulty of isolating the required products from the equilibrium mixture where their content is relatively small. A more effective procedure involves the formation of 4-methylpent-1-ene from 2-methylpent-1-ene and 2-methylpent-2-ene by the method of the so called "antithermodynamic isomerisation" in the presence of borides, which Ziegler developed[162,163]. The products of this reaction contain 45–70% of the required compound.

The vapour-phase dimerisation and codimerisation of alkenes in the presence of catalysts on carriers containing an alkali metal or its compound is characterised by a high degree of conversion of the starting material, improved selectivity, and long duration of the continuous operation of the catalyst. Potassium and sodium or their mixtures and more rarely lithium, rubidium, and caesium are usually recommended for the preparation of such catalysts. Inorganic oxides, for example MgO, $Al_2O_3$, CaO, ZnO, alumino- and magnesio-silicates[164-175], inorganic acid salts ($K_2CO_3$, $K_2SiF_6$, NaCl, KCl, etc.)[173,176,177], alkaline earth metal hydrides[179], metallic aluminium, magnesium, copper, silver, iron, cobalt, nickel, and their mixtures[180-184], and crystalline zeolites[185] are used as the carriers.

An active catalyst for the conversion of olefins was obtained by depositing potassium on magnesium oxide. It is pointed out that the selectivity of the dimerisation and codimerisation of alkenes with respect to the required $\alpha$-olefin improves when the carrier has been heat-treated at 500–1000°C.[166] It has also been suggested[167-173] that potassium and potassium amide on alumina be used. The authors believe that the composition of the propene dimer obtained in the presence of these catalysts is determined by the specific surface of the carrier. Judging from the data which they quote, the highest yield of $\alpha$-olefins is attained when the oxide has a small specific surface. The surface was reduced by the heat-treatment of the carrier at temperatures up to 1200°C, but the authors[167-169] did not take into account the fact that this entails also the conversion of the $\gamma$-form of the oxide into the $\alpha$-form, i.e. a change not only in the specific surface but also in other surface properties for example, acidity.

The study of the influence of the porosity of the carrier on the yield of 4-methylpent-1-ene in the dimerisation of propene[74] showed that, with decrease of pore radius, the content of this $\alpha$-olefin in the dimerised product diminishes and the yield of its $\beta$-, $\gamma$-, and $\omega$-isomers increases.

Alkali metal hydrides are more advantageous than the pure alkali metals because of the higher rate of dimerisation and the greatly reduced period required for the formation of the catalyst[186-191]. It is suggested that not all alkali metal hydrides but only the hydrides of the most reactive metals (potassium, rubidium, caesium, or their mixtures) be used on the following carriers: carbon black, potassium, rubidium, and caesium carbonates, or powdered glass[186,189,190]. A high activity of the catalyst and selectivity of the dimerisation of propene to 4-methylpent-1-ene (approximately 90–92%) were attained on a catalyst consisting of a mixture of potassium, copper, and sodium[192] or potassium[183] alkoxide. Catalysts comprising alkali metals or their hydrides and charcoal have been described[193-210]. Mainly methylpentenes with the multiple bond in an internal position have been obtained in their presence. Exceptions are catalysts containing an amino-group[193] as well as layer complexes having the overall formula $MC_X$ with a definite alkali metal : carbon ratio[195,197,198,209,210]. The physicochemical principles of the reactions in the presence of such complexes have been examined[211].

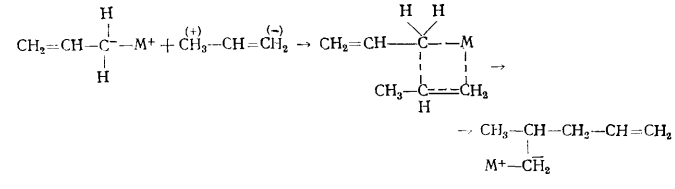
Comparison of various catalysts for the dimerisation of propene to 4-methylpent-1-ene[102,212-236] led to the conclusion that elemental alkali metals on alkali metal carbonates are the most effective catalysts[177,213-232]. It has been noted that the composition of the products of this reaction changes only slightly on passing from one alkali metal to another. The nature and surface properties of the carrier have a decisive influence on the direction of the reaction towards the formation of a particular isomer[102]. Thus, when the alkali metal is deposited on potassium carbonate (specific surface $S = 0.15$ m$^2$ g$^{-1}$), propene dimerises mainly to 4-methylpent-1-ene[213-220], while in the presence of $\gamma$-$Al_2O_3$ ($S = 250$ m$^2$ g$^{-1}$) the product is 2-methylpent-2-ene[167]. Mainly *cis*- and *trans*-4-methylpent-2-enes are formed on the "Na on $\alpha$-$Al_2O_3$" catalyst ($S = 14$ m$^2$ g$^{-1}$).[102,169]

However, the surface area is not apparently the only factor determining the efficiency of the carrier. For example, sodium deposited on a ceramic, pumice, or a faience carrier with a low surface area proved to be inactive in the dimerisation of propene[102].

Catalysts containing an alkali metal on inorganic alkali metal salts (halides, sulphates, silicates, and carbonates) showed a high activity[213,228].

The experimental data described cannot be accounted for in terms of a reaction mechanism providing for the intermediate formation of carbanions as separate kinetic species[58]. Evidently, when a carbanion is really the reaction centre, then in such a mechanism of the propagation reaction the capacity for oligomerisation should be shown only by electron-accepting vinyl compounds, because a carbanion is an electron-donating agent. Ethylenic and diethylenic hydrocarbons, which are electron-donating substances[237,238], should not combine with a carbanion and should not therefore oligomerise under the influence of substances capable of forming carbanions[237].

These findings can be best explained in terms of an anionic-coordination mechanism[239] based not on a carbanion but on an ionic aggregate containing the metal ion as well as the carbanion. In this case, the transition state consists of a four-membered ring[239] and the dimerisation of propene can be represented schematically as follows[102]:

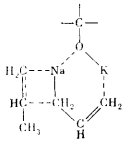


A definite coordination in the addition of the monomer to the active centre is probably promoted also by the polarisation of the olefin molecule as a result of the $\pi$–$\delta$ conjugation, which has been observed in many ways, for example with the aid of isotope exchange[5,240,241].

It was shown previously[212] that sodium catalysts show a low activity in the dimerisation of propene in the presence of alkali metals dispersed in inert hydrocarbon solvents. However, when sodium is deposited on an inorganic acid salt (for example, on potassium carbonate) or $\gamma$-$Al_2O_3$, catalysts for the dimerisation of propene more effective

than the potassium catalysts are obtained[228]. This phenomenon has been attributed by some workers to the displacement of potassium from the inorganic acid salt by sodium[74,242]. However, the hypothesis[243] that the activation of allylsodium compounds by inorganic acid salts proceeds in consequence of the formation on the surface of the carrier of the so called "double coordination complex" appears more likely. Such complexes are formed with compounds where the metal–carbon bond is conjugated with a double bond or a phenyl group[17,243]. They consist of ionic aggregates, where alkali metal atoms exhibit both basic and coordination valences[237,244]. The reaction is believed[244] to proceed via the adsorption of a monomeric molecule on the ionic aggregate with the coordination and activation of the former on the surface of the latter and the subsequent interaction with the anion located on the same site. The increase of activity is attributed to the enhancement of the polarisation of the $M^{\delta+}-\overset{\delta-}{C}<$ bond on formation of the complex. It has been shown that the activity of the catalyst increases when the distance $r$ in the inorganic salts employed, equal to the sum of the ionic radii, is greater than 2.75 Å and the complex contains different alkali metals[245].

The results of studies on the selection of catalysts for the dimerisation and codimerisation of olefins agree well with the investigations of polymerisation processes carried out by Morton[243,244]. This justifies the hypothesis that the activation of allylsodium by potassium carbonate is associated with the formation of a "double coordination complex" and that the selectivity of the reaction can be explained by the selective adsorption of a monomeric molecule in its field and that the transition state in the dimerisation of propene may be represented schematically as follows[102]:



These views on the reaction mechanism are confirmed by data[246] showing that the addition of mercury or transition metals to the "sodium on potassium carbonate" catalyst alters fairly appreciably the rate but not the proportions of reaction products. The authors concluded[246] that the rate-limiting stage of the reaction is the adsorption of propene. It has been shown[102,247] that the rate and selectivity of the dimerisation of propene depend on the content of metallic sodium in the catalyst. Hambling[247] attributed the change in selectivity to the isomerisation of 4-methylpent-1-ene catalysed by allylsodium. However, this mechanism appears unlikely, since the allyl carbanion is a comparatively weak base, while 4-methylpent-1-ene is a very weak acid. The Shaw mechanism[69], with chain termination via the dimer, where a strong base, namely the isohexenyl carbanion

$$M^+[CH_3-\underset{\displaystyle CH_2}{\underset{|}{CH}}-CH-CH=CH_2]^-$$

acts as the metallating agent, appears to be more likely.

The study of the composition of high-molecular-weight side products of the dimerisation of propene in the presence of the "sodium on potassium carbonate" catalyst showed that they consist mainly of $C_9$ olefins, formed via the mechanism involving the addition of the dimer to the active allyl centre responsible for the dimerisation[248].

In contrast to the dimerisation of propene, that of ethylene in the presence of the "Na on $K_2CO_3$" catalyst proceeds at insignificant rates, apparently owing to the difficulty of the substitution of a proton in the vinyl group[100]. The reaction products consist mainly of but-1-ene and 3-methylpent-1-ene. The latter is probably formed via the mechanism involving the addition of an ethylene molecule to the *s*-butenyl carbanion† [100,247].

But-1-ene dimerises at a higher rate than ethylene, because, as already pointed out, but-1-ene is metallated faster. The two structures of the carbanions formed under these conditions,

$$Na^+\left[\begin{array}{l}CH-CH=CH_2\\ |\\ CH_3\end{array}\right]^- \leftrightarrow Na^+\left[\begin{array}{l}CH=CH-CH_2\\ |\\ CH_3\end{array}\right]^-,$$

give rise to 3,4-dimethylhex-1-ene and 5-methylhex-2-ene following the addition of the next but-1-ene molecule[100], as was to be expected on the basis of the postulated mechanism.

The codimerisation of ethylene and but-1-ene in the presence of the "Na on $K_2CO_3$" catalyst is approximately an order of magnitude faster than the dimerisation of butenes. This can be explained by the involvement in the given reaction of a readily metallated alkene (but-1-ene and ethylene), which adds to the carbanion at a higher rate. The principal products of this reaction—3-methylpent-1-ene and hex-2-enes (with the former predominating)—are formed as a result of the addition of ethylene to the first or second structure of the s-butenyl carbanion respectively[100,247]. The codimerisation of ethylene with propene in the presence of this catalyst at 80–120°C gave 92 wt.% of pentenes, 5.2 wt.% of heptenes, and only 2.6 wt.% of hexenes. Thus the addition of ethylene to the allyl anion in the above temperature range is approximately 40 times faster than the addition of propene (pent-1-ene and 4-methylpent-1-ene predominate in the pentene and hexene fractions respectively)[247].

The yield of high-molecular-weight olefins, particularly $C_7$ and $C_8$ olefins, is much higher in the codimerisation reactions involving ethylene. Furthermore, the rate of formation of octenes in the codimerisation of ethylene and but-1-ene increases with increase of the content of ethylene in the starting material[103]. The composition of the $C_8$ olefins (the main products are 3-methylhept-1-ene, oct-4-enes, 3-ethyl-3-methylpent-1-ene, 3-methylhept-3-ene, 4-ethylhex-2-ene, and 5-methylhept-3-ene) shows that these alkenes are formed as a result of the successive addition of two ethylene molecules to the butenyl carbanion and not as a result of the dimerisation of butenes[103].

The heptenes formed as side products in the codimerisation of ethylene and propene in the presence of the "sodium on potassium carbonate" catalyst contain mainly 3-pent-1-ene and also admixture of *cis*- and *trans*-hept-3-enes and *cis*- and *trans*-4-methylhex-2-enes[247,249]. The formation of these alkenes can be explained by the addition of ethylene to three types of anions, which may be produced on metallation of straight-chain pentenes:

$$Na^+\left[\begin{array}{l}CH-CH=CH_2\\ |\\ CH_2\\ |\\ CH_3\end{array}\right]^- \quad (VI);$$

$$Na^+\left[\begin{array}{l}CH_2-CH=CH\\ \qquad\quad |\\ \qquad\quad CH_2\\ \qquad\quad |\\ \qquad\quad CH_3\end{array}\right]^- \quad (VII);$$

$$Na^+\left[\begin{array}{l}CH_3-CH-CH\\ \qquad\quad \|\\ \qquad\quad CH\\ \qquad\quad |\\ \qquad\quad CH_3\end{array}\right]^- \quad (VIII)$$

† Here and henceforth the abbreviation "...addition to carbanion..." has been adopted, which will be understood as "addition of an olefin molecule to the active centre containing the given carbanion".

The same olefins have been obtained in a direct synthesis of heptenes from ethylene and pent-1-ene [247,249]. However, the contents of 3-ethylpent-1-ene and hept-3-enes are approximately 86 and 11 wt.% respectively, which gives a somewhat higher ratio than that of the carbanions (VI) and (VII) in metallation products, which is 4 : 1. [17] The content of 4-methylhex-2-enes, the products of the addition of ethylene to the carbanion (VIII), is lower still, namely 2.6 wt.%, which might be accounted for by the low content of pent-2-enes in the reaction zone. However, in the codimerisation of ethylene and pent-2-enes, the reaction rate was somewhat higher, but the content of 4-methylhex-2-enes increased insignificantly [249]. An improved yield of straight-chain heptenes in this reaction was achieved only after the simultaneous alteration of the nature of the alkali metal as the "active component" and of the catalyst carrier. Thus, on replacing the "Na on $K_2CO_3$" catalyst by the "K on $Li_2CO_3$" catalyst, the yield of linear $C_7$ olefins was sharply increased (up to 50%). [250]

These results can be explained on the basis of a mechanism taking into account not only the relative stabilities and reactivities of various anions but also the influence of the cations derived from the organometallic compound and the inorganic carrier. The decisive factors responsible for the specificity of the action of the catalyst are apparently the stability and reactivity of the complex formed by the anion, the cation, and the inorganic alkali metal salt [102].

The possibility of employing $\beta$-olefins as the starting materials for codimerisation reactions is extremely attractive, since it makes it possible, in the first place, to obtain on their basis valuable $\alpha$-olefin monomers for the synthesis of heat-resistant plastics (with melting points in the range 350–420°C) [251] and, in the second place, to make use of new sources of starting materials, for example industrial petroleum fractions [252] and the disproportionation [253–255] or isomerisation products of lower mono-olefins [249]. By altering the composition of the starting material and the carrier for the alkali metal, a number of workers [254,256–261] obtained a wide range of methylpentene and ethylpentene positional isomers.

Reactions involving the addition of propene to olefins in the presence of the "Na on $K_2CO_3$" catalyst require the use of more severe temperature conditions (140–170°C) [262] than the reactions in which ethylene adds to the same alkenes (80–100°C) [247]. It has been shown that, for an equimolecular mixture of propene and but-1-ene, the rate of addition of propene to a mixture of allyl and butenyl anions is approximately 15 times higher than the rate of addition of but-1-ene. The presence of a methyl substituent at the butenyl anion lowers the rate of addition of olefins by a factor of seven compared with the allyl anion [247].

The effective oligomerisation reaction on catalysts with an acid-free carrier is as a rule preceded by a fairly long period involving the formation of the complex during which the olefins are metallated and active centres containing carbanions are formed. The duration of this period diminishes in the presence of alkali metal catalysts with an acid carrier. It can be shortened by treating the catalyst with hydrogen or a readily metallated olefin before the start of the reaction [223,256]. It has been suggested that alkali metal hydrides themselves be deposited instead of the treatment with hydrogen [191]. At the end of the induction period, the rate of reaction is stabilised for a long time [225,247], which supports the hypothesis that the reaction proceeds in the presence of a constant number of active centres. Activity is lost owing to the gradual shielding of the surface by the extensive condensation products, which are probably formed as a result of the dehydrogenation [63], dehydrocyclisation, and the so called "internal alkylation" described by Richey and coworkers [263]. As a result of the last reaction, cyclic compounds, for example methylcyclopentane, may be formed [68].

This type of catalyst may be regenerated with hydrogen [220,221], but this probably entails the hydrogenation of condensation products with a deficiency of hydrogen (one hydrogen atom for two carbon atoms) [68]. Although alkali metals are not transition metals, they catalyse the hydrogenation of aromatic molecules and their catalytic activity increases from lithium to rubidium. The most active catalyst of this reaction is sodium on potassium carbonate [242]. The possibility of the regeneration of alkali metal catalysts on carriers combined with the long period of their operation between regenerations (not less than 800 h) and high selectivity and activity [217,224,247,264], make these catalysts promising for the oligomerisation of olefins. It is not fortuitous that the first industrial process involving the dimerisation of propene to 4-methylpent-1-ene has in fact been achieved in the presence of these catalysts [264]; studies on their modification are being continued [180–185,246,265–267].

A tendency has arisen to employ alkali metals on carriers, particularly "Na on $K_2CO_3$" [268] or alkali metal complexes with carbon [269], in alkylation reactions which had been studied previously in the presence of dispersions of alkali metals or their complexes with aromatic hydrocarbons.

So many studies have been devoted to the polymerisation of diolefins in the presence of basic catalysts that even their simple enumeration is difficult within the framework of the present review. We shall only note that the view according to which these reactions proceed via "anionic-coordination" [239] or "coordination" [237] mechanisms, presupposing the formation of active centres containing organometallic compounds of alkali metals [270], has predominated in recent years. The reactions of dienes, which occur at higher rates, are undesirable side processes in the reactions of the less reactive mono-olefins, since the formation of dehydrocyclisation of high-molecular-weight diene polymers lead to the rapid deactivation of the catalyst. It is therefore recommended that the content of diene and acetylenic impurities in the olefinic starting materials be kept at the level of five parts per million [213]. It has been shown [271,272] that, in the presence of mono-olefins, dienes form not only homopolymers but also copolymers with the alkenes on the alkali metal catalysts.

Although the synthesis of polyolefins in the presence of alkali metal catalysts on carriers was achieved as early as 1954, [273] these studies were not developed further and research was continued mainly on the dimerisation and codimerisation of olefins. Reports concerning the preparation of $C_{10}$–$C_{16}$ oligomers with a narrow molecular weight distribution appeared only recently [274]. Using the "Na on $\gamma$-$Al_2O_3$" catalyst containing 0.2–2.1% of OH groups, it is possible to obtain detergent olefins [274] containing up to 50% of $\alpha$-olefins. This comparatively high content of surface hydroxyls distinguishes the above catalyst from those for the dimerisation of olefins, where the OH content is reduced to a minimum by the thermal activation of the carrier at 500°C.

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Thus examination of certain reactions of alkenes in the presence of basic catalysts has shown that they probably

occur with the intermediate formation of organic compounds of the alkali metals, the characteristics of the synthesis and reactions of which are of decisive importance for the specificity of the reactions investigated and the composition of their products. Being highly reactive compounds in consequence of the ionic character of the C—M bond, these substances accelerate the dimerisation, codimerisation, oligodimerisation, isomerisation, alkylation, and hydrogenation reactions of low-molecular-weight mono-olefins. The interaction of the carbanionic and metallic components of these compounds is most likely to be determined not only by electrostatic but also by exchange forces and depends significantly both on the structure of the carbanion and on the nature of the alkali metal. Free carbanions are apparently not formed in the transition state and there is merely an electron shift in the direction of the formation of $\rangle C^-$. The involvement of two catalyst centres in the transition state tends to increase the selectivity of the reaction. Modification of the catalysts (organic derivatives of alkali metals) by inorganic carriers and additives to the latter makes it possible to increase the activity and selectivity of the catalysts and in many cases constitutes an effective method for altering the mode of reaction. The results achieved using alkali metal catalysts on carriers show that promising methods for the processing of olefins can be devised on their basis.

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# Methods of Synthesis of Imidazopyrimidines with a Bridgehead Nitrogen Atom and Their Benzo-analogues

I.A.Mazur, B.E.Mandrichenko, and R.I.Katkevich

The methods of synthesis of imidazopyrimidines with a bridgehead nitrogen atom, namely imidazo[1,2-*a*]pyrimidines, imidazo[1,2-*c*]pyrimidines, and their benzo-analogues, are examined, particular attention being devoted to methods of synthesis of preparative value. Certain theoretical problems associated with the formation of these heterocyclic condensed systems are discussed.
The bibliography includes 157 references.

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## I. INTRODUCTION

Among the nitrogen-containing heterocycles which are constituents of alkaloids, vitamins, nucleic acids, enzyme systems, etc. imidazolines with a bridgehead nitrogen atom, namely imidazo[1,2-*a*]- and imidazo[1,2-*c*]-pyrimidines, have attracted attention in recent years. Derivatives of the latter type—the alkaloids alchornine, alchornidine, and alchorneine—have been recently isolated from plants of the genus *Alchornea*.[1-3]

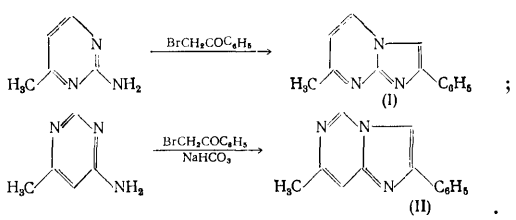
The search undertaken in recent years for biologically active imidazopyrimidines with a bridgehead nitrogen atom, which are structural analogues of purines, led to the detection among them of compounds with a broad spectrum of biological activity[4-18]. This resulted in an increased interest in the development of procedures and methods for the synthesis of these heterocyclic sytems.

The present review is in essence the first attempt at a survey and a critical examination of the literature data, mainly those obtained recently, on the methods of synthesis of imidazopyrimidines with a bridgehead nitrogen atom, since the information on this problem quoted in Shvachkin's review[19], published 20 years ago, is extremely limited and already obsolete. In the present review, a systematic account is given of all the available literature data and the methods of synthesis of imidazo[1,2-*a*]- and imidazo[1,2-*c*]-pyrimidine systems and the limits of their applicability and preparative value are estimated.

## II. ALKYLATION OF AMINOPYRIMIDINES AND AMINOIMIDAZOLES

### 1. Alkylation of 2(4)-aminopyrimidines

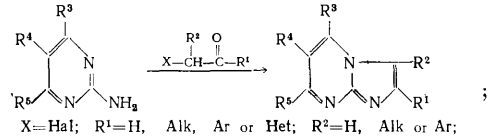
The classical method for the preparation of imidazo[1,2-*a*]- and imidazo[1,2-*c*]-pyrimidines, the alkylation of 2-amino- and 4-amino-pyrimidines, was achieved for the first time by Ochiai and Jamai[20] in 1939. By heating 2-amino-6-methyl- and 4-amino-6-methyl-pyrimidines with phenacyl bromide, they synthesised 7-methyl-2-phenylimidazo[1,2-*a*]-pyrimidine (I) and 7-methyl-2-phenylimidazo[1,2-*c*]-pyrimidine (II):



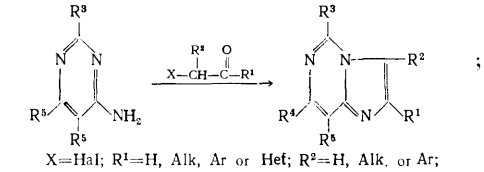

Subsequently, the method was applied to the synthesis of a whole series of unsubstituted and *C*- or *N*-substituted 2- and 4-aminopyridines[12-14,21-46]. The wide scope of this reaction, which is suitable for the synthesis of virtually all imidazopyrimidines with functional groups, is illustrated in Scheme 1.

The method discussed is fairly promising, since it permits the use of a whole series of alkylating agents and an appreciable variation of the experimental conditions. The alkylating agents employed were $\alpha$-bromo(chloro)-ketones and $\alpha$-bromo(chloro)aldehydes or their acetals. The alkylation process is usually carried out by heating equimolar amounts of the reactants to 60–100°C in an organic solvent (pure alcohols, dioxan, toluene and dimethylformamide) or in water. In order to prevent the formation of salts by the aminopyrimidines[46], which hinders the reaction, basic reagents are used: sodium hydroxide, sodium bicarbonate, and trialkylamines[31].

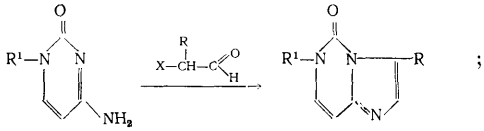
Scheme 1



X=Hal; $R^1$=H, Alk, Ar or Het; $R^2$=H, Alk or Ar; $R^1R^2$=$-(CH_2)_n-$; $R^3$=H, OH, Alk or Ar; $R^4$=H, OH, OAlk, Hal or $NO_2$; $R^5$=H or Alk; $R^4R^5$=$-(CH_2)_n-$.



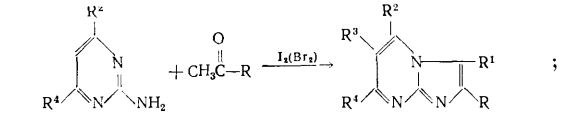
X=Hal; $R^1$=H, Alk, Ar or Het; $R^2$=H, Alk or Ar; $R^3$=H, Alk, OH or OAlk; $R^4$=H, OAlk or Hal; $R^5$=H or Hal.



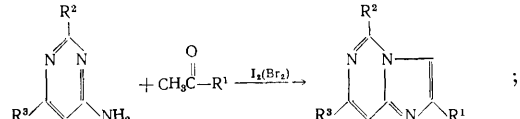
X=Cl or Br; R=H or Alk; $R^1$=Alk .

Apart from its advantages, the method suffers from a significant defect associated with the powerful lachrymatory action of α-halogenocarbonyl compounds. A version of the single-stage synthesis of imidazopyrimidine derivatives [47-49] (Scheme II), which excludes the stages involving the preparation and purification of the halogenocarbonyl component, is therefore of interest. A second undoubted advantage of this type of synthesis is the possibility of obtaining pure non-halogenated imidazopyrimidines and also their mono- and di-halogeno-derivatives, which is achieved by a strict control of the quantitative proportions of bromine and the other reagents.

Scheme 2

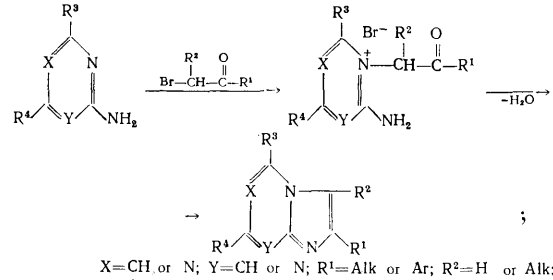


R=Alk or Ar; $R^1$=H or Br; $R^2$=H or OH; $R^3$=H or Br; $R^4$=H or Alk.



$R^1$=Alk or Ar; $R^2$=H or OAlk; $R^3$=OAlk or Cl; $R^4$=H or Br.

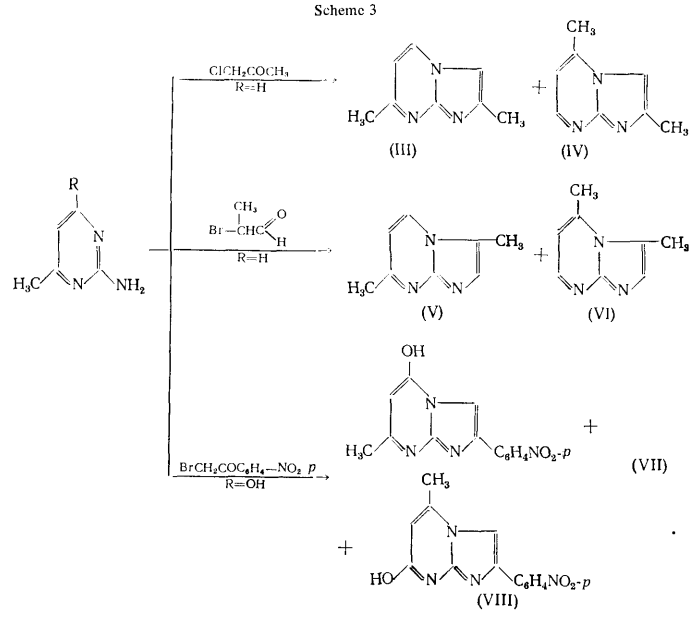
The interaction of aminopyrimidines with α-halogenoaldehydes (and α-halogenoketones) can proceed in theory via an initial stage involving the quaternisation of the pyrimidine nitrogen atom or via the formation of Schiff bases. Shvachkin [19] shares the view of Ochiai and Jamai [20], who believe that the initial step in this reaction is the formation of azomethines, which cyclise in the presence of bases. Recent studies [37,38,41-43,46] have shown that aminopyrimidines are quaternised, forming extremely labile salts, which are readily converted into imidazopyrimidines on heating or when an attempt is made to isolate the free bases. There is no doubt about the formation of the quaternary salts and it is convincingly supported by spectroscopic data:



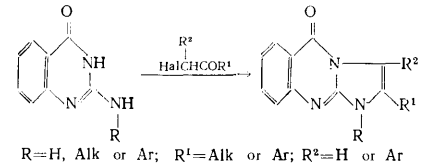
X=CH or N; Y=CH or N; $R^1$=Alk or Ar; $R^2$=H or Alk; $R^3$=H, OH or OAlk; $R^4$=H, Alk, OAlk or Hal.

The alkylation of asymmetric 2-aminopyrimidines [38,43,46] by α-halogeno ketones and α-halogenoaldehydes can involve the $N_{(1)}$ and $N_{(3)}$ atoms, which leads to an isomeric mixture of products (III) and (IV), (V) and (VI), and (VII) and (VIII) respectively. Determination of the isomeric composition of the reaction products showed that compounds (III), (V), and (VII) predominate, which can probably be accounted for by steric factors (Scheme 3).

Scheme 3



The alkylation method proved to be suitable for the synthesis of 1,5-dihydroimidazo[2,1-*b*]-5-quinazolone derivatives from 2-amino(alkyl or aryl-amino)-4-quinazolones and α-halogenoketones [49,50]:

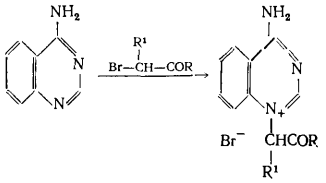


R=H, Alk or Ar; $R^1$=Alk or Ar; $R^2$=H or Ar

It is remarkable that, in contrast to the majority of α-amino-substituted nitrogen-containing heterocycles, which are alkylated at the endocyclic nitrogen atom adjoining the amino-group, 4-aminoquinazoline interacts with α-halogenoketones preferentially with formation of

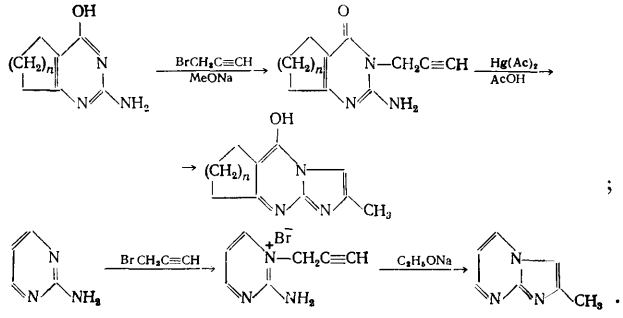
1-acylalkyl-4-aminoquinazolinium quaternary salts [49,51]. The attack by the alkylating agent on the $N_{(1)}$ atom can be explained on the basis of the molecular diagrams in Armarego's monograph [52].

The specificity of the alkylation of 4-aminoquinazolines by α-halogenoketones precluded the synthesis of imidazo-[1,2-*c*]quinazoline derivatives by this method [49,51]:



R=Alk, Ar or Het; R¹=H or Alk

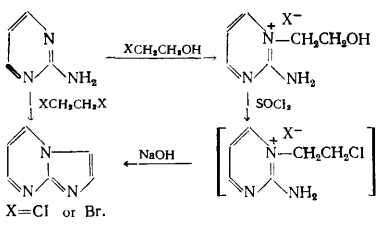
Together with α-halogenocarbonyl compounds, propargyl bromide can be used as the alkylating agent to obtain 2-methyl-substituted imidazopyrimidines [14,54,54]:



It follows from the above scheme that *N*-propargyl derivatives can be converted into methylated imidazo-pyrimidines in two different ways: by the Kucherov hydration of the triple bond with subsequent cyclisation of via the nucleophilic amination of the triple bond under the conditions of base catalysis.

β-Halogenoalcohols and 1,2-dihalogenoalkanes [46,49,55-57], which alkylate 2-amino-, 2-arylamino-, and 4-amino-pyrimidines and 2-amino(alkyl- or arylamino)-4-quin-azolones, have been used to synthesise hydrogenated analogues of imidazopyrimidines (quinazolines). [49,57]

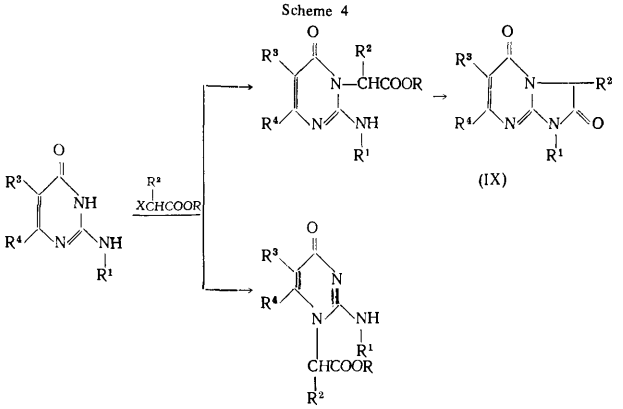
In practice it is better to use dihalogenoalkanes in this reaction, since the latter can then be carried out in one stage [46,56,57]:



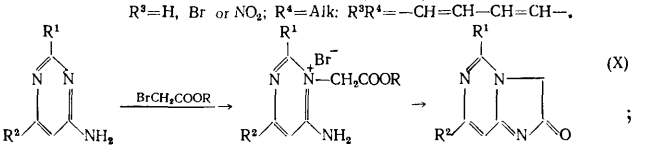
X=Cl or Br.

The use of α-halogenocarboxylic acids and their esters makes it possible to obtain a series of different 2-oxo-derivatives of imidazopyrimidine (quinazoline) from 2-amino- and 4-aminopyrimidines [46,49,58-60] and 2-amino-(alkyl- or arylamino)-4-quinazolinones [49] (Scheme 4).

Scheme 4



X=Cl, Br or I; R=H or Alk; R¹=H, Alk or Ar; R²=H or Alk; R³=H, Br or $NO_2$; R⁴=Alk; R³R⁴=—CH=CH—CH=CH—.



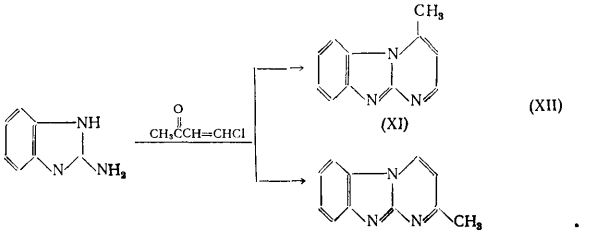
R=Alk; R¹=H or OAlk; R²=Cl or OAlk

It should be noted particularly that alkylation of asymmetric 2-aminopyrimidines by α-halogenocarboxylic acids (or esters) involves simultaneously the $N_{(1)}$ and $N_{(3)}$ atoms [46,49,58]. The intermediate *N*-carboxyalkyl-(alkoxycarbonylalkyl)pyrimidines (quinazolines) are extremely labile and frequently cyclise under reaction conditions to hydrogenated 2-oxo-derivatives of imidazo-pyrimidine (quinazoline). [46,49,58-60] The presence of active centres in compounds (IX) and (X) makes them important intermediates in the syntheses of potential biologically active substances or dyes [46,49,59,60].

The use of the anhydrides of α-halogenocarboxylic acids in the reaction leads to the initial formation of *N*-acyl derivatives of 2-aminopyrimidines, which cyclise under conditions which are relatively unsuitable for practical purposes and with fairly low yields [19,61-69].

## 2. Alkylation of 2-Aminoimidazoles

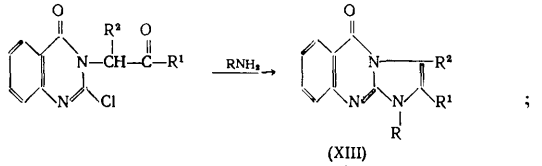
Imidazopyrimidines with a bridgehead nitrogen atom can be synthesised by alkylating 2-aminoimidazoles. On treatment with β-chlorovinyl methyl ketone, 2-amino-benzimidazole is known to be converted [70] into 4-methyl-pyrimido[1,2-*a*]benzimidazole (XI) and 2-methylpyrimido-[1,2-*a*]benzimidazole (XII) in proportions of 8 : 1.



Kochergin [71] demonstrated the possibility of obtaining tetrahydropyrimido[1,2-*a*]benzimidazole from 1-alkyl-2-aminobenzimidazole and 1,3-dihalogenopropane.

## III. AMINATION OF HALOGENO-, ALKYLTHIO-, AND ARYLOXY(ALKOXY)-DERIVATIVES OF PYRIMIDINE AND IMIDAZOLE

The amination of halogeno-, alkylthio-, and aryloxy-(alkoxy) derivatives of pyrimidine (quinazoline) and imidazole constitutes a method of preparation of imidazopyrimidines and their benzo-analogues which is no less important on a preparative scale. In most cases, this method is more laborious than the previous one, but it has nevertheless found applications in the synthesis of imidazopyrimidine systems and their hydrogenated analogues. The nucleophilic substitution of the halogeno-, alkylthio-, and aryloxy(alkoxy)-groups in the above systems is usually carried out in organic solvents over a wide temperature range. Armarego[72] and other workers[73,74] modified the general method somewhat. They synthesised imidazo[1,2-*a*]- and imidazo[1,2-*c*]pyrimidines from 2-chloro- and 4-chloro-pyrimidines and aminoacetals[72-74] in the presence of potassium iodide. The conversion of the initial chloropyrimidines into the more reactive iodopyrimidines made it possible to achieve quantitative yields of $\alpha$-pyrimidinylaminoacetals. Depending on the type of cyclising agents, the latter are converted into the corresponding imidazo-, 3-hydroxyimidazolino-, and 3-alkoxyimidazolino-pyrimidines (Scheme 5). The reaction with 4-chloroquinazoline proceeds similarly[4].



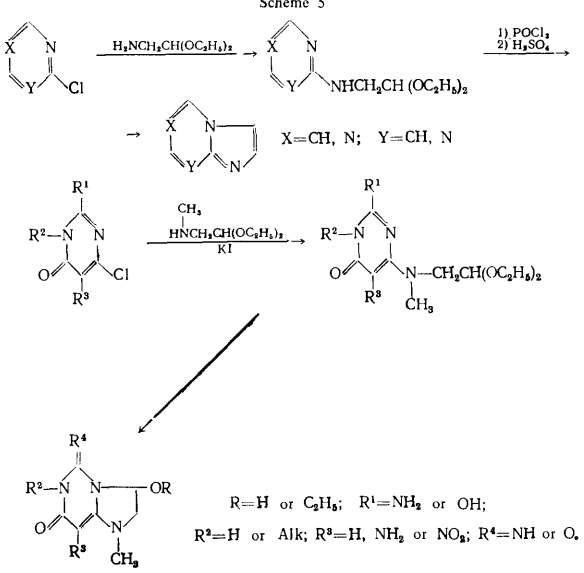
(XIII)

R=H, Alk or Ar; $R^1$=Alk, or Ar; $R^2$=H or Ar.

Pfleiderer et al,[74] who aminated 4-chloro-5-nitropyrimidine-2,6-diones with glucosamine in an aqueous alkaline medium, demonstrated the possibility, in principle, of obtaining 2-formyl-3-hydroxy-8-nitro-1,2,3,5,6,7-hexahydroimidazo[1,2-*c*]pyrimidine-5,7-dione and its 6-substituted derivatives.

An interesting method for the synthesis of imidazoquinazolin-5-ones has been proposed recently[49,75]: 3-acylalkyl-2-chloroquinazolin-4-ones are aminated with ammonia and primary amines[76] and are readily converted into compounds of type (XIII)

Scheme 5



X=CH, N; Y=CH, N

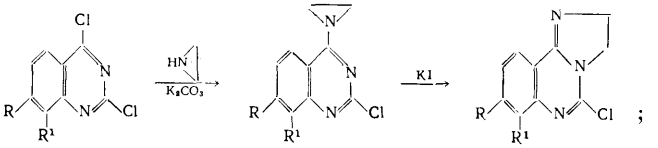
R=H or $C_2H_5$; $R^1$=$NH_2$ or OH; $R^2$=H or Alk; $R^3$=H, $NH_2$ or $NO_2$; $R^4$=NH or O.

There have been a number of communications[4,72,79-82,87,126,140-146] in which the results of studies of the interaction of chloro- and alkylthio-pyrimidines (quinazolines, purines) with aminoalcohols and their ethers are presented. In this case, the hydrogenated imidazopyrimidine systems are synthesised in two stages involving the formation of $\beta$-hydroxyalkylaminopyrimidines with their subsequent conversion into the corresponding cyclising $\beta$-chloro-derivatives. For this reason, it is better to use $\beta$-halogenoalkylamines instead of $\beta$-aminoalcohols in this reaction[77,79-86].

Hornyak and Lempert[87] replaced the stage involving the halogenation of the intermediate heterylaminoalcohols by their oxidation with chromium trioxide in acetic acid or anhydride. It is remarkable that the use of this procedure leads to the formation of 3-hydroxyimidazopyrimidines.

Reiter and coworkers[88,89] developed a method for the thermal cyclisation of $\beta$-aryloxyethylaminopyrimidines, which greatly simplified the preparation of imidazopyrimidines.

The method of synthesis of imidazolinoquinazolines, using aziridine as the aminating agent, is of some interest. According to patent data[11], the initial 2,4-dichloroquinazolines are selectively aminated in the 4-position under fairly mild conditions. Subsequent treatment of the aminated product with potassium iodide in acetone leads to the formation of a tricyclic product:

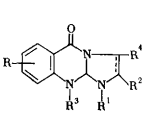


R=$R^1$=H or $OCH_3$.

The amination of 4-chloroquinazoline with ethylenediamine results in the formation of imidazolino[1,2-*c*]-quinazoline[90], but the ambiguity of the reaction pathway lowers sharply the advantage of this method.

Hydrogenated imidazo[1,1-*b*]quinazoline and pyrimido[1,2-*f*]xanthine systems have been obtained by treating 2-chloro-3-($\beta$-chloroethyl)quinazolin-4-one[91-93] and 8-bromo-7-($\gamma$-bromopropyl)theophylline[94] with ammonia, primary amines and hydroxylamine. The scope of this method is limited owing to the low availability of the labile halogeno-components.

A number of publications have appeared in recent years indicating the possibility of using alkylthio-derivatives of imidazoles and benzimidazoles for the synthesis of imidazopyrimidine systems. 2-Alkylthioimidazolines and their *N*-substituted derivatives[95-99] as well as 2-alkylthiobenzimidazoles[100,101] give rise to tri- and tetra-cyclic products on heating with *o*-aminobenzoic acids, their anhydrides, isatin, or isatoic acids:

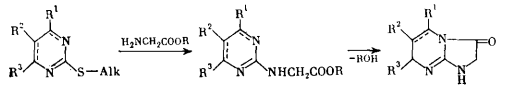


R=H, OH, OAlk, Hal, Het, $SO_2Cl$ or $SO_2NH_2$; $R^1$=H or Alk; $R^1R^2$=$-(CH_2)_4-$; $R^3$=H, Alk or Ar; $R^3R^4$=—CH=CH—CH=CH—; ═══ single or double bond.

Similar compounds may be obtained from 2-halogenoimidazoles[100-105].

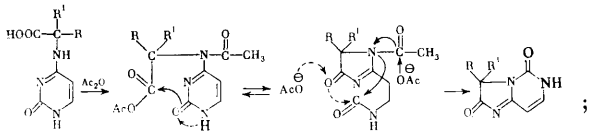
There exist two radical approaches to the solution of the problem of synthesising hydrogenated imidazopyrimidin-2(3)-ones. One of these involves the amination of halogeno- or alkylthio-pyrimidines by aminoacids or their esters. This method has been used successfully to synthesise hexahydroimidazo[1,2-*a*]pyrimidin-3-one[106-107], tetrahydroimidazo[1,2-*c*]pyrimidin-2-ones[69], tetrahydroimidazo[2,1-*a*]quinazolin-3-ones[108,109], dihydroimidazo[1,2-*c*]quinazolin-2-ones[49], and dihydroimidazo-[1,2-*i*]purin-2-ones[110-112].

The reaction of 2(4)-halogeno- or alkylthio-pyrimidines (quinazolines) with aminoacids or their esters, which is distinguished by its simplicity, proceeds with high yields on heating (as a rule in lower alcohols) to 20–100°C:



R=H or Alk; $R^1=R^2=2H$; $R^1R^2=-CH=CH-CH=CH-$; $R^3$=H or OH; ═══ single or double bond.

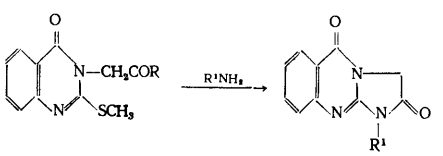
Tetrahydropyrimidin-2-ylaminoacetic acid and its esters obtained in this way[106,107] are unstable in the form of the hydrochlorides; their neutralisation leads to the formation of hexahydroimidazo[1,2-*a*]pyrimidin-3-one. In contrast to these, *N*-(4-oxoquinazolin-2-yl)aminoacetic acid is entirely stable and its cyclisation in the presence of dicyclohexylcarbodiimide or acetic anhydride proceeds preferentially along the "*a*" edge of the quinazoline ring with formation of cyclic 3-oxo-derivatives[108,109]. The reactions of *N*-(pyrimidin-4-yl, quinazolinyl, and adenin-6-yl)-α-aminocarboxylic acids under the conditions of cyclisation by glacial acetic acid or the acetic acid–acetic anhydride mixture have been described[49,69,110-112]. The thorough investigation by Ueda and Fox[69], where two alternative pathways to the cyclisation of *N*-(2-oxopyrimidin-4-yl)-α-aminocarboxylic acids were considered, is noteworthy. The authors showed that the only reaction products are 3-alkyl-1,2,3,5-tetrahydroimidazo-[1,2-*c*]pyrimidine-2,5-diones and proposed the following mechanism for their formation:



R=$R^1$=H or Alk.

Similar results were obtained in the cyclisation of *N*-(quinazolin-4-yl, adenin-6-yl)-α-aminocarboxylic acids[49,110-112]. Using a tracer atom method, Chheda and coworkers[110,111] finally confirmed in recent years the validity of Ueda's theoretical postulates.

Another version involves the use of the esters or amides of 2-methylthioquinazolin-3-ylacetic acid[91,108,109,113-116]:



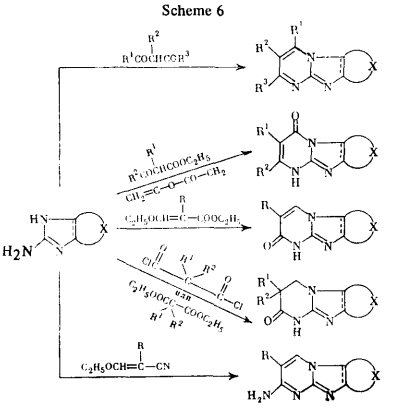
R=OAlk or $NH_2$; $R^1$=H, Alk or Ar.

Unfortunately, this method, which is synthetically more promising since it does not require the use of aminoacids or their esters, has not been extended to other systems.

## IV. CONDENSATION OF 2-SUBSTITUTED IMIDAZOLES WITH ALDEHYDES, 1,3-DICARBONYL COMPOUNDS, ACIDS, AND THEIR DERIVATIVES

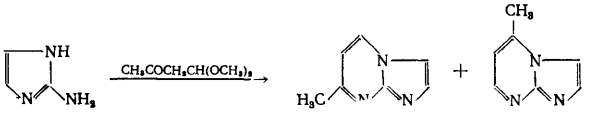
Condensation as a method of synthesis of imidazopyrimidine systems has been known for a long time. Using 2-aminoimidazoline and acetoacetic ester, Kawai[117] obtained for the first time in 1931 7-methyltetrahydroimidazo[1,2-*a*]pyrimidine. Subsequently the preparative possibilities of this method were widely investigated by many workers. The extensive study of this reaction was favoured by the relative availability of the initial 1,3-dicarbonyl compounds and 2-aminoimidazoles (benzimidazoles) and their hydrogenated analogues. This type of condensation (Scheme 6) is convenient for the synthesis of polynuclear heterocyclic systems with an imidazopyrimidine fragment. At the same time, one should note the ambiguity of this reaction, which leads to the formation of a mixture of isomeric products. Despite the difficulty of separating the isomers, this method can be regarded as sufficiently preparative, permitting the variation of the experimental conditions (temperature, reaction time, solvent, and pH of the medium).

Scheme 6

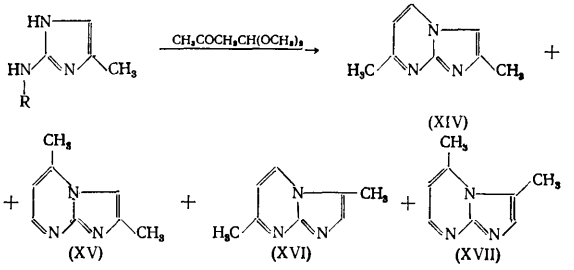


Here ═══ is a single or double bond and X are different substituents in the imidazole ring or the condensed benzene ring.

Imidazo[1,2-*a*]pyrimidine systems have been obtained by the condensation of 2-aminoimidazoles[30,34,38,118,119], 2-aminoimidazolines[117,120-125], and 2-aminobenzimidazoles[118,119,126-139] with 1,3-dicarbonyl compounds or substances which can be converted into these reagents under the reaction conditions. The 1,3-dicarbonyl compounds used were dialdehydes and their acetals, formylketones, diketones, ketoacids or their esters, diketens, dicarboxylic acids or their esters, and acid halides, as well as α,β-unsaturated acids, their chlorides, and esters. The composition of reaction products is determined by the structural characteristics of the reactants. Two isomeric products are usually obtained when 2-aminoimidazole or its 4,5-disubstituted derivatives with identical substituents are treated with asymmetric 1,3-dicarbonyl compounds[38,118,119,132,139]:

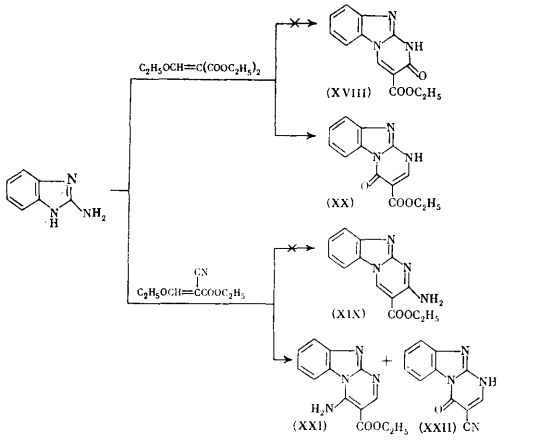


The condensation of 2-amino-4(5)-methylimidazole with the acetal of acetoacetaldehyde in a neutral medium leads to a four-component mixture of isomers (XIV)–(XVII), while in an acid medium a two-component mixture of compounds (XV) and (XVII) is obtained [38]:



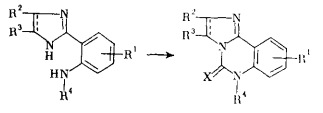
The study of Chow et al. [139], who investigated the reaction of 2-aminobenzimidazole with bifunctional carboxylic acid derivatives, merits special attention, as they obtained results conflicting with earlier conclusions [119]. De Cat and von Dormael [119] claim that the condensation of 2-aminobenzimidazole with diethyl ethoxymethylenemalonate leads to compound (XVIII) and the reaction with ethyl cyanoethoxymethyleneacetate gives rise to compound (XIX).

Chow et al. [139] reproduced these reactions under identical conditions and obtained, instead of compound (XVIII), its isomer (XX) and, instead of compound (XIX), the products were compounds (XXI) and (XXII):



In order to solve the structural problems, Chow et al. [139] carried out a series of chemical transformations of compounds (XX)–(XXII) and analysed their $^1$H NMR spectra. In view of all these considerations, their data are fairly convincing, in contrast to earlier investigations, whose conclusions are doubtful and require additional tests.

Imidazo[1,2-*c*]quinazolines, which are of biological value [4-10,17,18], become available as a result of the condensation of imidazole-containing compounds, which serve as the diamino-components, with aldehydes [7,8,10], carboxylic acids, their chlorides, and thioanhydrides [5,8,10,15,147-150]:



X=O or S; $R^1$=Alk or Hal; $R^2$=$R^3$=H or Alk; $R^2R^3$=—CH=CH—CH=CH—; $R^4$=H or Alk; ═══ single or double bond.

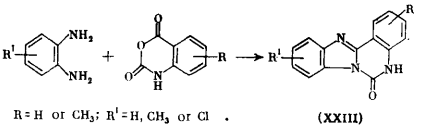
The study of Franchetti and Grifantini [151], who reduced 2-(*o*-nitrophenyl)-1-hydroxyimidazole 3-oxide with zinc to a tricyclic 5,6-dihydroimidazoquinazoline derivative, is of some interest.

Methods of synthesis of hexahydroimidazoquinazolines based on ethylenediamines and 1-acylaminobenzophenones have been patented [6,9].

The preparation of tetrahydroimidazo[1,2-*c*]quinazolines together with diazepines [152] or a mixture of imidazo[1,2-*c*]- and imidazo[2,1-*b*]-quinazolines [92] has been claimed.

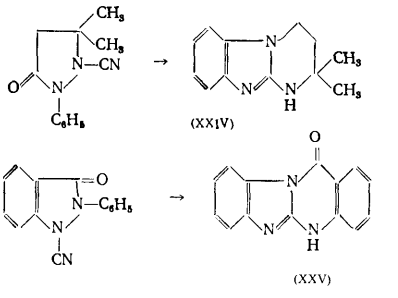
## V. OTHER METHODS OF SYNTHESIS

Apart from the general methods discussed above, there are specific procedures for the synthesis of imidazopyrimidines and their benzo-analogues, which are important in particular instances and which have not found extensive use. Thus compounds of type (XXIII) are formed when *o*-phenylenediamine is fused with isatoic acids [148,153]:



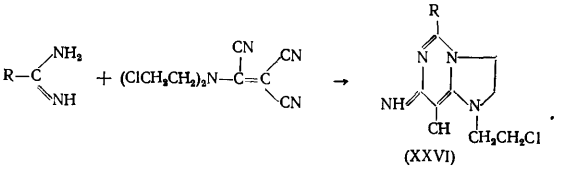
R=H or $CH_3$; $R^1$=H, $CH_3$ or Cl (XXIII)

The reaction of ethylenediamine with 2,6-dithiobenzothiazine—the thio-analogue of isatoic acid—proceeds similarly [154]. A novel method has been described for the synthesis of benzimidazopyrimidines (XXIV) and (XXV) by heating 2-cyano-1-phenyl-3,3-dimethylpyrazolidin-5-one and 1-cyano-2-phenylbenzopyrazolidin-3-one at 270°C [155]:

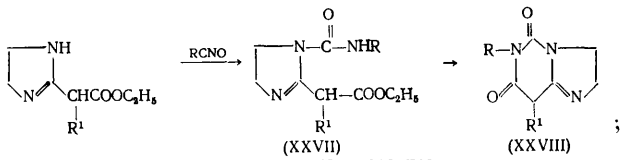


The authors do not discuss the mechanism of the formation of the above compounds.

1-β-chloroethyl-5-R-8-cyano-7-imino-1,2,3,7-tetrahydroimidazo[1,2-*c*]pyrimidines (XXVI) have been synthesised from amidines under the influence of bis-(β-chloroethylamine)tricyanoethylene [156]:



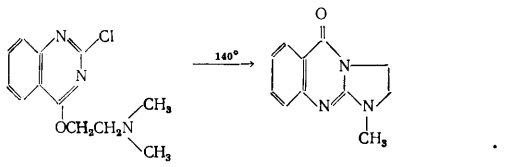
The use of cyanates in the reaction with ethyl imidazoline-2-acetates in benzene made it possible to obtain derivatives of hexahydroimidazo[1,2-*c*]pyrimidine-5,7-dione (XXVIII).[157] This process proceeds via a stage involving the formation of the intermediate (XXVII), which is converted into compound (XXVIII) on boiling in alcohol:



(XXVII) (XXVIII)

R=H or $C_6H_5$; $R^1$=H or $C_6H_5NHCO$.

It has been observed[92] that heating compound (XXIX) to 140°C for a short time results in the formation of traces of 1-methyltetrahydroimidazo[2,1-*b*]quinazolin-5-one:



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# The Chemistry of $\Delta^{\alpha\beta}$-Butenolides†

A.A.Avetisyan and M.T.Dangyan

Data on the chemistry of $\Delta^{\alpha\beta}$-butenolides are surveyed and described systematically and the available information in the literature about the methods of preparation of these compounds are discussed. The chemical reactions of $\Delta^{\alpha\beta}$-butenolides are examined and a brief account is given of the biological activity of unsaturated $\gamma$-lactones.
The bibliography includes 253 references.

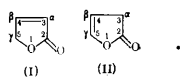
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## I. INTRODUCTION

There has been a growth of interest in the simplest unsaturated $\gamma$-lactones after the discovery of the antibiotic properties of many natural products—protoanemonin, clavacin, penicilloic acid, vitamin C, and others. They all exhibit their antibiotic activity in combination with strong bactericidal properties [1,2]. Numerous investigations have shown that the unusual specific action of these antibiotics is determined mainly by the presence of the unsaturated $\gamma$-lactone ring and also by the nature and positions of the functional groups present. The unsaturated $\gamma$-lactone ring is also encountered in many other biologically active compounds [3-6]. Fairly extensive experimental data have now accumulated on the synthesis and reactions of unsaturated $\gamma$-lactones. These studies have demonstrated the possibility of the wide-scale employment of $\gamma$-lactones in various branches of the national economy and also in organic synthesis.

$\alpha\beta$-Unsaturated $\gamma$-lactones (I) and $\beta\gamma$-unsaturated $\gamma$-lactones (II) are distinguished on the basis of the position of the double bond and chemical properties:



(I) (II)

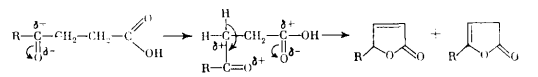
This review is a first attempt in the Soviet scientific literature at a survey and a systematic account of data on the chemistry of $\Delta^{\alpha\beta}$-butenolides published up to 1976.

## II. METHODS OF SYNTHESIS OF $\Delta^{\alpha\beta}$-BUTENOLIDES

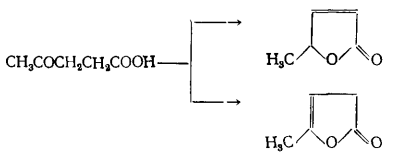
The available literature data on the methods of preparation of $\Delta^{\alpha\beta}$-butenolides can be in the main subdivided into several groups.

### 1. The Preparation of $\Delta^{\alpha\beta}$-Butenolides from Ketoacids and Their Derivatives

One of the commonest methods of the synthesis of $\Delta^{\alpha\beta}$-butenolides involves the intramolecular cyclisation of various keto- and diketo-acids and their derivatives. In order to achieve such synthesis, it is necessary that the oxo- and carboxy-groups in these compounds are in the $\gamma$-position; it is also essential that the ketoacid should be capable of existing in the enolic form:

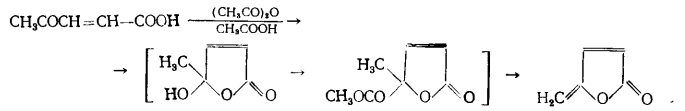


One of the first $\Delta\alpha\beta$-butenolides obtained was angelica lactone, synthesised as early as 1885 [7-12] from levulinic acid. On heating under atmospheric pressure, levulinic acid loses a water molecule and is converted into a mixture of two isomeric unsaturated $\Delta^{\alpha\beta}(\beta)$- and $\Delta^{\beta\gamma}(\alpha)$-angelica lactones:

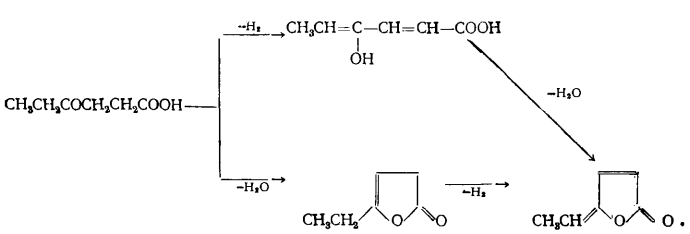


$\beta$-Angelica lactone is also obtained on heating levulinic acid with keten [13] (or with added toluene-*p*-sulphonic acid [14]) and on distillation of acetyl-levulinic acid [15].

When $\beta$-acetylacrylic acid is heated with a mixture of acetic anhydride and acetic acid in the presence of a small amount of concentrated sulphuric or toluene-*p*-sulphonic acid, $\gamma$-methylene-$\Delta^{\alpha\beta}$-butenolide (protonemonine) is obtained [16]:



Substituted protoanemonines have been obtained from levulinic acid homologues in the presence of complex catalysts [17]. The elimination of water and dehydrogenation can be carried out consecutively:



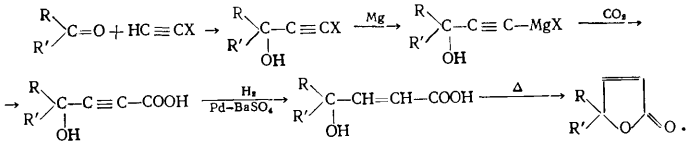
†2(5*H*)-furanones (Ed. of Translation).

$\Delta^{\alpha\beta}$-Butenolides are obtained by the reaction of $\beta$-benzoyl-$\alpha$-phenylpropionic acid and its derivatives with acetyl chloride[18], acetic anhydride[19], and sulphuric acid[20]. This reaction is acoompanied by the formation of $\beta\gamma$-isomers[21,22] and bislactones[23-26]. The reaction of esters of these acids with aromatic aldehydes in the presence of bases leads to $\gamma$-hydroxy-$\Delta^{\alpha\beta}$-butenolides[27-29].

When benzylidinepyruvic acid reacts with aromatic amines, the products are $\gamma$-aryl-$\alpha$-arylamino-$\Delta^{\alpha\beta}$-butenolides[30-33] whose condensation with $o$-nitrobenzaldehyde leads to $\alpha$-hydroxy-$\gamma$-($o$-nitrophenyl)-$\Delta^{\alpha\beta}$-butenolide[34]. The reaction of acrolein with cyanoacetic acid yields $\alpha$-cyano-$\Delta^{\alpha\beta}$-butenolides[35].

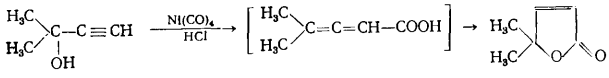
## 2. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from $\alpha\beta$-Unsaturated Carboxylic Acids and Their Derivatives

An important method for the synthesis of $\Delta^{\alpha\beta}$-butenolides is the intramolecular cyclisation of $\alpha\beta$-unsaturated carboxylic acids and their derivatives. When ethyl crotonate is heated with selenium dioxide, a $\Delta^{\alpha\beta}$-butenolide is obtained[36]. Acetylenecarboxylic acids are reduced to olefinic acids, which likewise can cyclise to the corresponding $\Delta^{\alpha\beta}$-butenolides on heating[37,38]:



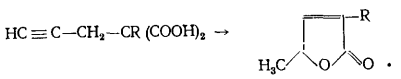
The intramolecular cyclisation of $\alpha\beta$-unsaturated carboxylic acids and their derivatives apparently proceeds via a mechanism which has been generally adopted for the formation of esters from acids and alcohols.

A variation of this reaction is the conversion of an acetylenic alcohol into $\Delta^{\alpha\beta}$-butenolide on heating with nickel carbonyl in a butanol–hydrochloric acid mixture[39]. It is suggested that the reaction proceeds via an allenecarboxylic acid:

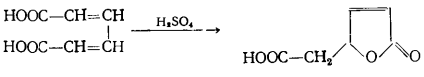


$\Delta^{\alpha\beta}$-Butenolide is also obtained when acetylene is heated with acetone and acetic anhydride in an autoclave at 100°C and under a pressure of 250 atm in the presence of dicobalt octacarbonyl[40,41].

In the presence of acid or alkaline catalysts, acetylenecarboxylic and acetylenedicarboxylic acids cyclise to $\Delta^{\alpha\beta}$-butenolides. The corresponding $\Delta^{\alpha\beta}$-butenolide and dilactones have been obtained by this reaction from various alkyl- and aryl-substituted malonic acids containing the propargyl or dipropargyl group[42-44]:

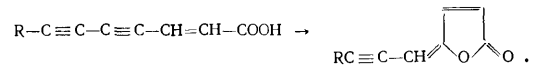


Carboxylic acids with two double bonds can be converted into lactones by treatment with sulphuric acid. Thus, the lactonisation of muconic acid results in the formation of $\gamma$-carboxymethyl-$\Delta^{\alpha\beta}$-butenolide[45,46]:



When monobasic or dibasic enynoic acids‡ are heated, they cyclise with formation of $\Delta^{\alpha\beta}$-butenolides of the type of protoanemonine derivatives[47-49].

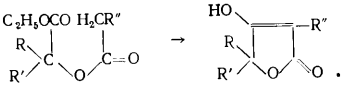
The cyclisation of endiynoic acids leads to $\Delta^{\alpha\beta}$-butenolides with an acetylenic group[54]:



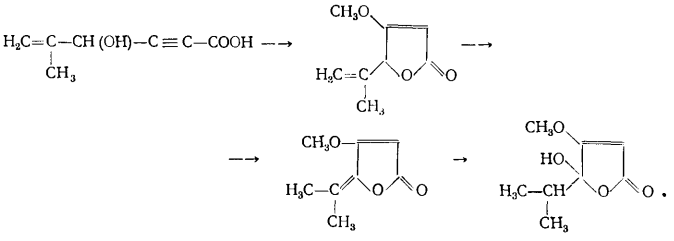
## 3. The Preparation of $\Delta^{\alpha\beta}$-Butenolides from Hydroxy- and Halogeno-Acids and Their Derivatives

The cyclodehydration of saturated and unsaturated hydroxyacids and their derivatives is widely used to synthesise $\Delta^{\alpha\beta}$-butenolides. Natural products such as vitamin C, dihydropenicilloic acid, etc. have been synthesised by this method.

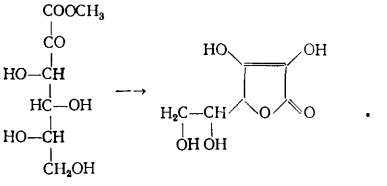
When $\alpha$-hydroxyacid diesters are heated in the presence of metallic sodium, tetronic acids are formed[55]:



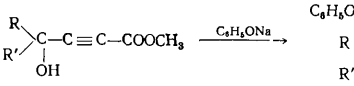
On heating, 3,4-dihydroxybutyric acid with phosphorus pentoxide, $\Delta^{\alpha\beta}$-butenolide is formed and can be obtained also from 3,4-dichlorobutyric acid when the latter is heated with potassium carbonate or a methanol solution of sodium hydroxide[56]. $\gamma$-Isopropenyl-$\beta$-methoxy-$\Delta^{\alpha\beta}$-butenolide has been synthesised by intramolecular cyclisation of 4-hydroxy-5-methylhex-5-en-2-ynoic acid in the presence of $BF_3$.HgO in methanol. The butenolide is converted by treatment with an aqueous alcoholic solution of alkali into $\gamma$-hydroxy-$\gamma$-isopropyl-$\beta$-methoxy-$\Delta^{\alpha\beta}$-butenolide (dihydropenicilloic acid)[57,58]:



When methyl 2-oxogulonate is heated in methanol solution in the presence of sodium carbonate in an atmosphere of nitrogen, the product is vitamin C (L-ascorbic acid)[59]:

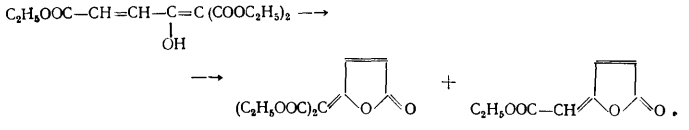


$\gamma\gamma$-Dialkyl-$\beta$-phenoxy-$\Delta^{\alpha\beta}$-butenolides have been obtained by the reaction of sodium phenoxide with the methyl esters of $\gamma$-hydroxyacetylenic acids[60]:

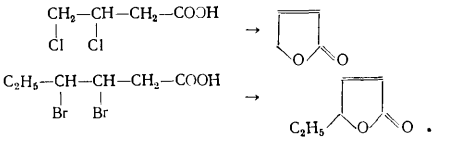


‡It is of interest that these acids cyclise to 2-pyrones under the influence of strongly basic catalysts[47,48,50-53].

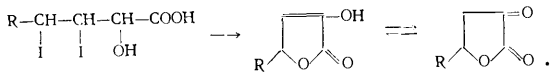
Muconic acid derivatives have been used[61] as the starting materials for the synthesis of unsaturated $\Delta^{\alpha\beta}$-butenolides; thus pyrolysis of diethyl $\beta$-hydroxy-$\alpha$-ethoxycarbonylmuconate leads to a mixture of diunsaturated lactones—derivatives of the type of protoanemonine:



Halogenocarboxylic acids and their derivatives have also been used as the starting materials for the synthesis of unsaturated $\Delta^{\alpha\beta}$-butenolides. The corresponding $\Delta^{\alpha\beta}$-butenolides are obtained by the dehydrohalogenation of $\beta\gamma$-dihalogenobutyric[62,63] and $\beta\gamma$-dibromocaproic[64] acids in the presence of sodium carbonate, sodium bicarbonate, or triethylamine:

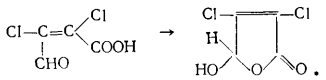


$\gamma$-Alkyl-$\alpha$-hydroxy-$\Delta^{\alpha\beta}$-butenolides, which are in equilibrium with the keto-forms, have been synthesised by the elimination of water from $\alpha$-hydroxy-$\beta\gamma$-diiodocarboxylic acids[65]:



$\beta$-Formyl-$\alpha\beta$-dihalogenoacrylic acids condensed with phenol, anisole, guaiacol, thymol, halogenobenzene, 1,2,3-trimethoxybenzene, and *o*-dimethoxybenzene in the presence of inorganic or Lewis acids to form $\gamma$-substituted $\Delta^{\alpha\beta}$-butenolides[66-69].

Halogenomuconate esters exist in the cyclic lactone form[70]:

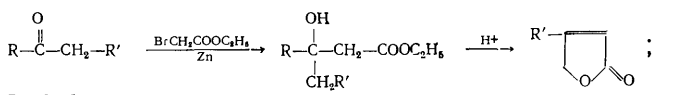


When chloromuconic acid condenses with acetophenone, nitromethane, or nitroethane in the presence of sodium hydroxide, $\gamma$-substituted $\alpha\beta$-dichloro-$\Delta^{\alpha\beta}$-butenolides are obtained[71,72]; the condensation of the acid with benzene and chlorobenzene yields respectively $\alpha\beta$-dichloro-$\gamma$-phenyl-$\Delta^{\alpha\beta}$-butenolide and $\alpha\beta$-dichloro-$\gamma$-(*p*-chlorophenyl)-$\Delta^{\alpha\beta}$-butenolide[24,73] and the condensation with aromatic compounds (phenol and anisole) in the presence of polyphosphoric acid gives rise to $\alpha\beta$-dichloro-$\Delta^{\alpha\beta}$-butenolides[68,74].

Bromomuconic acid reacts with acetophenone to form $\alpha\beta$-dibromo-$\gamma$-phenacyl-$\Delta^{\alpha\beta}$-butenolide[75].

## 4. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides by the Reformatsky Reaction

An important method for the synthesis of $\Delta^{\alpha\beta}$-butenolides and steroid lactones is the Reformatsky reaction. The starting materials in this case are $\alpha$-methoxy- or acetoxy-ketones. This method of synthesis of $\Delta^{\alpha\beta}$-butenolides has been used by many investigators[76-99]:



The acetoxyester is converted into the $\Delta^{\alpha\beta}$-butenolide by heating it in the presence of alkali metal hydrogen sulphates, anhydrous oxalic acid, or potassium phosphate[100]. The intramolecular Reformatsky reaction, i.e. the interaction of the above compounds with zinc or magnesium in inert solvents, constitutes a modification of this process[101].

## 5. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from the Corresponding $\Delta\beta\gamma$-Isomers

Under the influence of bases such as triethlyamine, piperidine, and benzylamine, $\Delta\beta\gamma$-butenolides are converted into the corresponding $\Delta^{\alpha\beta}$-isomers[8,102,103]. Acetic anhydride is sometimes used as the catalyst for this purpose[104,105].

## 6. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from Substituted $\gamma$-Butyrolactones

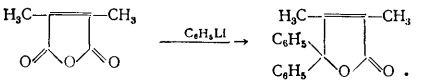
When saturated $\gamma$-lactones containing substituents (OH, $OOCCH_3$, SH, $NH_2$) in the $\alpha$- or $\gamma$-positions are treated with acids or salts, the HX molecule is split off with formation of a mixture of $\Delta^{\alpha\beta}$- and $\Delta^{\beta\gamma}$-isomers. Treatment of the mixture with a base leads to the pure $\Delta^{\alpha\beta}$-isomer[106,107].

For example, $\alpha$-chloro-$\beta$-cyclohexylbutyrolactone is converted into $\beta$-cyclohexyl-$\Delta^{\alpha\beta}$-butenolide under the influence of potassium acetate[108,109]. $\beta$-Aroyl-$\beta$-bromoacrylic acids, which exist in the cyclic form, have been converted into the corresponding $\Delta^{\alpha\beta}$-butenolides[110-112]. A solution of $\gamma$-benzoyl-$\beta$-phenylacrylic acid contains approximately 70% of $\gamma$-hydroxy-$\alpha\beta$-diphenyl-$\Delta^{\alpha\beta}$-butenolide[109].

Pyrolysis of saturated $\gamma$-lactones containing substituents (H, $C_7H_{15}$ or $C_2H_5$, OAc) in the $\gamma$-position, in the presence of sulphuric acid at 200–330°C, gives rise to $\gamma$-alkyl-$\Delta^{\alpha\beta}$-butenolides[114]. $\gamma$-Substituted $\Delta^{\alpha\beta}$-butenolides are obtained by the oxidative decarboxylation of $\gamma$-substituted paraconic acid in the presence of $Na_2S_2O_8$, $AgNO_3$, and $CuSO_4$.[115]

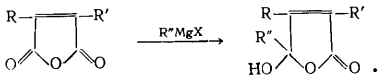
## 7. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from Substituted Maleic Acid Anhydrides

The next most important method of synthesis of $\Delta^{\alpha\beta}$-butenolides involves the interaction of a substituted maleic anhydride with organometallic compounds. Thus the reaction of dimethylmaleic anhydride with phenyllithium yields $\alpha\beta$-dimethyl-$\gamma\gamma$-diphenyl-$\Delta^{\alpha\beta}$-butenolide[116]:



$\gamma$-Alkyl-$\gamma$-hydroxy-$\Delta^{\alpha\beta}$-butenolides have been obtained by the reaction of mono- and di-alkylmaleic anhydrides with alkylmagnesium or arylalkylmagnesium halides[117].

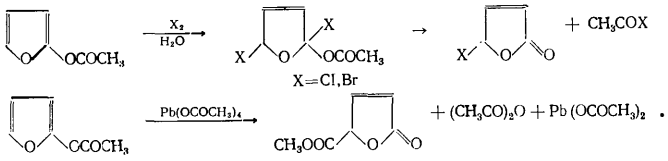
Dehydration of these butenolides leads to α-alkylidene-$\Delta^{\alpha\beta}$-butenolides [117]:



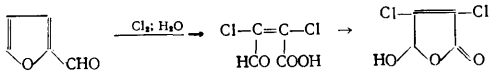
$\gamma\gamma$-Disubstituted $\alpha\beta$-dimethyl-$\Delta^{\alpha\beta}$-butenolides are obtained by the Friedel-Crafts reaction from dimethylmaleic anhydride and biphenyl in carbon disulphide [118].

## 8. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from Furan and Furancarboxylic Acid Derivatives

The reaction of 2-acetoxyfuran with halogens (chlorine or bromine) in the presence of water or lead tetraacetate results in the synthesis of γ-halogeno- or γ-acetoxy-$\Delta^{\alpha\beta}$-butenolides [119]:



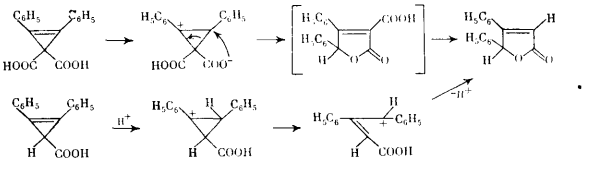
When bromine is allowed to react with pyromucic acid in the presence of water, a complex process takes place—decarboxylation, addition of bromine, and oxidation with formation of $\alpha\beta$-dibromo-γ-hydroxy-$\Delta^{\alpha\beta}$-butenolide [120]. $\alpha\beta$-Dichloro-γ-hydroxy-$\Delta^{\alpha\beta}$-butenolide is obtained when chlorine and furfural are added simultaneously to a concentrated solution of hydrochloric acid at 70°C [121]:



Acid hydrolysis of methyl 3,4-dihalogeno-2,5-dimethoxytetrahydrofurancarboxylates leads to $\alpha\beta$-dihalogeno-$\Delta^{\alpha\beta}$-butenolides [122].

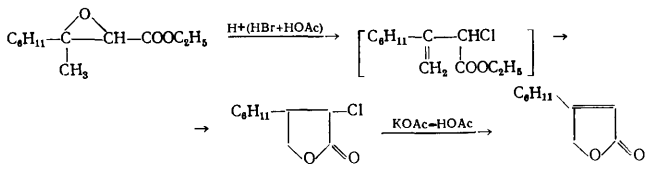
## 9. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from Cyclopropane Derivatives

The reaction of diphenylacetylene with diazomalonic ester in the presence of copper leads to 1,2-diphenylcyclopropane-3,3-dicarboxylic acid, the thermal decomposition of which results in the formation of $\beta\gamma$-diphenyl-$\Delta^{\alpha\beta}$-butenolide [123]. This butenolide is also obtained from acetic acid derivatives and from 1,2-diphenylcyclopropane-3-carboxylic acid in the presence of acid catalysts [124-126]:

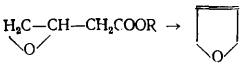


## 10. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from Epoxy-Compounds

$\Delta^{\alpha\beta}$-Butenolides are also obtained from epoxy-compounds. Thus ethyl 3-cyclohexyl-2,3-epoxybutyrate, which is readily formed by the Darzens reaction, is converted in the presence of catalysts into β-cyclohexyl-$\Delta^{\alpha\beta}$-butenolide [108,109]:



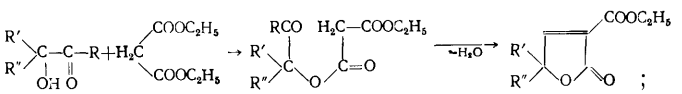
On treatment with sulphuric acid, esters of 3,4-epoxybutyric acid are converted into $\Delta^{\alpha\beta}$-butenolide [127]:



## 11. The Synthesis of $\Delta^{\alpha\beta}$-Butenolides from Hydroxyketo-Compounds

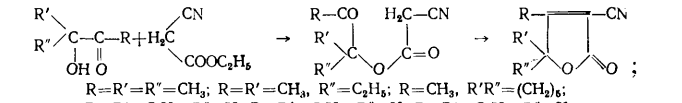
An important disadvantage of the above methods is the difficulty of introducing various functional groups into the unsaturated lactone ring. For this reason, the condensation of hydroxyketones with esters containing active methylene groups§ may be regarded as the most general method of synthesis of $\Delta^{\alpha\beta}$-butenolides with functional groups. The esters with active methylene groups employed are the acetoacetic, benzoylacetic, malonic, cyanoacetic, phenylacetic, and similar compounds, for example diketen.

Thus acyloins and tertiary α-ketoalcohols interact with ethyl malonate in the presence of alkaline catalysts to form substituted α-ethoxycarbonyl-$\Delta^{\alpha\beta}$-butenolides [128-133]. Sodium ethoxide is an effective catalyst for this reaction [132,133]:



R=R′=R″=CH$_3$; R=R′=CH$_3$, R″=C$_2$H$_5$; R=CH$_3$, R′R″=(CH$_2$)$_5$; R=R′=C$_2$H$_5$, R″=H; R=R′=C$_3$H$_7$, R″=H; R=R′=C$_4$H$_9$, R″=H; R=R′=C$_5$H$_{11}$, R″=H .

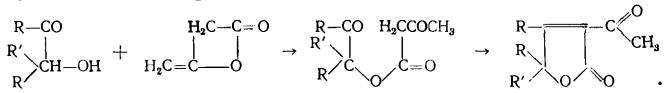
As is to be expected, cyanoacetic ester condenses with α-ketoalcohols in the presence of a basic catalyst more readily than malonic acid, the product being substituted α-cyano-$\Delta^{\alpha\beta}$-butenolides [133,134]:



R=R′=R″=CH$_3$; R=R′=CH$_3$, R″=C$_2$H$_5$; R=CH$_3$, R′R″=(CH$_2$)$_5$; R=R′=C$_2$H$_5$, R″=H; R=R′=C$_3$H$_7$, R″=H; R=R′=C$_4$H$_9$, R″=H; R=R′=C$_5$H$_{11}$, R″=H.

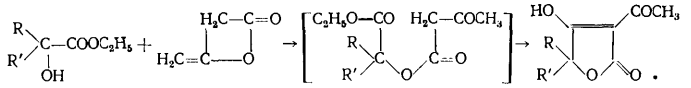
Under analogous conditions, benzoin reacts with cyanoacetic ester to form α-cyano-βγ-diphenyl-$\Delta^{\alpha\beta}$-butenolide [135].

The esters of acyloins and acetoacetic acid can undergo intramolecular condensation with formation of $\Delta^{\alpha\beta}$-butenolides. For example, acyloins and tertiary α-ketoalcohols react with diketen in the presence of pyridine or triethylamine to form acetoacetic acid esters, which cyclise on heating to substituted $\Delta^{\alpha\beta}$-butenolides [136-138]:

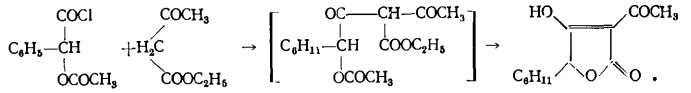


§Among the advantages of this method, one may note the ready availability of the initial compounds and the simple technology of the process.

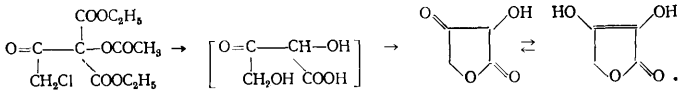
Under analogous conditions $\alpha$-hydroxyacid esters also react with diketen to form the corresponding $\Delta^{\alpha\beta}$-butenolides—acetyltetronic acids [136,139]



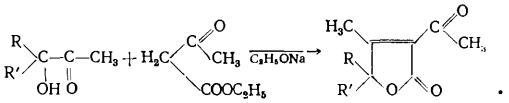
In order to synthesise tetronic acid derivatives, the chloride of acetoxy-mandelic acid was allowed to react with acetoacetic ester [140], which resulted in the formation of $\alpha$-acetyl-$\beta$-hydroxy-$\gamma$-phenyl-$\Delta^{\alpha\beta}$-butenolide:



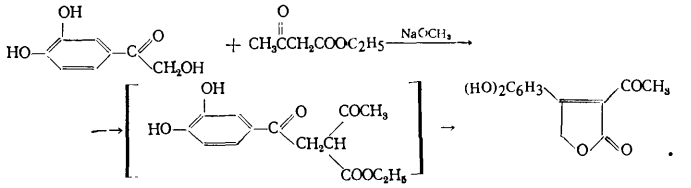
A number of acylated malonic and cyanoacetic acids have also been used for the same purpose [140]. Thus $\alpha$-hydroxytetronic acid has been obtained from diethyl acetoxychloroacetylmalonate in the presence of base [141]:



The condensation of tertiary $\alpha$-ketoalcohols with acetoacetic esters in the presence of sodium ethoxide proceeds with formation of the corresponding $\alpha$-acetyl-$\Delta^{\alpha\beta}$-butenolides [134]:

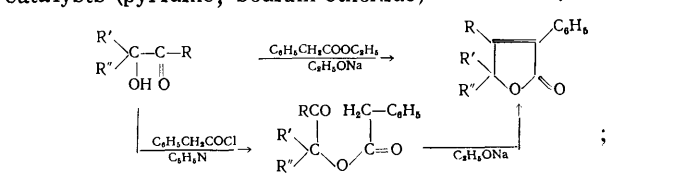


$\omega$-Hydroxyacetophenones containing hydroxy-groups in the benzene ring interact with acetoacetic ester in methanol solution to form $\Delta^{\alpha\beta}$-butenolides [142-144]:



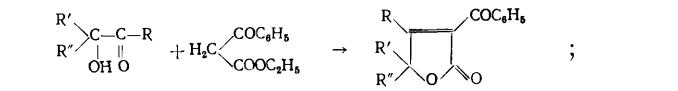
2-Methyl-3,3-di-($p$-tolyl)propionic acid, which gives rise to a mixture of $\Delta^{\alpha\beta}$-$\Delta^{\beta\gamma}$-isomers on heating with acetic anhydride, was obtained similarly from acetophenone and $\beta$-benzoacrylic [$\beta$-benzoylacrylic?] acid [108]. [This paragraph is completely erroneous. 2-Methyl-3,3-di-($p$-tolyl)-propionic acid is not mentioned in Ref. 108 nor in Refs. 142 to 144 (Ed. of Translation)].

Substituted $\alpha$-phenyl-$\Delta^{\alpha\beta}$-butenolides have been synthesised by the condensation of $\alpha$-ketoalcohols with phenylacetic ester and phenylacetyl chloride as well as substituted phenylacetic acids in the presence of basic catalysts (pyridine, sodium ethoxide) [128,129,145,146]:



R=R′=R″=$CH_3$; R=R′=$CH_3$, R″=$C_2H_5$; R=$CH_3$, R′R″=$(CH_2)_5$; R=R′=$C_2H_5$, $C_3H_7$ or $C_4H_9$, R″=H.

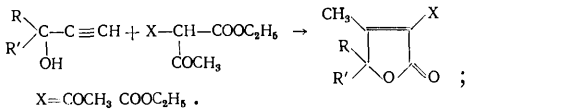
Secondary and tertiary $\alpha$-ketoalcohols are converted into the corresponding $\alpha$-benzoyl-$\Delta^{\alpha\beta}$-butenolides on condensation with benzoylacetic ester in the presence of sodium ethoxide [147,148]:



R=R′=R″=$CH_3$; R=R′=$CH_3$, R″=$C_2H_5$; R=$CH_3$R′R″=$(CH_2)_5$; R=R′=$C_2H_5$, $C_3H_7$,$C_4H_9$, R″=H.

The ability of the above esters to form lactones in condensation reactions with $\alpha$-ketoalcohols diminishes in the sequence cyanoacetic > acetoacetic > malonic > benzoylacetic > phenylacetic. A probable reaction mechanism has been proposed [132,133,138].

Acetylenic carbinols have also been used as starting materials for the synthesis of $\Delta^{\alpha\beta}$-butenolides. Thus Lacey [138] obtained $\alpha$-acetyl- or $\alpha$-ethoxy-carbonyl-$\Delta^{\alpha\beta}$-butenolides by the reaction of ethynylmethanols with acetylacetoacetic or acetylmalonic esters at 135–200°C:



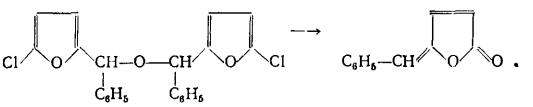
X=$COCH_3$ $COOC_2H_5$.

## 12. Oxidation with Peracids

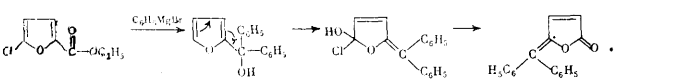
When 2,5-dimethylphenol is oxidised with peracids, the product is $\alpha\alpha'$-dimethyl-*cis*,*cis*-muconic acid, which is converted into $\gamma$-ethoxycarbonyl-$\alpha$-methyl-$\Delta^{\alpha\beta}$-butenolide on heating in ethanol [149].

## 13. The Synthesis of $\gamma$-Arylidene- and $\gamma$-Alkylidene-$\Delta^{\alpha\beta}$-Butenolides

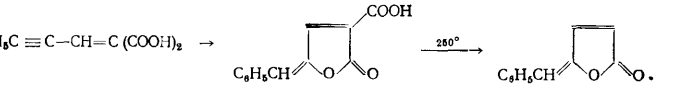
When bis-(5-chlorofuryl-2-methylphenyl) ether reacts with concentrated sulphuric acid, $\gamma$-benzylidene-$\Delta^{\alpha\beta}$-butenolide is formed [150]:



$\gamma$-Diphenylmethylene-$\Delta^{\alpha\beta}$-butenolide has been synthesised from ethyl 5-chlorofuran-2-carboxylate on treatment with phenylmagnesium bromide [150]:



When malonic acid reacts with phenylpropargylaldehyde, the product is phenylpropargylidenemalonic acid, which is converted into $\gamma$-benzylidene-$\alpha$-carboxy-$\Delta^{\alpha\beta}$-butenolide on heating to 190°C. [48] The decarboxylation of this product at 250°C leads to $\gamma$-benzylidene-$\Delta^{\alpha\beta}$-butenolide [48,151]:

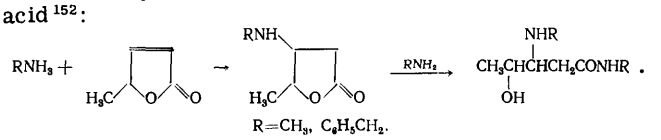


When mono- or di-alkylmaleic anhydrides are treated with a Grignard reagent at low temperatures, di- or trisubstituted $\gamma$-hydroxy-$\Delta^{\alpha\beta}$-butenolides are obtained [117]. Their dehydration with a mixture of acetic anhydride, acetic acid and sulphuric acid leads to $\gamma$-alkylidene or $\gamma$-arylidene-$\Delta^{\alpha\beta}$-butenolides [117].

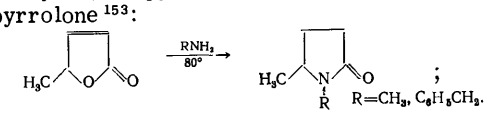
## III. CHEMICAL PROPERTIES OF $\Delta^{\alpha\beta}$-BUTENOLIDES

$\Delta^{\alpha\beta}$-Butenolides are very reactive. Owing to the presence of reactive centres such as the double bond and the lactone ring, they can react with nucleophiles and electrophiles and can undergo other reactions involving both the retention and the opening of the lactone ring.

$\Delta^{\alpha\beta}$-Butenolides react with ammonia and amines in different ways. Jones and Young [152] showed that, when angelica lactone reacts with aqueous methylamine and benzylamine solutions at room temperature, the amines add to the unsaturated carbon–carbon bond in the lactone ring [152]. Since the distribution of electron density in the lactone ring is such that there is a deficiency of electron density at the second and fifth carbon atoms in the ring, presumably nucleophiles attack one of these carbon atoms with subsequent dissociation of the $C_{(1)}-C_{(2)}$ or $C_{(1)}-C_{(5)}$ bond and formation of the corresponding derivative. The product obtained, which is a derivative of butyrolactone, therefore reacts with a second amine molecule to form the methylamide of $\gamma$-hydroxy-$\beta$-methylaminovaleric acid and the benzylamide of $\beta$-benzylamino-$\gamma$-hydroxyvaleric acid [152]:

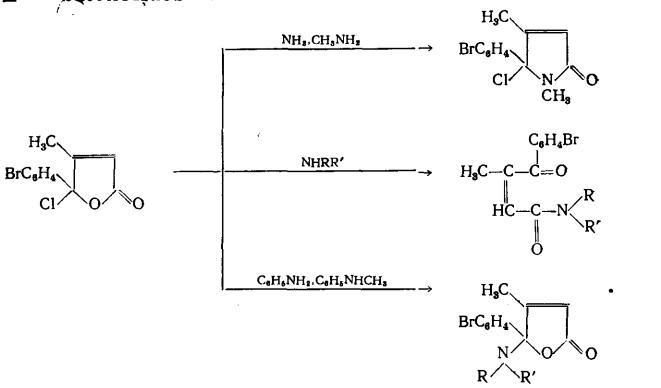



However, when angelica lactone is heated with an equimolar amount of methylamine or benzylamine to 80°C, 1,5-dimethyl-2(5*H*)-pyrrolone and 1-benzyl-5-methyl-2(5*H*)-pyrrolone [153]:

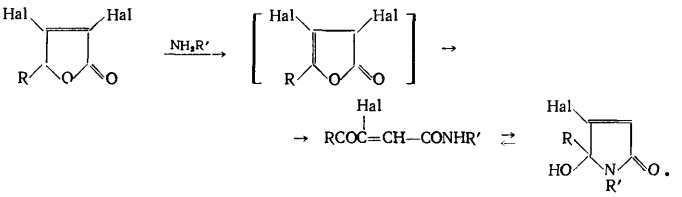



The reactions of halogenobutenolides with ammonia or amines can proceed in the following ways: opening of the butenolide ring with formation of the corresponding amide of a hydroxy- or an amino-acid [154–157], nucleophilic substitution of the halogen by an amino-residue [30,154–157], and addition of an amine to the C=C bond of the $\Delta^{\alpha\beta}$-butenolide ring [152]. The particular pathway followed in the reaction with a given nucleophile is apparently determined mainly by the thermodynamic stability of the addition products formed [158].

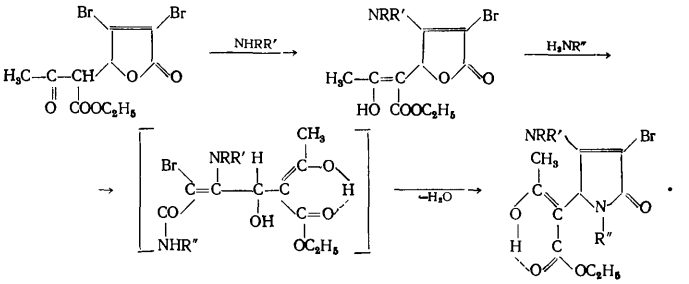
For example, when $\gamma$-(bromophenyl)-$\gamma$-chloro-$\beta$-methyl-$\Delta^{\alpha\beta}$-butenolide reacts with ammonia at room temperature in benzene, the product is a $\gamma$-hydroxylactam, the reaction with dimethylamine yields the alkylamide of *cis*-$\beta$-(*p*-bromobenzoyl)-$\beta$-methylacrylic acid, and the reaction with aniline or methylaniline results in the formation of $\gamma$-(*N*-arylamino)-$\gamma$-(bromophenyl)-$\beta$-methyl-$\Delta^{\alpha\beta}$-butenolides [30]:




It has been shown [156,157] that, when $\alpha\beta$-dihalogeno-$\Delta^{\alpha\beta}$-butenolides are treated with primary amines in methanol at temperatures between −5° and −10°C, the butenolide ring opens with formation of an amide, which readily cyclises under the reaction conditions and is in equilibrium with the corresponding lactam:

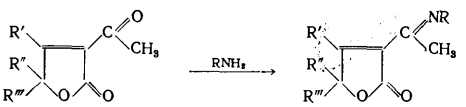



When $\alpha\beta$-dibromo-$\gamma$-($\alpha'$-ethoxycarbonylacetonyl)-$\Delta^{\alpha\beta}$-butenolide reacts with a twofold excess of a primary or secondary amine in methanol, the nucleophilic substitution of the halogen by the amino-residue takes place without involving the lactone ring; the products are $\beta$-amino-$\alpha$-bromo-$\Delta^{\alpha\beta}$-butenolides, which are converted into the corresponding $\Delta^{\alpha\beta}$-crotonolactams at room temperature in dioxan [159]:

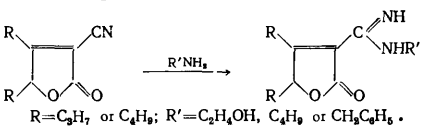



Bromine is substituted in the $\beta$-position, which can be explained by the fact that the electron density is a minimum at the corresponding carbon atom [160].

When substituted $\alpha$-acetyl-$\Delta^{\alpha\beta}$-butenolides react with primary amines, the nucleophilic attack by the amine is directed exclusively to the acetylcarbonyl group with formation of the corresponding amino-derivatives of $\alpha$-acetyl-$\Delta^{\alpha\beta}$-butenolides [161]:

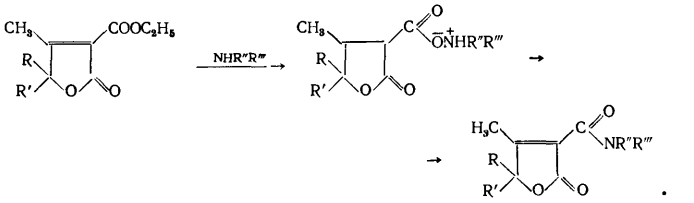



Primary amines add to the cyano-group of substituted $\alpha$-cyano-$\Delta^{\alpha\beta}$-butenolides with formation of the aminidines of the corresponding lactones [162]:

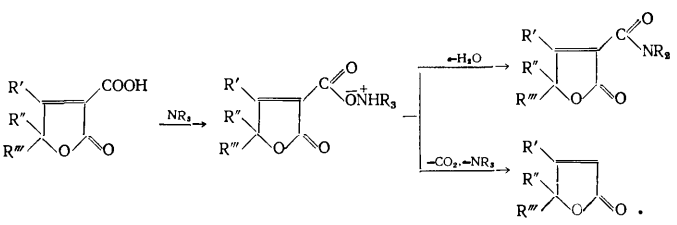



R=$C_3H_7$ or $C_4H_9$; R′=$C_2H_4OH$, $C_4H_9$ or $CH_2C_6H_5$.

The reaction of substituted $\alpha$-ethoxycarbonyl-$\Delta^{\alpha\beta}$-butenolides with primary and secondary amines proceeds via the nucleophilic attack by the amine exclusively on the ester group, with formation of the amides of salts of substituted $\gamma$-lactonoacids, i.e. the reactions proceed without the opening of the lactone ring [163–165]:

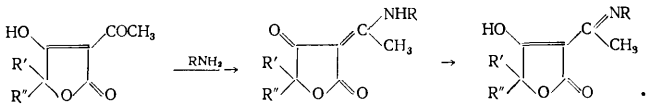


$\beta\gamma\gamma$-Trialkyl-$\alpha$-carboxy-$\Delta^{\alpha\beta}$-butenolides readily react with aqueous ammonia and aniline solutions and with primary and secondary amines to form the ammonium salts of $\alpha$-carboxy-$\Delta^{\alpha\beta}$-butenolides [164]:

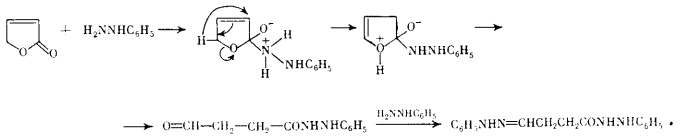


Depending on the nature of the amine, the salts decompose in two ways with formation of the amidolactones of $\alpha$-carboxy-$\Delta^{\alpha\beta}$-butenolides and $\beta\gamma\gamma$-trialkyl-$\Delta^{\alpha\beta}$-butenolides. In both cases the unsaturated lactone ring remains unchanged [164].

When $\alpha$-acetyltetronic acids are heated with ammonia and primary amines, imino-derivatives of tetronic acid are formed [139]:

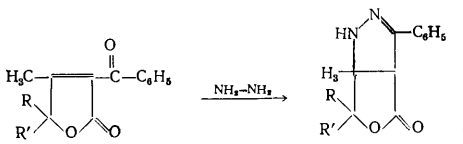


The reaction of $\Delta^{\alpha\beta}$-butenolides with phenylhydrazine entails the dissociation of the $C_{(1)}-C_{(2)}$ bond of the lactone ring with formation of the phenylhydrazide-phenylhydrazone of formylsuccinic acid [166]; the authors represent the reaction by the following scheme:



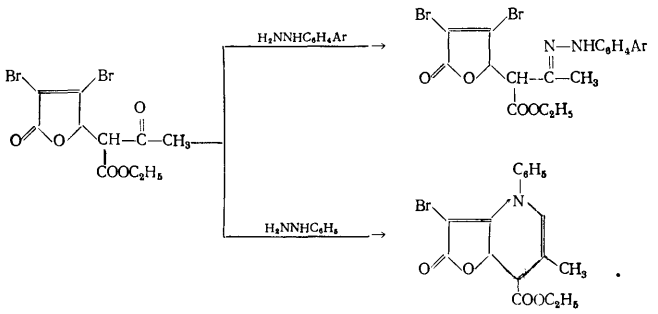
The reaction of $\alpha$- and $\beta$-acetyl-$\Delta^{\alpha\beta}$-butenolides with hydrazine, phenylhydrazine, and hydroxylamine at room temperature involves the oxo-group without the opening of the lactone ring and without addition to the double bond [161,167].

The reaction of hydrazine with substituted $\alpha$-benzoyl-$\Delta^{\alpha\beta}$-butenolides yields pyrazolines containing the $\gamma$-lactone ring [168]:



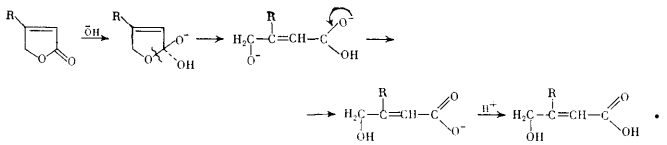
Similar pyrazolines were obtained also by the reaction of $\Delta^{\alpha\beta}$-butenolides with aliphatic diazo-compounds [169].

Kalnina and Gudriniece [159] showed that the reaction of $\alpha\beta$-dibromo-$\gamma$-($\alpha'$-ethoxycarbonylacetonyl)-$\Delta^{\alpha\beta}$-butenolide with $p$-nitro- and 2,4-dinitro-phenyl-hydrazines at room temperature yields the corresponding arylhydrazones, while the reaction of $\alpha\beta$-dibromo-$\Delta^{\alpha\beta}$-butenolide with phenylhydrazine involves also the elimination of hydrogen bromide and the closure of the tetrahydropyridazine ring [159]:

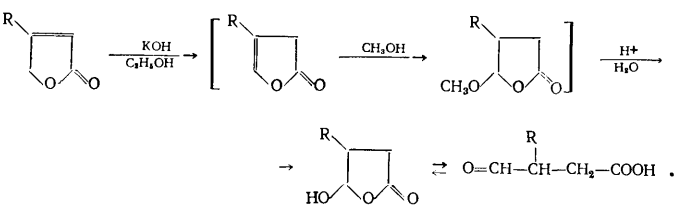


Thus the study of the reactions with ammonia and nitrogen-containing bases showed that, in contrast to the saturated analogues, the lactone ring in unsaturated substituted butenolides is unreactive towards nucleophiles. Comparative studies of the reactivities of the functional groups and the double bond clearly demonstrated the much weaker electrophilic properties of the double bond in these reactions.

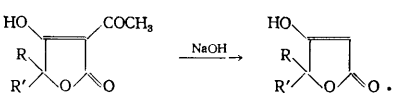
$\Delta^{\alpha\beta}$-Butenolides are hydrolysed with and without the opening of the lactone ring. The ease of ring opening in hydrolysis depends on the nature and positions of the substituents. Thus when $\beta$-substituted $\Delta^{\alpha\beta}$-butenolides were acted upon by alkali, two different reactions were noted [86]. In an aqueous medium, the lactone hydrolyses, forming the salt of the corresponding acid [86]:



In alcoholic solution, the double bond migrates irreversibly to the $\beta\gamma$-position and the resulting vinyl ether combines with the elements of the alcohol to form an acetal. After acidification, the acetal hydrolyses to the hydroxylactone, which exists in equilibrium with the non-cyclic formyl-substituted acid [86]:

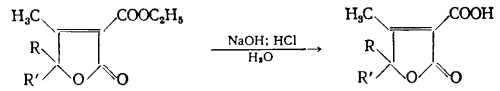


On treatment with aqueous solutions of alkali, the unsaturated lactone ring in $\alpha$-acetyl-$\gamma$-methyl- and $\alpha$-acetyl-$\gamma\gamma$-diphenyltetronic acids remain unchanged, the products being $\gamma$-alkyltetronic acids [139]:

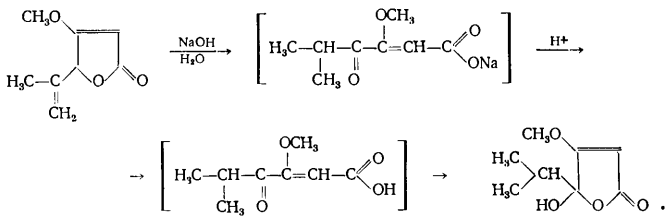


Alkaline and acid hydrolysis of substituted $\alpha$-ethoxycarbonyl-$\Delta^{\alpha\beta}$-butenolides involves only the ethoxycarbonyl

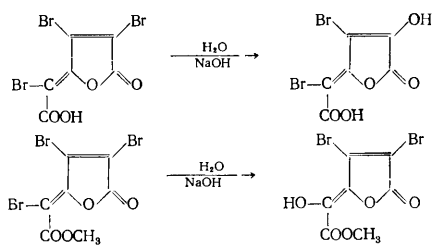
group with retention of the lactone ring and the formation of $\alpha$-carboxy-$\Delta^{\alpha\beta}$-butenolides [163,164]:



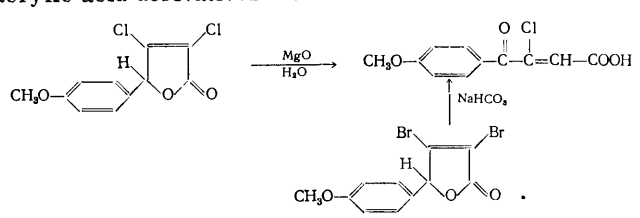
Killian et al.[170] showed that, when penicilloic acid reacts with a cold dilute solution of sodium hydroxide, dihydropenicilloic acid is formed. It is suggested that treatment with alkali involves a shift of the double bond with subsequent opening and reclosure of the lactone ring:



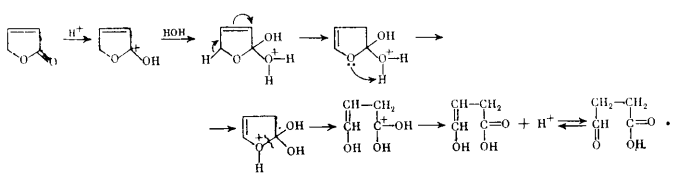
The alkaline hydrolysis of halogeno-$\Delta^{\alpha\beta}$-butenolides involves only the halogen with retention of the lactone ring. Thus the alkaline hydrolysis of the $\gamma$-lactone and the methyl ester of the $\gamma$-lactone of $\alpha\beta\delta$-tribromomuconic acid yields respectively the $\gamma$-lactone of $\beta\gamma$-dibromo-$\alpha$-hydroxymuconic acid[171] and the $\gamma$-lactone of the methyl ester of $\alpha\beta$-dibromo-$\delta$-hydroxymuconic acids[172]:



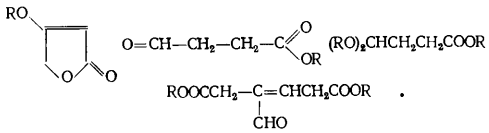
Hydrolysis of halogeno-$\Delta^{\alpha\beta}$-butenolides also proceeds on treatment with magnesium oxide in aqueous dioxan or in sodium bicarbonate solution with formation of acrylic acid derivatives[173]:



Acid hydrolysis of $\gamma$-lactones, which proceeds with opening of the lactone ring, has been described only for an unsaturated $\Delta^{\alpha\beta}$-butenolide[166]. The opening of the $\Delta^{\alpha\beta}$-butenolide ring in an acid medium is accompanied by the appearance of the formyl group and leads to the formation of 4-hydroxybut-3-enoic acid, which is converted into the tautomeric formylsuccinic acid[166]:

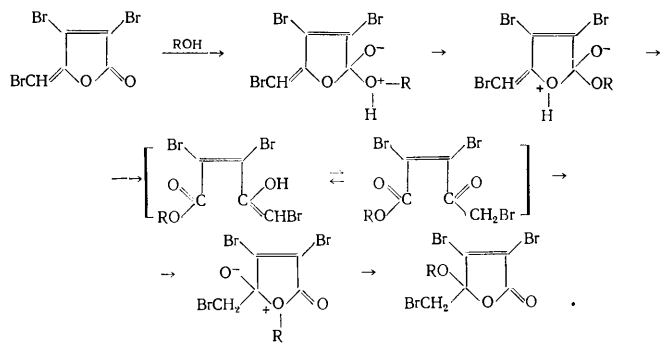


Alcoholysis of $\Delta^{\alpha\beta}$-butenolides takes place in the presence of acid catalysts (in the absence of catalysts, the reaction proceeds only slowly and requires prolonged heating) and leads to the formation of hydroxyacids. Thus heating of a $\Delta^{\alpha\beta}$-butenolide with alcohols leads to a mixture of products[12,166,174-176], which were isolated by fractional distillation and identified by the formation of various derivatives and by infrared and Raman spectroscopy:



$\Delta^{\alpha\beta}$-Butenolides react with alcohols in the presence of hydrogen chloride[43] or thionyl chloride[174] with formation of hydroxyacid esters.

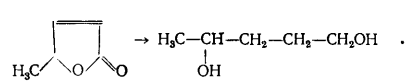
The reaction of $\alpha\beta$-dibromo-$\gamma$-bromomethylene-$\Delta^{\alpha\beta}$-butenolide with alcohols on boiling leads to the formation of $\gamma$-alkoxy-$\alpha\beta$-dibromo-$\gamma$-bromomethyl-$\Delta^{\alpha\beta}$-butenolides[177]. The initial products are apparently esters, whose conversion into a cyclic form involves the stabilisation of oxonium derivatives of $\Delta^{\alpha\beta}$-butenolides:



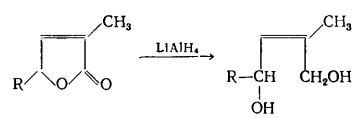
Systematic study of the catalytic hydrogenation of $\Delta^{\alpha\beta}$-butenolides showed that they readily react with hydrogen at the double bond, being converted into the corresponding butyrolactone derivatives[139,162,165,178,179]. Palladium black, Raney nickel, and palladium calcium on carbonate are used as catalysts.

The catalytic hydrogenation of $\alpha$-ethoxycarbonyl, $\alpha$-carboxy-, $\alpha$-carbamoyl, $\alpha$-acetyl, and $\alpha$-cyano-$\Delta^{\alpha\beta}$-butenolides over $Pd/CaCO_3$ proceeds selectively, involving the unsaturated bond of the lactone ring, and leads to the synthesis of the corresponding butyrolactone derivatives[139,162,165].

The effect of complex metal hydrides on $\Delta^{\alpha\beta}$-butenolides has been investigated[180-182]. $\Delta^{\alpha\beta}$-Butenolides are reduced by lithium tetrahydroaluminate to the corresponding diols. Thus pentane-1,4-diol is obtained when $\beta$-angelica lactone is treated with lithium tetrahydroaluminate[183]:



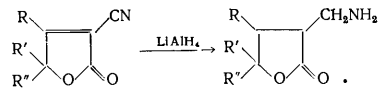
The reduction of $\alpha$-methyl-$\gamma$-phenyl-$\Delta^{\alpha\beta}$-butenolide and $\alpha$-methyl-$\gamma$-(2-naphthyl)-$\Delta^{\alpha\beta}$-butenolide leads to the corresponding diols[181]:



The opening of the lactone ring is observed also when $\Delta^{\alpha\beta}$-butenolides react with dimethyl- and diethyl-aluminium chlorides[184]. Ketoalcohols and the corresponding unsaturated and saturated diols are obtained for different

proportions of the lactone and lithium tetrahydroaluminate taken for the reaction[181-183].

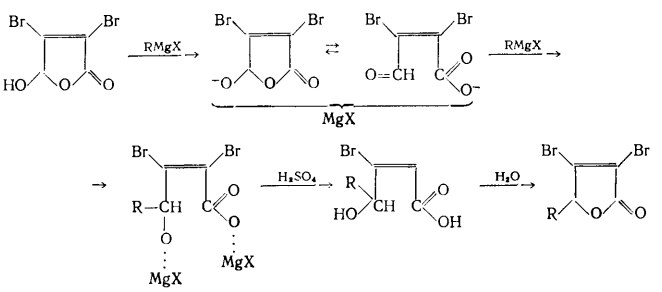
The reduction of substituted α-cyano-Δ$^{\alpha\beta}$-butenolides with lithium tetrahydroaluminate involves the cyano-group with simultaneous reduction of the unsaturated bond in the lactone and leads to α-aminomethylbutyrolactones[182]:



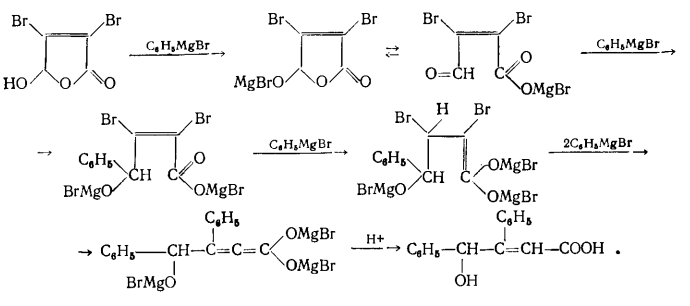
α-Hydroxymethyl-, α-(1-hydroxyethyl)-, and α-(1-hydroxybenzyl)-Δ$^{\alpha\beta}$-butenolides have been obtained under analogous conditions from α-ethoxycarbonyl, α-acetyl-, and α-benzoyl-Δ$^{\alpha\beta}$-butenolides[182].

Since Δ$^{\alpha\beta}$-butenolides can be regarded as dihydrofuranones, one may expect that they can be readily converted into furan derivatives. Thus α-acetyl-Δ$^{\alpha\beta}$-butenolides undergo a very interesting rearrangement. When α-acetyl-Δ$^{\alpha\beta}$-butenolides [i.e. 3-acetyl-2(5*H*)-furanones] are heated with a mixture of acetic and hydrochloric acids, furan-3-carboxylic acids are obtained[136,138,139].

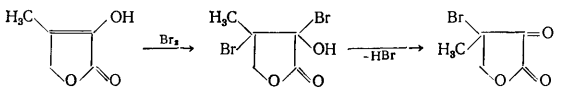
The reaction of Δ$^{\alpha\beta}$-butenolides aith organometallic compounds has been investigated. Δ$^{\alpha\beta}$-Butenolides behave in different ways in reactions with organomagnesium compounds. Thus, when bromomuconic acid is treated with alkylmagnesium halides in ethereal solution, γ-alkyl-αβ-dibromo-Δ$^{\alpha\beta}$-butenolides are obtained[75,154]:



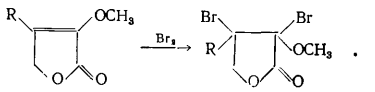
Bromomuconic acid reacts with phenylmagnesium bromide with much greater difficulty[75,154], undergoing a series of transformations: the reaction leads to a magnesium halide alkoxide:



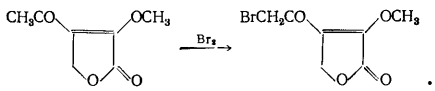
When the final organomagnesium compound is treated with dilute sulphuric acid, cinammic acid derivatives are obtained. The ability of the double bond in Δ$^{\alpha\beta}$-butenolides to undergo electrophilic reactions has also been investigated in relation to halogenation reactions. The latter proceed with retention of the lactone ring. It has been shown[185] that α-hydroxy-β-methyl-Δ$^{\alpha\beta}$-butenolide reacts with an equimolar amount of bromine, forming αβ-dibromo-α-hydroxy-β-methyl-γ-lactone, which splits off one molecule of hydrogen bromide and is converted into β-bromo-β-methyl-α-oxo-γ-lactone:



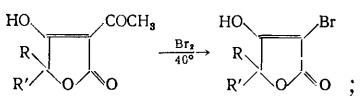
Bromination of β-alkyl-α-methoxy-Δ$^{\alpha\beta}$-butenolides leads to the formation of β-alkyl-αβ-dibromo-α-methoxybutyrolactones[186]:



In the presence of the acetyl group as a substituent, the bromination involves the latter with formation of β-bromoacetyl-α-methoxy-Δ$^{\alpha\beta}$-butenolide:

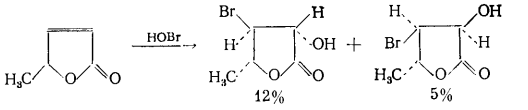


When α-acetyl-γγ-dimethyl- and α-acetyl-γγ-spirocyclohexane-tetronic acids are acted upon by bromine, the acetyl group is split off and the corresponding α-bromo-γγ-dimethyl- and α-bromo-γ-spirocyclohexane-tetronic acids are obtained[156]:



When α-acetyl-Δ$^{\alpha\beta}$-butenolides react with an equimolar amount of phosphorus pentachloride, α-(α-chlorovinyl)-Δ$^{\alpha\beta}$-butenolides are formed, while an excess of phosphorus pentachloride leads to the formation of α-(αβ-dichlorovinyl)-Δ$^{\alpha\beta}$-butenolides[187].

The reaction of β-angelica lactone with hypobromous acid results in the formation (in very low yields) of crystalline diastereoisomers of β-bromo-α-hydroxy-γ-valerolactone[188]:

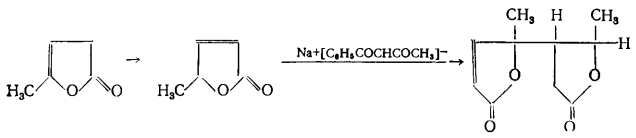


When hydrogen chloride or bromide combines with a Δ$^{\alpha\beta}$-butenolide, the product is β-chloro- or β-bromo-γ-butyrolactone[189]. In the latter case, 3,4-dibromobutyric acid is also formed[189].

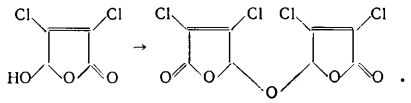
Δ$^{\alpha\beta}$-Butenolides react with diazomethane to form methylated products[34,151,167,190,191]. Thus the reaction of γ-benzylidene-α-methoxycarbonyl-Δ$^{\alpha\beta}$-butenolide with diazomethane yields the corresponding β-methylderivative. *C*-Methylation therefore proceeds more rapidly than the formation of the cyclopropane derivative. γ-Benzylidene-α-cyano-β-methyl-Δ$^{\alpha\beta}$-butenolide has been obtained similarly[151].

β-Angelica-lactone or a mixture of the α- and β-isomers dimerises at 20–200°C in the presence of tertiary amines, alkali metals, or alkali metal alkoxides and hydroxides[192-194]. It has been established that β-angelica lactones are more reactive than their α-isomers. The isomerisation of β-angleica lactones also proceeds in the presence of the sodium salt of benzylacetone or anhydrous potassium

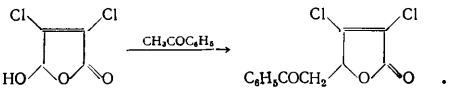
carbonate[195,196]; the authors suggest that the process proceeds as follows:



Dimerisation is also observed when $\alpha\beta$-dichloro-$\gamma$-hydroxyangelica lactone is dehydrated by benzenesulphonic acid[70]:

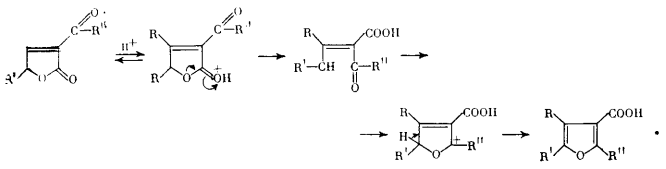


Dieckman and Platz[197] achieved for the first time the condensation of chloromuconic acid and acetophenone in the presence of an aqueous alcoholic solution of alkali, which gave a low yield of $\alpha\beta$-dichloro-$\gamma$-phenacyl-$\Delta^{\alpha\beta}$-butenolide:

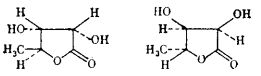


Later it was shown[75] that, when the condensation is carried out in an aqueous alkaline solution, the yield of $\gamma$-phenacyl-$\Delta^{\alpha\beta}$-butenolide increases appreciably[75].

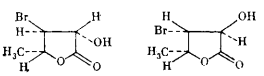
$\Delta^{\alpha\beta}$-Butenolides are readily oxidised by potassium permanganate to dihydroxylactones, which may be hydrolysed to the corresponding trihydroxyacids[103,198]. Thus $\alpha\gamma$-dimethyl-$\Delta^{\alpha\beta}$-butenolide is oxidised to $\alpha\beta$-dihydroxy-$\alpha\gamma$-diphenyl-$\gamma$-butyrolactone[199]. However, this reaction pathway is not general since, $\beta\gamma$-diphenyl-$\Delta^{\alpha\beta}$-butenolides, for example, does not form hydroxy-derivatives at all[103]:



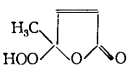
In the presence of osmium tetroxide in an aqueous sodium chloride solution, $\beta$-angelica lactone gives rise to a mixture of hydroxylactones[200]:



Stereoisomeric $\beta$-bromo-$\alpha$-hydroxy-$\gamma$-valerolactones are formed when $\beta$-angelica lactone is treated with hypobromous acid[188]:



$\beta$-Angelica lactone also undergoes autoxidation with formation of a hydroperoxy-compound[201]:



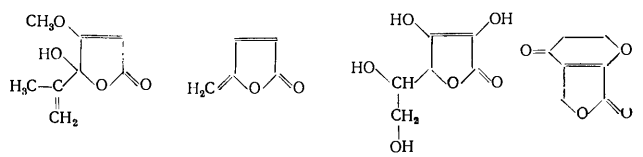
In the presence of silica or pumice at 450–650°C, it is pyrolysed with formation of methyl vinyl ketone[202].

In contrast to their saturated analogues ($\gamma$-butyrolactones)[203,204], $\Delta^{\alpha\beta}$-butenolides show little reativity in polymerisation reactions[205-207], but readily copolymerise with various vinyl monomers. Thus the $\Delta^{\alpha\beta}$-butenolide–styrene copolymer has been obtained in the presence of radical initiators[205]. The copolymerisation reactions of $\beta\gamma\gamma$-trialkyl-$\alpha$-ethoxycarbonyl-$\Delta^{\alpha\beta}$-butenolides with acrylonitrile, *N*-vinylcaprolactam, *N*-vinylpyrrolidinone, methyl acrylate, and vinyl acetate have been investigated[208,209]. The copolymers of $\alpha$-acetyl- and $\alpha$-cyano-$\beta\gamma\gamma$-trimethyl-$\Delta^{\alpha\beta}$-butenolides with styrene, acrylonitrile, methyl methacrylate, and *N*-vinylcaprolactam have been obtained[208,209]. The relative activity constants have been determined for certain pairs of monomers[208,209].

Dichloroprotoanemonine also readily copolymerises with vinyl monomers via a radical mechanism[210]. These reactions proceed with retention of the lactone ring and the formation of reactive copolymers.

## IV. BIOLOGICAL ACTIVITY OF UNSATURATED $\gamma$-LACTONES

The unsaturated lactone ring is present in many natural products[3-6,57,211,212] and physiologically active substances[211-218]. For example, it is a constituent of penicilloic acid, protoanemonine, vitamin C, clavacin, etc:

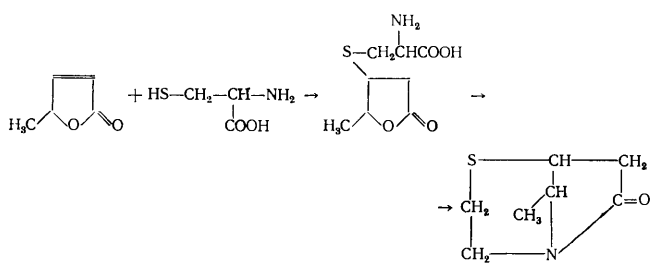


It has been established that the vitamin activity of L-ascorbic acid is due to the presence of the $\Delta^{\alpha\beta}$-butenolide system[211].

Both $\alpha$- and $\beta$-angelica lactones exhibit bactericidal properties[14]. Hydrolysis of the lactone as well as hydrogenation of the double bond entails the loss of activity by these compounds.

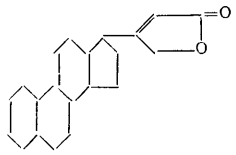
The antibiotic activity of unsaturated lactones has been explained by their ability to react readily with cystine and also with certain enzymes containing mercapto-groups which are important for the normal activity of microorganisms[219-221]. It has been suggested that the bactericidal activity of unsaturated lactones is associated with the ability of the lactone double bond to combine with the SH groups present in bacterial proteins, inhibiting thereby the processes involved in the growth of bacteria[220,221]. A special study has been made of the reaction of cysteine with certain unsaturated lactones, particularly with angelica lactone[220,221].

The reaction proceeds via the mechanism:

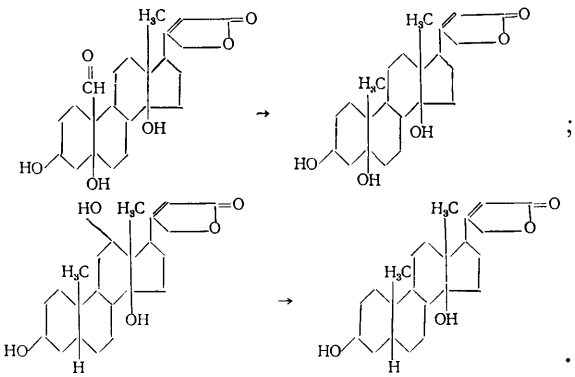


Protoanemonine is an effective antibacterial substance[221].

The class of natural products containing the unsaturated $\gamma$-lactone ring, namely natural steroids having the general structure [222-226]

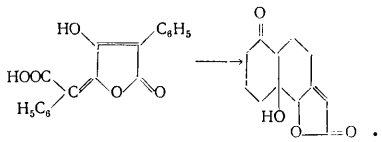


is of interest. Compounds of this type (cardenolides) promote the normal activity of the cardiac muscle in man and animals. Cardenolides are steroids containing a $\Delta^{\alpha\beta}$-butenolide ring in the side chain [223,227-250]. They include for example, strophanthidin, periplogenin, digoxigenin, digitoxigenin, etc:



Cardiac glucosides, incorporating the $\Delta^{\alpha\beta}$-butenolide ring, are present in the cardenolide, the aglycone, or the sugar residue [227].

Vulphinic acid [$\beta$-hydroxy-$\alpha$-phenyl-$\gamma$-(phenylcarboxymethylene)-$\Delta^{\alpha\beta}$-butenolide] and $\psi$-santonin, which exhibits a high physiological activity, also contain the $\Delta^{\alpha\beta}$-butenolide structure [21,251-253]:



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# Fundamental Hydrodynamic Characteristics of Polymers with Star and Comb Macromolecular Structures

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The review considers the majority of studies published up to 1976 and dealing with the hydrodynamic properties of polymers having star and comb macromolecular structures. Methods for the estimation of the degree of branching are presented and it is shown how the dependence of the intrinsic viscosity on molecular weight changes on passing from randomly branched macromolecules to star and comb macromolecules. The influence of the polydispersity of the branches on the size of the macromolecules and their rigidity parameters is examined.
The bibliography includes 110 references.

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NOTATION

$\eta_0$ = solvent viscosity;
$[\eta]$ = intrinsic viscosity of the polymer solution;
$[\eta]\theta, [\eta]l, [\eta]_g$ = intrinsic viscosities in a $\theta$-solvent and of linear and branched macromolecules respectively;
$M$ = molecular weight (M.W.); $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ are the number-average, weight-average, and $z$-average molecular weights;
$A$ = Kuhn segment; $Al$, $A_g$, $A_s$, and $A_b$ are the corresponding segments for linear and branched macromolecules and in the main and side chains of a branched macromolecule ("backbone" and "branches");
$S$ = number of monomeric units in the Kuhn segment; $S_s$ is the corresponding number for the main chain of a branched macromolecule;
$a$ = persistent length (correlation length);
$L$ = contour length of the macromolecule (the length of the macromolecule straightened without distortion of the valence angles); $L_s$ and $L_b$ are the corresponding values for the main and side chains;
$l$ = distance between two neighbouring branches;
$\lambda$ = projection of the monomeric unit in the direction of the main chain;
$[\overline{R}^2]^{1/2}$ = mean square radius of inertia; $[\overline{R}^2]_l^{1/2}$ and $[\overline{R}^2]_g^{1/2}$ are the corresponding radii for the linear and branched macromolecule;
$[\overline{h}^2]^{1/2}$ = mean square distance between the ends of the macromolecules;
$g$ = factor characterising the degree of branching of the macromolecule;
$\epsilon$ = swelling parameter of the polymeric coil;
$N$ = number of Kuhn segments in the macromolecule; $N_s$ and $N_b$ are the corresponding numbers for the main and side chains;
$f$ = number of branches in the branched macromolecule;
$m$ = average number of branching centres (points) per macromolecule;
$\Phi$ = Flory constant;
$h$ = ratio of the hydrodynamic radii of the branched and linear macromolecules with the same degrees of polymerisation;
$P$ = degree of polymerisation;
$F$ = translational friction constant;
$\alpha$ = swelling coefficient;
$\chi$ = parameter characterising the excess energy of the interaction of macromolecules in solution per solvent molecule;
$z$ = parameter characterising the number of collisions of the chain units within the limits of the coil per unit volume;
$\gamma$ = effective excluded volume of the segment;
$\mu$ = chemical potential of the system;
$C_m$ = coefficient of polymer–solvent interaction:

$$C_m = \left(\frac{3^3}{2^{5/2}\pi^{3/2}}\right)\left(\frac{\bar{v}^2}{V_1 \cdot N_A}\right)\left(\frac{M}{\overline{h}_\theta^2}\right)^{3/2},$$

Here the symbols have the following significance:
$V_1$ = molar volume of the solvent; $N_A$ = Avogadro number;
$v$ = specific partial volume of the polymer;
$\psi_1$ = entropy parameter of the system;
$T$ = temperature of the solution;
$A_2$ = second virial coefficient in the expansion of the osmotic pressure in terms of concentration;
$a, b, K_\eta, K_s$ = parameters of the equation relating $[\eta]$ to $M$;
$\varphi$ = variable.

## I. INTRODUCTION

The extensive development of the theory and practical applications of anionic polymerisation made it possible to obtain polymers with a strictly specified macromolecular structure. Thus virtually monodisperse polystyrenes have now been synthesised and investigated in detail[1-5]. The anionic polymerisation of organocyclosiloxanes in the presence of tri- and tetra-functional sodium initiators led to the synthesis of star polydimethylsiloxanes with a narrow molecular weight distribution (MWD).[6-9] The use of a trifunctional activator for the synthesis of branched polyamides[10] and the synthesis of a star dextran[11] and a star polyethylene[12] have been described.

The synthesis of polymers with a comb macromolecular structure has been developed on an even larger scale during the last decade. Numerous studies were published between 1965 and 1975, in which the properties of comb polymers and the difference of their behaviour in solution from that of polymers with a linear macromolecular structure were discussed.

The behaviour of polymers in solution is determined by many factors, the main ones being the chemical structure and the geometry of the macromolecules, the nature of the solvent, the molecular weight (M.W.) of the polymer, and the temperature of the solution. Thus the introduction of only a few long branches into the macromolecule of a linear polymer leads to an appreciable decrease in the size of the molecular coil in solution and hence to a decrease of $[\eta]$ relative to the linear polymer with the same chemical composition[13]. The most reliable data on the degree of branching of macromolecules can therefore be obtained by studying the properties of dilute solutions of polymers and the dependence of these properties on the size and number of branches in the macromolecule[4,13-20].

However, a quantitative interpretation of the experimental results is in most cases extremely difficult. A common disadvantage of the existing methods is the necessity to compare the results with the corresponding results for linear polymers having the same chemical composition and molecular weight[13].

If a branched macromolecule does not obey Gaussian statistics, it is necessary to compare the dimensions of molecules having not only the same molecular weight but also the same thermodynamic rigidity, i.e. with $A_g = A_l$. One must then take into account also the thermodynamic rigidity of the main ($A_s$) and side ($A_b$) chains of the branched macromolecule[21].

In certain cases, it is convenient to compare the experimental characteristics of the branched macromolecules with the analogous characteristics of the linear molecules whose molecular weight is equal to that of the main chain of the branched macromolecule, i.e. of the "backbone".[21]

The problem of determining the influence of the degree of branching on the parameters of the macromolecular coil is complicated by the existence of a wide variety of types of branching. It is usual to distinguish three types of branching: star, comb, and cascade branching[22-26]. In the comb and cascade branching, the molecule contains not one but several branching nodes, in contrast to star branching. Regular (equal lengths of the branches) and random (different lengths of the branches) structures are also characteristic of these three types of branching. One of the types of regular star branching has been examined by Tsvetkov[27]. In addition, it is possible to distinguish long-chain and short-chain branching. In certain cases, short-chain branching has only an insignificant influence on the properties of macromolecules in solution[24-26].

All the comb polymers known at present can be divided into two types: comb homopolymers and graft comb heteropolymers (copolymers). Comb homopolymers include polymers whose macromolecules have long straight-chain aliphatic side branches in each monomeric unit, for example, poly-$\alpha$-olefins, poly(alkyl acrylates), polyvinyl ethers, polyvinyl esters, etc.[28-39]. The structures of graft comb copolymers depend on the molecular parameters of the homopolymers incorporated in them[40-48].

Fairly numerous experimental studies of the properties in solution of polymers with the comb macromolecular structure have now been published[18,19,25,28-51]. However, the hydrodynamics of solutions of star polymers have been investigated only in relation to polystyrene[1-5,52] and polyorganosiloxanes[6-9].

Macromolecules with cascade random branching are the type most frequently synthesised. At high degrees of conversion, such macromolecules can be transformed into microgels and gels.

A comparative examination of the hydrodynamics of solutions of polymers with the comb and star macromolecular structures on the basis of the available theoretical[3,22,23,25,50-52,54,55] and experimental[2,18,19,21,25,53,56-60] data is of undoubted interest. For all types of branching, the dimensions of macromolecules are characterised solely by their average radius of inertia $[\bar{R}^2]_g^{1/2}$, since the concept of the distance between the ends of the polymer chain $[\bar{h}^2]^{1/2}$, defining the size of linear macromolecules, loses its significance in the present instance[22,24,57]. Usually $[\bar{R}^2]_g^{1/2} < [\bar{R}^2]_l^{1/2}$, so that the intrinsic viscosity $[\eta]_g < [\eta]_l$.

The degree of branching of macromolecules has come to be characterised by the factor $g$[22,25,50,55]:

$$g^{\epsilon} \simeq [\bar{R}_0^2]_g/[\bar{R}_0^2]_l \text{ and } g^{\circ} = [\eta_\theta]_g/[\eta_\theta]_l, \qquad (1)$$

where $\epsilon$ may assume values of 1/2, 1, and 3/2. The factor $g$ is determined by the number of segments in the backbone of the macromolecule and in the branches[61,62]:

$$g = \frac{N - \sum_b N_b}{N} = \frac{N_s}{N}.$$

However, the factor $g$ depends also on the number, rigidity, and polydispersity of the side branches, and on the length, rigidity, and polydispersity of the main chain[61].

Depending on the type of branching, short side branches, which usually do not have a significant influence on the macromolecular size, can affect the values of $[\bar{R}_\theta]_g^2$ in a $\theta$-solvent[50,51-54,56-60]. On the other hand, in effective solvents the presence of short branches can appreciably increase the size of the macromolecule[56-58].

## II. STAR MACROMOLECULES

Three-, tetra-, and poly-functional star macromolecules with single and multiple branching centres are known. Star macromolecules may be homogeneous, with the centre of the star and the branches consisting of atoms of the same kind (Fig. 1*a*), and heterogeneous (Fig. 1*b*). The branches of the star may be of the same or different length, short and long, mono- and poly-disperse.

In 1949, Zimm and Stockmayer[50] suggested that the degree of branching of homogeneous star polymers whose molecules have different branching functionalities (tri- and tetra-functional branching) be characterised by a quantity

$g$ proportional to the ratio of the mean square radii of inertia of the branched and linear macromolecules and to the ratio of the intrinsic viscosities:

$$g^{3/2} \simeq ([\bar{R}^2_\theta]_g/[\bar{R}^2_\theta]_l)^{3/2}; \quad g^{3/2} = [\eta_\theta]_g/[\eta_\theta]_l. \qquad (2)$$

The use of this relation is based on the hypothesis that the Flory equation for linear polymers [63]

$$[\eta_\theta]_l = \Phi_\theta [\bar{R}^2_\theta]^{3/2}_l/M$$

is valid also for branched specimens.

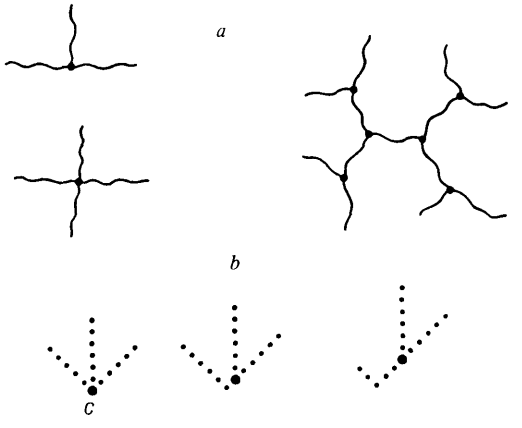



Figure 1. Graphical representation of the possible structures of a star macromolecule: *a*) homogeneous branching [27]; *b*) heterogeneous branching [98]; *c*) centre of the star.

However, Stockmayer and Fixmann [54] and Zimm and Kilb [27,55] showed that the effective hydrodynamic radius of the polymeric molecule is less sensitive to branching than the radius of inertia $[\bar{R}^2_\theta]^{1/2}$. In this case, the Flory equation for star macromolecules can be formulated as follows:

$$[\eta_\theta]_g = \Phi_\theta \frac{[\bar{R}^2_\theta]^{3/2}_g}{M} h^3. \qquad (3)$$

In 1953 Stockmayer and Fixmann [24,54] showed that the coefficient of friction of a branched macromolecule is related to the radius of inertia and the hydrodynamic radius:

$$F_{\theta g}/\eta_0 = \frac{\Phi^{1/3}_\theta}{2.5 \times 10^6} [\bar{R}^2_\theta]^{1/2} h, \qquad (4)$$

where $F_{\theta g}$ is the translational friction constant and

$$h^3 = [\eta_\theta]_g/[\eta_\theta]_l = f^{3/2}/[2 - f + \sqrt{2}\,(f-1)]. \qquad (5)$$

In this case $g^{1/2} < h^3 < g^{3/2}$.

Stockmayer and Fixmann [24,54] suggested that this relation remains valid for any branching model and can be used to find the functionality and the number of branching nodes, provided that the ratio $[\eta\theta]_g/[\eta\theta]_l$ is known.

However, Zimm and Kilb showed subsequently [55,61] that neither Eqn. (2) nor Eqns. (4) and (5) can be used with adequate reliability for the description of the behaviour of any star macromolecule in solution.

Zimm and Kilb [55,61] based their calculations on the model of a star molecule with $f$ branches and $N$ subchains, the centres of hydrodynamic interactions being located at the ends of the subchains. Zimm and Kilb examined two models of macromolecules with star branching: comprising one branching centre with four branches of equal length and one branching centre with two long and eight short branches. It was shown that the influence of branching on the hydrodynamic properties of macromolecules is somewhat smaller than on the size of the coil [22,26,55,62-64]. The increase of the hydrodynamic interaction factor only partly compensates the influence of the "contraction"† of the coils owing to branching on the hydrodynamic properties. The value of $\Phi$ for branched polymers exceeds by a factor of 6–27 that for linear polymers [2,65,66]. For this reason, Eqn. (4) is not rigorously justified, since the coefficient of friction and the viscosity, on which it is based, depend in different ways on the details of the structure of the macromolecule [23].

All this was taken into account in the studies of Zimm and Kilb [55,64], who showed that

$$[\eta_\theta]_g/[\eta_\theta]_l = g^{1/2},$$

for star macromolecules and

$$[\eta_\theta]_l/[\eta_\theta]_g \simeq \sqrt{3}.$$

Zimm and Kilb suggest that these equations can be applied with adequate approximation to any types of branched macromolecules [55,61]. However, it has been stated [61] that the Stockmayer–Fixmann and Zimm–Kilb calculations have been carried out for star macromolecules and that the *a priori* extension of the results to comb macromolecules is not always correct. Thus Kurata and Fukatsu [67] showed that, for statistically branched polymers, the ratio $P_g/P_l$, where $P \simeq \Phi^{1/2}/2.5 \times 10^6$, increases monotonically with increase of branching density, tending asymptotically to 1.34. For graft comb polymers, the ratio $P_g/P_l$ initially increases with increasing branching density, passes through a maximum, and then falls, tending to unity regardless of the functionality of the branching. These results show that, in translational motion of macromolecules, the effective hydrodynamic dimensions depend not only on the density but also on the type of branching. Stockmayer and Fixmann [54,61] suggest that the effective hydrodynamic dimensions are the same in translational and rotational motion.

## III. COMB MACROMOLECULES

### 1. Comb Homopolymers

Homopolymers with a comb macromolecular structure should be formally assigned to the class of linear polymers, since the length of the side branches is much smaller than the length of the main chain [32,68]. However, many specific properties make it necessary to treat comb polymers as a special type of branched polymer. Thus mainly orientation short-range order obtains in linear polymers and is to an overwhelming extent one-dimensional with a symmetry axis parallel to the molecular axis. In

† It is understood that the term "contraction" does not imply that the macromolecule actually contracts. The effective volume of the branched macromolecule is simply smaller than that of its linear analogue having the same molecular weight.

comb homopolymers, there is a possibility of two-dimensional order due to the intramolecular interaction of the long side branches and the intermolecular interaction between the main chains. Comb macromolecules tend to become ordered as a result of the association of the side chains, which is the reason for the ease of formation of ribbon structures[32,68]. Even in amorphous polymers with short side branches, order is observed, entailing the appearance of layer structures. The interaction of methylene chains in homopolymeric comb macromolecules has a decisive influence on the type of crystallisation, but the degree of ideality of the packing depends in many ways on the nature of the main chain[32,68]. An increase of the length of the side groups in comb homopolymers leads to an increase of the equilibrium rigidity of both the main chain of the macromolecule and of its side groups. This was demonstrated in a study of the behaviour of poly(methyl acrylate), poly(butyl acrylate), poly(octyl acrylate), and poly(octadecyl acrylate) in solution[37]. With increase of length of the side branches, the number of coiled conformations and the conformational stability of the macromolecules in solution increase[35].

It has been found for poly(cetyl methacrylate) that the length of the Kuhn segment is $A = 43$ Å.[34] This value exceeds by a factor of two the segmental dimensions of the majority of flexible chain molecules without complex side groups. It has been concluded[34] that the side chains of poly(cetyl methacrylate) molecules possess a high equilibrium rigidity and that there is an intramolecular orientation order in this polymer, exceeding the orientation order of Gaussian chains.

On the basis of the results of X-ray diffraction analysis of poly(hexadecyl acrylate) and poly(hexadecyl methacrylate), Shibaev and coworkers[33] showed that the side branches of poly(alkyl acrylates) and poly(alkyl methacrylates) in which the length of the side chains corresponds to ten and more carbon atoms form two-layer and one-layer types of hexagonal packing. The critical length of the side chain, equivalent to 9–10 carbon atoms, corresponds to the transition from the helical conformation of the macromolecules to layer structures with hexagonal packing of the side branches[32,68].

With increase of the length of the side chains in comb homopolymers [poly(phenyl methacrylate) and poly(chlorophenyl methacrylate)], the segmental anisotropy of the molecules becomes more pronounced, which can also be attributed to the influence of the interaction of the side groups, which becomes more intense with increase of their size[28].

## 2. Comb Heteropolymers (Copolymers)

In a study of the graft copolymers of poly(methyl methacrylate) and poly(butyl methacrylate) with polystyrene, which are distinguished by a high frequency of grafts and long main and side chains, it was shown[43] that, in all cases the hydrodynamic dimensions of the macromolecules of the graft comb copolymers in the same solvent are much smaller than those of the macromolecules of its constituent homopolymers having the same molecular weight (Fig. 2). However, the persistent chain length $a$, for example in the graft copolymer, is 50 Å, and the ratio $P = a/d = 1.8$, i.e. the macromolecules are rigid [$d$ is the diameter (thickness) of the macromolecule].

Studies by Birshtein and coworkers[69] have shown that comb homo- and hetero-polymers should be regarded as pseudorigid (see Table). The persistent length $a = [\overline{h^2_\theta}]/2L$ characterises the degree of coiling or the equilibrium flexibility of the polymer chain. In the absence of bulk-phase interactions (at the $\theta$-point), the statistical properties of polymer chains are determined mainly by the flexibility parameters $a$ (or the length of the Kuhn segment $A = 2a$) and the relative dimensions $L/a$. However, many important properties of polymer chains are influenced by the interactions not only along but also across the chain. These include the degree of foldability, the arrangement of polymers in the amorphous and crystalline states, the extent and nature of the bulk-phase interactions between the macromolecules in solution, etc. The above characteristics depend not only on the length of the rigid section but also on its thickness or, more precisely, on the relative quantity $a/d$ characterising the degree of extention of an individual persistent section of the chain ($a/d$ is the parameter of the local asymmetry of the macromolecule[69]).

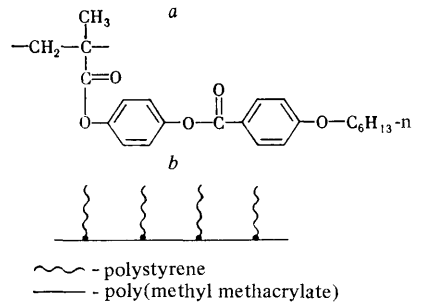



Figure 2. Comb macromolecules: *a*) comb homopolymers[29]; *b*) graft comb copolymers.

The main characteristic of pseudorigid polymers is large transverse dimensions of the chain. In the absence of a thick shell, the backbone of such pseudorigid comb macromolecules is appreciably flexible. However, when the chain is thick, the flexibility cannot be realised: the persistent length, i.e. the length of the section along which the chain bends, evidently cannot be smaller than its thickness. Therefore, for "thick" comb polymers of this kind, one must assume that $d \simeq a$, so that $a/d \simeq 1$. Thus pseudorigid macromolecules are characterised by a high value of $a$ for a small local asymmetry[69]. In essence, pseudorigid molecules constitute to some extent an analogue of flexible molecules magnified severalfold: the scale factor $a$ varies, but, for fixed relative dimensions $L/a$ and $a/d$, the physical picture remains unaltered[69].

However, polymers with long side groups can be justifiably regarded as similar to the usual flexible but short chains only when the frequency of the distribution of side groups is fairly high. Otherwise, the differences between the chemical natures of the side groups and the chain backbone will have an effect. The microstructure of the section through a macromolecule with long side groups is determined primarily by the properties of the side chains, in particular by their intrinsic local asymmetry[69].

Furthermore, in contrast to linear macromolecules, the long-range interactions in graft comb copolymers (as in uniformly branched macromolecules[21]) are intense, which leads to very considerable (but virtually isotropic) swelling of the macromolecules in effective solvents[48].

Types of polymers with different local asymmetry[69].

| Class of polymer | Polymer | $d$, Å | $a$, Å | $a/d$ |
|---|---|---|---|---|
| Flexible | Polystyrene | 10 | 9 | ~1.0 |
| | Polyethylene | 4 | 6 | 1.5 |
| Rigid | Trinitrocellulose | 8.3 | 100 | ~10 |
| | Polyphenylsilsesquioxane | 7 | 70 | 10 |
| | Poly(butyl isocyanate) | 8 | 500 | ~60 |
| Pseudorigid | Poly(n-alkyl acrylates) | 40 | 40 | 1 |
| | Poly(methyl methacrylate)–polystyrene grafted copolymers | 40 | 40 | 1 |

If the main chains of graft comb copolymers are capable of crystallisation and the side chains consist of irregular macromolecules (or conversely), then X-ray diffraction data suggest that order should persist in such a polymer even in the presence of a high content of the amorphous component[46].

It has been shown[53,56–60,70] that the theory of the worm-like chain is applicable to the description of the behaviour in solution of heteropolymeric comb macromolecules with short branches ($L_b \ll L_s$ and $l_b > L$). The rigidity of the main chain of such comb macromolecules proved to be much greater than that of the macromolecules of the corresponding homopolymers, since in graft macromolecules of this kind the conformation of the side chain is similar to that of a slightly bent rod. A unique combination of the considerable rigidity of the coil with its virtual impenetrability by the solvent has been observed, which is due to the large hydrodynamic (effective) diameter of such a worm-like chain.

## IV. CHARACTERISTICS OF THE BEHAVIOUR IN SOLUTION OF STAR AND COMB MACROMOLECULES

### 1. Non-Gaussian Chains

Linear macromolecules in thermodynamically ideal solutions can be regarded as impenetrable coils with a Gaussian distribution of the segments relative to the centre of gravity. Branching leads to compacting of the segments and their more uniform distribution in the bulk of the macromolecule. Conformational statistics of a branched molecule can therefore be non-Gaussian even in an ideal solvent[61,71,72].

The dimensions of star and comb macromolecules depend both on the lengths of the branch and the backbone ($L_V$ and $L_S$) and on the number of branches[73,74]. The comb macromolecule is characterised by the number of segments $N_b$ belonging to a single branch and the number of segments $N_S$ constituting the backbone of the macromolecule. For small values of $N_b$, the star molecule ceases to be a Gaussian coil and the same happens in the case of the comb macromolecule for small values of $N_b$ and $N_S$.

Calculation of the branching factor $g$ for star and comb macromolecules showed that, when $N_S$ and $N_b \geq 100$, then the macromolecule is a Gaussian coil in a $\theta$-solvent. Knowing the values of $g$ for such macromolecules, it is possible to calculate the number of branches using tabulated data[55,56,67,73,75]. When $N_b < 100$, the branches of the star macromolecule become non-Gaussian. The factor $g$ then diminishes with decrease of the number of segments in the branch. For example, when $f = 8$ and $N_b = 0.1$, 10, and 100, then $g = 0.075$, 0.325, and 0.340 respectively.

A similar dependence has been observed for comb macromolecules: for $f = 100$ and the ratio $N_b/N_S = 0.1$, we have $g = 0.038$ for $N_S = 1$ and $g = 0.114$ for $N_S = 100$. Thus the greater the rigidity of the backbone, the smaller the factor $g$.[73]

The radius of inertia of unperturbed star macromolecules is characterised by the relation[3]

$$[\bar{R}_\theta^2]_q = \frac{N_b A^2}{6}\left(\frac{3f-2}{f}\right), \tag{6}$$

the corresponding relation for comb macromolecules being

$$[\bar{R}_\theta^2]_g = \frac{A^2}{6}\left[N_s + 3N_b\frac{r}{1+r}\right], \tag{7}$$

where $r = N_b/l$.

On the other hand, if the branched macromolecule does not obey Gaussian statistics, the factor $g$ must be estimated by comparing the dimensions of macromolecules having not only the same molecular weights but also the same thermodynamic rigidities, i.e. $A_g = A_l$. One must bear in mind that the thermodynamic rigidities of the main and side chains of a branched macromolecule are the same[21].

On the other hand, when $A_g \neq A_l$, the experimental factor $g_e$ is related to the calculated factor $g_t$ in the following way:

$$g_e = g_t\frac{A_g\left[1-\frac{3A_g}{2L}+\frac{3A_g^2}{2L^2}-\frac{3A_g^3}{4L^3}\left(1-e^{-\frac{2L}{A_g}}\right)\right]}{A_l\left[1-\frac{3A_l}{2L}+\frac{3A_l^2}{2L^2}-\frac{3A_l^3}{4L^3}\left(1-e^{-\frac{2L}{A_g}}\right)\right]}. \tag{8}$$

For a Gaussian chain, Eqn. (8) is converted into the relation $g_e = g_t A_b/A_l$.

For a non-Gaussian star macromolecule, in which the chains are randomly oriented, the branching factor $g_t$ is related to the number of branches $f$ and the number of segments $N_b$ in one branch[21]:

$$g_t = \frac{1}{Bf}\left\{6f\left[\frac{1}{6}-\frac{1}{4N_b}+\frac{1}{4N_b^2}-\frac{(1-e^{-2N_b})}{8N_b^3}-3f(f-1)\right]\times\right.$$
$$\left.\times\left[1-\frac{1}{2N_b}+\frac{(1-e^{-2N_b})^2}{8N_b^2}\right]\right\}, \tag{9}$$

where

$$B = 1-\frac{3}{2N_b f}+\frac{3}{2N_b^2 f^2}-\frac{3}{4N_b^3 f^3}(1-e^{-2fN_b}).$$

When $N_b > 100$, the relation is converted into the familiar relation for Gaussian branched macromolecules:

$$g_t = \frac{3f-2}{f^2}. \tag{10}$$

For regularly branched non-Gaussian comb macromolecules, in which the main and side chains have the same thermodynamic rigidities, the branching factor $g_t$ is related to $\gamma = L_b/L_S$ and $f$ in a very complex manner[21].

For Gaussian chains ($N_S > 100$, $\gamma N_S > 100$), $g_t$ becomes

$$g_t = \left\{1 + \frac{\gamma f}{f+1}[(2f+1+3\gamma(f+1)] + \gamma^2 f(f-1)(1+3\gamma) + f\gamma^3\right\}(1+\gamma f)^{-3}. \quad (11)$$

If the main chain is Gaussian and the side chains are rigid rods, the[21] $g_t$ becomes[12]

$$g_t = \frac{1}{(1+\gamma f)^3}\left\{1 + \frac{\gamma f}{f+1}[2f+1+\gamma(f+1)\ (2\gamma N_s+1)] + \right. \quad (12)$$
$$\left. + \gamma^2 f(f-1)(1+\gamma^2 N_s+\gamma) + \frac{f\gamma^3}{2}(\gamma N_s - 1)\right\}.$$

These equations are applicable to the estimation of the rigidities of comb homopolymers and graft comb copolymers. The factor $g$ can be used to estimate quantitatively the degree of branching of the polymer. On comparing these results with those of Thurmond and Zimm[76], Kilb[64] and subsequently Kotlyar[77,78] and other workers[13,22] showed that the ratio of the intrinsic viscosities is a sufficiently reliable measure of the degree of branching:

$$g^{1/2} = [\eta_\theta]_g/[\eta_\theta]_l \cong [\eta]_g/[\eta]_l \cong g^n, \quad (13)$$

where $g^i$ is the degree of branching of an impenetrable macromolecule. This ratio varies with the solvent used. However, the estimate of $[\eta\theta]$g must be treated critically and the use of very effective solvents must be avoided[25,79,80], since

$$[\eta]_g/[\eta]_l > [\eta_\theta]_g/[\eta_\theta]_l,$$

the discrepancy being greater the more effective solvent and the higher the molecular weight of the polymer.

The knowledge of the factor $g_e$ makes it possible to determine with an adequate approximation the parameter $f$—the functionality of each point, provided that the number of branching points $m$ is known. For star polymers with one, two, and three branching points, we have[22]

$$g_\theta^2 = \begin{cases}(3f-2)/f^2 & \text{when } m=1\\ (18f^2-28f+11)/(2f-1)^2 & \text{when } m=2\\ (51f^2-90f+40)/(3f-2)^3 & \text{when } m=3\end{cases}. \quad (14)$$

Knowing $f$, it is possible to determine in turn the number of branching points $m$[55,67]:

$$g^i = \begin{cases}\left[\left(1+\frac{m}{7}\right)^{1/2}+\frac{4m}{9\pi}\right]^{-1/4} & \text{when } f=3\\ \left[\left(1+\frac{m}{6}\right)^{1/2}+\frac{4m}{9\pi}\right]^{-1/4} & \text{when } f=4.\end{cases} \quad (15)$$

All the above values have been tabulated[55,67,75]. When the lengths of the branches in the macromolecule are not the same and there is a possibility of both long and short chains, Eqn. (15) becomes[81,82]

$$g_\theta^i = \frac{1}{m+1}[1+m(1-2f+2f^2-2f^3)+m^2(-f+4f^2-4f^3)]. \quad (16)$$

## 2. The Degree of Branching and Swelling of Macromolecules

Another distinctive feature of branched macromolecules, particularly star and comb macromolecules, is as follows: under non-ideal conditions, the swelling of the macromolecular coil influences its size in opposition to the change in size caused by branching. The influence of the degree of branching is opposed to the influence of bulk-phase effects in effective solvents, where the segments are "diluted" in the bulk of the macromolecule[22,26,61,63].

Ptitsyn and Kron[22] showed that the bulk-phase effects influence the dimensions of the branched chains (the volume of the coil) much more than the dimensions of the corresponding linear chains, i.e. the nature of the excluded volume is determined by the probability of intramolecular contacts between the units in the coil. Furthermore, they showed[4,22] that the coefficient of volume expansion of a star molecule is a complex function:

$$\alpha_g^2 = \bar{R}_g^2/\bar{R}_{\theta g}^2 = 1 + \frac{134}{105}\chi z;\ z = \left(\frac{3}{2\pi}\right)^{3/2}\frac{N^{1/2}v}{6}. \quad (17)$$

For $\alpha_g$ close to unity, we have

$$\alpha_g^2 = 1 + \frac{134}{105}\frac{z}{g_\theta^3} + \ldots,$$

so that $\chi = 1/g_\theta^3$. For linear chains, $\chi = 1$. Ptitsyn and Kron[22] showed that Eqn. (17) is applicable only in the vicinity of the $\theta$-point, where the bulk-phase effects are small. For large values of $\alpha_g$, the equation for the swelling of branched macromolecules is analogous to Flory's equation for the swelling of a linear coil:

$$\alpha^5 - \alpha^3 = \frac{134}{105}\chi z. \quad (18)$$

Then we have $\bar{R}_g^2 \sim g_\theta^{4/5}$ when $\alpha \gg 1$, while $\bar{R}_{\theta g}^2 \sim g_\theta^2$, i.e. the bulk-phase effects partly compensate the decrease in the size of the macromolecule due to branching (the star shape).

When $\alpha \gg 1$, we have $\alpha_g = \alpha_l \chi^{1/3}$, whence

$$g \equiv [\bar{R}_g^2/\bar{R}_l^2]^{1/2} = g_\theta \frac{\alpha_g}{\alpha_l} \simeq g_\theta \chi^{1/2}. \quad (19)$$

Since $\chi \simeq \mu/g_\theta^3$, it follows that $g = \mu^{1/3}$. The parameter $\mu$ depends on the type of branching model and increases with increase of $m$. For high degrees of branching, $g \simeq \mu^{1/3}$, i.e. the ratio of the sizes of the branched and linear macromolecules with the same molecular weights tends to a constant value in an effective solvent as $f$ increases, while in a $\theta$-solvent it tends to zero[22].

The factor $g_\theta$ can decrease rapidly with increase of the molecular weight[22], which leads to a weaker dependence of $\bar{R}_{\theta g}^2$ on $M$ for branched chains than for linear chains. Consequently the sizes of macromolecules in effective solvents, characterised by $[\bar{R}_g^2]^{1/2}$, are relatively insensitive to the degree of branching and cannot be used together with the ratio $\bar{R}_{\theta g}^2/M$ for the quantitative estimation of the degree of branching.

## 3. The $\theta$-Temperatures

The third distinctive feature of star and comb polymers was noted in studies by Benoit and coworkers[3,4]. Whereas the equation for the swelling of a linear polymer in effective solvents is

$$\alpha^5 - \alpha^3 = 2C_{ml}\psi_1(1-\theta/T)M^{1/2}, \quad (20)$$

where the coefficient $C_m$ for a given polymer and solvent is independent of the molecular weight of the polymer, for branched polymers Eqn. (20) assumes the following form:

$$\alpha^5 - \alpha^3 = 2C_{ml}\psi_1(1-\theta/T)M^{1/2}g^{3/2} + \left(\frac{2}{3}\right)\frac{C_{ml}}{\alpha^3}g^{-3}. \quad (21)$$

In this case $g = [\bar{R}_\theta^2]_g/[\bar{R}_\theta^2]_l$. The swelling coefficient $\alpha$ increases slowly with increasing molecular weight and depends on the properties of the solvent, the dependence

being more pronounced the higher the value of $\psi_1(1 - \theta/T)$, i.e. the more effective the solvent. When $T = \theta$, $\alpha = 1$.

Eqn. (21) shows that the swelling coefficient $\alpha$ for branched polymers (particularly for comb and star polymers) is not unity when $T = \theta$.[3,4] If the temperature at which $\alpha = 1$ is designated by $\theta_\alpha$. Eqn. (21) can be formulated thus:

$$\frac{\theta}{\theta_\alpha} - 1 = \frac{C_{ml} g^{-1/2}}{3 C_{ml} \psi_1 M^{1/2}}. \qquad (22)$$

According to this expression, the decrease in the molecular weight of the polymer or the increase in the reduced ratio results in a deviation of $\theta_\alpha$ from Flory's $\theta$-point. $\theta_\alpha$ is always greater than $\theta$ and becomes equal to $\theta$ only when $M \to \infty$.

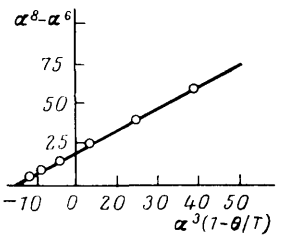



Figure 3. Determination of the $\theta$-temperature by extrapolating a plot of $\alpha^8 - \alpha^6$ against $1 - \theta/T$ for star and comb polymers[3].

If the expansion (swelling) factor of the macromolecule $\alpha$ is designated by $\alpha_\theta$ at Flory's temperature, Eqn. (21) can be written as follows:

$$\alpha_\theta^8 - \alpha_\theta^6 = \frac{2}{3} C_{ml} \cdot g^{-3}, \qquad (23)$$

i.e. $\alpha_\theta$ is independent of $M$, depending only on $g$.

On the basis of the foregoing, one should consider two temperatures: one at which $A_2 = 0$, i.e. $\theta_{A_2}$ and the other, Flory's $\theta$-temperature, at which $A_2$ is not zero, i.e. is equal to $A_{2\theta}$. Incidentally $\theta_{A_2}$ does not differ very significantly from the $\theta$-temperature‡. Thus one may speak of the existence of two characteristic temperatures for star and comb polymers, namely the $\theta_\alpha$ temperature at which $\alpha = 1$ and $\theta_{A_2}$, the temperature at which $A_2 = 0$. Both temperatures differ from Flory's classical§ $\theta$-temperature, and the relation[3,4]

$$\theta_\alpha < \theta_{A_2} < \theta$$

holds most frequently.

However, Vrii[83] and Casassa[84] claim that the relation $\theta_\alpha < \theta < \theta_{A_2}$ is valid.

In order to find $\theta_\alpha$ (and hence $\bar{R}^2_{\theta g}$), the sizes of the branched macromolecules are determined in any solvent at different temperatures and plots of the type shown in Figs. 3 and 4 are constructed[3,4].

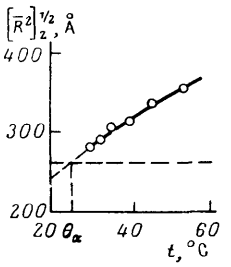



Figure 4. Determination of the $\theta$-temperatures for star and comb polymers from the variation of $[\bar{R}^2]_z^{1/2}$ with increasing temperature of the solution[3].

The swelling factors $\alpha_R$ for star and comb polymers are equal[4,83,85]:

$$\alpha_{Rg}^2 = \bar{R}^2_{\theta g} / \bar{R}^2_{\theta r}.$$

The viscometric coefficient of expansion for polymers with randomly branched macromolecules and star macromolecules $\alpha_\eta$ is given correspondingly by the expressions

$$\alpha_{\eta g^*} = [\eta]_{g^*} / [\eta_\theta]_{g^*}; \quad \alpha_{\eta g} = [\eta]_g / [\eta_\theta]_g.$$

The relation between $\alpha_{\eta g^*}$ and $\alpha_{\eta g}$ can be formulated as follows:

$$\alpha^3_{\eta g^*} - 1 = \frac{3}{2}(\alpha^3_{\eta g} - 1). \qquad (24)$$

The relations between $\alpha^3_{\eta g} - 1$ and $(1 - \theta/T)M^{1/2}$ and between $\alpha_{\eta g^*}$ and $\alpha_{\eta g}$ are linear for branched polymers with different functionalities (Figs. 5 and 6). Fig. 6 shows that $\alpha_{\eta g}$ for star macromolecules is always greater than for randomly branched macromolecules[5].

‡ In order to avoid terminological and semantic confusion, we may note that, according to Flory, the only sign of the $\theta$-state, i.e. of the pseudoideality of the solution, is not the equality of the swelling parameter $\alpha$ to unity, but the equality of the second virial coefficient to zero. This should be remembered in considering $\theta$-points with different subscripts.

§ When $\alpha = 1$ and $A_2 = 0$ simultaneously.

4. Dependence of $[\eta]$ on $M$

The degree of branching of macromolecules is reflected in the nature of the dependence of $[\eta]$ on $M$.[24,55,63,75,76,86-89] The plot of $\lg[\eta]$ against $\lg M$ for cascade polymers may become curved in the presence of macromolecules with different degrees of branching and the greater the increase of the degree of branching with increasing molecular weight of the polymer the smaller the value of $a$ and the larger the value of $K$ in the Mark-Kuhn-Houwink equation [Eqn. (25)]:

$$[\eta]=K_\eta M^{a-\varphi};\ S_0=K_s M^{1-b}\equiv K_s M^{1-\left(\frac{a-\varphi+1}{3}\right)}=K_s M^{1-\left(b-\frac{\varphi}{3}\right)}. \quad (25)$$

The relation $b = (a + 1)/3$ holds for branched polymers.

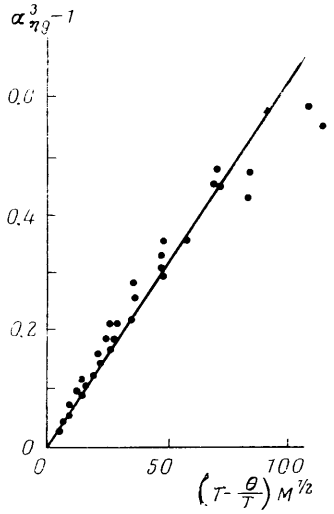



Figure 5. Increase of the swelling coefficient of star polystyrene with $(1 - \theta/T)M^{1/2}$.

Zimm and Stockmayer[50] showed that $a$ can vary as follows with the degree of branching:

$$a_g=a_l+(2-a_l)\frac{d\ln g}{d\ln P}. \quad (26)$$

Since $d \ln g/d \ln P < 0$, we have $a_g < a_l$.

According to Zimm and Kilb[55,75], for a high degree of branching in effective solvents, Eqn. (25) becomes

$$[\eta]=K_\eta M^{a-0.25}, \quad (27a)$$

while in a $\theta$-solvent we have

$$[\eta]_{\theta g}=K_\theta \cdot M^{0.25}. \quad (27b)$$

Thus the parameter $a$ in Eqn. (25) is always smaller for branched polymers than for linear polymers (star polymers are an exception). In a $\theta$-solvent, the parameter becomes equal to 0.25, in contrast to 0.5 for linear polymers.

The dependence of the parameter $g^i = [\eta_\theta]_g/[\eta_\theta]_l$ on $M$ is determined by the dependence of the number of branching units $m$ on $M$. For single-centre star macromolecules, the factor $m$ is independent of $M$.

As early as 1948, Flory showed that the parameter $a$ in Eqn. (25) for star molecules with $f = 1$, **2**, or 3 is the same as the value of $a$ for linear macromolecules. Flory observed the variation of $a$ only with increase of $f$ (for $f$ = 8), which can probably be explained by the breakdown of the star properties.

It has been shown[52] for star polystyrene that the parameters $a$ and the swelling factors $\alpha^3_\eta$ for linear and star polystyrenes are identical. The parameter $a$ remains constant even in solvents which are not $\theta$-solvents.

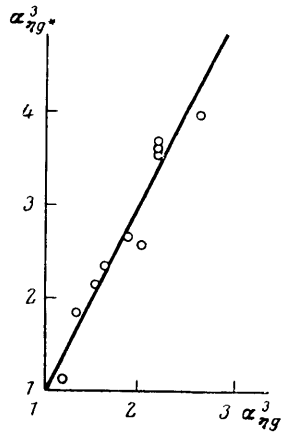



Figure 6. Relative change in the viscometric swelling coefficient of star ($\alpha^3_{\eta g}$) and randomly branched ($\alpha^3_{\eta g*}$) polystyrene[5].

For polymers with the comb structure of macromolecules, the dependence of $[\eta]$ on $M$ is different[90-93]. As noted above, a characteristic feature of a comb macromolecule is the great rigidity of its main chain accompanied by an appreciable density in the distribution of segments in the part of the volume adjoining the main chain (owing to the branches)[53,56-60]. As noted by Tsvetkov and coworkers[70,90,94] the best model for the description of the hydrodynamic properties of such a molecule is a wormlike chain, the main parameters of which are the contour length $L$, the hydrodynamic diameter $d$, and the persistent length $a$ (formally equal to half the statistical Kuhn segment $A$).

The use of the worm-like chain model, the viscosity data, and data for translational and rotational friction can yield reliable data on the conformational characteristics of the macromolecules of comb heteropolymers[93]. As for rigid-chain polymers, the sizes of the macromolecules of comb polymers vary little with the solvent, which makes it possible to neglect the influence of bulk-phase effects on their conformational properties[93].

A characteristic feature of many comb copolymers is their relatively low intrinsic viscosity compared with that of the linear homopolymer having the same structure as the main chain of the comb copolymer and the same molecular weight. This led some investigators to the idea of a globular structure of the molecules of comb copolymers. However, in reality the hydrodynamic properties of comb copolymers are fully consistent with those of a linear worm-like chain[93].

The value $a = 0.5$ in Eqn. (25) is not limiting for comb copolymers. We have[93]

$$M/[\eta] = \frac{1}{0.43\,N_A}(M/LA)^{3/2}M^{1/2} = \left(\frac{2.3\lg A}{d} - 1.6\right)\cdot\frac{M^2}{L^2}\cdot\frac{1}{A}. \quad (28)$$

For a fairly large diameter of the macromolecule ($d > 0.2$ Å), the dependence of $M/[\eta]$ on $\sqrt{M}$ can be represented by a straight line, which makes a negative intercept on the ordinate axis. With increase of $M$, the intrinsic viscosity $[\eta]$ evidently increases more slowly than does $M^{0.5}$, i.e. we have $a < 0.5$ depending on $[\eta] = KM^a$. This case has been examined (for $S = 33$).[93,94]

If the structure of the chain of a comb copolymer corresponds to the condition $A/d \simeq 1$, it follows from Eqn. (28) and the expression[93]

$$S_s = A/\lambda = \frac{M_0}{\lambda^2(1-x_1)}\cdot(0.43\,N_A\,d\,y/d\,z)^{-3/2} \quad (29)$$

(where $x_0$ is the mole fraction of component $B$ forming the branches of the comb macromolecule) that

$$S_s = [M_0[\eta]/0.43\,N_A P^{1/2}(1-x_0)]^{-3/2}\lambda^{-2}. \quad (30)$$

Eqn. (30) shows that the rigidity of the main chain of the comb macromolecule may be determined directly from the intrinsic viscosity[93].

It must be emphasised again that the cause of the great rigidity and order of the macromolecules of comb copolymers investigated[53,56-60,90,94] should be sought in the interaction of the branches. These interactions lead to the formation of intramolecular structures with a high degree of orientation order. Such structures may be a consequence of the strong dispersion interaction of the polystyrene chains constituting the branches of graft comb macromolecules. Relations of this kind have been traced for the homologous series of graft comb copolymers of poly(methyl methacrylate) with styrene, the contour length of the main chain of which $L$ varies from 9000 to 3700 Å.[90,93]

A rare instance (see Table) of comb copolymers [grafted copolymers of poly(methyl methacrylate) with styrene] whose contour length $L$ is comparable to their persistent length has been examined[90]. Low values of the exponential coefficients $a$ and $b$ ($a < 0.5$) have been noted for such copolymers: $[\eta] = 0.11\times10^{-4}M^{0.43}$ and $S_0 = 1.2\times10^{-15}M^{0.54}$. In this case, the contour length of the macromolecule $L$ is modelled by a persistent chain with a contour length $L$ equal to the length of the main chain of poly(methyl methacrylate):

$$L = \frac{M(1-x_1)\lambda}{M_0}, \quad (31)$$

where $M_0$ is the molecular weight of the monomer unit of the main chain.

In conclusion of the discussion of comb macromolecules, we emphasise yet again that the different "anomalies" in their properties compared with their linear analogues or homologues can be due to three different causes, linked directly with the configuration (structure) of the macromolecules.

1. In comb homopolymers, more than 80% of the molecular weight is as a rule contained in the branches. Depending on the structure of these branches, gel formation may begin already at low concentrations, regardless of the degree of stereoregularity, owing to the crystallisation of sections of the branches or, according to Tsvetkov[29], a long-range order, similar to that in liquid crystals, may arise within the chains. The first version is characteristic of poly(alkyl acrylates) or poly(alkyl methacrylates) and the second is characteristic of polymers whose side groups are capable of forming thermotropic or lyotropic liquid crystals in the "free state".

These anomalies in the two versions persist for a fairly long time also on diluting the "long-chain" units by short-chain units (for example, methyl methacrylate or acrylate units), i.e. on passing from a comb homopolymer to a statistical comb copolymer with infrequent long side chains. However, after the attainment of a "critical" dilution, the effects of intrachain and interchain ordering, leading to "anomalies", vanish.

2. In comb heteropolymers, i.e. in graft copolymers, the anomalies arise from segregation effects due to the different natures of the backbone chain and the branches¶. The hydrodynamic (but not thermodynamic!) behaviour of such macromolecules is simulated by a "thick" impenetrable worm-like chain.

3. In "classical" branched comb homopolymers, there are no longer any selective effects; however, the increased density in the distribution of segments—a direct consequence of branching—leads to a decrease ("slight contraction") of the hydrodynamic volume of the macromolecules and hence to a change in the "normal" parameters in Eqns. (25) for the intrinsic viscosity and the translational friction constant.

## V. THE INFLUENCE OF POLYDISPERSITY ON THE BRANCHING PARAMETERS

The branching parameters of macromolecules are influenced significantly not only by the type of branching and the length and frequency of the branches, but also by parameters such as the molecular weights, the polydispersities of the main and side chains, and the distribution of branches with respect to molecular weight. This is manifested particularly clearly in the study of long-chain branching[1,95-101].

The number-average molecular weight of a branched macromolecule with $f$ branches varies as follows with the number of branches relative to the molecular weight of a linear polymer having the same chemical composition[1,95,96]:

$$\overline{M}_{nf}/\overline{M}_{nl} = f. \quad (32)$$

The variation of $f$ is associated solely with the number of branches regardless of their length. A higher-order molecular weight ($\overline{M}_w$, $\overline{M}_z$, etc.) is influenced also by the size of the chains. Comparison of different average molecular weights ($\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$) of branched and linear specimens therefore yields information not only about the number but also about the size of the branches. For example, the large change in $\overline{M}_n$ associated with a slight change in $\overline{M}_w$ indicates a large number of short branches.

¶See "Entsiklopediya Polimerov" (The Encyclopaedia of Polymers), Vol. II, "Makromolekula" (The Macromolecule).

Conversely, a small number of long branches (comparable in length to the main chain) leads to an appreciable decrease of $\bar{M}_w$ with a relatively slight change in $\bar{M}_n$.[95]

The knowledge of the average molecular weights of branched and linear polymers makes it possible to calculate other branching parameters. This was done by Budtov and coworkers[95,102] for the comb esters of poly(vinyl alcohol) with long-chain branching and by Burchard[103,104] for star polymers. Such branching parameters include the distribution of the branching centres among molecules with different molecular weights, the polydispersities of the branches and backbones with respect to length, and the average molecular weights of the centre of the star and its branches in the case where the centre has a chemical structure different from that of the branches (Fig. 1*b*).[103] Burchard showed that in the latter case the masses of the centre and of the star are given by the following expressions respectively:

$$m_c = \frac{(1-\beta)\bar{M}_{wc}}{\alpha f\bar{M}_{wg} + (1-\beta)\bar{M}_{wc}}\ ;\ m_g = \frac{\alpha f\bar{M}_{wg}}{\alpha f\bar{M}_{wg} + (1-\beta)\bar{M}_{wc}}\ . \qquad (33)$$

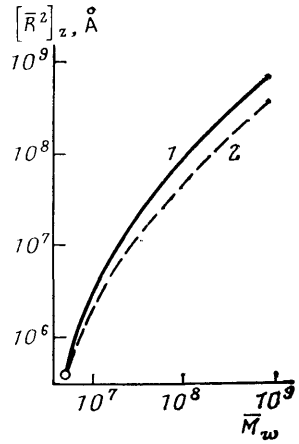



Figure 7. Variation of the mean square radius of inertia with increase of the molecular weight of a polyfunctional star macromolecule[97]: 1) polymer with the "most probable" distribution of branches; 2) monodisperse branches.

For a homodisperse centre, $\bar{M}_{nc} = \bar{M}_{wc}$; in the case of branches with the "most probable" distribution $\bar{M}_{ng} = \bar{M}_{wg}(1-\beta)$ ($\bar{M}_{ng}$, $\bar{M}_{nc}$, and $\bar{M}_{ns}$ are the number average molecular weights of the centre and branches of a star macromolecule respectively, $\bar{M}_{wg}$ is the weight-average molecular weight of the star macromolecule, and $\beta$ is the probability of the interaction of the branches with one another). Evidently this equation is valid also for comb polymers.

The relations examined above were derived for a star macromolecule with polydisperse branches[103]. The mean square radii of inertia of star macromolecules with polydisperse and monodisperse branches are significantly different. This difference increases particularly markedly with increased molecular weight of the star polymer (Fig. 7). For the same functionality of branching, the factor $g$ of star polymers depends on the polydispersity of the branches.

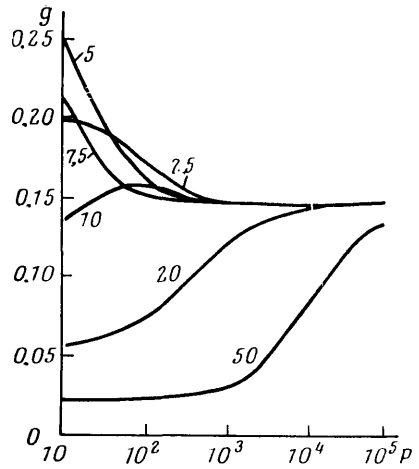



Figure 8. Variation of the factor $g$ with increase of the degree of polymerisation for star macromolecules having a large centre[97]. The numerals against the curves represent the ratio $l_c/l_s$.

Fig. 8 shows that, for the "most probable" distribution with respect to the lengths of the branches ($\alpha = 1$), the value of $g$ for a homodisperse star polymer is smaller than for a polydisperse star polymer. For the same degree of polymerisation of a star polymer $P$, the rigidity factor $g$ of a star with a large centre depends significantly on the effective length of the bond $l_c$ between two centres and the length of the bond $l_s$ between two branches, as can be seen in Fig. 8. The average hydrodynamic radii of inertia of such polymers with polydisperse branches $[\bar{R}^2]_z^{1/2}$ vary in accordance with the following law[103]:

$$[\bar{R}^2]_{zi} = \frac{l_s^2}{4}\frac{\bar{M}_{wg}}{\bar{M}_s} = \frac{l_s^2}{4(1-\beta)}[2+(f-1)\alpha], \qquad (34)$$

where $\beta$ is the probability of the interaction of the branches with one another.

For a polymer with monodisperse branches, we have

$$[\bar{R}^2]_{zi}^{1/2} = \frac{l_s^2}{6}\frac{\bar{M}_{wg}}{\bar{M}_s} = \frac{l_s^2}{6}N[1-(f-1)\alpha]. \qquad (35)$$

Thus the parameter $g$ cannot be used by itself without a far-reaching study of other branching parameters, the molecular weight, and the molecular weight distribution of the polymer, its branches, and the centre of the macromolecule, with both star and comb structures[91,92].

Budtov and Godunova[102] proposed a method for the estimation of the polydispersities of the branches and backbones from the lengths for comb polymers and a method for estimating the distribution of branching nodes.

The following relations are valid for the number-average and weight-average molecular weights of comb polymers $\bar{M}_{ng}$ and $\bar{M}_{wg}$:

$$\bar{M}_{ng} = \bar{M}_{ns} + f_n\bar{M}_{nb} \qquad (36)$$

$$\bar{M}_{ng}\ \bar{M}_{wl} = \bar{M}_{ws}\ \bar{M}_{ns} + f_n\bar{M}_{bs}\bar{M}_{wb}, \qquad (37)$$

$$\bar{M}_{ng}\bar{M}_{wg} = \bar{M}_{ws}\bar{M}_{ns} + 2\bar{M}_{ns}B_{ws} + f_n\bar{M}_{bs}B_w,$$

where $\bar{M}_{ns}$, $\bar{M}_{ws}$, $\bar{M}_{nb}$, and $\bar{M}_{wb}$ are the number-average and weight-average molecular weights of the backbones and branches and $f_n$ is the number-average number of branches per molecule,

$$B_w = \frac{\sum_i B_i^2}{\sum_i B_i}; \quad B_{ws} = \frac{\sum_i \bar{M}_{si} B_i}{\sum_i \bar{M}_{si}}, \tag{38}$$

(here $B_i = \Sigma_k f_{ik} \bar{M}_{bk}$ is the mass of all the branches of the $i$th molecule, and $f_{ik}$ is the number of branches in the $i$th molecule with the molecular weight equal to $\bar{M}_{bk}$).

The branched structure is characterised by the polydispersity of the backbones and branches:

$$\alpha_s = \frac{\bar{M}_{ws}}{\bar{M}_{ns}}; \quad \alpha_b = \frac{\bar{M}_{wb}}{\bar{M}_{nb}}. \tag{39}$$

If

$$\bar{M}_{ns} \leq \bar{M}_{ng},$$

then

$$\bar{M}_{ns} = \frac{\bar{M}_{ng}}{\alpha_b/\alpha_s + f_n}\left[\frac{\alpha_b}{\alpha_s} + f_n\sqrt{\frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}} - \frac{\alpha_b}{\alpha_s f_n}\left(1 - \frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}}\right)}\right], \tag{40a}$$

$$\bar{M}_{nb} = \frac{\bar{M}_{ng}}{\alpha_b/\alpha_s + f_n}\left[1 - \sqrt{\frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}} \frac{\alpha_b}{\alpha_s f_n}\left(1 - \frac{\bar{M}_{wl}}{\alpha_s \bar{M}_{ng}}\right)}\right]. \tag{40b}$$

In all cases, $f_n = \bar{M}_{ng}/\bar{M}_{nl} - 1$. The limits of the variation of $\alpha_s$ and $\alpha_b$ may be as follows:

$$\alpha_s \geqslant \frac{\bar{M}_{wl}}{\bar{M}_{ng}}; \quad \alpha_b \leqslant f_n \cdot \frac{\bar{M}_{wl}/\bar{M}_{ng}}{1 - \bar{M}_{wl}/\alpha_s \bar{M}_{ng}}. \tag{41}$$

The lower limit of the polydispersity of the branches $\alpha_b \geqslant 1$ and the upper limit of the polydispersity of the backbone is defined by the condition

$$\alpha_s \leqslant \frac{\bar{M}_{wl}/\bar{M}_{ng}}{1 - f_n \bar{M}_{wl}/\bar{M}_{ng}}. \tag{42}$$

At the same time, the polydispersities of the backbones and branches, $\alpha_s$ and $\alpha_b$, should be smaller than the polydispersities of linear and branched specimens:

$$\bar{M}_{wl}/\bar{M}_{ng} \leqslant \alpha_s; \quad 1 \leqslant \alpha_b \leqslant \bar{M}_{wl}/\bar{M}_{nl}. \tag{43}$$

The relations obtained are fairly general and make it possible to estimate reliably branching parameters such as $\bar{M}_{ns}$, $\bar{M}_{nb}$, $\alpha_s$, and $\alpha_b$.

If it is assumed that the mass of all the branches is smaller than that of the backbone, we obtained from Eqn. (38)[102]

$$B_{ws} \simeq \frac{\bar{M}_{ng} \cdot \bar{M}_{wg} - \bar{M}_{ws} \cdot \bar{M}_{ns}}{2\bar{M}_{ns}}, \tag{44}$$

which leads to yet another branching parameter:

$$f_{ws} = B_{ws}/\bar{M}_{wb}. \tag{45}$$

Substitution in Eqn. (45) of various model distribution functions and of the equations for the dependence of $f_i$ and $M_{B_i}$ on $B_{S_i}$ leads to the conclusion that $f_{ws} \geqslant f_w$ ($f_w$ is the number-average number of branches per molecule).

Comparison of $f_n$ and $f_{ws}$ permits a qualitative conclusion concerning the distribution of branching nodes among molecules having different molecular weights.

For a faster quantitative determination of the dependence of the branching parameters of star and comb polymers on their hydrodynamic properties and for the determination of molecular weights in the presence of long-chain branching, nomograms [97,103-106] and matrix methods [107] have been proposed in a number of studies.

The experimental studies carried out by Frenkel and coworkers [99-101] in order to test the influence of the polydispersity of the initial homopolymers on the final polydispersity of the graft comb copolymers showed that, for example, the molecular weight distribution (MWD) in a graft copolymer of cellulose with polyacrylonitrile and poly(methyl methacrylate) and the distribution of the molecular weights of polyacrylonitrile and poly(methyl methacrylate) as well as the cellulose chains is narrower than in homopolymerisation. The Schultz inhomogeneity parameter $U = \bar{M}_w/\bar{M}_n - 1$ varies from 0.25 to 0.57 under these conditions [101].

The study of the graft polymerisation of methyl methacrylate on wool [100] showed that the molecular weight distribution of the graft poly(methyl methacrylate) chains is unimodal and narrower than in free homopolymerisation.

Such narrowing of the molecular weight distribution of the chains compared with the free polymerisation of the monomer constituting the branches is due (other conditions being equal) to the same segregation effects which give rise to the anomalies in the hydrodynamic and thermodynamic behaviour of graft comb copolymers. Segregation occurs for high positive values of the thermodynamic parameter $\chi_{AB}$, which can be treated, by analogy with the Flory–Huggins parameter $\chi_1$, as the change in the free energy of the polymer A, playing the role of the "solvent", when a bound (in the chain of a second polymer) unit or segment of type B is introduced into it (or conversely). The theory of $\chi_{AB}$ is fairly complex and we cannot consider it here. However, it follows from it that the free energy of a macromolecule increases continuously as branches of another polymer grow on it. For this reason, a moment is inevitably reached when further growth of the branches become energetically unfavourable. This leads to a sharp increase of the chain termination rate constant or a decrease of the chain propagation rate constant or both simultaneously. Since the width of the molecular weight distribution is determined unambiguously by the ratio of the rate of termination $r_t$ to the rate of propagation $r_p$, the normal distribution of the molecular weights of the branches must be

$$q_n(P) = \alpha(P)\, e^{-\int_i^P \alpha(P)\, dP}, \tag{46}$$

where $\alpha = r_t/r_p$ and $P$ is the degree of polymerisation at any instant. Eqn. (46) shows immediately that, when $d\alpha/dP > 0$ (this happens precisely because of segregation and to a greater extent the higher the value of $\chi_{AB}$), the statistical width of the molecular weight distribution, estimated from the ratio $\bar{P}_w/\bar{P}_n$, should diminish.

Graft polymerisation is frequently accompanied by the partial degradation of the chains on which grafting takes place; the equalisation of the molecular weight distribution can now proceed with respect to two parameters $M_A$ and $M_B$. Some evidence for such equalisation has been obtained recently in the analysis of the grafting of acrylamide on cellulose [109].

## VI. CONCLUSION

If we disregard three-dimensional polymerisation or polycondensation, the problem of the branching of macromolecules arose initially as a side effect in linear polymerisation at the expense of higher degrees of conversion when polymerisation is carried out under technological conditions.

The marked influence of branching on the set of physical characteristics and the practical properties of articles made of polymers required the development of analytical methods for the determination of the degree of branching, mainly in order to monitor the polymerisation process itself. However, the difficulty of direct linear analysis required the development of model concepts. Star and comb polymers cannot arise as a result of a random process. However, it is more convenient to carry out experiments with such polymers in order to test theoretical relations. Special syntheses of polymers of this kind were therefore undertaken and it was found that, in contrast to statistically branched polymers, they may possess "intrinsic useful properties", which is a situation characteristic of the development of the chemistry and physics of polymers at the present stage where research techniques are converted into applied methods and model compounds are converted into real materials (in a broad sense of the last term).

This applies particularly to two of the three types of comb polymers examined--capable of forming ordered (and regular) structures via their branches and of forming microheterogeneous "alloys" as a result of segregation (graft copolymers). Segregation has now found wide-scale applications in the industrial manufacture of impact-resistant polystyrene plastics.

The applications of star polymers are associated, in principle, with imparting catalytic functions to the latter.

The purely analytical aspect still retains its importance--in all cases where branching develops via a cascade mechanism it becomes uncontrollable and can lower significantly the useful characteristics of the polymer. Since, as in the case of the molecular weight distribution or the inhomogeneity of the composition of the copolymers, the quantitative branching characteristics reflect fine details of the kinetics and mechanism of the polymerisation or polycondensation, the study of these characteristics is not only of interest from the standpoint of "control" but is also of independent interest. (A completely up to date example is provided by the analysis of the side reactions in the formation of ladder polysiloxanes [110].)

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# Polarography of Coumarins (Chromen-2-ones)

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The mechanism of the reduction of natural and synthetic coumarins at a dropping mercury electrode is examined. The dependence of the half-wave potential on chemical structure is demonstrated by means of correlation equations and quantum-chemical characteristics. The polarographic properties are interpreted in terms of other physicochemical characteristics (optical, adsorption, polarisation, kinetics of important chemical reactions, microwave-spectroscopic, etc.). Polarography can be applied in various fields of the chemistry of coumarins (in the study of adsorption, complex formation, inhibition of chain oxidations, and the mechanism of organic reactions). A list of 200 references is included.

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## I. INTRODUCTION

Coumarins are typical heterocyclic compounds, present as structural units in the molecules of tanning agents, antibiotics, phytocides, and a large group of polyphenolic compounds[1-3]. Considerable interest in this group of natural compounds arose from the specificity[1,2] and the breadth of their biological action[3,4]. They have since found wide application in analytical chemistry as luminescent and other indicators[5], optical brightening agents in the textile industry[6], sensitisers in copying techniques[7], aroma-producing substances in foodstuffs, printing, and perfumery industries[1], organic reagents in laser technology[8], toxic chemicals in agriculture[9], and pharmaceutical preparations[1,10] in medicine. In view of the specificity of their physicochemical properties further application of coumarins is envisaged in the production of organic semiconductors, scintillation materials, quantum generators, vitamins, and various organic reagents.

Further investigation of the physicochemical properties of these compounds is of great interest for expanding their fields of application, studying the peculiarities of their electronic structure, elucidating their biological role and aspects of their biosynthesis, and revealing effective new methods of preparation. Polarography has gained a lasting position among other physicochemical methods of examining organic compounds and enables a vast range of theoretical and practical problems to be solved. Results obtained by the polarographic investigation of coumarins can be transferred to other heterocyclic compounds and classes of organic substances.

A considerable number of papers have now appeared on the polarography of coumarins, but there is no critical review of existing achievements in this field with an indication of future lines of research. The present Review discusses not only the polarography of coumarins but also aspects of that of other classes of organic compounds (carbohydrates, cardiac glycosides, chromones, and flavonoid compounds, cinnamic and hydroxycinnamic acids) to the extent necessary for the interpretation of polarographic data and other physicochemical investigations on coumarins.

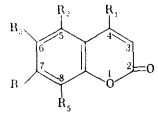
## II. MECHANISM OF ELECTRODE REACTIONS

A necessary condition for a heterocyclic compound to be electrochemically active is that the ring should be conjugated and the compound polarisable. The most objective criteria of the presence of conjugation are provided by spectral data characterising the distribution of $\pi$-electron density in the molecule and by the dipole moments. Thus several workers have shown[1,11-13] that hydrogenation of the $C_{(3)}=C_{(4)}$ double bond in the 2-pyrone ring of coumarin entails disappearance of fluorescence, characteristic absorption bands, and reducibility at a dropping mercury electrode[14], because of the disruption of conjugation in the pyrone ring. The dipole moment together with the conjugation characteristic indicates also the degree of polarisability of the molecule[15,16]. Dipole moments lying in the range 4.0–8.0 D have been determined experimentally and calculated by an additive vector scheme for several compounds of the coumarin series[16-19]. The dipole moment of coumarin itself has been measured[16] as 4.5 D.

Voitkevich showed[20] that increase in the dipole moment of aliphatic and aromatic compounds is accompanied by increase in their depolarising power at a dropping mercury electrode. However, there may be departures from this general rule, since electrochemical reduction and oxidation depend on many factors and are complicated by adsorption, protonation, dimerisation, solvation, etc. In several cases the dipole moments of the electrochemically active group are more significant than that of the whole molecule. Furthermore, the electrochemical activity of a molecule can be assessed more accurately from the dipole moment not under static conditions, as is usually done, but in an excited state[21].

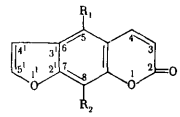
Several workers have shown that both coumarin itself and its derivatives are reduced at a dropping mercury electrode[14,22-60] when various salts—lithium, ammonium, and potassium chlorides, tetraethylammonium iodide and its base, and also Britton–Robinson buffer solutions—are used as supporting electrolyte. Various media have been employed—alcoholic (methanol, ethanol, and propan-1(and 2)-ols), aqueous alcohols, dimethylformamide, and acetone.

The subjects of investigation were natural coumarins of the coumarin (I)



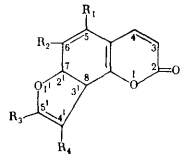
(I)

psoralen (II)



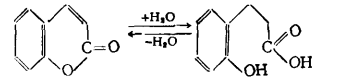
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and angelicin (III)



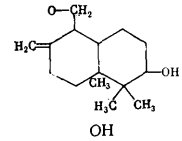
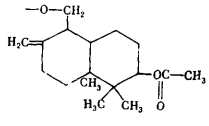
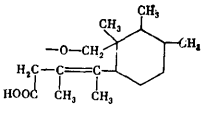
(III)

series, whose principal polarographic characteristics are given in Tables 1–3. These show that coumarin derivatives are reduced at a dropping mercury electrode in two stages, producing in aqueous methanol two waves with tetraethylammonium iodide, and one wave with lithium chloride, as supporting electrolyte. A single wave is obtained also in Britton–Robinson buffer solutions. However, two reduction waves are formed in tetraethylammonium hydroxide used as base in the buffer mixture. The first wave at pH > 10 decreases in height with time, owing to cleavage of the lactone ring[1,33–36,56,62–70]:



The influence of the nature of the base, the substituent, and the solvent on the kinetics of this process has been investigated[56]. Fission of the lactone ring can be affected by daylight and by ultraviolet radiation[1,36].

**Table 1.** Chemical structure and polarographic constants of compounds of the coumarin series*.

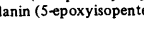
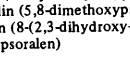
| Compound | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_6$ | $-E_{1/2}$, V(s.c.)**, in $(C_2H_5)_4NI$ I | $-E_{1/2}$, V(s.c.)**, in $(C_2H_5)_4NI$ II | $-E_{1/2}$, V(s.c.)**, in LiCl I | $K_D$, *** $\mu A\ s^{1/2}\ mM^{-1}\ mg^{-2/3}$ I | $K_D$, *** $\mu A\ s^{1/2}\ mM^{-1}\ mg^{-2/3}$ II |
|---|---|---|---|---|---|---|---|---|---|---|
| Coumarin | H | H | H | H | H | 1.40 | 1.97 | 1.30 | 4.20 | 3.70 |
| 6-Methylcoumarin | H | H | $CH_3$ | H | H | 1.42 | 1.92 | 1.78 | 4.07 | 3.50 |
| Umbelliferone (7-hydroxycoumarin) | H | H | H | OH | H | 1.47 | 1.65 | 1.88 | 1.30 | 1.01 |
| 4-Methylumbelliferone | $CH_3$ | H | H | OH | H | 1.61 | 1.74 | 1.74 | 1.77 | 1.54 |
| Herniarin (7-methoxycoumarin) | H | H | H | $OCH_3$ | H | 1.44 | 1.94 | 1.77 | 4.07 | 3.50 |
| Coumarin-7-yl acetate | H | H | H | $O-C(O)CH_3$ | H | 1.35 | 1.80 | 1.66 | 4.00 | 3.33 |
| 7-Isopentenyloxycoumarin | H | H | H | $O-CH_2-CH=C(CH_3)_2$ | H | 1.51 | 2.08 | 1.87 | 2.98 | 2.55 |
| 7-Geranyloxycoumarin | H | H | H | $O-CH_2-CH=CCH_2-CH_2CH=C(CH_3)_2$ (CH) | H | 1.51 | 1.86 | — | 2.32 | — |
| Umbelliprenin (7-farnesyloxycoumarin) | H | H | H | $O(CH_2CH=C-CH_2)_2-CH_2CH=C(CH_3)_2$ ($CH_3$) | H | 1.51 | 2.05 | 1.84 | 3.38 | 3.10 |
| Farnesiferol A (7-(8-hydroxy-6,7,7-trimethyl-3-methylene-[4,4,0]dec-2-ylmethoxy)-coumarin) | H | H | H |  | H | 1.86 | — | 1.90 | 1.76 | — |
| Aesculetin (6,7-dihydroxycoumarin) | H | H | OH | OH | H | 1.50 | 1.78 | — | 0.51 | 0.73 |
| Aesculin (6-glucosyl-7-hydroxycoumarin) | H | H | $OC_6H_{11}O_5$ | OH | H | 1.59 | 1.74 | 1.70 | 1.48 | 2.07 |
| Osthole (8-isopentenyloxy-7-methoxycoumarin) | H | H | H | $OCH_3$ | $CH_2CH=C(CH_3)_2$ | 1.53 | 2.08 | 1.90 | 4.86 | 2.92 |
| Fraxinol (6-hydroxy-5,7-dimethoxycoumarin) | H | $OCH_3$ | OH | $OCH_3$ | H | 1.53 | 1.93 | 1.81 | 3.37 | 2.53 |
| Fraxinyl (5,7-dimethoxycoumarin-6-yl) acetate | H | $OCH_3$ | $O-C(O)-CH_3$ | $OCH_3$ | H | 1.43 | 1.88 | 1.70 | 3.72 | 3.00 |
| Farnesiferyl acetate | H | H | H |  | H | 1.67 | — | — | 2.70 | — |
| Galbanic acid (7-(2-(4-carboxy-1,2-dimethylprop-1-enyl)-1,5,6-trimethylcyclohexyloxy)coumarin) | H | H | H |  | H | 1.70 | 1.84 | — | 2.00 | 2.00 |

* Potential of dropping mercury electrode monitored potentiometrically[61].

** I = first wave; II = second wave.

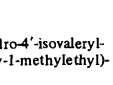
*** With tetraethylammonium iodide as supporting electrolyte in 75% methanol.

**Table 2.** Chemical structure and polarographic constants of compounds of the psoralen series*.

| Compound | $R_1$ | $R_2$ | $-E_{1/2}$, V(s.c.e.)**, in $(C_2H_5)_4NI$ I | $-E_{1/2}$, V(s.c.e.)**, in $(C_2H_5)_4NI$ II | $-E_{1/2}$, V(s.c.e.)**, in LiCl I | $K_D^{***}$, $\mu A\ s^{1/2}\ mM^{-1}\ mg^{-2/3}$ I | $K_D^{***}$, $\mu A\ s^{1/2}\ mM^{-1}\ mg^{-2/3}$ II |
|---|---|---|---|---|---|---|---|
| Psoralen (furo[3,2-*g*]coumarin) | H | H | 1.44 | 1.95 | 1.83 | 3.1 | 2.30 |
| Bergaptol (5-hydroxypsoralen) | OH | H | 1.43 | — | — | — | — |
| Bergapten (5-methoxypsoralen) | $OCH_3$ | H | 1.45 | 1.86 | 1.85 | 3.34 | 2.85 |
| Isoimperatorin (5-isopentenyloxypsoralen) | $O-CH_2CH=C(CH_3)_2$ | H | 1.45 | — | — | — | — |
| Oxypeucedanin (5-epoxyisopentenyloxypsoralen) |  | H | 1.67 | 2.00 | 1.73 | 3.42 | 2.76 |
| Xanthotoxol ( 8-hydroxypsoralen) | H | OH | 1.50 | 2.00 | 1.79 | 3.20 | 2.38 |
| Xanthotoxin (8-methoxypsoralen) | H | $OCH_3$ | 1.38 | 1.85 | 1.66 | 4.12 | 3.57 |
| Xanthotoxyl (psoralen-8-yl)acetate | H | $O-C(O)-CH_3$ | 1.35 | — | — | 1.01 | — |
| Imperatorin (8-isopentenyloxypsoralen) | H | $O-CH_2-CH=C(CH_3)_2$ | 1.42 | 1.35 | 1.80 | 3.05 | 2.90 |
| Isopimpinellin (5,8-dimethoxypsoralen) | $OCH_3$ | $OCH_3$ | 1.45 | 1.81 | 1.79 | — | — |
| Biacangelicin (8-(2,3-dihydroxy-3-methylbutoxy)-5-methoxypsoralen) | $OCH_3$ |  | 1.41 | 1.93 | — | 2.00 | 1.80 |
| Cnidilin (5-isopentenyloxy-8-methoxypsoralen) | $O-CH_2-CH=C(CH_3)_2$ | $OCH_3$ | 1.45 | 1.91 | 1.81 | — | — |
| Cnidicin (5,8-di-isopentenyloxypsoralen) | $O-CH_2-CH=C(CH_3)_2$ | $O-CH_2-CH=C(CH_3)_2$ | 1.41 | 1.86 | 1.78 | — | — |
| Alloimperatorin (8-hydroxy-5-isopentenylpsoralen) | $CH_2-CH=C(CH_3)_2$ | OH | 1.56 | 1.80 | — | 1.37 | 1.30 |

* Potential of dropping mercury electrode monitored potentiometrically[61].
** I = first wave; II = second wave.
*** With tetraethylammonium iodide as supporting electrolyte in 75% methanol.

**Table 3.** Chemical structure and polarographic constants of compounds of the angelicin series*.

| Compound | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $-E_{1/2}$, V(s.c.e.)**, in $(C_2H_5)_4NI$ I | $-E_{1/2}$, V(s.c.e.)**, in $(C_2H_5)_4NI$ II | $-E_{1/2}$, V(s.c.e.)**, in LiCl I | $K_D^{***}$, $\mu A\ s^{1/2}\ mM^{-1}\ mg^{-2/3}$ I | $K_D^{***}$, $\mu A\ s^{1/2}\ mM^{-1}\ mg^{-2/3}$ II |
|---|---|---|---|---|---|---|---|---|---|
| Angelicin (fuoro[2,3-*h*]coumarin) | H | H | H | H | 1.48 | 1.89 | 1.80 | 2.41 | 1.50 |
| Isobergapten (6-methoxyangelicin) | H | $OCH_3$ | H | H | 1.55 | 1.94 | 1.86 | 2.70 | 2.20 |
| Sphondin (5-methoxyangelicin) | $OCH_3$ | H | H | H | 1.45 | 1.90 | 1.88 | 4.12 | 3.57 |
| Pimpinellin (5,6-dimethoxyangelicin) | $OCH_3$ | $OCH_3$ | H | H | 1.53 | 2.08 | 1.81 | 2.20 | 2.00 |
| Oreosolone (5'-isopropenylangelicin) | H | H |  | H | 1.47 | 1.94 | 1.82 | 1.61 | 1.50 |
| Oreosolol (5'-(1-hydroxy-1-methylethyl)-angelicin) | H | H |  | H | 1.48 | — | — | 2.20 | — |
| Methyl oreosolyl ether (5'-(1-methoxy-1-methylethyl)angelicin) | H | H |  | H | 1.48 | — | — | 1.89 | — |
| Peucenidin (5'-(1-acetoxy-1-methylethyl)-4',5'-dihydro-4'-senecioylangelicin) | H | H |  |  | 1.43 | 1.99 | 1.79 | 0.3 | 0.90 |
| Athamantin (4',5'-dihydro-4'-isovaleryl-oxy-5'-(1-isovaleryloxy-1-methylethyl)-angelicin) | H | H |  |  | 1.60 | 2.12 | 1.77 | 1.34 | 1.00 |
| Libonatin (4'-acetoxy-4',5'-dihydro-5'-(2-methylbut-2-enoyl)angelicin) | H | H |  | $O-C(O)-CH_3$ | 1.47 | | 1.80 | 1.02 | 3.40 |

* Potential of dropping mercury electrode monitored potentiometrically[61].
** I = first wave; II = second wave.
*** With tetraethylammonium iodide as supporting electrolyte in 75% methanol.

Investigation of the kinetics and the mechanism of cleavage of the lactone ring not only is of theoretical interest in connection with the chemistry of lactones, on whose physicochemical and kinetic characteristics very few data are available, but also is one of the most important aspects of the chemistry of coumarins, since a considerable number of their fundamental chemical reactions (hydrogenation, azo-coupling, methylation, oxidation,

halogenation, mercuration, and arsenation) are based on preliminary cleavage of the lactone ring in alkaline medium and are widely used for the identification[1-3,68,71-72], quantitative analysis[71-73], preparative isolation[1,73], and synthesis[68,73] of these compounds. Experimental results confirm that the lactone ring opens in alkaline medium. The initial wave of coumarin is obtained when the solutions are acidified to neutral pH[14,36]. Reaction velocities at high rates of cleavage of the lactone ring are determined by oscillographic polarography[35].

The morphology of the waves from coumarin derivatives and their relative heights exhibit several special features. Waves due to hydroxycoumarins are diffuse, showing a considerable tendency to coalesce owing to the small differences in half-wave potentials caused by the formation of intermolecular hydrogen bonds. The hydroxycoumarins—fraxinol and aesculetin—on polarographic reduction give an intense lemon-yellow coloration, the optical density of the solutions remaining constant for a long time[14]. Spectral investigations have shown that the formation of coloured products is due to conversion of the coumarin into a quinonoid system. Only one wave is recorded with farnesiferol, clearly owing to the impossibility of obtaining the second stage of reduction in tetraethylammonium iodide as supporting electrolyte. With the acylangelicins—peucenidin and libanotin—the second wave is threefold the height of the first wave, as a consequence of further reduction at the second stage of residues of organic acids present in side-chains. These features together with the considerable differences among half-wave potentials for several coumarins—coumarin itself, aesculetin, umbelliprenin, farnesiferol, psoralen, xanthotoxol—may form a basis for the identification and qualitative analysis of coumarins.

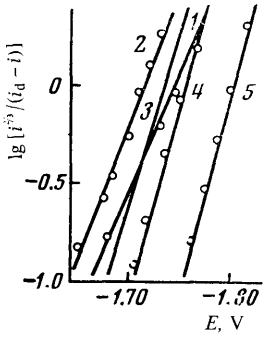



Figure 1. Dependence of $\lg[i^{2/3}/(i_d - i)]$ on $E$ for the first wave of coumarin in 3% tetraethylammonium iodide in methanolic (vol.%) solutions: 1) 12.5; 2) 25.0; 3) 37.5; 4) 62.5; 5) 87.5.

The linear concentration dependence of the limiting current[14,27-30,35-39,41-60] and also the temperature coefficients (1.2–2.0% $deg^{-1}$) indicate a limiting diffusion current of coumarin derivatives when they are reduced at a dropping mercury electrode. These relationships have been verified with various supporting electrolytes (lithium chloride, tetraethylammonium iodide, Britton–Robinson buffer) in aqueous, alcoholic (methyl, ethyl, propyl, and isopropyl), and aqueous–alcoholic solutions, in dimethylformamide alone and mixed with water and with alcohols, and in acetone. With the quaternary ammonium iodide a linear concentration dependence of the limiting current has been established[14] for both reduction stages in the concentration range 0.1–0.001 mass %, which formed the basis for the development of methods for the quantitative analysis of coumarins in various materials[35,41-57,60]. The observed limiting currents are consistent with the Ilkovič equation[74].

Čapka[27] used the diffusion coefficients of acetophenone and benzophenone in comparing the limiting currents, and reached the erroneous conclusion that coumarins undergo two-electron reduction at the potential of the first wave.

Polarographic coulometry[75], with graphical analysis of the voltage–current curves by means of the Heyrovský[76] and Mairanovskii[77] equations, has shown that the first stage in the reduction of coumarins in various supporting electrolytes takes place reversibly, with addition of a single electron followed by slow dimerisation (Fig. 1). Cyclic polarograms obtained at a suspended drop also show reversibility of the electrode process. The half-wave potential becomes more negative with increase in the alcohol concentration. Fig. 1 shows that this involves little change in the reversibility.

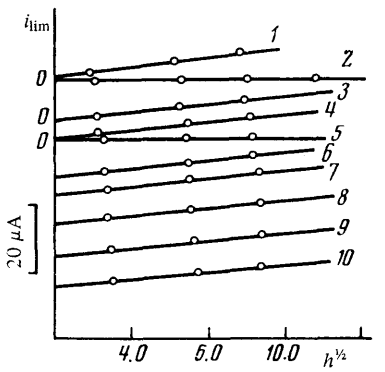
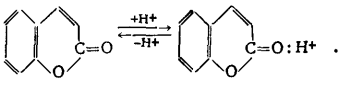



Figure 2. Dependence of limiting current of first wave of coumarin on $h^{1/2}$ in solutions of ionic strength 0.39 at different pH-values: 1) 3.29; 2) 3.79; 3) 4.10; 4) 4.50; 5) 5.02; 6) 7.10; 7) 8.36; 8) 8.91; 9) 10.36; 10) 11.2.

The half-wave potential at the first reduction stage remains unchanged over the pH range 6–9. In the second stage, recorded only in Britton–Robinson buffer solutions containing tetraethylammonium hydroxide as base, the half-wave potential depends on the pH, which can be explained by polarography of cinnamic and hydroxycinnamic[78-80] acids, in whose reduction the dissociation of their phenolic and carboxylic groups plays a considerable part[81]. Therefore the first and second half-wave potentials of hydroxycoumarins change with increase in pH. The second stage in the cathodic reduction of still undecomposed coumarin in the presence of tetraethylammonium hydroxide is accompanied by reduction of hydroxycinnamic acids formed by cleavage of the lactone ring in the coumarins. The second wave is therefore complicated in character. The half-wave potential of hydroxycinnamic acids, like that

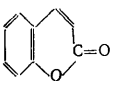
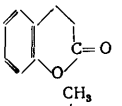
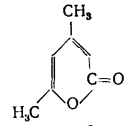
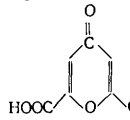
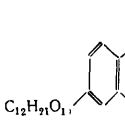
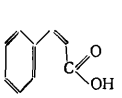
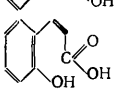
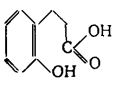
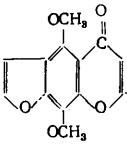
of cinnamic acids[76,82-88], is markedly dependent on pH, and hence that of the second wave of coumarins also depends on pH under the above conditions.

The occurrence of kinetic currents at acid pH values (Fig. 2, curves *2* and *5*), the variation of the half-wave potential over the pH range 4.1–6.0, the electronic structure, quantum-chemical calculations[89], the basicity constants[90], and also the mechanism of formation of oxonium salts[91-93] prove that coumarin molecules undergo protonation:



Thus coumarins exhibit a diffusion current at pH 4.10–10.36; a coumarin wave cannot be recorded at pH < 3.29, owing to superposition of the discharge of hydrogen ions on the reduction of coumarin. Investigations of the dependence of $I_d$ on $h^{1/2}$ at various pH[14] indicate a kinetic current over the pH range 3.29–4.10, whose magnitude is determined by the rate of protonation of coumarin. In alkaline medium (pH > 10.3) the strength of the current is limited by the rate of cleavage of the lactone ring. The second reduction wave of coumarins and the wave of cinnamic acids are not recorded at all in supporting electrolytes that are more easily reduced than are tetra-alkylammonium salts, whence Knobloch[28,29] wrongly concluded that cinnamic acids are polarographically inactive.

**Table 4.** Half-wave potentials of model compounds polarographed in 75% methanol*.

| Compound | Structural formula | $-E_{1/2}$, V(s.c.e.), in | | | | | |
|---|---|---|---|---|---|---|---|
| | | 3% $(C_2H_5)_4NI$ | | 3% LiCl | | Britton-Robinson buffer | |
| | | I | II | I | II | I | II |
| Coumarin |  | 1.40 | 1.97 | 1.32 | — | 1.67 (pH 7.10) | — |
| 3,4-Dihydrocoumarin |  | — | — | — | — | — | — |
| 4,6-Dimethyl-2-pyrone |  | 1.72 | 1.94 | 1.90 | 2.20 | — | — |
| Chelidonic acid |  | 1.40 | 1.96 | — | — | 1.50 (pH 9.15) | — |
| Hesperedin |  | 1.80 | — | — | — | — | — |
| Cinnamic acid |  | 1.38 | 1.85 | 1.67 | — | — | — |
| *cis-o*-Hydroxycinnamic acid |  | 1.40 | 1.97 | 1.99 | — | — | — |
| *trans-o*-Hydroxycinnamic acid |  | 1.44 | 1.89 | 1.86 | — | — | — |
| Kellin** |  | 1.56 | 2.10 | 1.57 | 1.80 | — | — |

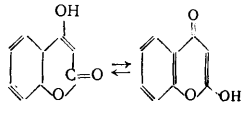
*Dihydrocoumarin was prepared by hydrogenating coumarin in alkaline medium with molecular hydrogen in the presence of a palladium catalyst[94,95]; 4,6-dimethyl-2-pyrone was synthesised from acetoacetic ester[68]; and chelidonic acid was obtained by N. F. Komissarenko from Far Eastern lily of the valley (*Convallaria keiskei Mig.*) in the Phytochemistry Laboratory of the Kharkov Chemical and Pharmaceutical Scientific Research Institute.

**With 3% tetraethylammonium iodide as supporting electrolyte kellin has a third wave with $E_{1/2}$ = −2.35 V.

Various model compounds have been examined[14] in order to interpret the mechanism of polarographic reduction of coumarins at a dropping mercury electrode. The results (Table 4) show that polarographic activity is due to the presence of the conjugated chain CH : CH.CO.O in the 2-pyrone structure. This chain disappears on hydrogenation of the $C_{(3)} : C_{(4)}$ double bond, in contrast to chromones, which have an O : C.CH : C.O chain in the 4-pyrone structure. Coumarins containing substituents having double bonds that are either isolated from or only slightly conjugated with the 2-pyrone ring (farnesan in umbelliprenin, isopentenyl in imperatorin and osthole, ester groups in athamantin) do not show the enhanced electrochemical activity of these groups observed in peucenidin and libanotin.

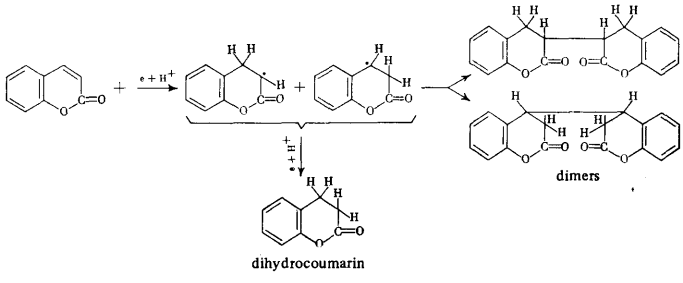
Chromatographic, mass-spectral and spectral (ultraviolet and infrared), and combined chromatographic and mass-spectrometric examination of the products of electrolysis at a dropping mercury electrode and at a controlled potential on a macroelectrode[14], as well as preparative electrolysis[36,39], show that the electrode reaction results in formation of dihydrocoumarin and dimers of coumarin. Other compounds have also been detected in preparative electrolysis, which may be products of hydrogenation by hydrogen[96,97] formed during electrolysis and of subsequent reaction of the products with radicals and with the electrode material[98].

In contrast to chromones and chalcones, coumarins exhibit intense infrared absorption bands due to the carbonyl group[1,11,13] and diminished reactivity towards cationic reactants[68], so that it may be concluded that this group is more weakly protonated in coumarin derivatives than in chalcones[22,23,99-102], flavonoid compounds[22,23,103-111], and chromones[22,23,104-112], whose half-wave potentials depend on the pH and which produce a catalytic current[28,29,77]. Such a current has been observed[43,49] with kellin, a pharmaceutical preparation. Chromones are genetically so close to coumarins in chemical structure that conversion of 4-hydroxycoumarins into 2-hydroxychromone is observed[29]:

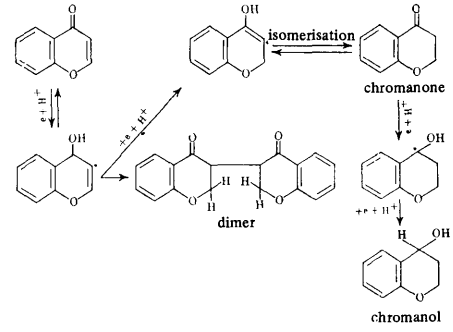


Reducibility at a dropping mercury electrode is observed also with other classes of compounds containing a 2-pyrone ring (cardiac glycosides)[113-117].

The results of the investigations enable schemes to be postulated for reduction at a dropping mercury electrode—for coumarins




and for chromones




The same mechanism of reduction has been suggested by Stradyn'[23] and by Perrin[22] in fundamental reviews on the polarography of heterocyclic organic compounds.

Carbohydrates present in side-chains in coumarins, cardiac glycosides, flavonoid compounds, and chromones are not reduced at a dropping mercury electrode, since their reduction requires the presence of a carbonyl form, which cannot be produced in solution owing to the absence of ring–chain tautomerism in the glycosidic state[24,76]. In the case of furochromones[111,112] (kelloglycoside) the introduction of the carbohydrate residue converts a single-wave into a two-wave polarogram. The polarograms of kellin and the glycoside in various supporting electrolytes are quite complicated, containing diffusion and catalytic waves. In acid medium the electrode process is complicated by formation of protonated complex compounds (oxonium salts), and in alkaline medium by cleavage of the 4-pyrone ring, so that kinetic currents may also be observed.

The reduction of coumarin derivatives at a dropping mercury electrode is accompanied by adsorption phenomena[14,32,118-120] depending on the structure of the electrical double layer[17,32,120].

## III. CHEMICAL STRUCTURE AND HALF-WAVE POTENTIAL

One of the most important tasks of the polarography of organic compounds is to find relations between chemical structure and half-wave potential, since knowledge of this correlation will enable the electrochemical activity of organic compounds to be assessed, to a certain extent the mechanism of electrochemical processes, their kinetics, the structure of the products of electrolysis, and also several important physicochemical constants (ionisation potential, electron affinity, redox potential of biochemically important systems), defined directly or indirectly in terms of the half-wave potential, which have played some part in assessing the results of quantum-chemical calculations on the molecules of benzenoid aromatic compounds[121-123]. Such relations can be gauged in several ways—(i) by qualitative and semi-quantitative comparison of half-wave potentials with the electronic structure of functional groups, with conjugation, steric, and inductive effects[24,25,64,76,124], (ii) by means of correlation equations[125-129], (iii) by quantum-chemical methods[121-123,130-131], and (iv) from the relation between the half-wave potential and other physicochemical constants (refraction, dipole moments, ultraviolet and infrared spectra, mass spectra, and microwave spectroscopy—nuclear magnetic and electron spin resonance) containing considerable information on the chemical structure of the molecules[25,74,121,132]—on which

several reviews have been published[25,121,132-136], besides individual chapters in special monographs[74,130,131], devoted to a detailed examination of the relation between half-wave potentials and chemical structure.

In order to trace a correlation with the structure of coumarins and to reach conclusions on the influence of substituents on the half-wave potential, the Reviewer has selected series both of naturally occurring compounds and of products of chemical reactions[40]. Such comparison cannot be based on published values, since half-wave potentials have been obtained by different workers under different conditions (different supporting electrolytes, solvents, and apparatus). The individual values may be contradictory even under the same conditions, and several compounds when tested did not exhibit any polarographic activity (derivatives of 4-hydroxycoumarins)[37,38].

Table 1 gives the chemical structure and the half-wave potentials of derivatives of coumarin, psoralen, and angelicin. Only the values for the first wave, corresponding to a reversible process, were used for the comparison. Table 1 shows that alkylated coumarins, containing donor substituents, are reduced with greater difficulty than are the corresponding unsubstituted compounds. The 2-pyrone ring in the coumarin system is reduced more readily than is 2-pyrone itself, because of conjugation with the aromatic benzene system.

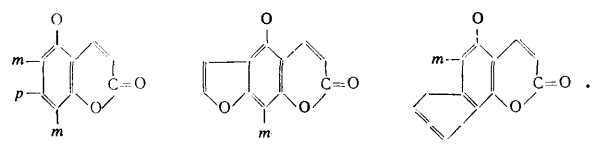
The fusion of a furan ring with the coumarin system in psoralen and angelicin derivatives hinders reduction of the furocoumarins owing to the donor influence of the furan heteroatom. Introduction of ester substituents lowers the half-wave potential of the corresponding hydroxy-compounds (umbelliferone, fraxinyl, xanthotoxyl, and peucenidinyl acetates, libanotin, and athamantin). Coumarin ethers exhibit the considerable electron-donating activity of the radicals, reflected in more negative half-wave potentials. The lengthening of the unconjugated chain in geranyl- and 7-farnesyl-oxycoumarins produces no change in the half-wave potential of 7-isopentenyloxycoumarin. This proves the absence of steric hindrance by groups to reduction of the $C_{(3)}:C_{(4)}$ double bond in benzo-2-pyrone.

Among simple coumarins the highest reduction potential is shown by farnesiferol A, probably because of the specific conformation of the farnesyl group, causing steric hindrance to reduction of the $C_{(3)}:C_{(4)}$ double bond at a dropping mercury electrode[124,137,138]. The half-wave potentials of 5-mono- and 5,8-di-substituted psoralen derivatives lie in the narrow range from −1.41 to −1.45 V, with the exception of xanthotoxol and alloimperatorin, in which the 8-hydroxyl produces a displacement of electron density owing to conjugation with the carbonyl of the 2-pyrone through the heteroatomic oxygen. Angelicin derivatives substituted at position 5 or in the furan ring have values between −1.43 and −1.48 V; the 6-substituted derivatives have more negative half-wave potentials.

Correlation equations have been used to find a quantitative relation with chemical structure, and half-wave potentials have been compared with the energy of the lowest vacant level. Naturally occurring coumarins contain substituents mainly in the benzene ring, at a considerable distance from the reactive centre—the $C_{(3)}:C_{(4)}$ double bond—that undergoes electrochemical hydrogenation. It is therefore advisable to use the Hammett equation, representing the inductive and mesomeric influence of substituents[22,125-129,139,140], whose application has been described in detail by Zuman[127,128]. According to its physical meaning the Hammett equation is applicable mainly to benzenoid compounds, but several workers have shown that it can be used for heterocyclic compounds[22,23,126,141]. Its application requires accurate knowledge of the position of a substituent with respect to the reaction centre, a problem that is made more difficult by the location of substituents and centre in different rings.

In one paper Zuman[58] stated that the Hammett equation must be used for coumarin derivatives substituted in the benzene ring, but the Taft equation[125,126,139] for those substituted in the pyrone ring; yet no information is available on how to control the position of a substituent. Several workers have shown that the orienting effects of substituents depend on the electron density on the carbon atoms[130,142,143].

Published molecular diagrams of coumarin, psoralen, and angelicin[12,89,131] and those calculated by the Reviewer using the LCAO-MO method to the Hückel approximation suggest that the orientation of substituents can be represented by



The test compounds cannot be regarded as belonging to a single reaction series, for they are based on different structures—coumarin, angelicin, and psoralen—although all the compounds are reduced at a dropping mercury electrode by the same mechanism. Furthermore, the influence of a substituent in a given ring changes with its orientation relative to the heteroatoms. In view of these considerations, some of the natural coumarins having tabulated values of $\sigma$ were divided, on treatment of their half-wave potentials, into the reaction series

(*a*) coumarin, 6-methylcoumarin, umbelliferone, 4-methylumbelliferone, herniarin, coumarin-7-yl acetate

(*b*) aesculin, aesculetin, fraxinol, fraxinyl acetate

(*c*) psoralen, xanthotoxol, xanthotoxin, xanthotoxyl acetate.

For other compounds either tabulated values of $\sigma$ are not available or the Hammett equation is inapplicable.

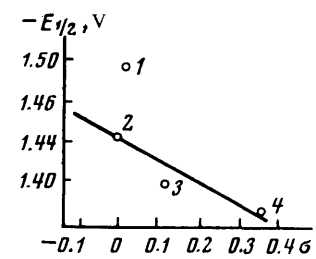



**Figure 3.** Correlation of half-wave potentials of reaction series (*a*) with Hammett $\sigma$ constants for: 1) *p*-OH; 2) *p*-$OCH_3$; 3) *m*-$CH_3$; 4) H; 5) *p*-$OCOCH_3$.

The results plotted in Figs. 3 and 4 show that reaction series (*a*) and (*c*) satisfy the Hammett equation. Departures from the correlation can be explained by absence of additivity, between the electrochemical activity of the coumarins at the dropping mercury electrode and the $\sigma$ values, resulting from intra- and inter-molecular hydrogen bonding, adsorption, dimerisation, and solvation effects.

The Reviewer has assessed the rigour with which the Jaffé correlation[125,126,144] is satisfied only on reaction series (*a*), for which the principal correlation parameters have the values $\eta = 0.974$, $\rho = 0.13$, and $S = 0.058$. The positive value of $\rho$ indicates that the reaction is electrophilic in character: i.e. the introduction of electron-donating substituents retards hydrogenation of the double bond, whereas electron-accepting substituents accelerate it (respectively more and less negative half-wave potentials). The small $\rho$ for series (*a*) indicates the low polarity of the transition state. Values of $\sigma$ have been taken from the paper by McDaniel and Brown[145].

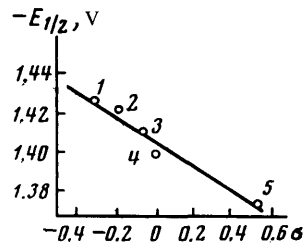



Figure 4. Correlation of half-wave potentials of reaction series (*c*) with Hammett $\sigma$ constants for: 1) *m*-OH; 2) H; 3) *m*-$OCH_3$; 4) *m*-$OCOCH_3$.

Coumarin has 11 molecular orbitals, of which 6 are bonding and 5 antibonding. All 12 $\pi$-electrons can be distributed among bonding molecular orbitals to form a closed system. The energies of delocalisation and of aromatisation for coumarin are respectively $3.36\beta$ and $0.575\beta$†. Of the 14 molecular orbitals in the psoralen molecule 8 are bonding and 6 are antibonding; the 16 mobile $\pi$-electrons of psoralen also occupy all the bonding orbitals and form a closer electron system. Thus the compounds studied form closed electron shells with 8, 12, and 16 $\pi$-electrons. The Hückel rule is inapplicable to them, since the 2-pyrone ring is not a regular polygon owing to the presence of the carbonyl group, and the $4n + 2$ $\pi$-electrons rule is not satisfied.

The polarographic activity of organic compounds involves the donation of electrons from the highest occupied level and the acceptance of electrons by the lowest vacant level, so that the half-wave potential is a linear function of the energy of these levels, and can be measured by the electron affinity or the ionisation potential[130-132,146]. This provides a ready explanation of the satisfactory correlation of this potential with various physical and chemical[74,131,147-152] properties of organic compounds.

A theoretical basis for the possibility of correlating half-wave potentials with the energy of the lowest vacant orbital was first provided by Maccoll[153]. This dependence for the coumarin, psoralen, and angelicin series (Fig. 5) shows that half-wave potentials may be predicted for furocoumarins. Departures from this dependence exhibited by acetylated derivatives and diols (aesculetin) in the coumarin series can be explained by insufficient allowance in quantum-chemical calculations for exchange interaction between adjacent groups and interaction of groups with the solvent or by distortion of the potentials by adsorption, solvation, protonation, and dimerisation of intermediate products.

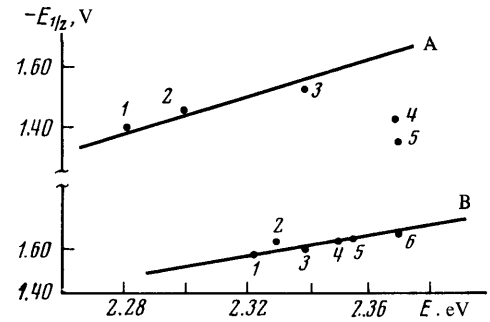



Figure 5. Correlation of energies of lowest vacant orbitals $E$ and the polarographic half-wave potentials for the coumarin series (*A*): 1) coumarin; 2) umbelliferone; 3) fraxinol; 4) fraxinyl acetate; 5) umbelliferone acetate; and for the psoralen and the angelicin series (*B*): 1) psoralen; 2) angelicin; 3) xanthotoxin; 4) sphondin; 5) begapten; 6) isopimpinellin.

## IV. PHYSICOCHEMICAL PROPERTIES AND HALF-WAVE POTENTIAL

It is of great theoretical and practical interest to find the interrelationship between the polarographic characteristics and the physicochemical properties of organic molecules, for the reasons outlined below.

1. It will become possible to assess the relation between the half-wave potential and chemical structure—more precisely to understand how this potential reflects features in the electronic structure of molecules (inductive and mesomeric effects), conformational characteristics (steric effects), the distribution of electron density, the polarisability and polarity of molecules, electrochemical activity, reactivity, and in several cases also the biological action of the substance.

2. Comparison of half-wave potentials with redox potentials will give information on the reversibility of an electrode process, and sometimes polarography may become an independent method for determining redox potentials, since it is more sensitive than the potentiometric method and can be applied over a wider composition range of the medium (quinones, vitamins).

3. Comparison of half-wave potentials with spectral characteristics will permit estimation of the degree of homolysation of molecules[154-156] and the parameters in the equation relating these potentials with the energy of the orbitals, with some indication of the mechanism of electron transfer in the electrochemical step.

4. Comparison of half-wave potentials with dipole moments and refractions enables the electrochemical activity of individual functional groups or structural units of the molecule to be estimated, and also the direction of the polarisation vector to be assessed.

†Here $\beta$ represents the resonance integral used in quantum-chemical calculations[130].

5. The relation between the diffusion-current constant (from the Ilkovič equation) and the molecular mass enables the latter to be evaluated, and also to some extent the degree of sphericity of the molecule (which occurs in the main condition for the Stokes–Einstein equation to be satisfied).

6. Comparison of half-wave potentials for the oxidation of organic compounds with mass-spectral characteristics (ionisation potential, peak appearance potential) will enable the ionisation potential to be evaluated.

7. Comparison of the half-wave reduction potentials with the energy of the longer-wavelength band of the donor (charge-transfer complex) will enable the electron affinity to be evaluated.

8. Comparison of half-wave potentials for polarographic oxidation and reduction will enable the alternance and non-alternance of hydrocarbons to be assessed.

Undoubtedly we could still find quite a few important aspects of the theoretical and practical applicability of the correlation of polarographic characteristics with other physicochemical characteristics of the molecules.

The Reviewer has compared half-wave potentials for the polarographic reduction of coumarins with (i) the energy of the longer-wavelength ultraviolet absorption band, (ii) the dipole moments, (iii) mass-spectral characteristics, (iv) the chemical shift in the nuclear magnetic resonance spectra, and (v) the electron affinity, besides comparing the diffusion-current constants in the first wave of coumarins in 5% tetraethylammonium iodide solution as supporting electrolyte with the molecular mass.

## 1. Half-wave Potential and Ultraviolet Spectra of Coumarins

Comparison of half-wave potentials with ultraviolet absorption band energies is based on the identity of primary physicochemical steps in an electrochemical reaction and in photoexcitation. Watson and Matsen[157]‡ used Maccoll's relation[153] to show that for many compounds the dependence of the half-wave potential on the energy of transition of an electron from the highest occupied to the lowest vacant orbital can be established directly:

$$-E_{1/2}={}^1/_2\, h\nu+\text{const.},$$

where $\nu$ is the frequency of the longer-wavelength absorption band.

A defect in most papers in this field is non-observance of the dimensions of the units in which $E_{1/2}$ and $\lambda_m(\nu)$ are expressed. The former is measured in *volts*, and the latter in *nanometres*. If both parameters are expressed in *electron-volts*, the values of $E_{1/2}$ will partly take into account also the mechanism of reduction at the dropping mercury electrode, since $E_{1/2}$ will have to be multiplied by the number of electrons involved in the electrochemical step.

Grabovskii[157] showed that the relations between the reduction potential and the energy of the electron transition may assume different forms depending on the nature of the substituent and the electron transition. There may be other approaches to a physical explanation of the correlation between half-wave potential and ultraviolet spectral data.

Several substances undergoing an electrochemical reaction at a dropping mercury electrode form charge-transfer complexes with components of the supporting electrolyte and act as acceptors, so that the relation[158]

$$h\nu=I_D-E_A+C$$

holds for them, where $h\nu$ (in eV) is the energy of charge transfer, $I_D$ (eV) the ionisation potential of the donor, $E_A$ (eV) the electron affinity of the acceptor, and $C$ a constant. As several workers have shown, a linear dependence exists between $h\nu$ and $E_A$, as between $h\nu$ and $I_D$, and since the reduction half-wave potential of an organic molecule most often corresponds to $E_A$,[159] this potential should vary linearly with the energy of the longer-wavelength absorption band. On the other hand, the frequency of variation in the variable dipole moment $P$ is described by the formula[160]

$$P=P_0\cos(2\pi\nu t),$$

(in which $P_0$ is the constant dipole moment of the molecule, $\nu$ the frequency of vibration of the molecule, and $t$ the time), which shows that the frequency depends on the dipole moment. In several cases the half-wave potential is a linear function of the dipole moment[20,74], so that a linear relation should exist between this potential and the energy of the corresponding absorption band.

The spectrum of coumarins contains 4–6 strong absorption bands (molar extinction coefficients 3000–30 000). The bands are due to $\pi-\pi^*$ transitions[11,12], but $n-\pi^*$ transitions may also occur (masked by $\pi-\pi^*$ transitions). The polarographic reduction of naturally occurring coumarins at a dropping mercury electrode is due, by analogy with other organic compounds, to the presence of a system of delocalised $\pi$ electrons in the 2-pyrone ring, and is accomplished by passage of electrons from the electrode to the lowest vacant level in the molecule.

The long-wavelength bands corresponding to $\pi-\pi^*$ transitions characterise the energetic state of the functional part of the molecule (containing the conjugated $\pi$-electron system), which is also electrochemically active, so that it is the energy of such a band that must be compared with the half-wave potential. The ultraviolet band energies of coumarins were obtained (in electron-volts) from the corresponding $\lambda_m$ values by means of the classical Bohr frequency rule $h\nu = hc/\lambda = \epsilon_2 - \epsilon_1$.[160] Relative energies of polarographic reduction of the molecules of coumarins $\epsilon$ can be determined as the product of the polarographic half-wave potential $E_{1/2}$ and the number of electrons $n$ taking part in the electrochemical step. The half-wave potentials of the first, reversible wave are usually taken in finding the correlation of spectral and polarographic characteristics, as in the present case.

A linear dependence of the half-wave potential of the first wave on the longer-wavelength ultraviolet absorption maximum has indeed been established for the series—coumarin, psoralen, and angelicin—with the potential falling as the band energy increases[41]. However, since the correlation is based on the energy of the whole band corresponding to $\pi-\pi^*$ transitions predominantly of the $C_{(3)}:C_{(4)}$ double bond, not of part of it, the whole energy of polarographic reduction of the double bond must obviously be taken, i.e. the half-wave potential of the second wave, corresponding to the sum of the electron affinities of the coumarin molecule and of its radical. It is probable that, as in polarography, the transfer of electrons in a spectroscopic experiment takes place in stages (transfer of the first electron followed by that of the second, and so on).

‡This reference appears to be in error (Ed. of Translation).

The polarographic and spectral characteristics found by the Reviewer for naturally occurring coumarins show (Table 5) a deviation of 0.4–0.5 eV from a linear relation only with five compounds (angelicin, acetylumbelliferone, imperatorin, 4-methylumbelliferone, and xanthotoxin): with all the remaining compounds a precise correlation between optical and electrochemical characteristics is observed, which enables half-wave potentials in the coumarin series to be calculated from the energy of the longer-wavelength absorption band.

**Table 5.** Electrochemical and optical characteristics of naturally occurring coumarins.

| Compound | $-E_{1/2}$, V | $\epsilon$, eV | $\lambda_m$, nm | $h\nu$, eV |
|---|---|---|---|---|
| Coumarin | 1.97 | 3.94 | 309 | 4.00 |
| 6-Methylcoumarin | 1.92 | 3.84 | 320 | 3.88 |
| Umbelliferone | 1.84 | 3.68 | 324 | 3.83 |
| Acetylumbelliferone | 1.80 | 3.60 | 310 | 4.00 |
| Fraxinol | 1.93 | 3.86 | 308 | 4.03 |
| Osthole | 2.08 | 4.16 | 321 | 3.87 |
| Aesculin | 1.74 | 3.98 | 333 | 3.73 |
| Acetylfraxinol | 1.88 | 3.76 | 312 | 4.00 |
| Psoralen | 1.95 | 3.90 | 292 | 4.25 |
| Angelicin | 1.89 | 3.78 | 289 | 4.30 |
| Aesculetin | 1.78 | 3.56 | 347 | 3.60 |
| Isopimpinellin | 1.81 | 3.62 | 308 | 3.95 |
| Imperatorin | 1.85 | 3.70 | 299 | 4.15 |
| Bergapten | 1.86 | 3.72 | 309 | 4.00 |
| 7-Isopentenyloxycoumarin | 2.08 | 4.16 | 322 | 3.86 |
| Sphondin | 1.90 | 3.80 | 303 | 4.10 |
| Umbelliprenin | 2.05 | 4.10 | 309 | 4.00 |
| Cnidicin | 1.86 | 3.72 | 308 | 4.06 |
| Cnidilin | 1.91 | 3.82 | 308 | 4.06 |
| Xanthotoxin | 1.85 | 3.70 | 298 | 4.16 |
| Xanthotoxol | 2.00 | 4.00 | 306 | 4.06 |
| 4-Methylumbelliferone | 1.74 | 3.48 | 315 | 3.93 |
| Farnesiferol | 1.86 | 3.72 | 322 | 3.86 |

## 2. Mass-spectral Characteristics and Half-wave Potentials

Electron bombardment of coumarin produces molecular ions[161–163], whose measured appearance potential was corrected for the contact potential of the nickel–molybdenum system (the ion source)[164]. This can be accepted as the ionisation potential, which in the Reviewer's experiments was around 4.0 eV. The correlation of spectral, mass-spectral, and polarographic data enables spectral characteristics to be used to find ionisation potentials, and the equality of the latter to the half-wave potentials as a criterion of the degree of homolysation of the molecule[154, 155] and the consequent possibility of formation of a charge-transfer complex, since the half-wave potentials can be used to find electron affinities[159].

## 3. Electron Affinity and Half-wave Potential

Since half-wave potentials are often used to estimate electron affinities, it was of interest to compare these quantities. Experimental determination of electron affinity is usually based on the examination of charge-transfer complexes, the theory of which was developed by Mulliken[165], or on polarography[159,166]. The Reviewer has calculated electron affinity $A$ by Scott and Becker's method[167] based on the equation

$$A = -\alpha^2 - \left(m_{\overline{N}} - \frac{\eta+1}{\eta} N\right)\beta^0,$$

obtained from approximate quantum-chemical calculations, in which $\alpha^2 = -9.878$ eV, $\beta^0 = 2.110$ eV, $m_{\overline{N}}{}^{12}$ is the Hückel coefficient of the highest occupied orbital or of the anion, $\eta$ is the number of $\pi$ electrons in the neutral molecule, and $N$ is a constant.

**Table 6.**

| Compound | $\eta$ | $m_{\overline{N}}$ (Ref.12) | $-A$, eV | $-E_{1/2}$, V |
|---|---|---|---|---|
| Coumarin | 12 | 1.2391 | 3.70 | 1.40 |
| Herniarin | 12 | 1.1903 | 3.80 | 1.44 |
| 4-Methylumbelliferone | 12 | 1.2000 | 3.93 | 1.61 |
| Psoralen | 16 | 1.1200 | 3.65 | 1.44 |

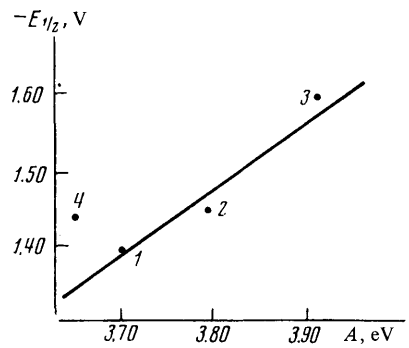



Figure 6. Relation between half-wave potential and electron affinity of coumarins: 1) coumarin; 2) herniarin; 3) 4-methylumbelliferone; 4) psoralen.

The calculated results are given in Table 6. The graphical relation between the two quantities shows (Fig. 6) that the polarographic half-wave potential varies linearly with the electron affinity of the coumarins.

## 4. Dipole Moments and Half-wave Potentials

Data on the dipole moments of coumarins are extremely limited, but the Reviewer's attempts to calculate them by quantum-chemical methods[15,168,169] gave overestimates.

For most substances the wave is considered[20] to move to less negative potentials with increase in the dipole moment. The present case constitutes an exception to the general rule (Fig. 7), which merits special examination.

## 5. Nuclear Magnetic Resonance and Half-wave Potential

The fine structure of an organic molecule is characterised by the chemical shift and the spin distribution constant, which is why n.m.r. spectroscopy[170,171] finds such great use for confirming the conformations of molecules, the distribution of electron density on the atoms, found by other physicochemical methods (spectroscopy, dipole moments) and by quantum-chemical methods. Comparison of polarographic and n.m.r. results is of the greatest

interest, since it enables the electrochemically active units of the molecule, i.e. the sites of lowest electron density, to be determined.

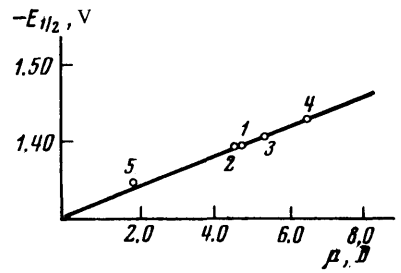



**Figure 7.** Relation between half-wave potentials and dipole moments (determined according to Debye) for coumarins: 1) coumarin; 2) coumarin-6-sulphonic acid; 3) 6-methylcoumarin; 4) 6-aminocoumarin; 5) 6-nitrocoumarin.

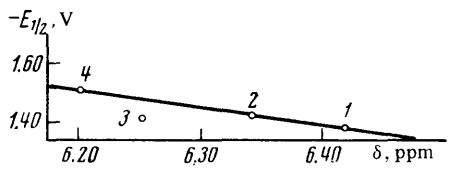



**Figure 8.** Relation between half-wave potential and chemical shift for coumarins: 1) coumarin; 2) fraxinyl acetate; 3) herniarin; 4) 7-hydroxyisopentenyloxycoumarin.

Nuclear magnetic resonance data for coumarins[12,172-174] show that the $C_{(3)}:C_{(4)}$ double bond is the site of lowest electron density, and the 2-pyrone carbonyl group the site of maximum electron density, in agreement with quantum-chemical calculations[12,131] and the vector diagram of the dipole moment of the coumarin molecule. This is confirmed by the comparison of half-wave potentials and chemical shifts plotted in Fig. 8.

### 6. Diffusion-current Constants and Molecular Mass

Increase in molecular mass entails a decrease in the diffusion-current constant (Fig. 9). This provided a method for estimating the molecular masses of coumarins, and also for estimating the constant from the latter, which is very important in calculating the number of electrons and interpreting the mechanism of electrode reactions.

## V. METHODS OF POLAROGRAPHIC ANALYSIS

The polarographic method of analysis is widely used for coumarins[30,31,35,41-46,48,51,54,57,175] and the related chromones[43,175]. The techniques employed are based on displaying the depolarising ability of these compounds at a dropping mercury electrode in the cathodic potential range. Novel physicochemical properties of coumarins detected in this way are of the greatest interest.

Investigation of the mechanism of the chain autoxidation of sulphites revealed that naturally occurring coumarins have a considerable inhibiting effect[46]. A linear dependence exists between the duration of inhibition and the concentration of the coumarins (within the range $10^{-4}$–$10^{-6}$M), which can be used in quantitative analysis. Different coumarins have different ranges of linearity. The inhibiting effect is detected from the change in the rate of fall of the maximum oxygen content in the presence of a sulphite by polarography with 0.01% potassium chloride solution as supporting electrolyte. The sensitivity of this method of analysis ($10^{-7}$ M) is hundredfold that of methods based on the electrochemical reduction of coumarins ($10^{-5}$ M). It will give good results in the analysis of polarographically inactive coumarins (dihydrocoumarin, 4-hydroxycoumarin derivatives) and of coumarins that have poorly developed polarographic waves (hydroxycoumarins).

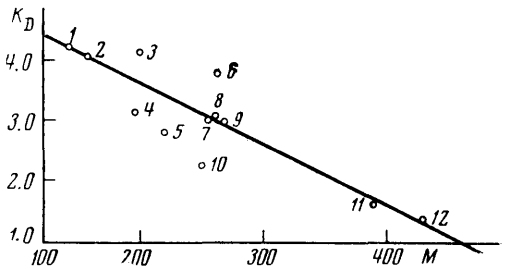



**Figure 9.** Dependence of $K_D$ on molecular mass for the coumarins: 1) coumarin; 2) 6-methylcoumarin; 3) xanthotoxin; 4) psoralen; 5) isobergapten; 6) 7-isopentenyloxycoumarin; 7) fraxinol; 8) imperatorin; 9) fraxinyl acetate; 10) pimpinellin; 11) farnesiferol; 12) athamantin.

A very urgent problem in the chemistry of coumarins is the determination of molecular mass. Hitherto it has been found via the diffusion coefficient by the use of diffusion currents, which is time-consuming and not always accurate. The molecular mass can be determined experimentally by polarography using a standard compound. This gives a formula, based on the Ilkovič and Stokes–Einstein equations[156], from which diffusion coefficients are absent[47,176]:

$$M_x = \left( \frac{10^{16} I_{st}^4 \cdot M_{st} \cdot c_x^4}{I_x^4 \cdot c_{st}^4} \right)^{1/4},$$

where $M_X$ is the molecular mass of the test coumarin, $I_{st}$ and $I_X$ (in μA) are the limiting currents of standard and test coumarin solutions, $M_{st}$ is the molecular mass of the standard coumarin derivative, $c_{st}$ (mM) is the concentration of the standard coumarin solution, and $c_X$ (%) that of the test solution. The relative error of the determination is ±2.5%. The method developed by the Reviewer is far simpler than the mass-spectral method with respect to equipment and more reliable than Rast's method. The methods of analysis of coumarins are applicable also to other classes of organic compounds, and have entered the USSR State Pharmacopoeia[102].

The use of chromatographic methods—paper, thin-layer, and gel—for the preliminary separation of mixtures of coumarins and chromones extends the possibilities of polarography in the investigation and the analysis of these compounds[98,177-180].

## VI. APPLICATION OF POLAROGRAPHY TO THE CHEMISTRY AND BIOLOGY OF COUMARINS

### 1. Kinetics of Cleavage of the Lactone Ring

As already mentioned, the kinetics of cleavage of the lactone ring is not only of practical interest, from the point of view of finding optimum conditions for the analysis, synthesis, and isolation of coumarins, but also of theoretical interest, since by analogy with benzoic esters the determination of rate constants should permit establishment of a scale of the values of $\sigma$ required for the correlation of chemical structure with the physicochemical properties of coumarins.

The polarographic method is absolute in recording the lactone form of coumarin in solution, since the cleaved form—hydroxycinnamic acid—is not established in several supporting electrolytes. Other methods (spectrophotometric, conductometric, potentiometric) enable relative measurements to be made[64-66]. An oscillographic technique enables measurements to be made at high rates of fission of the lactone ring.

Table 7. Rate constants ($M^{-1}$ $s^{-1}$) of cleavage of the lactone ring of coumarin in various media.

| Solvent compound | concn., vol.% | LiOH | NaOH | KOH | $(C_2H_5)_4$ NOH |
|---|---|---|---|---|---|
| Water | 100.0 | 0.338 | 0.347 | 0.388 | 0.130 |
| Methanol | 25.0 | — | 0.227 | — | — |
| Methanol | 30.8 | — | 0.101 | — | — |
| Methanol | 50.0 | 0.073 | 0.069 | 0.082 | — |
| Methanol | 70.0 | — | 0.020 | — | — |
| Ethanol | 19.0 | — | 0.146 | — | — |
| Ethanol | 30.8 | — | 0.131 | — | — |
| Ethanol | 50.0 | 0.132 | 0.124 | 0.129 | — |
| Ethanol | 70.0 | — | 0.056 | — | — |
| Propan-1-ol | 19.0 | — | 0.162 | — | — |
| Propan-1-ol | 30.8 | — | 0.075 | — | — |
| Propan-1-ol | 50.0 | 0.032 | 0.0638 | 0.054 | 0.059 |
| Propan-1-ol | 70.0 | — | 0.062 | — | — |
| Propan-1-ol | 96.0 | — | 0.645 | — | — |
| Propan-2-ol | 19.0 | — | 0.266 | — | — |
| Propan-2-ol | 30.8 | — | 0.124 | — | — |
| Propan-2-ol | 50.0 | 0.106 | 0.124 | 0.108 | 0.131 |
| Propan-2-ol | 70.0 | — | 0.116 | — | — |
| Dimethylformamide | 50.0 | 0.035 | 0.036 | 0.047 | — |

Application of polarography[56] and colorimetry[72,182] to isomolar series[181] shows that coumarin reacts in equimolecular proportions with a base. The reaction is of the second order[67,183]. The investigations have been made in aqueous-alcoholic solutions in the presence of various bases—ammonium, lithium, sodium, potassium, and tetraethylammonium hydroxides—and reaction rate constants have been determined for various concentrations of the alcohol (Table 7). The reaction does not take place in purely alcoholic solvents (methanol, ethanol, propan-1(or 2)-ol). The rate constant increases with decrease in the mole fraction of the organic solvent and in the inductive effect of the substituent but with increase in the strength of the base. The more negative the half-wave potential of coumarin, the more difficult is cleavage of the lactone ring. All the researches show that this process depends on many factors and involves water molecules.

### 2. Complex Formation in the Coumarin Series

Polarography is widely used to investigate complex formation[75,76,184]. The first polarographic study of the formation by aesculetin of complexes with copper, gold, tin, and rhodium salts has been made by the Reviewer. Copper salts give stable complexes, but the process is protracted, taking place in several stages with formation of a mixture of complexes differing in chemical structure, as chromatography[1,185,186] and spectroscopy[187,188] have shown. Earlier spectral results[187] are dubious in view of the close similarity in physicochemical properties of the components of the aggregate complex.

The presence of a complex is established polarographically from the difference between the half-wave potentials of metal and coumarin. The stoichiometric ratio of copper and aesculetin in the complex has been determined[162]. The other complexes—with rhodium, gold, and tin—have only been identified polarographically during their formation.

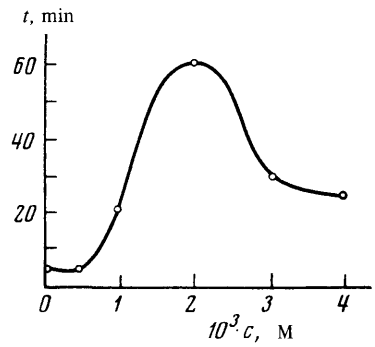



Figure 10. Dependence of the duration $t$ of inhibition by coumarin of the chain autoxidation of sodium sulphite on its concentration $c$.

### 3. Inhibition of Chain Reactions

A form of chain reaction is the autoxidation of sulphites[189-193], which can conveniently be investigated by a polarographic method, since the reaction is studied by measuring the concentration of oxygen in the solution. The Reviewer has been the first to use polarography to investigate this reaction. Coumarins exert a considerable inhibiting effect[194] (Fig. 10), which consists in significant retardation of the rate of autoxidation by interaction of the added coumarin molecules with radicals appearing during the reaction. The inhibiting effect becomes stronger with increase in the molecular mass of the coumarin, in the degree of branching of the molecule, and in the number of phenolic groups.

The mechanism of this reaction, involving ion–radical processes, models redox processes occurring in the living organism. Therefore the useful pharmacological action of many medicinal and biologically active compounds, including coumarin derivatives, is accompanied by a harmful inhibiting effect on redox processes in healthy cells of the organism. In the case of pathological processes (cancer) the inhibiting effect may be of positive value: indeed several coumarins are used for the treatment of malignant diseases[195]. Detailed investigation of the mechanism of the inhibiting effect of coumarins (based on mathematical equations and models) will help to reveal the biological functions of coumarins in plant and animal organisms at a higher level, and thereby establish a more exact model of the dependence of pharmacological action on chemical structure.

The formation of hydrogen peroxide during the autoxidation of sulphites has also been shown by a polarographic method—from the increase in height of the second oxygen wave—which has permitted a more thorough investigation of the mechanism of this reaction. On this basis it is possible to study the mechanism of the aging of coumarins, and also to develop methods for their accelerated aging, enabling the useful life of coumarin preparations to be predicted.

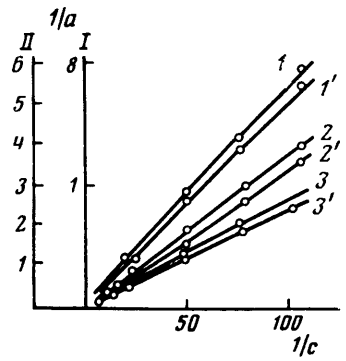



**Figure 11.** Adsorption isotherms for xanthotoxin on silica gel with: I) column chromatography; II) thin-layer chromatography (primed numerals) and different mobile phases: 1) chloroform; 2) acetone; 3) methanol.

## 4. Adsorption Phenomena

The investigation of adsorption phenomena at the mercury–solution interface is one of the most important fields in the electrochemistry and the physical chemistry of surface phenomena, permitting a more profound and detailed interpretation of polarographic investigations. The occurrence of adsorption phenomena in solutions of coumarins has been established[17,32] from the character of the electrocapillary curves and the Gibbs adsorption isotherms[118,119] plotted from data obtained by means of a dropping mercury electrode. Coumarin is desorbed on the negative branch of the electrocapillary curve. Adsorption phenomena supplement certain information on electrochemical reactivity, and also model exchange processes at biological membranes. In combination with column chromatography, furthermore, the polarographic method enables adsorption isotherms (Fig. 11) to be obtained for coumarins[196,197].

A new method of plotting the adsorption isotherms of organic compounds[53], based on thin-layer chromatography, involves measurement of the difference between the distances advanced by the solvent front and by the substance $\Delta lf$.

## 5. Solubility of Coumarins

The great sensitivity of the polarographic method and the possibility of electrochemical reduction in the most diverse media enable it to be widely used to determine the solubility of coumarins by polarographing saturated solutions after dilution with the appropriate solvent.

**Table 8.** Solubility of coumarin in various solvents at 20°C ($c$ is the content of the substance in grams per 100 ml solution).

| Solvent | $c$ | Solvent | $c$ |
|---|---|---|---|
| Methanol | 15.10 | Butanol | 6.35 |
| Ethanol | 8.30 | Pentanol | 4.10 |
| Propan-1-ol | 5.80 | Dioxan | 39.40 |
| Propan-2-ol | 7.20 | Acetone | 44.40 |

At the same time the solubility was determined refractometrically[41,198]. Table 7 shows that the solubility increases with the number of carbon atoms in the alcohol molecule.

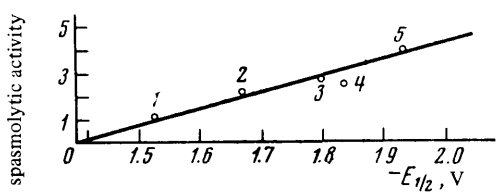



**Figure 12.** Dependence of spasmolytic action of coumarins (according to results obtained in the Pharmacology Laboratory of the Kharkov Chemical and Pharmaceutical Scientific Research Institute) on the half-wave potential: 1) coumarin; 2) umbelliferone; 3) 4-methylumbelliferone; 5) aesculin; 6) aesculetin.

## 6. Half-wave Potential and Biological Activity

The biological activity of organic molecules can be assessed from a combination of pharmacological, biochemical, and physicochemical investigations. Considerable progress can be made in this field by the application of polarography according to the following scheme: (i) comparative estimation, based on the half-wave potentials,

of oxidation and reduction, ionisation potentials, and electron affinities, parametrising the principal physicochemical and biological properties of organic molecules; (ii) comparative assessment of the quantum-chemical parameters and the degrees of homolysation of organic molecules by comparing the polarographic half-wave potentials with quantities—energy of longer-wavelength absorption band, refraction, dipole moments—obtained by other physicochemical methods; (iii) experimental determination of inhibiting effect on chemical models and enzyme systems from the duration of inhibition found from the fall in wave height; (iv) determination of metabolic products; (v) comparative study of chemical and electrochemical stability of pharmacologically important units in the molecules; and (vi) determination of resorptive adsorption capacity.

We have compared the half-wave potentials with the spasmolytic activities of naturally occurring coumarins (Fig. 12) from Khadzhai's results[199]. The greater the electron density of the 2-pyrone ring in the coumarin system the greater the spasmolytic activity (e.g. the activity of simple coumarins is far lower than that of furocoumarins, which applies also to the half-wave potentials).

A polarographic method has been used also to study the photo-oxidation of furocoumarins[200] in the living organism from the consumption of oxygen.

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# Thermochemistry of Organic Compounds of Transition Metals

V.I.Tel'noi and I.B.Rabinovich

Experimental enthalpies of formation of carbonyl, cyclopentadienyl, arene, and alkoxyl compounds of transition metals are discussed with methods for their determination. Mean dissociation energies calculated therefrom for the bonds formed by the metals in these compounds vary regularly with the nature of the ligand and the position of the metal in the Periodic System. All the thermochemical quantities cited have been recalculated on the basis of current values of the initial data. A list of 112 references is included.

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## I. INTRODUCTION

Organic compounds of transition metals have acquired applied importance e.g. in the industrial production of several pure metals from their carbonyls, the manufacture of metal oxide films from alkoxy-compounds of the metals, as catalysts and antiknock additives, and for other purposes. On the other hand, the great interest taken in these compounds by research workers is due to their structural features and their reactions, as well as the specific nature of the $\pi$ bond formed by transition metals with organic ligands.

Although the systematic study of the properties of organic compounds of transition metals began comparatively recently—after the discovery of ferrocene in 1951—very many experimental and theoretical investigations have now been made on the molecular structure of and the nature of the chemical bonds in these compounds, on developing methods for the preparation of novel classes of such compounds, and on elucidating the mechanism of their reactions. Far less work has been done on the thermodynamic parameters of these compounds. Nevertheless, significant information is already available even on these aspects, but it has been published in diverse scientific periodicals, and has not been summarised. Yet such data are necessary for technical calculations of processes involving these compounds, and are important also for the theory of the chemical bond and of heterogeneous catalysis. In particular, the calculation of reaction enthalpies requires knowledge of the enthalpies of formation of the reactants. The same data are necessary in order to compute the energies of dissociation of chemical bonds. For these reasons the present Review will survey published information on the enthalpies of formation of organic transition-metal compounds.

The enthalpy of formation $\Delta H_f^\circ$ of an organic compound Org (from the elements in phase states that are stable under the given conditions) is usually calculated from its enthalpy of combustion $\Delta H_c^\circ$:

$$\Delta H_f^0(\text{Org}) = \sum \nu_i \Delta H_f^0(i) - \Delta H_c^\circ(\text{Org}),$$

where $\Delta H_f^\circ(i)$ is the enthalpy of formation of the $i$th combustion product (from tables), and $\nu_i$ is its stoichiometric coefficient in the equation for the combustion of the organic compound. The enthalpy of formation of the test compound can similarly be calculated from the measured enthalpy of any other reaction involving it and known values of $\Delta H_f^\circ$ for all the other reactants.

Many published enthalpies of formation of organic transition-metal compounds have been calculated from their experimental enthalpies of combustion. Several difficulties of technique are usually encountered during the determination of the latter in a bomb calorimeter—(*a*) complicated purification of test compounds, (*b*) their rapid oxidisability (sometimes spontaneous combustion) in air, (*c*) the explosive character of combustion in the bomb, (*d*) possibility of formation of products of incomplete combustion, (*e*) possibility of reactions between combustion products, and (*f*) complexity of analysis of combustion products—which complicate the extraction of reliable results.

With easily oxidisable crystalline organometallic compounds serious difficulties arise in preventing premature oxidation before ignition. The use of glass or polymer ampoules, which are widely employed in the study of liquids, is rarely successful because of the dispersal of crystals inside the bomb by the extremely rapid combustion. Sometimes, therefore, the weighed portion of the compressed or powdered test substance is placed in molten paraffin wax, the latter is allowed to solidify, and the two are burned together. Not only does this protect the test substance from oxidation in the preliminary stage of the experiment but it also promotes more complete combustion. A disadvantage of this method is the fairly large correction needed for the enthalpy of combustion of the paraffin wax.

Good et al.[1] determined the enthalpy of formation of decacarbonyl dimanganese by combustion in a rotating bomb. This method entailed dissolution of the combustion products in the bomb in order to establish a definite final state of the reaction system. The necessity of selecting an appropriate solvent in each specific case, the appearance of new sources of errors, and the laborious character of the series of operations prevent widespread adoption of this method.

Both thermal decomposition (into metal and carbon monoxide) and high-temperature iodination have been recommended[2] for the calorimetric investigation of carbonyls.

In the subsequent discussion of published results the method of determination will be indicated and attention will be paid to the surmounting of experimental difficulties. The observed heats of combustion from which heats of formation have been calculated are given and discussed. Values in the Review for the mean energy of dissociation $\overline{D}$ of metal–ligand bonds in compounds $ML_n$ have been calculated as one-$n$th of the enthalpy of atomisation $\Delta H_{at}^\circ$ of the compound in the gaseous state, which is given by the equation

$$\Delta H_{at}^0(ML_n,(g)) = \Delta H_f^0(M,(g)) + n\Delta H_f^0(L,(g)) - \Delta H_f^0(ML_n,(g)).$$

Methods for calculating values of $\overline{D}$ in compounds RML are described in connection with specific compounds.

In the present Review values of enthalpies of combustion or of other reactions $\Delta H_r^\circ$ are accompanied by the accuracy indicated in the original papers. Values of enthalpies of formation and of mean bond dissociation energies have been recalculated by the Reviewers on the basis of current values for the enthalpies of formation of atoms and substances. Calculation of dissociation energies of metal–ligand bonds in cyclopentadienyl compounds is complicated by the absence of a reliably established value for the enthalpy of formation of the cyclopentadienyl radical: thus this function has been given as 45.4 ± 10,[3] ~50,[4,5] 63,[6] 53 ± 12,[7] and 47 ± 4 [8] kcal mole$^{-1}$; the Reviewers have adopted the arbitrary value $\Delta H_f^\circ(C_5H_5,g)$ = 50 kcal mole$^{-1}$. Values of the enthalpies of formation of other substances used by Reviewers in thermochemical calculations are listed in Table 1. Values in the Review are expressed in thermochemical calories (1 cal = 4.184 J) and relate to a standard pressure (always denoted by a ° sign) and the standard temperature of 298.15 K. The letters in parentheses accompanying chemical formulae (c, l, g, and s) denote respectively the crystalline, liquid, and gaseous states and a solution.

Table 1. Enthalpies of formation used in the calculations.

| Substance* | $\Delta H_f^0$, kcal mole$^{-1}$ | Ref. | Substance* | $\Delta H_f^0$, kcal mole$^{-1}$ | Ref. |
|---|---|---|---|---|---|
| $Br_2$($n$CCl$_4$)(s) | 0.71±0.02 | 9 | n-$C_5H_{11}O$(g) | −23.5±2.0 | 12 |
| Cl(g) | 28.993±0.006 | 9 | t-$C_5H_{11}O$(g) | −29.0±2.0 | 12 |
| $Cl_2$($n$CCl$_4$)(s) | −4.6±0.1 | 9 | $C_2H_5OH$(l) | −66.20 | 11 |
| CO(g) | −26.416±0.031 | 9 | n-$C_3H_7OH$(l) | −72.79 | 11 |
| $CO_2$(g) | −94.052±0.011 | 9 | iso-$C_3H_7OH$(l) | −76.04 | 11 |
| $CH_3$(g) | 34.0±1.0 | 9 | n-$C_4H_9OH$(l) | −77.87 | 11 |
| $C_6H_6$(g) | 77.7±2.0 | 10 | iso-$C_4H_9OH$(l) | −79.73 | 11 |
| $C_6H_5CH_2$(g) | 45±1 | 10 | s-$C_4H_9OH$(l) | −81.90 | 11 |
| $C_6H_5CH_3$(g) | 11.95±0.15 | 11 | t-$C_4H_9OH$(l) | −85.87 | 11 |
| $C_6H_4$(g) | 19.82±0.12 | 11 | n-$C_5H_{11}OH$(l) | −85.55 | 11 |
| $C_6H_5Cl$(g) | 12.39±0.16 | 11 | t-$C_5H_{11}OH$(l) | −90.71 | 11 |
| 1,3,5-$C_6H_3(CH_3)_3$(g) | −3.84±0.34 | 11 | Co(g) | 102.4±1.0 | 9 |
| 1,2,4-$C_6H_3(CH_3)_3$(g) | −3.33±0.27 | 11 | $CoCl_2$(c) | −74.1±0.5 | 9 |
| $C_6H_5C_2H_5$(g) | 7.12±0.20 | 11 | $CoBr_2$(c) | −51.55±0.50 | 9 |
| o-$C_6H_4(C_2H_5)_2$(g) | −4.53±0.5 | 11 | CoO(c) | −57.1±0.3 | 9 |
| $C_6H_5$-iso-$C_3H_7$(g) | 0.94±0.26 | 11 | $Co_3O_4$(c) | −212±2 | 9 |
| o-$C_6H_4$(iso-$C_3H_7$)$_2$(g) | −17±1 | 13 | Cr(g) | 95 0±1.0 | 9 |
| cyclo-$C_7H_8$(g) | 43.47 | 11 | $CrCl_2$(c) | −94.5±1.0 | 9 |
| $CH_3O$(g) | 2.0±2.0 | 9 | $CrI_2$(c) | −37.5±1.5 | 9 |
| $C_2H_5O$(g) | −6.0±1.0 | 9 | $Cr_2O_3$(c) | −272.6±0.4 | 9 |
| n-$C_3H_7O$(g) | −11.2±2.0 | 10 | Fe(g) | 98.7±0.3 | 9 |
| iso-$C_3H_7O$(g) | −12.6±2.0 | 10 | $FeI_2$(c) | −27.8±2.0 | 9 |
| n-$C_4H_9O$(g) | −17±2 | 10 | $Fe_2O_3$(c) | −196.5±1.0 | 9 |
| iso-$C_4H_9O$(g) | −18±2 | 10 | $Fe_3O_4$(c) | −267.0±0.5 | 9 |
| s-$C_4H_9O$(g) | −20±2 | 10 | H(g) | 52.098±0.006 | 9 |
| t-$C_4H_9O$(g) | −23±2 | 10 | HCl(g) | −21.94±0.08 | 9 |
| HCl(200$H_2O$)(s) | −39.63±0.02 | 9 | HCl(51.3$H_2O$)(s) | −39.42±0.02 | 9 |
| HCl(400$H_2O$)(s) | −39.70±0.02 | 9 | Os(g) | 188.9±1.5 | 9 |
| Hf(g) | 148.2±1.0 | 9 | Pr(g) | 89.1±0.3 | 14 |
| $HfCl_4$(g) | −210.46±0.58 | 9 | $Pr_6O_{11}$(c) | −1365.6 | 16 |
| $HfCl_4$(c) | −236.7±0.3 | 9 | Pt(g) | 135.3±0.5 | 9 |
| $HfO_2$(c) | −267.1±0.5 | 9 | Re(g) | 185.4±1.5 | 9 |
| $HNO_3$(16$H_2O$)(s) | −49.37±0.12 | 9 | $HReO_4$(20$H_2O$)(s) | −191±1 | 9 |
| $H_2O$(l) | −68.3149±0.0096 | 9 | Rh(g) | 133.0±0.5 | 9 |
| I(g) | 25.52±0.01 | 9 | Ru(g) | 157.0±1.5 | 9 |
| $I_2$(g) | 14.92±0.02 | 9 | Sc(g) | 91.0±0.2 | 14 |
| Ir(g) | 160.0±1.5 | 9 | $Sc_2O_3$(c) | −456.4±0.5 | 17 |
| La(g) | 103.0±0.1 | 14 | Ta(g) | 187.9±1.0 | 9 |
| $La_2O_3$(c) | −458 | 15 | $Ta_2O_5$(c) | −489.3±0.4 | 9 |
| Mn(g) | 68.0±0.5 | 9 | Ti(g) | 113.2±1.0 | 9 |
| $MnI_2$(c) | −63.6±1.0 | 9 | $TiCl_4$(g) | −182.4±0.7 | 9 |
| MnO(c) | −92.0±0.1 | 9 | $TiCl_4$(l) | −192.2±0.9 | 9 |
| $MnO_2$(c) | −124.6±0.2 | 9 | $TiO_2$(c) | −225.6±0.2 | 9 |
| $Mn_2O_3$(c) | −228.9±0.2 | 9 | Tm(g) | 59.1±0.2 | 14 |
| $Mn_3O_4$(c) | −331.6±0.2 | 9 | $Tm_2O_3$(c) | −451.4±1.4 | 18 |
| Mn($NO_3$)$_2$ (10.3$H_2O$) (s) | −148.8±0.2 | 9 | V(g) | 123.0±1.0 | 9 |
| Mo(g) | 156.9±0.7 | 9 | $V_2O_5$(c) | −371.0±2.3 | 9 |
| $MoCl_4$(g) | −105±10 | 9 | W(g) | 304.8±1.0 | 9 |
| $MoO_3$(c) | −178.1±0.1 | 9 | $WCl_6$(g) | −119.1±0.5 | 9 |
| Nb(g) | 172.7±1.0 | 9 | $WO_3$(g) | −201.4±0.2 | 9 |
| $Nb_2O_5$(c) | −453.6±0.4 | 9 | Y(g) | 101.5±0.2 | 14 |
| Ni(g) | 102.5±0.5 | 9 | $Y_2O_3$(c) | −455.4±0.5 | 19 |
| NiO(c) | −57.3±0.1 | 9 | Yb(g) | 36.3±0.1 | 14 |
| | | | $Yb_2O_3$(c) | −433.7±0.5 | 20 |
| | | | Zr(g) | 143 4±1.5 | 9 |
| | | | $ZrCl_4$(g) | −207.77±0.35 | 9 |
| | | | $ZrCl_4$(c) | −234.17±0.28 | 9 |
| | | | $ZrO_2$(c) | −260.0±0.2 | 9 |

*Here and subsequently: g = gaseous state; l = liquid state; c = crystalline state; and s = solution.

## II. CARBONYL COMPOUNDS

### 1. Tetracarbonylnickel

Among determinations of the enthalpy of combustion of tetracarbonylnickel[21-23] the most soundly based[23] paid special attention to analysis of the products, including carbon and nickel monoxides. The solid products contained together with the latter a considerable quantity (9–21%) of metallic nickel. After correction for the incomplete oxidation of nickel, the enthalpy obtained for the process

$$Ni(CO)_4(l) + 2.5O_2(g) \rightarrow NiO(c) + 4CO_2(g)$$

was $\Delta H_c^\circ = -282.2 \pm 0.5$ kcal mole$^{-1}$, whence $\Delta H_f^\circ[Ni.(CO)_4, l] = -151.3 \pm 0.5$ kcal mole$^{-1}$.

The enthalpy of formation has been calculated also from equilibrium data on formation of the tetracarbonyl from metallic nickel and gaseous carbon monoxide[24-26], and these results have been critically examined[23,27,28]. The value $-149 \pm 2$ kcal mole$^{-1}$ was suggested[28] for the enthalpy of formation of tetracarbonylnickel in the liquid state. From the above results[23-28] Skinner[29] recommended the value $\Delta H_f^\circ[Ni(CO)_4, l] = -150.4 \pm 1.5$ kcal mole$^{-1}$. Together with the enthalpy of vaporisation $\Delta H_v^\circ[Ni(CO)_4] = 6.6 \pm 0.3$ kcal mole$^{-1}$ this gives $\Delta H_f^\circ[Ni.(CO)_4, g] = -143.8 \pm 1.5$ kcal mole$^{-1}$ and $\bar{D}(Ni-CO) = 35.2 \pm 0.4$ kcal mole$^{-1}$. Many carbonyls are partly associated in the gas phase[30]. In view of the comparative instability of these aggregates, however, disregard of association does not significantly distort the results calculated for $\bar{D}(M-CO)$.

The mean dissociation energy of the nickel–carbonyl bond has been determined also by electron bombardment[31,32]. The difference between the appearance potential of the $Ni^+$ ion in the process $Ni(CO)_4 + e \rightarrow Ni^+ + 4CO + 2e$ and the first ionisation potential of nickel gave values of $\bar{D}$ of $39.3 \pm 1.0$ and $43 \pm 1$ kcal mole$^{-1}$ respectively[31,32]. These overestimates in relation to the calorimetric results were attributed[31,32] to the presence of excess energy in the mass-spectrometric breakdown products of the initial compound.

### 2. Pentacarbonyliron

Early results for the enthalpy of combustion[33,34] cannot be accepted because of the absence of a detailed description of the experiments[33,34]. In later work[35] each enthalpy measurement was followed by careful analysis of the gaseous combustion products for carbon dioxide and of the solid products for the presence of metallic iron and the oxides FeO, $Fe_2O_3$, and $Fe_3O_4$. Most of the iron (72 to 96%) had been oxidised to the sesquioxide. After correction for incomplete oxidation of carbon and iron the enthalpy of the reaction

$$Fe(CO)_5(l) + 3.25O_2(g) \rightarrow 0.5Fe_2O_3(c) + 5CO_2(g)$$

became $\Delta H_c^\circ = -385.9 \pm 1.7$ kcal mole$^{-1}$, which correspond to $\Delta H_f^\circ[Fe(CO)_5, l] = -182.6 \pm 1.8$ kcal mole$^{-1}$. Using the published value[36] $\Delta H_v^\circ = 9.6 \pm 0.3$ kcal mole$^{-1}$, we obtain $\Delta H_f^\circ[Fe(CO)_5, g] = -173.0 \pm 1.8$ kcal mole$^{-1}$ and $\bar{D}(Fe-CO) = 28.1 \pm 0.4$ kcal mole$^{-1}$. Electron bombardment gives[31] for this dissociation energy the value 33 kcal mole$^{-1}$. It is interesting that considerably less energy is required for detachment of the first carbonyl group from the pentacarbonyl: thus mass spectrometry yields[37] $D[Fe(CO)_4-CO] \simeq 16$ kcal mole$^{-1}$.

### 3. Nonacarbonyldi-iron and Dodecacarbonyltri-iron

Skinner et al.[38] have studied the thermal decomposition of the nonacarbonyl at 553–573 K and its ionisation at 524–573 K. The results indicate that the enthalpy of the process $Fe_2(CO)_9(c) \rightarrow 2Fe(c) + 9CO(g)$ occurring at the standard temperature is $99 \pm 3$ kcal mole$^{-1}$, which corresponds to $\Delta H_f^\circ[Fe_2(CO)_9, c] = -337 \pm 3$ kcal mole$^{-1}$. Thermal decomposition and iodination of the dodecacarbonyl have been studied[38] over the range 494–544 K. Conversion of the results to 298.15 K gave for $Fe_3(CO)_{12}.(c) \rightarrow 3Fe(c) + 12CO(g)$ the value $\Delta H_r^\circ = 125 \pm 4$ kcal mole$^{-1}$, corresponding to $\Delta H_f^\circ[Fe_3(CO)_{12}, c] = -442 \pm 4$ kcal mole$^{-1}$.

The enthalpies of sublimation were estimated[38] as $18 \pm 5$ and $23 \pm 5$ kcal mole$^{-1}$ for the nonacarbonyl and dodecacarbonyl respectively. From these results we obtain for $\Delta H_f^\circ(g)$ the corresponding values $-319 \pm 6$ and $-419 \pm 7$ kcal mole$^{-1}$.

### 4. Decacarbonyldimanganese and Decacarbonyldirhenium

Good et al.[1] determined the enthalpy of formation of the manganese carbonyl by combustion in a rotating bomb, the products being dissolved in aqueous nitric acid and hydrogen peroxide. For the reaction

$$Mn_2(CO)_{10}(c) + 4HNO_3(16H_2O, s) + 6O_2(g) \rightarrow 2Mn(NO_3)_2(10.3H_2O, s) + 10CO_2(g) + 2H_2O(l)$$

they obtained $\Delta H_c^\circ = -777.0 \pm 0.8$ kcal mole$^{-1}$, and hence $\Delta H_f^\circ[Mn_2(CO)_{10}, c] = -400.5 \pm 1.0$ kcal mole$^{-1}$. Recent measurements[2] of the enthalpy of iodination in a Calvet microcalorimeter have given for the process

$$Mn_2(CO)_{10}(c) + 2I_2(g) \rightarrow 2MnI_2(c) + 10CO(g)$$

the value $\Delta H_r^\circ = -12.6 \pm 1.5$ kcal mole$^{-1}$, which corresponds to $\Delta H_f^\circ[Mn_2(CO)_{10}, c] = -408.6 \pm 1.5$ kcal mole$^{-1}$.

Determination of the enthalpy of combustion of the rhenium carbonyl in a stationary calorimetric bomb has given[39] for the reaction

$$Re_2(CO)_{10}(c) + H_2O(l) + 8.5O_2(g) \rightarrow 2HReO_4(20H_2O, s) + 10CO_2(g)$$

the value $\Delta H_c^\circ = -857.9 \pm 0.6$ kcal mole$^{-1}$, whence $\Delta H_f^\circ[Re_2(CO)_{10}, c] = -396.3 \pm 2.1$ kcal mole$^{-1}$. Other workers[38] have measured the enthalpies of thermal decomposition and of high-temperature iodination of the same compound. For the process $Re_2(CO)_{10}(c) \rightarrow 2Re(c) + 10CO(g)$ under standard conditions they find that $\Delta H_r^\circ = 131 \pm 5$ kcal mole$^{-1}$, which yields $-395 \pm 5$ kcal mole$^{-1}$ for the heat of formation.

Table 2. Thermochemical parameters (in kcal mole$^{-1}$) of dimanganese and dirhenium decacarbonyls.

| Carbonyl | $\Delta H_f^0$ (c) | $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $\bar{D}$ (M–CO) |
|---|---|---|---|---|
| $Mn_2(CO)_{10}$ | $-404.6 \pm 2.0$ | $19.2 \pm 0.5$ | $-385.4 \pm 2.0$ | $23.6 \pm 0.4$ |
| $Re_2(CO)_{10}$ | $-395.6 \pm 2.0$ | $22.3 \pm 0.1$ | $-373.3 \pm 2.0$ | $43.5 \pm 0.5$ |

Thus the use of different methods to determine enthalpy of formation has given mutually consistent results for both manganese and rhenium carbonyls. We have therefore used their average values in the thermochemical calculations (Table 2). The enthalpies of sublimation $\Delta H^{\circ}_{s}$ have been discussed in detail[40]. Mass-spectrometric data have been used to calculate mean bond dissociation energies: $D[(CO)_5Mn-Mn(CO)_5] = 21 \pm 3$ [41] and $D[(CO)_5Re-Re(CO)_5] = 44.7$ [42] kcal mole$^{-1}$. It is noteworthy that $\bar{D}(Re-CO)$ is almost double $\bar{D}(Mn-CO)$.

## 5. Manganese and Rhenium Pentacarbonyls

Skinner et al.[40] have measured the enthalpies of the high-temperature iodination of several methylated and halogenated manganese and rhenium pentacarbonyls, which gives the calculated enthalpies of formation in Table 3. The enthalpies of sublimation of methylmanganese and methylrhenium pentacarbonyls have been calculated from the experimental[43,44] temperature dependence of their vapour pressure.

Table 3. Thermochemical parameters (kcal mole$^{-1}$) of manganese and rhenium pentacarbonyls.

| Carbonyl | $-\Delta H^{0}_{f}$(c) | $\Delta H^{0}_{s}$ | $-\Delta H^{0}_{f}$(g) | $\bar{D}$ (M—$CH_3$) |
|---|---|---|---|---|
| $CH_3Mn(CO)_5$ | 189.8±2.2 | 15.0±0.5 | 174.8±2.3 | 26.7±3.2 |
| $ClMn(CO)_5$ | 241.2±3 | — | — | — |
| $BrMn(CO)_5$ | 231.8±2 | — | — | — |
| $CH_3Re(CO)_5$ | 198.8±2.2 | 16.0±0.5 | 182.8±2.3 | 53.1±3.8 |

Values of $\bar{D}(M-CH_3)$ have been calculated by means of the formula

$$\bar{D}(M-CH_3) = \Delta H^{0}_{f}(M,g) + \Delta H^{0}_{f}(CH_3,g) + 5\Delta H^{0}_{f}(CO,g) - \Delta H^{0}_{f}[CH_3M(CO)_5,g] - 5\bar{D}(M-CO)$$

on the assumption that $\bar{D}(M-CO)$ is the same in these compounds and in the corresponding decacarbonyls $M_2(CO)_{10}$. Table 3 shows that $\bar{D}(Re-CH_3)$ is twice $\bar{D}(Mn-CH_3)$: i.e. the same ratio is found between the metal–methyl bond dissociation energies as for the metal–carbonyl bonds in the rhenium and manganese decacarbonyls.

## 6. Tricarbonylcyclopentadienylmanganese

Determination of the enthalpy of combustion

$$C_5H_5Mn(CO)_3(c) + 8.7O_2(g) \rightarrow MnO_2(c) + 8CO_2(g) + 2.5H_2O(l)$$

as $\Delta H^{\circ}_{c} = -918 \pm 2$ kcal mole$^{-1}$ was recognised[45] to involve the possible formation of products of incomplete oxidation. Other workers[46] checked the completeness of combustion by determining manganese and carbon dioxides in the products; they found complete oxidation to manganese dioxide and obtained the value $-922 \pm 2$ kcal mole$^{-1}$. We recommend the mean of these results[45,46]: $\Delta H^{\circ}_{c} = -920 \pm 2$ kcal mole$^{-1}$, from which we calculate[30] $\Delta H^{\circ}_{f}[Mn(CO)_3.C_5H_5,c] = -127.8 \pm 2$ kcal mole$^{-1}$. Using $\Delta H^{\circ}_{s} = 12.5 \pm 0.8$ kcal mole$^{-1}$, we have $\Delta H^{\circ}_{f}[Mn(CO)_3C_5H_5,g] = -115.3 \pm 2.1$ kcal mole$^{-1}$.

## 7. Chromium, Molybdenum, and Tungsten Hexacarbonyls

The results of the first investigation[47] of the thermochemical properties of the three hexacarbonyls, involving measurement of their enthalpies of combustion in a stationary calorimetric bomb, were discussed in detail by workers[48] who redetermined these enthalpies. Analysis of the solid products revealed[48] that the oxides were accompanied by a certain quantity of unoxidised metal, which entailed appropriate corrections to the enthalpies of formation. The above results[47,48] have recently been carefully checked by Skinner et al.[49–51], using not only combustion in a stationary bomb but also their calorimetric methods of thermal decomposition and high-temperature iodination.

Table 4. Enthalpies of formation (kcal mole$^{-1}$) of chromium, molybdenum, and tungsten hexacarbonyls.

| Carbonyl | $-\Delta H^{0}_{f}$(c) | Method of determination | Ref. |
|---|---|---|---|
| $Cr(CO)_6$ | 249.3±0.5 | combustion, $\Delta H^{0}_{c} = -451.3 \pm 0.5$ | 47 |
| | 257.5±0.5 | combustion, $\Delta H^{0}_{c} = -443.1 \pm 0.5$ | 48 |
| | 234.3±1.8 | iodination, $\Delta H^{0}_{r} = 23.4 \pm 1.0$ | 2 |
| | 234.7±0.6 | combustion, $\Delta H^{0}_{c} = -465.9 \pm 0.5$ | 52 |
| | 238.9±4.5 | combustion, $\Delta H^{0}_{c} = -461.8 \pm 4.0$ | 51 |
| | 233.8±0.5 | decomposition, $\Delta H^{0}_{r} = 75.3 \pm 0.2$ | 51 |
| $Mo(CO)_6$ | 235.8±0.5 | combustion, $\Delta H^{0}_{c} = -506.7 \pm 0.5$ | 47 |
| | 235.0±0.3 | combustion, $\Delta H^{0}_{c} = -507.5 \pm 0.3$ | 48 |
| | 229.5±1.0 | decomposition, $\Delta H^{0}_{r} = 71.0 \pm 1.0$ | 2 |
| | 236.8±1.0 | combustion, $\Delta H^{0}_{c} = -505.7 \pm 0.9$ | 49 |
| | 236.4±0.4 | decomposition, $\Delta H^{0}_{r} = 77.9 \pm 0.4$ | 49 |
| $W(CO)_6$ | 226.0±0.5 | combustion, $\Delta H^{0}_{c} = -539.7 \pm 0.5$ | 47 |
| | 227.9±0.3 | combustion, $\Delta H^{0}_{c} = -537.8 \pm 0.3$ | 48 |
| | 229.7±1.2 | combustion, $\Delta H^{0}_{c} = -536.0 \pm 1.0$ | 50 |
| | 229.3±0.5 | decomposition, $\Delta H^{0}_{r} = 70.8 \pm 0.4$ | 50 |

All published experimental values of the enthalpies of formation of chromium, molybdenum, and tungsten hexacarbonyls are listed in Table 4. The enthalpies of combustion in the third column are based on the reactions

$$Cr(CO_6)(c) + 3.75O_2(g) \rightarrow 0.5Cr_2O_3(c) + 6CO_2(g)$$
$$M(CO)_6(c) + 4.5O_2(g) \rightarrow MO_3(c) + 6CO_2(g)$$
M – Mo or W.

The enthalpy of iodination of chromium hexacarbonyl relates to the process

$$Cr(CO)_6(c) + I_2(g) \rightarrow CrI_2(c) + 6CO(g).$$

The enthalpies of thermal decomposition correspond to the reactions

$$M(CO)_6(c) \rightarrow M(c) + 6CO(g)$$
M – Cr, Mo or W.

Table 4 shows good mutual agreement among values obtained for the enthalpy of formation of chromium hexacarbonyl on the basis of its iodination[2], combustion[52], and decomposition[51]. Hence we have used the average value

for our thermochemical calculations. The earlier results[47,48] for chromium hexacarbonyl must be regarded as incorrect. The most accurate values for the enthalpies of formation of molybdenum and tungsten hexacarbonyls are those of Skinner et al.[49,50], since for each substance they obtained results in good agreement by two different methods.

Table 5 gives recommended[53] enthalpies of sublimation. Values of $\bar{D}$(M–CO) in the last column have been calculated by the Reviewers from selected values of $\Delta H_f^\circ$.[M(CO)$_6$, g]. As for Group VII transition metals (Table 2), this bond dissociation energy increases considerably with the atomic number of the metal.

Table 5. Recommended thermochemical parameters (kcal mole$^{-1}$) of chromium, molybdenum, and tungsten hexacarbonyls.

| Carbonyl | $-\Delta H_f^0$ (c) | $\Delta H_s^0$ | $-\Delta H_f^0$ (g) | $\bar{D}$ (M–CO) |
|---|---|---|---|---|
| $Cr(CO)_6$ | 234.3±0.4 | 17.1±0.1 | 217.2±0.4 | 25.6±0.1 |
| $Mo(CO)_6$ | 236.6±0.2 | 17.6±0.2 | 219.0±0.3 | 36.2±0.1 |
| $W(CO)_6$ | 229.5±0.7 | 18.3±0.3 | 211.2±0.8 | 42.9±0.2 |

Table 6. Thermochemical parameters (kcal mole$^{-1}$) of arenechromium tricarbonyls.

| Carbonyl | $-\Delta H_f^0$ (c) | $\Delta H_s^0$ | $-\Delta H_f^0$ (g) | $\Delta H_r^{0*}$ |
|---|---|---|---|---|
| $(C_6H_6)Cr(CO)_3$ | 106±2 | 21.8±1 | 84.2±2.2 | 120±3 |
| $(C_6H_5CH_3)Cr(CO)_3$ | 114±2 | 22.6±1 | 91.4±2.2 | 119±3 |
| $[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$ | 136.5±2 | 25.9±1 | 110.6±2.2 | 122,5±3 |
| $[C_6(CH_3)_6]Cr(CO)_3$ | 166.5±3 | 29.5±1 | 137.0±3.2 | 132±4 |
| $(C_6H_5Cl)Cr(CO)_3$ | 111±5 | 24.5±1 | 86.5±5.1 | 115±5 |
| (cyclo-$C_7H_8$)$Cr(CO)_3$ | 74±3 | 22.5±1 | 51.5±3.2 | 111±4 |

*The enthalpies of decomposition of the compounds into chromium and the ligands.

## 8. Arenechromium Tricarbonyls

Skinner et al.[54,55] have used high-temperature calorimetry to study the thermal decomposition and the iodination of several compounds of type $Cr(CO)_3$Arene. Standard enthalpies of formation calculated from the results are given in Table 6 together with the measured[55] enthalpies of sublimation.

The last column in Table 6 indicates the enthalpies of decomposition

$$(\text{Arene})Cr(CO)_3(g) \rightarrow Cr(g) + \text{Arene}(g) + 3CO(g).$$

It was assumed[55] that the energy of dissociation of the chromium–carbonyl bond is the same in all these chromium compounds, 25.6 kcal mole$^{-1}$ as in chromium hexacarbonyl. To this approximation they found that the ligands formed the sequence

$$\text{cyclo-}C_7H_8 \simeq C_6H_5Cl < C_6H_6 \simeq C_6H_5CH_3 \simeq \simeq C_6H_3(CH_3)_3 < C(CH_3)_6$$

according to the mean energy of dissociation of the bonds formed with chromium. However, the hypothesis that $\bar{D}$(Cr–CO) has the same value in these carbonyl derivatives requires experimental confirmation.

## 9. Mesitylenemolybdenum Tricarbonyl

The Reviewers have measured the enthalpy of combustion by the method of Ref. 46. Determinations of molybdenum trioxide and carbon dioxide established the absence of products of incomplete combustion. They found for the reaction

$$[C_6H_3(CH_3)_3]Mo(CO)_3(c) + 15O_2(g) \rightarrow MoO_3(c) + 12CO_2(g) + 6H_2O(l)$$

the value $\Delta H_c^\circ = -1598 \pm 1$ kcal mole$^{-1}$, which corresponds to $\Delta H_f^\circ[Mo(CO)_3C_6H_3(CH_3)_3, c] = -119 \pm 1$ kcal mole$^{-1}$.

## 10. Carbonyl Compounds of Cobalt

Calorimetric determinations[56,57] have yielded for the enthalpies $\Delta H_r^\circ$ of the reactions

$$Co_2(CO)_8(c) + 2Br_2(n\text{-}CCl_4, s) \rightarrow 2CoBr_2(c) + 8CO(g);$$
$$Co_3(CCl)(CO)_9(c) + 4.5Cl_2(n\text{-}CCl_4, s) \rightarrow 3CoCl_2(c) + 9CO(g) + CCl_4(l);$$
$$Co_3(CBr)(CO)_9(c) + 4.5Br_2(n\text{-}CCl_4, s) \rightarrow 3CoBr_2(c) + 9CO(g) + CBr_4(n\text{-}CCl_4, s).$$

the respective values $-19.5 \pm 0.5$, $-107.5 \pm 1.6$, and $-191.4 \pm 1.0$ kcal mole$^{-1}$. Skinner et al.[38], using thermal decomposition and high-temperature iodination, found that the enthalpies of the processes

$$Co_2(CO)_8(c) \rightarrow 2Co(c) + 8CO(g)$$
$$Co_4(CO)_{12}(c) \rightarrow 4CO(c) + 12CO(g)$$

occurring under standard conditions were respectively $87 \pm 1$ and $124 \pm 4$ kcal mole$^{-1}$.

Table 7. Thermochemical parameters (kcal mole$^{-1}$) of cobalt carbonyls.

| Carbonyl | $-\Delta H_f^0$ (c) | $\Delta H_s^0$ | $-\Delta H_f^0$ (g) |
|---|---|---|---|
| $Co_2(CO)_8$ | 297.1±1.0 | 15.6±0.8 | 281.5±1.3 |
| $Co_4(CO)_{12}$ | 441±4 | (23±5) | 418±7 |
| $Co_3(CCl)(CO)_9$ | 280.5±2.2 | 23.8±0.4 | 256.7±2.2 |
| $Co_3(CBr)(CO)_9$ | 280.3±2.4 | 28.1±0.6 | 252.2±2.5 |

The enthalpies of formation of cobalt carbonyls calculated from the above data[38,56,57] are given in Table 7. The value found in Refs. 56 and 57 for the enthalpy of formation of octacarbonyldicobalt agrees with the calculated[38] value ($-296.3 \pm 1.2$ and $-298 \pm 2$ kcal mole$^{-1}$). The average of these results is therefore given in Table 7. The enthalpy of sublimation of the dodecacarbonyl has been estimated[38]. Those of the remaining compounds have been calculated[57] from the temperature dependence of their vapour pressure studied by Knudsen's effusion method over the range 288–318 K.

From the mass-spectrometric value of $D[(CO)_4Co–Co(CO)_4] = 14.5 \pm 2.0$ kcal mole$^{-1}$ and $\Delta H_f^\circ[Co_2(CO)_8, g] = -281.5 \pm 1.3$ kcal mole$^{-1}$, we calculate that $\bar{D}$(Co–CO) = $32.6 \pm 0.4$ kcal mole$^{-1}$.

## 11. Carbonyl Compounds of Ruthenium, Rhodium, Osmium, and Iridium

Skinner et al.[38,58] have used thermal decomposition and high-temperature iodination to determine the enthalpies of formation of polynuclear carbonyls of these platinum

metals. Table 8 lists the results together with the estimated enthalpies of sublimation.

The molecule of a polynuclear carbonyl in general contains three types of chemical bonds—terminal and bridging metal–carbonyl bonds and metal–metal bonds—whose energies of rupture are denoted [38] by the respective symbols $\overline{T}$, $\overline{B}$, and $\overline{M}$. Table 8A gives the enthalpies of the dissociation processes

$$M_m(CO)_n(g) \rightarrow m\,M(g) + n\,CO(g)$$

with the types and numbers of bonds undergoing rupture.

Table 8. Thermochemical parameters (kcal mole$^{-1}$) of ruthenium, rhodium, osmium, and iridium carbonyls.

| Carbonyl | $-\Delta H_f^0$ (c) | $\Delta H_s^0$ | $-\Delta H_f^0$ (g) |
|---|---|---|---|
| $Ru_3(CO)_{12}$ | 459±5 | (24±5) | 435±7 |
| $Rh_4(CO)_{12}$ | 435±3 | (24±5) | 411±6 |
| $Rh_6(CO)_{16}$ | 578±4 | (28±5) | 550±6 |
| $Os_3(CO)_{12}$ | 418±5 | (25±5) | 393±7 |
| $Ir_4(CO)_{12}$ | 435±4 | (25±5) | 410±7 |

Table 8A.

| Carbonyl | Enthalpy of dissociation, kcal mole$^{-1}$ | No. of bonds broken on dissociation |
|---|---|---|
| $Fe_2(CO)_9$ | 281±6 | $6\overline{T}+6\overline{B}+\overline{M}$ |
| $Fe_3(CO)_{12}$ | 401±7 | $10\overline{T}+4\overline{B}+3\overline{M}$ |
| $Co_2(CO)_8$ | 275±2 | $6\overline{T}+4\overline{B}+\overline{M}$ |
| $Co_4(CO)_{12}$ | 511±7 | $9\overline{T}+6\overline{B}+6\overline{M}$ |
| $Ru_3(CO)_{12}$ | 589±7 | $12\overline{T}+3\overline{M}$ |
| $Rh_4(CO)_{12}$ | 626±6 | $9\overline{T}+6\overline{B}+6\overline{M}$ |
| $Rh_6(CO)_{16}$ | 925±7 | $12\overline{T}+8\overline{B}+11\overline{M}$ |
| $Os_3(CO)_{12}$ | 643±7 | $12\overline{T}+3\overline{M}$ |
| $Ir_4(CO)_{12}$ | 733±7 | $12\overline{T}+6\overline{M}$ |

Table 8B.

| Carbonyl | $\overline{T}$, kcal mole$^{-1}$ | $\overline{M}$, kcal mole |
|---|---|---|
| $Ru_3(CO)_{12}$ | 42 | 29 |
| $Rh_4(CO)_{12}$ | 40 | 27 |
| $Rh_6(CO)_{16}$ | 40 | 27 |
| $Os_3(CO)_{12}$ | 46 | 31 |
| $Ir_4(CO)_{12}$ | 46 | 31 |

The energies of rupture of these bonds were calculated [38,58] on the assumption that $\overline{T}$, $\overline{B}$, and $\overline{M}$ each have the same value in $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, when we obtain for $\overline{B}$ and $\overline{M}$ the values 15.5 and 19.3 kcal mole$^{-1}$ respectively. The further assumption that corresponding bond dissociation energies are equal in $Co_2(CO)_8$ and $Co_4(CO)_{12}$ gives corresponding values of 15.0 and 22.0 kcal mole$^{-1}$. Hence for the iron and cobalt carbonyls we have $\overline{M} \simeq 0.68\overline{T}$ and $\overline{B} \simeq 0.5\overline{T}$. On the assumption of the same energy distribution among bonds also in polynuclear carbonyls of ruthenium, rhodium, osmium, and iridium, the values in Table 8B were calculated [38] for $\overline{T}$ and $\overline{M}$ in these compounds. This calculation is tentative in character, because of the use of estimates of enthalpies of sublimation, and also the hypothesis of constant ratios between $\overline{T}$, $\overline{B}$, and $\overline{M}$ in carbonyls differing significantly in composition and structure.

## III. CYCLOPENTADIENYL COMPOUNDS

### 1. Dicyclopentadienyls of 3*d* elements

Cotton and Wilkinson [4] calculated the enthalpy of formation of crystalline ferrocene from its enthalpy of combustion measured in a stationary calorimetric bomb. Chemical analysis showed that the solid product was a mixture of $Fe_2O_3$ and $Fe_3O_4$, which was allowed for in the calculations. (The quantity of iron oxidised to the sesquioxide did not exceed 18%.) They obtained the value $\Delta H_f^\circ$. $[(C_5H_5)_2Fe, c] = 33.8 \pm 1.3$ kcal mole$^{-1}$. These workers also measured the enthalpy of combustion of dicyclopentadienylnickel [59], found by chemical analysis that the solid products comprised a mixture of unoxidised nickel and the monoxide, and established that the quantity of nickel oxidised did not exceed 50%. They calculated that $\Delta H_f^\circ[(C_5H_5)_2Ni, c] = 63.0 \pm 0.6$ kcal mole$^{-1}$.

More recent measurements have been made [60–62] of the enthalpies of combustion both these compounds and of the dicyclopentadienyl derivatives of vanadium, chromium, manganese, and cobalt. These yielded the values [61,62] $40.3 \pm 0.4$ and $68.2 \pm 0.4$ kcal mole$^{-1}$ for the enthalpies of formation of crystalline ferrocene and dicylcopentadienylnickel respectively. In view of the experimental difficulties in the thermochemical study of this class of compound, the agreement between the results [4,59,61,62] for the two derivatives must be regarded as satisfactory. Average values are therefore given for them in Table 9.

Table 9. Thermochemical parameters (kcal mole$^{-1}$) of dicyclopentadienyls of 3*d* metals.

| Compound | $-\Delta H_c^0$ (c) | $\Delta H_f^0$ (c) | $\Delta H_s^0$ | $-\Delta H_f^0$ (g) | $\overline{D}$ (M–$C_5H_5$) |
|---|---|---|---|---|---|
| $(C_5H_5)_2V$ | 1502±2 | 34±2 | 14±1 | 48±2 | 88±1 |
| $(C_5H_5)_2Cr$ | 1461.0±0.5 | 42.6±0.5 | 16.7±0.4 | 59.3±0.6 | 67.8±0.6 |
| $(C_5H_5)_2Mn$ | 1440.7±0.5 | 48.1±0.5 | 18.1±0.4 | 66.2±0.6 | 50.9±0.4 |
| $(C_5H_5)_2Fe$ | 1408.1±1.0 | 37.0±1.0 | 17.5±0.2 | 54.5±1.0 | 72.6±0.6 |
| $(C_5H_5)_2Co$ | 1395.5±0.5 | 56.3±0.6 | 16.8±0 5 | 73.1±0.8 | 64.6±0.6 |
| $(C_5H_5)_2Ni$ | 1405.0±1.0 | 65.6±1.0 | 17.3±0.3 | 82.9±1.0 | 59.8±0.6 |

Table 9A.

| Compound | Combustion products | Compound | Combustion products |
|---|---|---|---|
| $(C_5H_5)_2V$ | $VO_2$(10%)+$V_2O_5$ | $(C_5H_5)_2Fe$ | $Fe_2O_3$ (7–14%)+$Fe_3O_4$ |
| $(C_5H_5)_2Cr$ | $Cr_2O_3$ (100%) | $(C_5H_5)_2Co$ | Co (7–25%)+CoO (54–71%)+$Co_3O_4$ (12–25%) |
| $(C_5H_5)_2Mn$ | MnO (10–24%)+$Mn_3O_4$ | $(C_5H_5)_2Ni$ | Ni (16–50%)+NiO |

Table 9B.

| Bond | V–$C_5H_5$ | Cr–$C_5H_5$ | Mn–$C_5H_5$ | Fe–$C_5H_5$ | Co–$C_5H_5$ | Ni–$C_5H_5$ |
|---|---|---|---|---|---|---|
| $\overline{D}$, kcal mole$^{-1}$ | 90; 91 | 90; 69 | 72 | 75; 72 | 78 | 69; 69 |

In order to prevent premature oxidation and to achieve complete combustion the test substances were placed [60-62] under vacuum conditions in a known mass of molten paraffin wax, which was allowed to solidify, after which the experiments were made on the composite specimens. Because of its stability, ferrocene was ignited in several experiments in polyethylene ampoules. The mass of the organometallic compound taken for an experiment was established by determining the quantity of carbon dioxide among the combustion products. The solid products were subjected to quantitative X-ray examination and chemical analysis, which gave the compositions listed in Table 9A.

The enthalpies of combustion in Table 9 were based on the processes

$$\left.\begin{array}{l}(C_5H_5)_2V(c) + 55/4O_2(g) \rightarrow 1/2V_2O_5(c)\\ (C_5H_5)_2Cr(c) + 53/4O_2(g) \rightarrow 1/2Cr_2O_3(c)\\ (C_5H_5)_2Mn(c) + 79/6O_2(g) \rightarrow 1/3Mn_3O_4(c)\\ (C_5H_5)_2Fe(c) + 79/6O_2(g) \rightarrow 1/3Fe_3O_4(c)\\ (C_5H_5)_2Co(c) + 13O_2(g) \rightarrow CoO(c)\\ (C_5H_5)_2Ni(c) + 13O_2(g) \rightarrow NiO(c)\end{array}\right\} + 10CO_2(g) + 5H_2O(l)\ .$$

Enthalpies of sublimation were calculated from the temperature dependence [60-65] of vapour pressure. The mean $M-C_5H_5$ bond dissociation energies in Table 9 (where M = V, Cr, Mn, Fe, Co, Ni) were found by means of the equation

$$\bar{D}(M-C_5H_5) = 1/2\,\{\Delta H_f^0(M, g) + 2\Delta H_f^0(C_5H_5, g) - \Delta H_f^0[(C_5H_5)_2M, g]\}\ .$$

Mass-spectrometric study of these compounds yielded the values in Table 9B. [66,67]

Thus values of $\bar{D}(M-C_5H_5)$ obtained mass-spectrometrically in all cases exceed the corresponding thermochemical values. This is attributed to excess energy in the mass-spectrometric breakdown products of the initial compounds, which is difficult to allow for.

## 2. Cyclopentadienyl Compounds of Titanium, Zirconium, and Hafnium

The Reviewers [60,68-70] have measured the enthalpies of combustion of cyclopentadienyltitanium trichloride and of a series of compounds of general formula $(C_5H_5)_2MR_2$, where M = Ti, Zr, Hf and R = Cl, $CH_3$, $C_6H_5$, $C_6H_5CH_2$, $C_6H_5OCO$. A stationary calorimetric bomb made of a special chromium–nickel steel was used for experiments on the combustion of chlorinated compounds, in order to avoid reaction of the combustion products with the material of the bomb. Conversion into hydrogen chloride of all the chlorine present in a chlorinated compound, which was necessary to obtain a quite definite thermochemical equation, was accomplished by introducing an appropriate quantity of hydrazine hydrochloride into the bomb, in aqueous solution on the glass cloth covering its internal surface. The mass of substance taken for combustion was determined from the quantity of carbon dioxide formed. X-Ray diffraction revealed the crystalline dioxides of the metals among the products. Chemical analysis of the solid products indicated the absence of unoxidised or incompletely oxidised metals.

Table 10. Thermochemical parameters (kcal mole$^{-1}$) of cyclopentadienyl compounds of titanium, zirconium, and hafnium.

| Compound | $-\Delta H_c^0$ (c) | $\Delta H_f^0$ (c) | $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $\bar{D}$ (M–$C_5H_5$) | $\bar{D}$ (M–R) |
|---|---|---|---|---|---|---|
| $(C_5H_5)TiCl_3$ | 737.8±1.6 | −145.5±1.6 | (25±2) | −120.5±3 | 62±3 | — |
| $(C_5H_5)_2TiCl_2$ | 1427.2±1.8 | −91.6±1.8 | 28.4±0.5 | −63.2±1.8 | 64.3±1.0 | — |
| $(C_5H_5)_2Ti(CH_3)_2$ | 1914±2* | 13±2 | (19±1) | 32±2 | — | 60±2 |
| $(C_5H_5)_2Ti(CH_2C_6H_5)_2$ | 3349.3±1.2 | 46.8±1.2 | (20±2) | 66.8±2 | — | 54±2 |
| $(C_5H_5)_2Ti(OCOC_6H_5)_2$ | 2935±3 | −231±3 | — | — | — | — |
| $(C_5H_5)_2ZrCl_2$ | 1427.5±0.7 | −128.6±0.7 | 25.1±0.5 | −103.5±0.9 | 85.7±1.0 | — |
| $(C_5H_5)_2Zr(CH_3)_2$ | 1927.6±0.5 | −10.6±0.5 | 19.4±0.5 | 8.8±0.7 | — | 65.6±1.1 |
| $(C_5H_5)_2Zr(C_6H_5)_2$ | 3081.2±2.6 | 65.9±2.6 | (22±1) | 87.9±3 | — | 69.8±2.0 |
| $(C_5H_5)_2HfCl_2$ | 1432.0±0.6 | −128.1±0.6 | 25.5±0.5 | −102.8±0.8 | 85.8±0.6 | — |

*Value corrected by the authors [68].

Values of $\Delta H_c^\circ$ in Table 10 for alkylated or arylated compounds relate to their oxidation to the crystalline metal dioxide, gaseous carbon dioxide, and liquid water. Combustion of the chlorinated compounds is represented by the equations

$$(C_5H_5)TiCl_3(c) + 6.5O_2(g) \rightarrow TiO_2(c) + 5CO_2(g) + H_2O(l) + 3HCl(400H_2O, s)$$
$$(C_5H_5)_2MCl_2(c) + 13O_2(g) \rightarrow MO_2(c) + 10CO_2(g) + 4H_2O + 2HCl(200H_2O, s)$$
M–Ti, Zr or Hf.

Values of the enthalpy of sublimation in parentheses (Table 10) have been estimated from values of this function for compounds of similar composition and structure. Values of $\Delta H_s^\circ$ in the remaining cases have been calculated from the temperature dependence of vapour pressure measured by the Knudsen effusion method. We regard as incorrect the values of −1366 ± 5 and −1398 ± 5 kcal mole$^{-1}$ obtained [71] for the enthalpies of combustion of dicyclopentadienyl-titanium and -zirconium dichlorides, because of inaccurate determination [71] of the composition of the products.

The bond dissociation energies in the last two columns in Table 10 have been calculated by means of the equations

$$\bar{D}(M-C_5H_5) = 1/2\,\{\Delta H_f^0(M, g) + 2\Delta H_f^0(C_5H_5, g) + 2\Delta H_f^0(Cl, g) - \Delta H_f^0[(C_5H_5)_2MCl_2, g] - 2\bar{D}(M-Cl)\};$$
$$\bar{D}(M-R) = 1/2\,\{\Delta H_f^0(M, g) + 2\Delta H_f^0(C_5H_5, g) + 2\Delta H_f^0(R, g) - \Delta H_f^0[(C_5H_5)_2MR_2, g] - 2\bar{D}(M-C_5H_5)\}.$$

The values of $\bar{D}(M-C_5H_5)$ have been obtained on the assumption that metal–chlorine bond dissociation energies are approximately the same in the dicyclopentadienylmetal dichlorides as in the corresponding tetrachlorides. Thus within the limits of experimental error the Ti–Cl bonds have the same length in $(C_5H_5)_2TiCl_2$ as in $TiCl_4$ (2.24 ± 0.01 [72] and 2.21 ± 0.03 Å [73]); and this applies also to the Zr–Cl bonds in $(C_5H_5)_2ZrCl_2$ and $ZrCl_4$ (2.31 ± 0.01 [74] and 2.33 ± 0.05 Å [73]). The bond dissociation energies in the tetrachlorides have been calculated from the data in Table 1 as respectively 102.9 ± 0.3, 116.8 ± 0.4, and 118.6 ± 0.3 kcal mole$^{-1}$ for $\bar{D}(Ti-Cl)$, $\bar{D}(Zr-Cl)$, and $\bar{D}(Hf-Cl)$. It is significant that such calculation gives closely similar bond dissociation energies $\bar{D}(Ti-C_5H_5)$ in $C_5H_5TiCl_3$ and $(C_5H_5)_2TiCl_2$ (Table 10). This is consistent with structural measurements indicating that all the carbon atoms in these compounds are equidistant from the

titanium atom [75]. Since the error in the value adopted $\Delta H_f^\circ(C_5H_5, g) = 50$ kcal mole$^{-1}$ is unknown (Section I), it is not included in the error in the determination of $\overline{D}(M-C_5H_5)$ given in Table 10.

Study of the thermochemistry of a compound having the empirical formula $(C_5H_5)_2Ti$ was based [60] on the assumption of a monomeric ferrocene-like structure. However, it has been established [76] that this compound has a more complicated structure. Therefore the Reviewers' earlier value [60,77] of $\overline{D}(Ti-C_5H_5) = 108$ kcal mole$^{-1}$ is not the mean dissociation energy of the titanium–cyclopentadienyl bond, but represents the total enthalpy of several processes.

In the calculation of $\overline{D}(M-R)$ it has been assumed that the metal–cyclopentadienyl bond dissociation energy is the same in corresponding compounds $(C_5H_5)_2MCl_2$ and $(C_5H_5)_2MR_2$. It must be noted that the unreliability of the value of $\Delta H_f^\circ(C_5H_5, g)$ does not affect the accuracy of the calculated $\overline{D}(M-R)$ values.

The above results show clearly that $\overline{D}(Zr-C_5H_5)$ and $\overline{D}(Hf-C_5H_5)$ are closely similar and exceed $\overline{D}(Ti-C_5H_5)$ by 21 kcal mole$^{-1}$. Like the above relations among values of $\overline{D}(M-CO)$ for transition metals (Table 2–5) this corresponds to the rule [78] that the dissociation energy of the bonds formed with a given ligand (atom) increases with the atomic mass of the transition metal down a particular subgroup.

The mean dissociation energy of the zirconium–phenyl bond exceeds that of the zirconium–methyl bond by 4.2 kcal mole$^{-1}$. It is interesting that a difference of the same order is always found for non-transition metals [79]. The enthalpy of combustion $\Delta H_c^\circ = -2995 \pm 3$ kcal mole$^{-1}$ measured [68] for $(C_5H_5)_2Ti(C_6H_5)_2(c)$ led to an abnormally high dissociation energy calculated for the titanium–phenyl bond. For this reason the value given [68] for the enthalpy of combustion must be regarded as tentative.

### 3. Cyclopentadienyl Compounds of Molybdenum and Tungsten

The Reviewers have used a calorimeter with a stationary bomb to measure [69,80] the enthalpies of combustion of compounds $(C_5H_5)_2MX_2$, where M = Mo, W and X = H, Cl, I. For the combustion of chlorinated compounds reaction between the walls of the bomb and the products of combustion was prevented by the insertion of a tightly fitting tantalum pot, whose inner surface was covered with glass cloth impregnated with 10 ml of water containing 0.05 mass % of hydrogen peroxide (to ensure completely conversion of chlorine into hydrogen chloride). In all experiments the mass of hydrochloric acid found among the combustion products coincided, within the limits of experimental error, with that calculated from the mass of the initial compound. The quantity of substance taken for combustion was determined from the amount of carbon dioxide among the products. X-Ray determinatin indicated that the solid products were the crystalline trioxides of the metals. No unoxidised or incompletely oxidised metal was detected. The enthalpies of combustion [69,80] listed in Table 11 are based on the reactions

$$(C_5H_5)_2MH_2(c) + 14.5O_2(g) \rightarrow MO_3(c) + 10CO_2(g) + 6H_2O(l)$$
$$(C_5H_5)_2MCl_2(c) + 13.5O_2(g) \rightarrow MO_3(c) + 10CO_2(g) + 4H_2O(l) + 2HCl(200H_2O, s)$$
$$(C_5H_5)_2MI_2(c) + 14O_2(g) \rightarrow MO_3(c) + 10CO_2(g) + 5H_2O(l) + I_2(c).$$

The enthalpies of sublimation of the "hydrides" were calculated from the temperature dependence of vapour pressure measured [80] by the Knudsen effusion method. Those for the remaining compounds were estimated on the basis of their monomeric character is the gas phase.

Table 11. Thermochemical parameters (kcal mole$^{-1}$) of cyclopentadienyl compounds of molybdenum and tungsten.

| Compound | $-\Delta H_c^0$(c) | $\Delta H_f^0$(c) | $\Delta H_s^0$ | $\Delta H_f^0$(g) |
|---|---|---|---|---|
| $(C_5H_5)_2MoH_2$ | 1575.1±0.6 | 46.6±0.6 | 22.1±0.5 | 68.7±0.8 |
| $(C_5H_5)_2MoCl_2$ | 1448.2±0.6 | −22.9±0.6 | (24±1) | 1.1±1.2 |
| $(C_5H_5)_2MoI_2$ | 1467.4±0.5 | 7.2±0.5 | (24±1) | 31.2±1.1 |
| $(C_5H_5)_2WH_2$ | 1611.7±0.6 | 59.9±0.6 | 23.0±0.5 | 82.9±0.8 |
| $(C_5H_5)_2WCl_2$ | 1477.4±0.6 | −17.0±0.6 | (25±1) | 8.0±1.2 |
| $(C_5H_5)_2WI_2$ | 1511.5±0.7 | 28.0±0.7 | (25±1) | 53.0±1.2 |

The calculation of $\overline{D}(M-C_5H_5)$ and $\overline{D}(M-X)$ for these compounds was similar to the above calculation of bond dissociation energies for titanium, zirconium, and hafnium compounds $(C_5H_5)_2MR_2$. It was assumed that here $\overline{D}(Mo-Cl)$ and $\overline{D}(W-Cl)$ are approximately equal to those in the hexachlorides (72.6 ± 1.7 and 83.0 ± 0.2 kcal mole$^{-1}$) calculated from the data in Table 1. This postulate should correspond to approximate equality of metal–chlorine internuclear distances between the molybdenum and tungsten test compounds and their respective hexachlorides. Unfortunately, the structural data required for comparison are lacking. However, the molybdenum–chlorine bond length is known to be 2.47 Å [81] in $(C_5H_5)_2$.$MoCl_2$, but 2.27 ± 0.02 Å [73] in molybdenum pentachloride. Since a decrease in the energy of rupture of a bond corresponds to an increase in its length, and $\overline{D}(Mo-Cl)$ is 9.1 kcal mole$^{-1}$ smaller in molybdenum hexachloride than in the pentachloride (calculated from standard data [9]), the bond is probably longer in the hexachloride, and the postulated approximate equality of $\overline{D}(Mo-Cl)$ in $(C_5H_5)_2MoCl_2$ and $MoCl_6$ is likely to be correct. The calculated results in Table 12 show that both $\overline{D}(M-C_5H_5)$ and $\overline{D}(M-X)$ are larger for tungsten than for molybdenum.

### 4. Cyclopentadienyl Compounds of Platinum

A massive microcalorimeter has been used [82] to measure the enthalpies of combustion of crystalline cyclopentadienyltrimethylplatinum and dicyclopentadienyldimethylplatinum as respectively −1270.8 ± 0.5 and −1706.3 ± 1.7 kcal mole$^{-1}$, the products being gaseous carbon dioxide, liquid water, and crystalline platinum. These values were used to calculate the corresponding heats of formation $\Delta H_f^\circ(c)$ are 40.3 ± 0.5 and 31.2 ± 1.7 kcal mole$^{-1}$.

The enthalpy of sublimation of the trimethyl derivative was calculated from the temperature dependence of the vapour pressure studied by the Knudsen effusion method, which gave $\Delta H_s^\circ = 18.6 \pm 0.5$ kcal mole$^{-1}$ for the range 290–305 K. The enthalpy of sublimation of the dicyclopentadienyl compound was taken to be 20 ± 1 kcal mole$^{-1}$. We then have for the heats of formation in the gaseous state $\Delta H_f^\circ(g)$ the respective values 58.9 ± 0.7 and 51.2 ± 1.9 kcal mole$^{-1}$.

On the assumption that bond dissociation energies are constant in these compounds, comparison of the heats of formation in the gaseous state yields $\overline{D}(Pt-C_5H_5) = 75 \pm 3$ and $\overline{D}(Pt-CH_3) = 51 \pm 1$ kcal mole$^{-1}$.

Table 12. Mean dissociation energies (kcal mole$^{-1}$) in cyclopentadienyl compounds of molybdenum and tungsten.

| Compound | $\overline{D}$ (M–$C_5H_5$) | $\overline{D}$ (M–H) | $\overline{D}$ (M–I) |
|---|---|---|---|
| $(C_5H_5)_2MoCl_2$ | 84.3±1.8 | — | — |
| $(C_5H_5)_2MoI_2$ | 84.3±1.8 | — | 54.1±2.0 |
| $(C_5H_5)_2MoH_2$ | 84.3±1.8 | 61.9±1.9 | — |
| $(C_5H_5)_2WCl_2$ | 94.4±0.8 | — | — |
| $(C_5H_5)_2WI_2$ | 94.4±0.8 | — | 57.0±1.1 |
| $(C_5H_5)_2WH_2$ | 94.4±0.8 | 68.6±1.0 | — |

### 5. Tricyclopentadienyl Derivatives of Rare-earth Metals

Enthalpies of combustion have been measured[83] for the tricyclopentadienyl compounds of scandium, yttrium, lanthanum, praseodymium, thulium, and ytterbium. X-ray diffraction has established formation of the crystalline oxide $Pr_6O_{11}$ but the crystalline sesquioxides of the other five rare-earth metals. Neither unoxidised metals nor oxides of other compositions were detected among the products of combustion. Table 13 lists the standard enthalpies of combustion to gaseous carbon dioxide, liquid water, and the metal oxide. It includes the standard enthalpies of formation in crystalline and gaseous states together with the mean $M-C_5H_5$ bond dissociation energies.

Table 13. Thermochemical parameters (kcal mole$^{-1}$) of tricyclopentadienyls of rare-earth metals.

| Compound | $-\Delta H_c^0$ (c) | $\Delta H_f^0$ (c) | $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $\overline{D}$ (M–$C_5H_5$) |
|---|---|---|---|---|---|
| $(C_5H_5)_3Se$ | 2148±1 | −3.2±1 | 26.2±1 | 23.0±1.5 | 72.7±0.5 |
| $(C_5H_5)_3Y$ | 2140±1 | −10.8±1 | 26.7±1 | 15.9±1.5 | 78.5±0.5 |
| $(C_5H_5)_3La$ * | 2146±1 | −6.4±1 | 27.4±1 | 21.0±1.5 | 77.3±0.5 |
| $(C_5H_5)_3Pr$ | 2144±2 | −6.7±2 | 30.0±1 | 23.3±2.0 | 71.9±1.0 |
| $(C_5H_5)_3Tm$ | 2137±1 | −11.8±1 | 26.6±1 | 14.8±1.5 | 64.8±0.5 |
| $(C_5H_5)_3Yb$ | 2147±1 | 7.0±1 | 26.0±1 | 33.0±1.5 | 51.1±0.5 |

*We have used the value $\Delta H_f^\circ(La_2O_3, c) = -458$ kcal mole$^{-1}$ taken from tables[15] in calculating $\Delta H_f^\circ[(C_5H_5)_3La, c]$. In Ref. 84 the enthalpy of formation of lanthanum sesquioxide was given as −428.6 kcal mole$^{-1}$, which is significantly lower than the values for scandium and yttrium sesquioxides (−456.4 and −455.4 kcal mole$^{-1}$). This casts doubt on the accuracy of the latter results[84], since the enthalpies of formation of the same type of oxides of other transition metals increase with the atomic number of the metal (Table 1).

Heats of formation of the gaseous cyclopentadienyls have been calculated from enthalpies of sublimation found from the temperature dependence of vapour pressure[85,86] over the range 473–673 K. We assumed that the enthalpies of sublimation of these compounds at 298.15 K exceed by 3 ± 1 kcal mole$^{-1}$ the experimental values for the above temperature range. Mass-spectrometric results were used[87] to calculate the enthalpy of the process

$$(C_5H_5)_3Yb(g) \rightarrow (C_5H_5)_2Yb(g) + C_5H_5(g),$$

as 58 ± 5 kcal mole$^{-1}$. Together with data in Table 13 this yields $\Delta H_f^\circ[(C_5H_5)_2Yb, g] = 41 \pm 5$ and $\overline{D}(Yb-C_5H_5) = 48 \pm 3$ kcal mole$^{-1}$. Hence the energies of dissociation of the ytterbium–cyclopentadienyl bond in tri- and di-cyclopentadienylytterbium are closely similar, which indicates a low energy of transition of ytterbium from the bivalent to the tervalent state.

## IV. ARENE COMPOUNDS

### 1. Dibenzenevanadium

The enthalpy of combustion of dibenzenevanadium

$$(C_6H_6)_2V(c) + 16.25O_2(g) \rightarrow 0.5V_2O_5(c) + 12CO_2(g) + 6H_2O(l)$$

was determined[88] as $\Delta H_c^\circ = -1732.7 \pm 1.8$ kcal mole$^{-1}$, which corresponds to $\Delta H_f^\circ[(C_6H_6)_2V, c] = 8.7 \pm 2.4$ kcal mole$^{-1}$. Premature oxidation was prevented by placing the compound in glass ampoules. However, the combustion products were not analysed[88], so that the above value for the enthalpy of combustion cannot be accepted as reliable, in view of the tendency of vanadium to exist in various states of oxidation (VO, $V_2O_3$, $VO_2$, and $V_2O_5$).

For the enthalpy of sublimation Fischer et al.[88,89] give the value 8.9 kcal mole$^{-1}$. However, this has been shown[90] to be incorrect, for $\Delta H_s^\circ \simeq 18$ kcal mole$^{-1}$. From this we find that $\Delta H_f^\circ[(C_6H_6)_2V, g] = 26.7 \pm 2.6$ kcal mole$^{-1}$, whence we obtain also $\overline{D}(V-C_6H_6) = 77.0 \pm 1.4$ kcal mole$^{-1}$.

### 2. Dibenzenechromium

The enthalpy of combustion in a stationary calorimetric bomb was given[91] as $\Delta H_c^\circ = -1696 \pm 8$ kcal mole$^{-1}$. The dibenzenechromium was placed in molten thymol to eliminate premature oxidation. More accurate determination was regarded[91] as impossible because of the large heat of combustion, the need to use auxiliary materials, and the difficulties in calculating several corrections. However, this is unconvincing, since the work[91] involved defects of method. The quantity of heat produced by the combustion of thymol amounted to 50–70% of the total quantity evolved in the bomb during the experiment. The heat of combustion, which was required to calculate the appropriate correction, was found with an error of ~0.2%. It can easily be reckoned that this will lead to an error of 3–6 kcal mole$^{-1}$ in $\Delta H_c^\circ[(C_6H_6)_2Cr, c]$.

Furthermore, determination of carbon dioxide and analysis of the solid products showed[91] that a high degree of combustion was not achieved: the quantity of the former was considerably smaller than expected, and the solid products contained elementary chromium. Since neither free nor combined carbon was detected in the solid phase, it was concluded[91] that the gaseous products included carbon monoxide, whose quantity was calculated.

Appropriate corrections for incomplete oxidation of carbon and chromium (respectively 5–49 and 3–21 kcal mole$^{-1}$) were made in processing the experimental results. However, such a procedure for determining the quantity of carbon monoxide among the combustion products is not exact, since carbon-containing products of thermal decomposition of the initial compound may be formed in the absence of a high degree of combustion.

A subsequent determination[92] of the enthalpy of combustion of dibenzenechromium gave $\Delta H_c^\circ = -1725.4 \pm 2.0$ kcal mole$^{-1}$. It is impossible to assess the reliability of this value because of the absence of any detailed description of the experiment[92].

Because of the sharp divergence between these results[91,92] the Reviewers redetermined the enthalpy of combustion of dibenzenechromium[93]. The compound was purified by repeated vacuum sublimation, and placed in polyethylene ampoules in the bomb. The mass taken for combustion was established by determining carbon dioxide in the products. Analysis of the solid products showed that neither unoxidised chromium nor unoxidised carbon was present, and a qualitative test for carbon monoxide in the gaseous products (which were passed through aqueous palladium dichloride) gave a negative result. The values obtained were $\Delta H_c^\circ = -1710 \pm 2$ and $\Delta H_f^\circ[(C_6H_6)_2Cr, c] = 35 \pm 2$ kcal mole$^{-1}$. Other workers[54] studied the high-temperature iodination of dibenzenechromium and obtained for the heat of formation 34 ± 2 kcal mole$^{-1}$, which agrees with the Reviewers' value[93] within the limits of experimental error.

Taking the average of these results[54,93] and using the heat of sublimation[94] $\Delta H_s^\circ = 19.6 \pm 0.5$ kcal mole$^{-1}$, we have $\Delta H_f^\circ[(C_6H_6)_2Cr, c] = 35.4 \pm 1.0$ and $\Delta H_f^\circ[(C_6H_6)_2Cr, g] = 54.1 \pm 1.1$ kcal mole$^{-1}$, and find from the latter that $\bar{D}(Cr-C_6H_6) = 40.2 \pm 0.7$ kcal mole$^{-1}$. This result agrees well with the mass-spectrometric values[95,96] of 40.5 and 39 kcal mole$^{-1}$, but is lower than the mass-spectrometric value[97] of 46 kcal mole$^{-1}$. It is interesting that considerably less energy is required to detach the first benzene ring than to detach the second: thus[96] $D_1(C_6H_6-CrC_6H_6) = 23$ and $D_2(Cr-C_6H_6) = 55$ kcal mole$^{-1}$.

### 3. Compounds of Chromium with Alkylated Benzenes

A stationary calorimetric bomb was used[92] to measure the enthalpies of combustion of compounds formed by chromium with methylated benzenes, and the Reviewers have studied[98] ethyl and isopropyl derivatives of dibenzenechromium by the same method. The enthalpies obtained for combustion of these compounds to crystalline chromium(III) oxide, gaseous carbon dioxide, and liquid water, together with the calculated standard enthalpies of formation and the mean chromium–ligand bond dissociation energies, are given in Table 14. Analytical data were absent[92] for solid and gaseous combustion products from compounds (I) and (II). In view of the closely similar results obtained for them (as was to be expected for compounds having the same composition and similar structures), however, the values given for the enthalpies of combustion are probably feasible: the formation of products of the incomplete combustion of (I) and (II) of the same nature and mass is improbable because of the non-standard conduct of the experiments. The solid combustion products from compounds (III)–(VI) were subjected[98] to X-ray examination and chemical analysis, when products of the incomplete oxidation of chromium were not detected.

Table 14 contains for compound (VI) the chromium–isopropylbenzene bond dissociation energy, calculated by means of the equation

$$\bar{D}(Cr-C_6H_5C_3H_7) = \Delta H_f^\circ(Cr, g) + \Delta H_f^\circ[C_6H_4(C_3H_7)_2, g] + \\ + \Delta H_f^\circ(C_6H_5C_3H_7, g) - \Delta H_f^\circ[(VI), g] - \bar{D}[Cr-C_6H_4(C_3H_7)_2]$$

on the assumption that $\bar{D}[Cr-C_6H_4(C_3H_7)_2]$ has the same value in (V) and (VI).

The enthalpies of sublimation of (I) and (II) were calculated[92] from the measured temperature dependence of vapour pressure as respectively 15.4 and 8.0 kcal mole$^{-1}$. The marked difference between these values casts doubt on their accuracy. In order to calculate $\Delta H_f^\circ(g)$ the Reviewers have assumed that the enthalpies of sublimation of these compounds differ little from the value for dibenzenechromium and are ~20 kcal mole$^{-1}$. The enthalpies of vaporisation of compounds (III)–(VI) have been taken from the literature[90,94,99–101].

Table 14 shows that the chromium–ligand bond dissociation energy in compounds (I)–(VI) is the same within the limits of experimental error. Mass spectrometry gave[97] for $\bar{D}[Cr-C_6H_3(CH_3)_3]$ in compound (I) the value 61 kcal mole$^{-1}$, which is considerably larger than the corresponding thermochemical value. The discrepancies often met between published thermochemical and mass-spectrometric results are due mainly to the absence of a reliably established mechanism of the breakdown of an organometallic compound on electron bombardment and also to the presence of excess energy in the breakdown products.

### 4. Diarenechromium Halides

Enthalpies of combustion have been measured and standard enthalpies of formation calculated[93] for dibenzenechromium chloride and bromide, and ditoluene, di-*m*-xylene, dimesitylene-, and dibiphenyl-chromium iodides

**Table 14.** Thermochemical parameters (kcal mole$^{-1}$) of compounds of chromium with alkylated benzenes.

| No. | Compound | $-\Delta H_c^0$ | $\Delta H_f^0$ | $\Delta H_s^0$ | $\Delta H_v^0$ | $\Delta H_f^0$ (g) | $\bar{D}$ (Cr – Ligand) |
|---|---|---|---|---|---|---|---|
| (I) | [1,3,5-$C_6H_3(CH_3)_3]_2Cr$(c) | 2638.0±3.0 | −11.0±3.0 | 20±1 | — | 9.0±3.1 | 39.1±1,6 |
| (II) | [1,2,4-$C_6H_3(CH_3)_3]_2Cr$(c) | 2640.0±1.9 | −9.0±1.9 | 20±1 | — | 11.0±2.2 | 38.7±1,3 |
| (III) | $(C_6H_5C_2H_5)_2Cr$(l) | 2340.1±0.8 | 15.9±0.8 | — | 18±2 | 33.9±2.2 | 37.7±1,3 |
| (IV) | [*o*-$C_6H_4(C_2H_5)_2]_2Cr$(l) | 2962.5±1.7 | −11.3±1.7 | — | 18±2 | 6,7±2.6 | 39.6±1.5 |
| (V) | [*o*-$C_6H_4$(iso-$C_3H_7)_2]_2Cr$(l) | 3576.6±1.8 | −46.7±1.8 | — | 24±2 | −22.7±2.6 | 41.8±1.5 |
| (VI) | [*o*-$C_6H_4$(iso-$C_3H_7)_2$]Cr($C_6H_5$ iso-$C_3H_7$)(l) | 3106.5±1.6 | −29.7±1.6 | — | 24±2 | −5.7±2.5 | 42.8±2.2 |

(Table 15). A tightly fitting tantalum pot prevented interaction between the walls of the bomb and the halides. In the determination of the enthalpy of combustion of dibenzenechromium chloride complete conversion of chlorine into hydrogen chloride was ensured by covering the inside surface of the bomb also with glass cloth impregnated with aqueous hydrazine dihydrochloride. Absence of unoxidised or incompletely oxidised chromium and carbon was shown in every experiment by analysis of the combustion products. Furthermore, hydrogen bromide was absent from the products of the combustion of dibenzenechromium bromide, and hydrogen chloride from those of the chloride.

Skinner et al.[54] obtained for the thermal decomposition

$$(C_6H_6)_2CrI(c) \rightarrow Cr(c) + 2C_6H_6(g) + 0.5I_2(g)$$

the enthalpy $\Delta H_r^\circ = 35 \pm 1$ kcal mole$^{-1}$, which corresponds to $\Delta H_f^\circ[(C_6H_6)_2CrI, c] = 12 \pm 1$ kcal mole$^{-1}$. In determining the enthalpy of combustion the Reviewers[102] paid especial attention to purifying the compound, and obtained for the process

$$(C_6H_6)_2CrI(c) + 15.75O_2(g) \rightarrow 0.5Cr_2O_3(c) + 12CO_2(g) + 6H_2O(l) + 0.5I_2(c)$$

the value† $\Delta H_c^\circ = -1684.8 \pm 0.5$ kcal mole$^{-1}$, corresponding to $\Delta H_f^\circ[(C_6H_6)_2CrI, c] = 10.0 \pm 0.5$ kcal mole$^{-1}$, close to Skinner's result[54].

Table 15. Thermochemical parameters (kcal mole$^{-1}$) of diarenechromium halides.

| Compound | $-\Delta H_c^0$ (c) | Combustion products | $\Delta H_f^0$ (c) |
|---|---|---|---|
| $(C_6H_6)_2CrCl$ | 1670±3 | $Cr_2O_3$ (c), $CO_2$ (g), $H_2O$ (l), HCl (400 $H_2O$, s) | −10±3 |
| $(C_6H_6)_2CrBr$ | 1674±2 | $Cr_2O_3$ (c), $CO_2$ (g), $H_2O$ (l), $Br_2$ (l) | −1±2 |
| $(C_6H_5CH_3)_2CrI$ | 1983±1 | $Cr_2O_3$ (c), $CO_2$ (g), $H_2O$ (l), $I_2$ (c) | −17±1 |
| $(m\text{-}C_6H_4(CH_3)_2)_2CrI$ | 2297±2 | $Cr_2O_3$ (c), $CO_2$ (g), $H_2O$ (l), $I_2$ (c) | −27±2 |
| $(1,3,5\text{-}C_6H_3(CH_3)_3)_2CrI$ | 2604±2 | $Cr_2O_3$ (c), $CO_2$ (g), $H_2O$ (l), $I_2$ (c) | −45±2 |
| $(C_6H_5C_6H_5)_2CrI$ | 3113±2 | $Cr_2O_3$ (c), $CO_2$ (g), $H_2O$ (l), $I_2$ (c) | 36±2 |

Table 16. Thermochemical parameters (kcal mole$^{-1}$) of tetra-alkoxytitanium compounds $(RO)_4Ti$.

| R | $\Delta H_r^0$ | $-\Delta H_f^0$ [$(RO)_4Ti$ (l)] | $\Delta H_o^0$ | $-\Delta H_f^0$ [$(RO)_4Ti$, (g)] | $\bar{D}$ (RO—Ti) |
|---|---|---|---|---|---|
| $C_2H_5$ | — | 349.0±1.4 | (24±2) | 325.0±2.5 | 102.8±1.0 |
| n-$C_3H_7$ | 0.602±0.00 | 376±4.2 | (18±2) | 358±4 | 107±2 |
| iso-$C_3H_7$ | 10.57±0.09 | 379±1.6 | (17±2) | 362±3 | 106±2 |
| n-$C_4H_9$ | −1.98±0.02 | 398±1.6 | (22±2) | 376±3 | 105±2 |
| iso-$C_4H_9$ | 0.305±0.002 | 403±1.5 | (22±2) | 381±2 | 105±2 |
| s-$C_4H_9$ | 6.88±0.05 | 404±1.5 | (22±2) | 382±2 | 104±2 |
| t-$C_4H_9$ | 15.8±0.12 | 411±1.5 | 15.8±0.8 | 395±2 | 104±2 |
| n-$C_5H_{11}$ | −2.29±0 03 | 429±2.2 | (25±2) | 404±2 | 106±2 |
| t-$C_5H_{11}$ | 11.27±0.08 | 458±2 | 18.5±0.9 | 439±2 | 109±2 |

### 5. Dibenzenemolybdenum

The enthalpy of combustion was found[88] to be $\Delta H_c^\circ$. $[(C_6H_6)_2Mo, c] = -1789.8 \pm 2.2$ kcal mole$^{-1}$, but no analysis of the combustion products was reported[88]. The assumed equation

$$(C_6H_6)_2Mo(c) + 16.5O_2(g) \rightarrow MoO_3(c) + 12CO_2(g) + 6H_2O(l).$$

yielded $\Delta H_f^\circ[(C_6H_6)_2Mo, c] = 73.2 \pm 2.2$ kcal mole$^{-1}$. Using[88,101] $\Delta H_S^\circ = 22 \pm 1$ kcal mole$^{-1}$, we find that $\Delta H_f^\circ[(C_6H_6)_2Mo, g] = 95.2 \pm 2.4$ kcal mole$^{-1}$. Mass spectrometry gives[104] $\bar{D}(Mo-C_6H_6) = 59$ kcal mole$^{-1}$.

## V. ALKOXY-COMPOUNDS

### 1. Alkoxy-compounds of Titanium

Determinations[105] of the enthalpies of the processes

$$TiCl_4(l) + 4C_2H_5OH(l) \rightarrow (C_2H_5O)_4Ti(l) + 4HCl(g)$$
$$TiCl_4(l) + 4C_2H_5OH(l) \rightarrow (C_2H_5O)_4Ti(l) + 4HCl(51.3H_2O, s)$$

gave respectively 19.5 ± 0.4 and −49.1 ± 0.6 kcal mole$^{-1}$, from which calculation gave for the enthalpy of formation of liquid tetraethoxytitanium the values −349.7 ± 1.8 and −348.4 ± 2.0 kcal mole$^{-1}$ in good agreement.

The enthalpy of formation of solid tetraethoxytitanium was calculated[106] from the enthalpy of combustion determined in a stationary calorimetric bomb: for the process

$$(C_2H_5O)_4Ti(c) + 12O_2(g) \rightarrow TiO_2(c) + 8CO_2(g) + 10H_2O(l)$$

the value $\Delta H_c^\circ = -1308.6 \pm 1.2$ was obtained, whence it was found that $\Delta H_f^\circ[(C_2H_5O)_4Ti, c] = -352.6 \pm 1.2$ kcal mole$^{-1}$. The enthalpy of fusion of this compound was estimated[106] as 3–6 kcal mole$^{-1}$. Good agreement is evident between these results[105,106].

Averaging the results[105] gave $\Delta H_f^\circ[(C_2H_5O_4)_4Ti, l] = -349.0 \pm 1.4$ kcal mole$^{-1}$, which was used to find[107] enthalpies of formation of several other alkoxytitanium compounds. For this purpose calorimetric determinations were made[107] of the enthalpies of the reactions

$$(C_2H_5O)_4Ti(l) + 4ROH(l) \rightarrow (RO)_4Ti(l) + 4C_2H_5OH(l),$$

where R = n-$C_3H_7$, iso-$C_3H_7$, n-$C_4H_9$, iso-$C_4H_9$, s-$C_4H_9$, t-$C_4H_9$, n-$C_5H_{11}$, and t-$C_5H_{11}$. The results of these measurements ($\Delta H_r^\circ$) and those of the corresponding calculations are given in Table 16.

The heats of formation of tetra-n-butoxy- and tetra-t-pentyloxy-titanium were checked[107] by studying the thermochemistry of the processes

$$[(C_2H_5)_2N]_4Ti(l) + 4n\text{-}C_4H_9OH(l) \rightarrow n\text{-}C_4H_9O)_4Ti(l) + 4(C_2H_5)_2NH(l),$$

$$[(C_2H_5)_2N]_4Ti(l) + 4t\text{-}C_5H_{11}OH(l) \rightarrow (t\text{-}C_5H_{11}O)_4Ti(l) + 4(C_2H_5)_2NH(l),$$

for which $\Delta H_r^\circ$ was respectively −69.4 ± 0.6 and −55.4 ± 0.4 kcal mole$^{-1}$. From the value found[107] for the heat of formation of tetrakisdiethylaminetitanium $\Delta H_f^\circ(l) = -116.8$ kcal mole$^{-1}$ and the known values for the alcohols and diethylamine it was calculated[107] that $\Delta H_f^\circ[(n\text{-}C_4H_9O)_4Ti, l] = -399$ and $\Delta H_f^\circ[(t\text{-}C_5H_{11}O)_4Ti, l] = -457$ kcal mole$^{-1}$, in good agreement with the values in Table 16.

Enthalpies of vaporisation (Table 16) were estimated[107] from the experimental values for tetra-t-butoxy- and tetra-t-pentyloxy-titanium, with allowance for depolymerisation of the compounds on evaporation. Table 16 shows that values of $\bar{D}$(RO—Ti) are little affected by the nature of the radical, and the mean must be taken as 105 ± 2 kcal mole$^{-1}$.

† In an earlier determination[103] we had obtained the low value $\Delta H_c^\circ = -1664$ kcal mole$^{-1}$, probably owing to inadequate purification of the specimen of dibenzenechromium iodide.

Shaulov et al.[108] used combustion in a stationary calorimetric bomb, and obtained for the enthalpies of formation of tetraisopropoxytitanium and tetra-n-butoxytitanium the respective values $-372.3 \pm 1.2$ and $-392.7 \pm 4.2$ kcal mole$^{-1}$, which differed by a few kilocalories per mole from those in Ref. 107 (Table 16).

Lappert et al.[109] determined the enthalpy of the process

$$TiCl_4(l) + 4iso\text{-}C_3H_7OH(l) \rightarrow (iso\text{-}C_3H_7O)_4Ti(l) + 5HCl(g)$$

and obtained $\Delta H_r^\circ = 19.3 \pm 1.2$ kcal mole$^{-1}$, which corresponds to $\Delta H_f^\circ[(iso\text{-}C_3H_7O)_4Ti, l] = -389 \pm 2$ kcal mole$^{-1}$. This value exceeds by 10 and 17 kcal mole$^{-1}$ respectively those obtained by the above workers[107,108]. The reasons for the discrepancy in these results[107-109] are obscure. Nevertheless, the detailed discussion[107] of the experimental conditions and the necessary corrections lead to acceptance of the results in Ref. 107 as the most soundly based.

## 2. Alkoxy-compounds of Vanadium and Chromium

Bradley and Hillyer[110] determined the enthalpies of the reactions of vanadium tetrachloride and of tetra-t-butoxyvanadium with aqueous hydrochloric acid, and found the enthalpy of the overall process

$$VCl_4(l) + 4t\text{-}C_4H_9OH(l) \rightarrow (t\text{-}C_4H_9O)_4V(l) + 4HCl(51.3H_2O, s)$$

to be $-22.7 \pm 0.9$ kcal mole$^{-1}$. Table 17 gives the enthalpy of formation of tetrabutoxyvanadium calculated from this result together with that of tetra-t-butoxychromium calculated[110] from its enthalpy of hydrolysis in aqueous sulphuric acid, allowing for the possibility of disproportionation of quadrivalent chromium to the tervalent and sexivalent states.

Table 17. Thermochemical parameters (kcal mole$^{-1}$) of alkoxy-derivatives of vanadium and chromium.

| Compound | $-\Delta H_f^0$ (l) | $\Delta H_v^0$ | $-\Delta H_f^0$ (g) | $\bar{D}$(t-C$_4$H$_9$O-M) |
|---|---|---|---|---|
| (t-C$_4$H$_9$O)$_4$V | 344±1 | (15.8±1) | 328.2±1.4 | 90±2 |
| (t-C$_4$H$_9$O)$_4$Cr | 321±1 | (15.8±1) | 305.2±1.4 | 77±2 |

The enthalpies of vaporisation of these complexes were equated[110] to the experimental value for tetra-t-butoxytitanium (Table 16).

## 3. Alkoxy-compounds of Zirconium and Hafnium

Lappert et al.[109] found that the enthalpy $\Delta H_r^\circ$ of the process

$$MCl_4(l) + 4iso\text{-}C_3H_7OH(l) \rightarrow (iso\text{-}C_3H_7O)_4M(c) + 4HCl(g)$$

was respectively $21.4 \pm 1.8$ and $10.4 \pm 1.8$ kcal mole$^{-1}$ when M = Zr and Hf. Enthalpies of formation of the alkoxy-compounds of zirconium and hafnium calculated from the results are given in Table 18. Enthalpies of sublimation were estimated[109] from the enthalpy of vaporisation of tetraisopropoxytitanium (Table 16) and their assumed value of 3 kcal mole$^{-1}$ for the enthalpy of fusion.

Comparison of the values in Table 18 with that in Table 16 for $\bar{D}$(RO–Ti) indicates that

$$\bar{D}(iso\text{-}C_3H_7\text{–}Ti) < \bar{D}(iso\text{-}C_3H_7O\text{–}Zr) < \bar{D}(iso\text{-}C_3H_7O\text{–}Hf)$$

i.e. $\bar{D}$(RO–M) increases with increase in the atomic number of the metal as Group IV of the Periodic System is descended.

Table 18. Thermochemical parameters (kcal mole$^{-1}$) of alkoyx-derivatives of zirconium and hafnium.

| Compound | $-\Delta H_f^0$ (c) | $\Delta H_s^0$ | $-\Delta H_f^0$(g) | $\bar{D}$(iso-C$_3$H$_7$O-M) |
|---|---|---|---|---|
| (iso-C$_3$H$_7$O)$_4$Zr | 429±1.8 | (20±5) | 409±5 | 126±2 |
| (iso-C$_3$H$_7$O)$_4$Hf | 443±1.8 | (20±5) | 423±5 | 130±2 |

## 4. Alkoxy-compounds of Niobium and Tantalum

The Reviewers[111] have determined the enthalpies of combustion of the penta-alkoxy-compounds $(RO)_5M$, in which M = Nb, Ta and R = $CH_3$, $C_2H_5$, n-$C_3H_7$. X-Ray phase analysis showed that the solid combustion products were niobium and tantalum pentoxides respectively. No products of incomplete oxidation of the metals were detected. Combustion of the test compounds was represented by the equation

$$(C_nH_{2n+1}O)_5M(l, c) + 7.5O_2(g) \rightarrow 0.5M_2O_5(c) + 5nCO_2(g) + (5n + 2.5)H_2O(l).$$

The values obtained for the enthalpies of combustion and the standard enthalpies of formation calculated from them are given in Table 19 together with the mean RO–M bond dissociation energies. Enthalpies of vaporisation were calculated from the temperature dependence of vapour pressure measured by the Knudsen effusion method. The enthalpies of fusion of crystalline niobium and tantalum methoxides were estimated as $3 \pm 1$ kcal mole$^{-1}$.

Table 19. Thermochemical parameters (kcal mole$^{-1}$) of alkoxy-compounds of niobium and tantalum.

| Compound | $-\Delta H_c^0$ | $-\Delta H_f^0$ | $\Delta H_s^0$ | $\Delta H_v^0$ | $-\Delta H_f^0$(g) | $\bar{D}$ (RO–M) |
|---|---|---|---|---|---|---|
| (CH$_3$O)$_5$Nb(c) | 871.5±0.4 | 337.9±0.6 | 19.2±2.5 | — | 318.7±2.6 | 100.3±2.0 |
| (C$_2$H$_5$O)$_5$Nb(l) | 1642.6±0.4 | 378.6±0.6 | — | 18.9±2.0 | 359.7±2.1 | 99.8±1.0 |
| (n-C$_3$H$_7$O)$_5$Nb(l) | 2426.4±0.8 | 406.7±1.0 | — | 24.4±1.6 | 382.3±1.8 | 99.8±2.0 |
| (CH$_3$O)$_5$Ta(c) | 878.3±0.4 | 349.0±0.6 | 21.1±3.2 | — | 327.9±3.3 | 105.2±2.0 |
| (C$_2$H$_5$O)$_5$Ta(l) | 1647.3±0.5 | 391.8±0.7 | — | 18.9±2.0 | 273.9±2.1 | 105.5±1.0 |
| (n-C$_3$H$_7$O)$_5$Ta(l) | 2430.2±0.8 | 420.7±1.0 | — | 26.6±2.1 | 394.1±2.3 | 105.2±2.0 |

Comparison of the RO–M bond dissociation energies in Table 19 with the RO–V value in Table 17 indicates that

$$\bar{D}(RO\text{–}V) < \bar{D}(RO\text{–}Nb) < \bar{D}(RO\text{–}Ta).$$

Thus, as in other cases, the RO–M bond dissociation energy increases with atomic number of the metal.

## VI. CONCLUSION

The most reliable values for the enthalpies of formation $\Delta H_f^\circ$ of organic compounds of transition metals and the mean bond dissociation energies $\bar{D}$ calculated from them are assembled in Tables 20–23. The experimental results collected in them and illustrated by Figs. 1–4 reveal corresponding rules for the mean energy of dissociation of the chemical bonds formed by transition metals in their organic compounds.

Table 20. Thermochemical parameters (kcal mole$^{-1}$) of carbonyl compounds of transition metals.

| Carbonyl | $-\Delta H_f^0$* | $-\Delta H_f^0$(g) | $\bar{D}$(M-CO) |
|---|---|---|---|
| $Ni(CO)_4$(l) | 150.4±1.5 | 143.8±1.5 | 35.2±0.4 |
| $Fe(CO)_5$(c) | 182.6±1.8 | 173.0±1.8 | 28.1±0.4 |
| $Fe_2(CO)_9$(c) | 337±3 | 319±6 | — |
| $Fe_3(CO)_{12}$(c) | 442±4 | 419±7 | — |
| $Mn_2(CO)_{10}$(c) | 404.6±2.0 | 385.4±2.0 | 23.6±0.4 |
| $CH_3Mn(CO)_5$(c) | 189.8±2.2 | 174.8±2.3 | — |
| $ClMn(CO)_5$(c) | 241.2±3 | — | — |
| $BrMn(CO)_5$(c) | 231.8±2 | — | — |
| $C_2H_5Mn(CO)_3$(c) | 127.8±2 | 115.3±2.1 | — |
| $Cr(CO)_6$(c) | 234.3±0.4 | 217.2±0.4 | 25.6±0.1 |
| $(C_6H_6)Cr(CO)_3$(c) | 106±2 | 84.2±2.2 | — |
| $(C_6H_5CH_3)Cr(CO)_3$(c) | 114±2 | 91.4±2.2 | — |
| $[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$(c) | 136.5±2 | 110.6±2.2 | — |
| $[C_6(CH_3)_6]Cr(CO)_3$(c) | 166.5±3 | 137.0±3.2 | — |
| $(C_6H_5Cl)Cr(CO)_3$(c) | 111±5 | 86.5±5.1 | — |
| $(cyclo\text{-}C_7H_8)Cr(CO)_3$(c) | 74±3 | 51.5±3.2 | — |
| $Mo(CO)_6$(c) | 236.6±0.2 | 219.0±0.3 | 36.2±0.1 |
| $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$(c) | 119±1 | — | — |
| $W(CO)_6$(c) | 229.5±0.7 | 211.2±0.8 | 42.9±0.2 |
| $Co_2(CO)_8$(c) | 297.1±1.0 | 281.5±1.3 | 32.6±0.4 |
| $Co_4(CO)_{12}$(c) | 441±4 | 418±7 | — |
| $Co_3(CCl)(CO)_9$(c) | 280.5±2.2 | 256.7±2.2 | — |
| $Co_3(CBr)(CO)_9$(c) | 280.3±2.4 | 252.2±2.5 | — |
| $Re_2(CO)_{10}$(c) | 395.6±2.0 | 373.3±2.0 | 43.5±0.5 |
| $CH_3Re(CO)_5$(c) | 198.8±2.2 | 182.8±2.3 | — |
| $Ru_3(CO)_{12}$(c) | 459±5 | 435±7 | (42) |
| $Rh_4(CO)_{12}$(c) | 435±3 | 411±6 | (40) |
| $Rh_6(CO)_{16}$(c) | 578±4 | 550±6 | (40) |
| $Os_3(CO)_{12}$(c) | 418±5 | 393±7 | (46) |
| $Ir_4(CO)_{12}$(c) | 435±4 | 410±7 | (46) |

*This column gives either $\Delta H_f^\circ$(c) or $\Delta H_f^\circ$(l), the appropriate symbol—(c) or (l)—being placed immediately after the formula of the compound.

1. For a given ligand the mean dissociation energy of its bond with a transition metal increases with the atomic number of the metal in a given group of the Periodic System. This energy is considerably smaller for transition metals of the first series than for those of the second series, whereas metals of the second and third series usually have closely similar values. The interest of this rule established by the Reviewers [61,70,77,78,80,111] is enhanced by the fact that non-transition elements exhibit the opposite relationship: the mean energy of dissociation of the bonds formed by an element with a given radical diminishes with increase in the atomic number of the element down a group in the Periodic System [79].

2. For a given transition metal M we find in all cases that

$$\bar{D}(M-OR) > \bar{D}(M-C_5H_5) > \bar{D}(M-C_6H_6) > \bar{D}(M-CO).$$

3. Any effect of alkyl substituents in the benzene ring in diarenechromium compounds on the mean chromium–ligand bond dissociation energy lies within the experimental error of its determination [77,98].

Table 21. Thermochemical parameters (kcal mole$^{-1}$) of cyclopentadienyl compounds of transition metals.

| Compound | $\Delta H_f^0$ (c) | $\Delta H_f^0$(g) | $\bar{D}$(M-C5H5) |
|---|---|---|---|
| $(C_5H_5)_2V$(c) | 34±2 | 48±2 | 88±1 |
| $(C_5H_5)_2Cr$(c) | 42.6±0.5 | 59.3±0.6 | 67.8±0.6 |
| $(C_5H_5)_2Mn$(c) | 48.1±0.5 | 66.2±0.6 | 50.9±0.4 |
| $(C_5H_5)_2Fe$(c) | 37.0±1.0 | 54.5±1.0 | 72.6±0.5 |
| $(C_5H_5)_2Co$(c) | 56.3±0.6 | 73.1±0.8 | 64.6±0.6 |
| $(C_5H_5)_2Ni$(c) | 65.6±1.0 | 82.9±1.0 | 59.8±0.8 |
| $(C_5H_5)TiCl_3$(c) | −145.5±1.6 | −120.5±3.0 | 62±3 |
| $(C_5H_5)_2TiCl_2$(c) | −91.6±1.8 | −63.2±1.8 | 64.3±1.0 |
| $(C_5H_5)_2Ti(CH_3)_2$(c) | 13±2 | 32±2 | — |
| $(C_5H_5)_2Ti(CH_2C_6H_5)$(c) | 46.8±1.2 | 66.8±2.0 | — |
| $(C_5H_5)_2Ti(OCOC_6H_5)_2$(c) | −231±3 | — | — |
| $(C_5H_5)_2ZrCl_2$(c) | −128.6±0.7 | −103.5±0.9 | 85.7±1.0 |
| $(C_5H_5)_2Zr(CH_3)_2$(c) | −10.6±0.5 | 8.8±0.7 | — |
| $(C_5H_5)_2Zr(C_6H_5)_2$(c) | 65.9±2.6 | 87.9±3.0 | — |
| $(C_5H_5)_2HfCl_2$(c) | −128.1±0.6 | −102.6±0.8 | 85.8±0.6 |
| $(C_5H_5)_2MoH_2$(c) | 46.6±0.6 | 68.7±0.8 | — |
| $(C_5H_5)_2MoCl_2$(c) | −22.9±0.6 | 1.1±1.2 | 84.3±1.8 |
| $(C_5H_5)_2MoI_2$(c) | 7.2±0.5 | 31.2±1.1 | — |
| $(C_5H_5)_2WH_2$(c) | 59.9±0.6 | 82.9±0.8 | — |
| $(C_5H_5)_2WCl_2$(c) | −17.0±0.6 | 8.0±1.2 | 94.4±0.8 |
| $(C_5H_5)_2WI_2$(c) | 28.0±0.7 | 53.0±1.2 | — |
| $(C_5H_5)Pt(CH_3)_3$(c) | 40.3±0.5 | 58.9±0.7 | 75±3 |
| $(C_5H_5)_2Pt(CH_3)_2$(c) | 31.2±1.7 | 51.2±1.9 | 75±3 |
| $(C_5H_5)_3Sc$(c) | −3.2±1 | 23.0±1.5 | 72.7±0.5 |
| $(C_5H_5)_3Y$(c) | −10.8±1 | 15.9±1.5 | 78.5±0.5 |
| $(C_5H_5)_3La$(c) | −6.4±1 | 21.0±1.5 | 77.3±0.5 |
| $(C_5H_5)_3Pr$(c) | −6.7±2 | 23.3±2.0 | 71.9±1.0 |
| $(C_5H_5)_3Tm$(c) | −11.8±1 | 14.8±1.5 | 64.8±0.5 |
| $(C_5H_5)_3Yb$(c) | 7.0±1 | 33.0±1.5 | 51.1±0.5 |

Table 22. Thermochemical parameters (kcal mole$^{-1}$) of arene compounds of transition metals.

| Compound | $\Delta H_f^0$* | $\Delta H_f^0$(g) | $\bar{D}$(M-Ligand) |
|---|---|---|---|
| $(C_6H_6)_2V$(c) | 8.7±2.4 | 26.7±2.6 | 77.0±1.4 |
| $(C_6H_6)_2Cr$(c) | 34.5±1.0 | 54.1±1.1 | 40.2±0.7 |
| $[1,3,5\text{-}C_6H_3(CH_3)_3]_2Cr$(c) | −11.0±3.0 | 9.0±3.1 | 39.1±1.6 |
| $[1,2,4\text{-}C_6H_3(CH_3)_3]_2Cr$(c) | −9.0±1.9 | 11.0±2.2 | 38.7±1.3 |
| $(C_6H_5C_2H_5)_2Cr$(l) | 15.9±0.8 | 33.9±2.2 | 37.7±1.3 |
| $[o\text{-}C_6H_4(C_2H_5)_2]_2Cr$(l) | −11.3±1.7 | 6.7±2.6 | 39.6±1.5 |
| $[o\text{-}C_6H_4(iso\text{-}C_3H_7)_2]_2Cr$(l) | −46.7±1.8 | −22.7±2.6 | 41.8±1.5 |
| $[o\text{-}C_6H_4(iso\text{-}C_3H_7)_2]Cr(C_6H_5\text{-}iso\text{-}C_3H_7)$(l) | −29.7±1.6 | −5.7±2.5 | 42.8±2.2 |
| $(C_6H_6)_2CrCl$(c) | −10±3 | — | — |
| $(C_6H_6)_2CrBr$(c) | −1±2 | — | — |
| $(C_6H_6)_2CrI$(c) | 11±1 | — | — |
| $(C_6H_6)_2CrI$(c) | −17±1 | — | — |
| $(C_6H_5CH_3)_2CrI$(c) | −27±2 | — | — |
| $[m\text{-}C_6H_4(CH_3)_2]_2CrI$(c) | −45±2 | — | — |
| $[1,3,5\text{-}C_6H_3(CH_3)_3]_2CrI$(c) | 36±2 | — | — |
| $(C_6H_5C_6H_5)_2CrI$(c) | 73.2±2.2 | 95.2±2.4 | 50.7±1.2 |
| $(C_6H_6)_2Mo$(c) | | | |

*See footnote to Table 20.

Table 23. Thermochemical parameters (kcal mole$^{-1}$) of alkoxy-compounds of transition metals.

| Compound | $-\Delta H_f^0$* | $-\Delta H_f^0$ (g) | $\bar{D}$(RO-M) |
|---|---|---|---|
| $(C_2H_5O)_4Ti$(l) | 349.0±1.4 | 325.0±2.5 | 102.8±1.0 |
| $(n\text{-}C_3H_7O)_4Ti$(l) | 376±4.2 | 358±4 | 107±2 |
| $(iso\text{-}C_3H_7O)_4Ti$(l) | 379±1.6 | 362±3 | 106±2 |
| $(n\text{-}C_4H_9O)_4Ti$(l) | 398±1.6 | 376±3 | 105±2 |
| $(iso\text{-}C_4H_9O)_4Ti$(l) | 403±1.5 | 381±2 | 105±2 |
| $(s\text{-}C_4H_9O)_4Ti$(l) | 404±1.5 | 382±2 | 104±2 |
| $(t\text{-}C_4H_9O)_4Ti$(l) | 411±1.5 | 395±2 | 104±2 |
| $(n\text{-}C_5H_{11}O)_4Ti$(l) | 429±2.2 | 404±2 | 106±2 |
| $(t\text{-}C_5H_{11}O)_4Ti$(l) | 458±2 | 439±2 | 109±2 |
| $(t\text{-}C_4H_9O)_4V$(l) | 344±1 | 328.2±1.4 | 90±2 |
| $(t\text{-}C_4H_9O)_4Cr$(l) | 331±1 | 305.2±1.4 | 77±2 |
| $(iso\text{-}C_3H_7O)_4Zr$(c) | 429±1.8 | 409±5 | 126±2 |
| $(iso\text{-}C_3H_7O)_4Hf$(c) | 443±1.8 | 423±5 | 130±2 |
| $(CH_3O)_5Nb$(c) | 337.9±0.6 | 318.7±2.6 | 100.3±2.0 |
| $(C_2H_5O)_5Nb$(c) | 378.6±0.6 | 359.7±2.1 | 99.8±1.0 |
| $(n\text{-}C_3H_7O)_5Nb$(l) | 406.7±1.0 | 382.3±1.8 | 99.8±2.0 |
| $(CH_3O)_5Ta$(c) | 349.0±0.6 | 327.9±3.3 | 105.2±2.0 |
| $(C_2H_5O)_5Ta$(l) | 391.8±0.7 | 273.9±2.1 | 105.5±1.0 |
| $(n\text{-}C_3H_7O)Ta$(l) | 420.7±1.0 | 394.1±2.3 | 105.2±2.0 |

*See footnote to Table 20.

4. In the series—vanadium, chromium, manganese, and iron—the mean methyl–cyclopentadienyl bond dissociation energy depends on the atomic number of the element qualitatively in the same way as does the enthalpy of atomisation of the metal (Fig. 5). This evidently means that the specific electronic structure of atoms of 3*d* elements has a qualitatively similar influence on $\pi$-bond formation in sandwich compounds and on that of a metallic bond in the elements. Despite the closely similar enthalpies of atomisation of iron, cobalt, and nickel (Table 1), however, the energy of dissociation of the Fe–$C_5H_5$ bond exceeds by 8 kcal mole$^{-1}$ the value of $\bar{D}$(Co–$C_5H_5$), which in turn is 5 kcal mole$^{-1}$ larger than $\bar{D}$(Ni–$C_5H_5$). A correlation between $\bar{D}$(M–$C_5H_5$) and the enthalpy of atomisation of the metal is observed also in a series of tricyclopentadienyl compounds of rare-earth metals—lanthanum, praseodymium, thulium, and ytterbium (Tables 1 and 13).

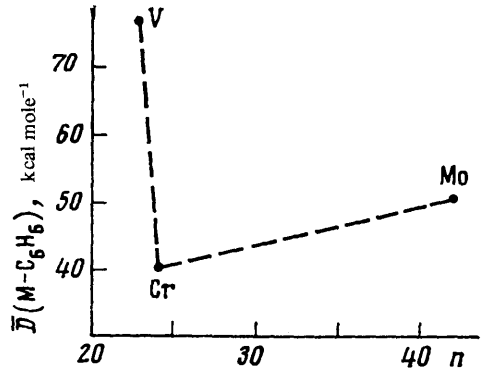



Figure 3. Variation of mean M–$C_6H_6$ bond dissociation energy with atomic number of metal.

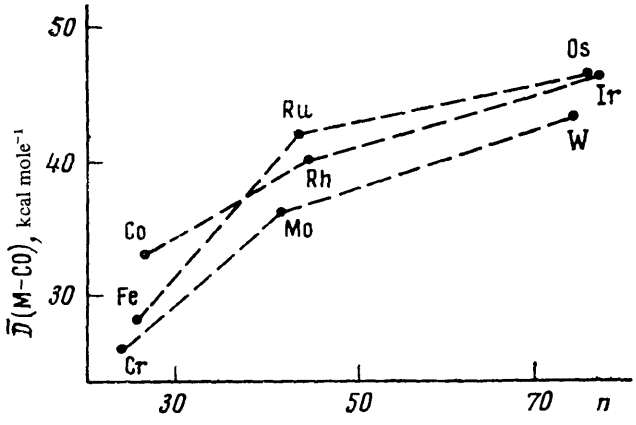



Figure 1. Variation of mean M–CO bond dissociation energy with atomic number of metal.

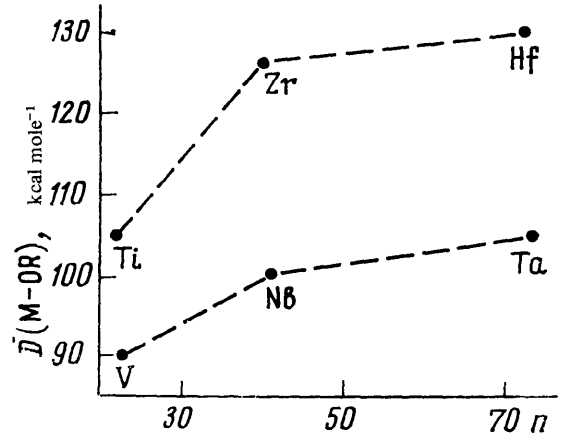



Figure 4. Variation of mean M–OR bond dissociation energy with atomic number of metal.

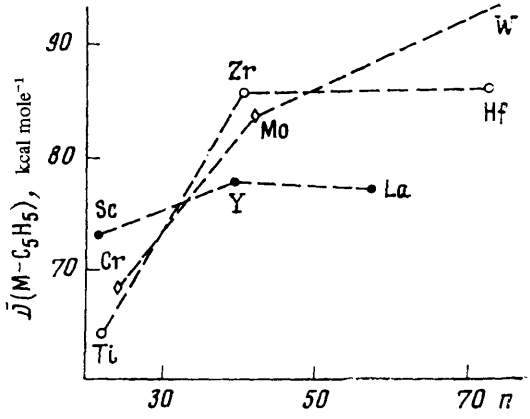



Figure 2. Variation of mean M–$C_5H_5$ bond dissociation energy with atomic number of metal.

Armstrong and his coauthors[112] have recently used the CNDO–MO method to describe the electronic properties of unsubstituted metallocenes of transition metals of the 3*d* series. They have calculated the charges on the metal atoms and the degree of completion of their orbitals; they have also computed the metal–carbon bond orders, which they assume[112] to be a quantitative measure of the interaction between metal and ring. According to the negative charges on the metal atoms in these compounds in the ground state the metals form the sequence

Fe>Cr>Co>Ni>V>Mn;

and according to the bond orders the sequence

Fe>Cr>Mn>V>Co>Ni,

whereas the experimental values of $\bar{D}$(M–$C_5H_5$) yield

V>Fe>Cr>Co>Ni>Mn.

Hence it is only for the series

$(C_5H_5)_2Fe$, $(C_5H_5)_2Cr$, $(C_5H_5)_2Co$, $(C_5H_5)_2Ni$

that a qualitative correspondence exists between the trend of variation in the experimental mean M–$C_5H_5$ bond dissociation energy and the bond order calculated from the

electronic structure of the metallocene. No analogous calculations have yet been made for other series of organic compounds of transition metals[112]. It must be supposed that further extension of experimental thermochemical investigations of these compounds, together with the development of quantum-mechanical calculations of the electronic characteristics of their molecules, will provide a deeper insight into the laws governing the energy parameters of organic compounds of metals.

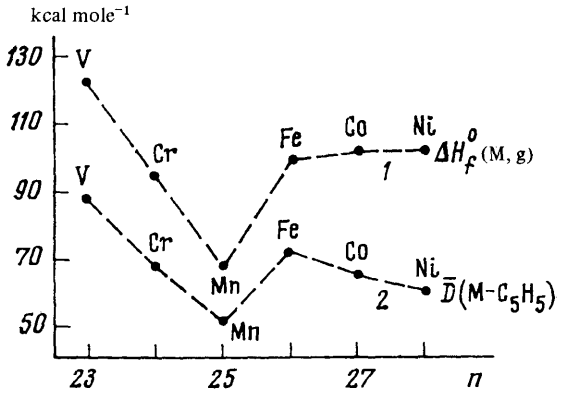



Figure 5. Influence of atomic number of metal in the 3*d* series of the Periodic System on: 1) enthalpy of atomisation of metal; 2) mean M–$C_5H_5$ bond dissociation energy.

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# Structural Aspects of Solid-phase Polymerisation

V.E.Shklover, N.G.Bokii, and Yu.T.Struchkov

The two main mechanisms of this new method—polymerisation in non-crystalline, armorphous zones and topochemical polymerisation—are closely connected with the morphology of the products. Especially detailed attention is paid to examples of topochemical polymerisation, by means of which it is possible in several cases to obtain single crystals of polymers. A list of 94 references is included.

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## I. INTRODUCTION

Whereas the polymerisation of monomers in the liquid phase has been well studied, solid-phase polymerisation has attracted the attention of research workers comparatively recently. Such reactions should differ significantly from the corresponding reactions in the liquid, since their course is largely determined by the environment and by the orientation of the monomer molecules in the crystal. Some of the most complete surveys of various aspects of the extremely complicated process of solid-phase polymerisation are listed here[1-6]. The present Reviewers have not attempted complete coverage of all the published information on solid-phase polymerisation, but have confined their attention to structural and crystal-chemical aspects of the possibilities and extent of polymerisation in solid organic (and organometallic) compounds. For example, the Review does not consider channel polymerisation, a review of which[2] does not, unfortunately, pay due regard to the work of Soviet researchers.

The two main types of mechanism—topochemical polymerisation and polymerisation in non-crystalline zones—were first distinguished in a review[1]. Topochemical polymerisation consists in a direct transition from monomer molecules to polymer chains without disruption of the crystal lattice of the monomer and without formation of non-crystalline intermediates[1,7,8]. The opposite type of solid-phase polymerisation takes place in non-crystalline zones, formed at the monomer–polymer interface and resembling a melt or a gas phase in character. This yields an amorphous polymer, which may then crystallise. The concept of a topotactic process—i.e. one in which a solid phase is formed with its crystallographic directions related to those of the crystal of the initial substance—is used to describe reactions in the solid state irrespective of the mechanism of polymerisation: in other words, topotactic reactions involve an unambiguous correspondence between the lattices of the initial (monomer) phase and the resulting (polymer) phase.

A necessary condition for the occurrence of topochemical solid-phase reactions consists in maximum displacements of the equilibrium positions of atoms in the interacting molecules with sufficiently intense thermal motion (vibration). This is the fundamental principle of lattice-controlled reactions formulated by Schmidt[9,10], and by Kargin and Kabanov[1] in its application to solid-phase polymerisation. The molecules in a crystal of a monomer are separated by van der Waals distances, and are usually too far apart for direct formation of chemical bonds between them. Therefore the reactivity of a solid is determined in principle by the mobility of individual units of the crystal lattice, i.e. molecules. In order that polymerisation should take place by a topochemical mechanism the distances between active (reactive) atoms in neighbouring molecules firstly should not exceed a certain value, respectively[11] 4.0 Å for C...C and C...N, 3.95 Å for P...N, and 3.7 Å for C...O interactions. Monomers in whose crystals active carbon atoms of neighbouring molecules are 4.3–4.7 Å apart are unable to polymerise in the solid phase. From these results the maximum distance $R$ between atoms A and B in neighbouring molecules at which polymerisation in the crystal is still possible can be estimated as $R = R_A + R_B + 0.5$ Å, where $R_A$ and $R_B$ are the van der Waals radii of atoms A and B. Secondly, solid-phase polymerisation is more probable, under otherwise similar conditions, with shorter than with longer distances between the reactant atoms in the crystal[12]. We must mention that this work[11,12] was concerned with the dimerisation of molecules, which in some cases can be regarded as a first step in polymerisation.

In the solid phase the actual polymerisation may be followed by relaxation processes, which change the morphology of the polymer formed initially[6,8]. This complicates the correlation between the mechanism of polymerisation and the morphology of the polymer obtained.

In order to make the account of solid-phase polymerisation more systematic, we shall discuss separately the solid-phase polymerisation of cyclic monomers and of unsaturated monomers containing multiple bonds. Both topochemical and non-topochemical polymerisation can take place in either group of monomers. The same division has been used previously[4].

## II. POLYMERISATION OF CYCLIC MONOMERS

A mechanism based on the arrangement of the molecules in a crystal of the monomer was suggested[8] for the solid-phase polymerisation of such cyclic monomers as e.g. trioxan and hexamethylcyclotrisiloxane. These molecules form stacks (Fig. 1) with the number of contacts between atoms of adjacent molecules in a stack larger, and the corresponding intermolecular distances shorter, than those between molecules in different stacks. Therefore polymerisation takes place in a stack with ring cleavage to form extended polymeric helices.

Another limiting case is the polymerisation of monomers in layers of molecules. This should yield planar zigzag molecules.

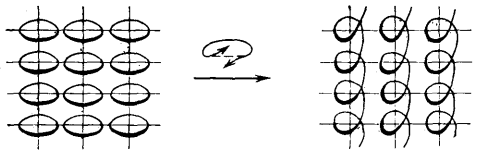


Figure 1. Polymerisation of cyclic molecules, present as stacks in the monomer crystal, to form helical polymer chains.

Table 1. Crystallographic data and physical constants of cyclic oligomers of formaldehyde and two modifications of polyoxymethylene.

| Oligomer or polymer | $(-CH_2-O-)_3$ (TOX) | $(-CH_2-O-)_4$ (TEX) | $(-CH_2-O-)_5$ (POX) | $(-CH_2-O-)_6$ (HOX) | $(-CH_2-O-)_n$ (POM) | |
|---|---|---|---|---|---|---|
| System | trig. | mon. | orh. | trig. | trig. | orh.* |
| Space group | *R3c* | *C2/c* | *Pbcn* | $R\bar{3}$ | $P3_1$ | $P2_12_12_1$ |
| Cell const. | | | | | | |
| *a*, Å | 9.320 | 11.455 | 8.135 | 7.917 | 4.47 | 4.77 |
| *b*, Å | 9.320 | 4.160 | 10.642 | 7.917 | 4.47 | 7.65 |
| *c*, Å | 8.196 | 12.232 | 7.645 | 11.345 | 17.39** | 3.56** |
| $\gamma$ or $\beta$, ° | 120 | 108.4 | | 120 | 120 | |
| Mol. in cell | 6 | 4 | 4 | 3 | | |
| Mol. symmetry | $C_{3v}-3m$ | $C_2-2$ | $C_2-2$ | $C_3-3$ | one helix 9/5*** | two helices 2/1*** |
| Density, g cm$^{-3}$ | | | | | | |
| meas. | 1.39 | 1.435 | 1.480 | 1.440 | 1.40—1.45 | 1.52 |
| X-ray | 1.406 | 1.442 | 1.507 | 1.457 | 1.49 | 1.54 |
| M.p., °C | 64 | 114 | 61 | 72.5 | 178—187 | (75—80)**** |

*Detected only in the polymerisation of hexoxodan.
**Axis of polymer chain.
***In the notation $n/m$ for a helix $n$ is the number of monomer units and $m$ the number of turns of the helix, both in the repeat distance.
****Orthorhombic–trigonal transition point.

## 1. Oligomers of Formaldehyde

The action of $\gamma$-rays on single crystals of cyclic oligomers of formaldehyde—1,3,5-trioxan (TOX), 1,3,5,7-tetroxocan (TEX), 1,3,5,7,9-pentoxecan (POX), and 1,3,5,7,9,11-hexoxodan (HOX)—leads to polymerisation with cleavage of the ring and formation of a crystalline polyoxymethylene (POM)† (Table 1).[13-15] In all cases the polyoxymethylene chain grows in certain crystallographic directions of the monomer crystal: i.e. a quite definite mutual orientation is exhibited by the crystallographic directions of monomer and polymer crystals. Thus the polymerisation of these monomers is a topotactic process.

† Only the trigonal modification of polyoxymethylene is formed in all cases other than in the polymerisation of the hexoxodan (see later).

The possibility of obtaining macrocrystals of polyoxymethylene by the polymerisation of crystals of the trioxan has been known for a long time[16-18]. Morphological investigations have shown that, except with gaseous surface initiation, the polyoxymethylene consists of crystalline fibres well oriented both mutually and with respect

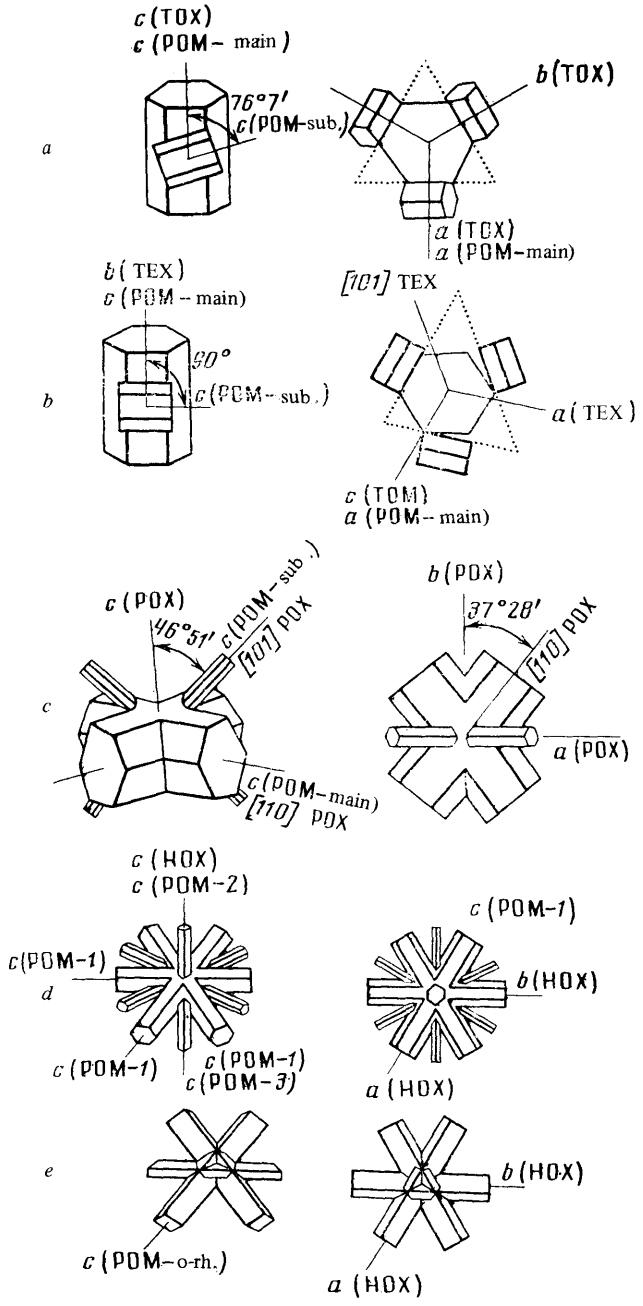



Figure 2. Diagram showing orientations of crystals of trigonal polyoxymethylene relative to crystals of: *a*) trioxan; *b*) tetroxocan; *c*) pentoxecan; *d*) hexoxodan; *e*) orthorhombic polyoxymethylene relative to a hexoxodan crystal. The dotted lines (*a* and *b*) show the relative orientations of the subcrystals.

to the crystallographic directions of the single crystal of the monomer[6,18]. Polyoxymethylene crystals obtained by solid-phase polymerisation possess unusual physical properties in comparison with crystals obtained from solutions or melts[6,19]. It was suggested[20,21] that those obtained by the solid-phase polymerisation of trioxan consist of elongated chains. A serious difficulty in studying the relation between the orientation of the growing fibres and the mechanism of the formation of polymer chains in a crystal matrix has been twinning of the polyoxymethylene: i.e. formation of a crystal having the predominant orientation (henceforward termed the "main crystal") is accompanied by that of crystals growing in other preferred directions[13,22]. The volume of such "subcrystals" becomes negligible when the temperature of polymerisation is raised. The subcrystals disappear also when the polymer is heat-treated at 170°C.[23]

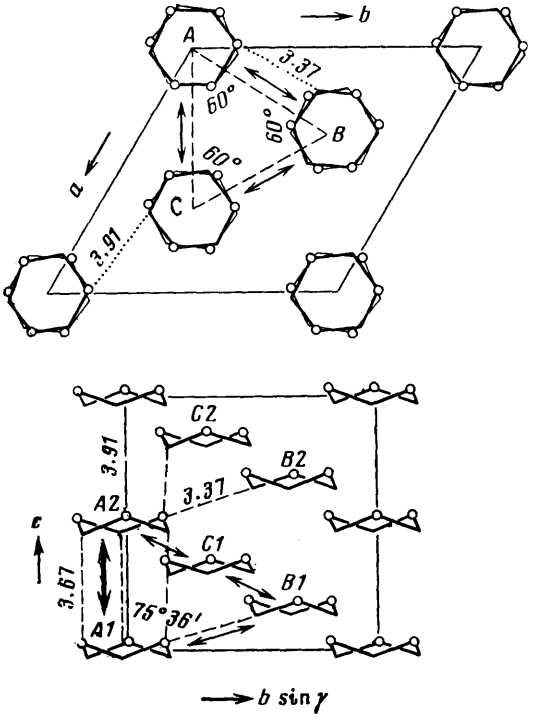



Figure 3. Packing of molecules in a crystal of trioxan. The thick and thin double arrows show the directions of the polymer chains in the main polyoxymethylene crystal and its subcrystals respectively. As also in Figs. 4, 6, and 7, the open circles indicate oxygen atoms.

The *c* axis of the main crystal of polyoxymethylene (the axis of the polymer chain) coincides with that of the initial trioxan crystal, but the (100) plane of the polymer is perpendicular to the *a* axis of the monomer (Fig. 2*a*). The *c* axes of the subcrystals are inclined to that of the main crystal at an angle of 76°7′, and their (100) planes are parallel to the (100) plane of the latter; the relative arrangement of the subcrystals corresponds to threefold axial symmetry. The tetroxocan can be polymerised[13] by precisely the same methods as with trioxan, but the morphology of the resulting polyoxymethylene is somewhat different: the *c* axis of the polymer (the axis of the chain) is parallel to the *b* axis of the monomer; and the *a* axis of the polyoxymethylene is parallel to the *c* axis of the tetroxocan (Fig. 2*b*). As in the polymerisation of trioxan, the X-ray diffraction patterns of the polyoxymethylene obtained from tetroxocan have additional, weaker reflections, indicating the formation of twin subcrystals in addition to the main crystal, but their orientation relative to the latter is different: the *c* axes of the subcrystals are perpendicular to that of the main crystal, and their (100) planes are parallel to the *c* axis of the main crystal. The directions of the *c* axes of the subcrystals are exactly parallel to the [100] (*a* axis), [001] (*c* axis), and [101] directions of the tetroxocan crystal. The twinned structure of the crystalline polyoxymethylene fibres is lost if polymerisation is conducted at temperatures above 80°C (and also when the polymer is annealed). In spite of this, however, density fluctuations are preserved in directions perpendicular to the axes of the polyoxymethylene macromolecules.

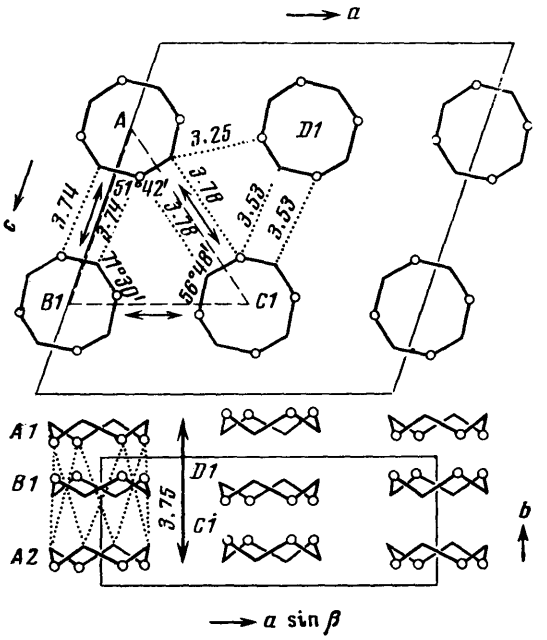



Figure 4. Packing of molecules in a crystal of tetroxocan. The thick arrow (below) and the thin double arrows (above) show the directions of the polymer chains of the main crystal and the subcrystals respectively.

Trioxan and tetroxocan molecules are stacked in the direction of growth of the polymer chain of the main crystals in such a way that the carbon atoms of one molecule are relatively close to the oxygen atoms of the neighbouring molecule (Figs. 3 and 4). The trioxan crystal includes three equivalent C...O distances of 3.67 Å in this direction (the *c* axis), and the tetroxocan crystal eight C...O distances of 3.75 Å (in the direction of the *b* axis).

**Table 2.** Parameters of the molecular packing of trioxan, tetroxocan, and pentoxecan in certain crystallographic directions (see Figs. 3, 4, and 6).

| Oligomer | Trioxan | | | Tetroxocan | | | | Pentoxecan | | | Polyoxymethylene | | | POM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Direction* | $A1...2A^{**}$ | $A1...B1^{***}$ | $A1...C1$ | $A1...A2^{**}$ | $A1...B1^{***}$ | $A1...C1$ | $A1...D1$ | [100] | [010] | [001] | $A...D^{**}$ [110] | $C...D^{***}$ [101] | $A...C, B...D$ [011] | |
| Distance between mol. centres of gravity, Å**** | 4.18 | 5.60 | 6.10 | 4.18 | 6.44 | 6.92 | 6.09 | 8.19 | 10.69 | 7.68 | 6.74 | 5.62 | 5.74;7.48; mean 6.61 | — |
| Distance per monomer unit, Å***** | 1.39 | 1.87 | 2.03 | 1.05 | 1.52 | 1.73 | 1.43 | 1.64 | 2.14 | 1.54 | 1.35 | 1.12 | 1.32 | 1.93 |
| Shortest C...O distance, Å | 3.67 | 3.37 | 3.91 | 3.75 | 3.74 | 3.78 | 3.25 | 4.76 | 6.43 | 6.79 | 3.39;3.40&3.79 | 3.45;3.67&3.84 | 3.59 & 3.76 | |
| Mol. cross-section, $Å^2$****** | 25.5 | 19.0 | 17.5 | 33.1 | 22.7 | 20.0 | 24.2 | 20.5 | 15.7 | 21.9 | 25.0 | 30.0 | 25.6 | 17.3 |
| Angle with $c$ (TOX) or $b$ (TEX) axis | 0° | 75°36′ | 62°50′ | 0° | 75°54′ | 88° | 66° | — | — | — | — | — | — | — |

*Two notations—directions between centres of gravity of molecules and crystallographic—are used. Where they coincide, both are given.

**Direction of polymer chain of main crystal.

***Direction of polymer chain of subcrystal.

****These lengths may differ somewhat from the repeat distances in the corresponding crystallographic directions. For example, the distance between the centres of gravity of the tetroxocan molecules $A1$ and $A2$ is 4.18 Å, but the repeat distance in the [010] direction (along the $b$ axis) is 4.16 Å.

*****Distance per monomer unit if polymerisation occurs in the given direction.

******Area per molecule perpendicular to the given direction.

Table 2 shows that the distances between the centres of gravity of the molecules are shorter in these directions ($A1...A2$ and $A...B$ respectively, both of 4.18 Å) than in others. This should result in maximum probability of interaction between molecules in these directions of the monomer crystals.

Trioxan crystals belong to the polar class $C_{3v}$, so that the vectors of the dipole moments have the same orientation relative to the $c$ axis. Such a structure, involving strong dipole interaction, tends to favour polymerisation[24]. Tetroxocan crystals belong to the non-polar class $C_2$, but molecules arranged along the $b$ axis, the preferential direction of polymer growth, form the same stacks as in trioxan. It is interesting that X-ray examination indicates that thermal motion in the tetroxocan crystal is most intense precisely in the direction of the $b$ axis[14]. The shortest C...O distance (3.37 Å) in trioxan is found between molecules $A1$ and $B1$ (Fig. 3). Subcrystals are formed in this direction and also in the equivalent $B1...C1$ and $C1...A2$ directions. Analysis of the reflection intensities on the X-ray patterns showed that the proportion of each of the subcrystals was ~15%, giving a total of ~45% for all subcrystals[14]. In the tetroxocan crystal the closest intermolecular contacts occur in the directions of the $a$ and $c$ axes, but such contacts are few. Thus the growth of polymer chains in this direction is explained by the larger number of C...O collisions during thermal motion and by the dipole interaction in the same direction.

The distance between monomer units along the axis of the polyoxymethylene helix is 1.93 Å, whereas in a "monomeric" crystal of tetroxocan, for example, four monomer units fit into the repeat distance of 4.18 Å along the $b$ axis, so that one monomer unit occupies only 1.05 Å. This discrepancy is smaller in the trioxan crystal, 1.39 Å per monomer unit in the direction of the $c$ axis. However, the form of the "monomeric" crystals of trioxan and tetroxocan remains unchanged on polymerisation. Resolution of this contradiction depends on elucidating the role of the subcrystals in polymerisation. The distance of 1.87 Å per monomer unit of trioxan in the $A1...B1$ direction‡ (the direction in which subcrystals are formed) is closely similar to the 1.93 Å between monomer units along the axis of the polyoxymethylene helix; furthermore, the cross-section of a molecule perpendicular to the $A1...B1$ direction is similar to that of the helix perpendicular to its axis (19.0 and 17.3 $Å^2$). Therefore the development of polymerisation in $A1...B1$ direction causes only slight stress in the trioxan crystal and seems adequate for relieving the stresses produced by growth of the main crystal[21]. At high temperatures the latter stresses can be removed by the strong thermal motion[25], with decrease in the number of subscrystals.

A relation has been discovered between the direction of dislocations in trioxan crystals and the direction of growth of polyoxymethylene[26]. If dislocations in trioxan favour polymerisation, as in many other crystalline monomers[27], a mechanism is possible in which a short polyoxymethylene chain formed initially is oriented along a dislocation, whose space it uses for its growth[6]. The formation of dislocations may well depend on a volume deficiency arising on polymerisation in the direction of the $c$ axis in the trioxan crystal[28]. The growth of polymerisation may lead to further development of dislocations, so that these two structure-dependent processes develop in parallel.

Two alternative molecular models of the structure of crystalline polyoxymethylene fibres have been suggested[6] in connection with the molecular mechanism of the solid-phase polymerisation of trioxan and the dampening effect of subcrystals. In the first model the difference in orientation between individual segments of the polymer chain (Fig. 5$a$) leads to the appearance of differently oriented

‡ Polymerisation does not occur in the $A1-C1$ direction, which would appear suitable with terms of the distance per monomer unit and the cross-section of the molecules, because of the large C...O distances (Table 2).

crystallites, which form the main crystal and the subcrystals[29,30]. On the other hand, microfilaments may consist entirely of segments having elongated chains and segments having "folded" chains (Fig. 5*b*).[31] The former model (Fig. 5*a*) is to be preferred, and provides a better explanation of the behaviour of polyoxymethylene when annealed.

As along the *c* axis in trioxan, the packing of tetroxocan molecules along the *b* axis is too dense for a uniform polyoxymethylene helix to be formed in this direction without additional displacement of molecules. Furthermore, the cross-section of the tetroxocan molecule is considerably larger than that of the polymer helix (Table 2). About 50% of the molecules in the series of polymerising along the *b* axis are forced to move from their lattice positions during polymerisation[26,32].

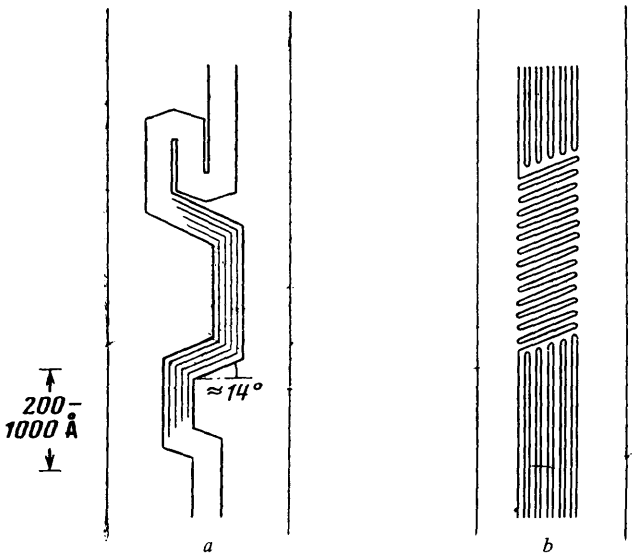



Figure 5. Alternative models (*a* and *b*) of the structure of crystalline polyoxymethylene fibres obtained by the solid-phase polymerisation of trioxan.

In the polymerisation of pentoxecan[14,33] the axis of the polymer chain (the *c* axis) lies in the [110] direction of the monomer, while the *a* axis of the polyoxymethylene is perpendicular to the *c* axis of the monomer (Fig. 2*c*). Since pentoxecan crystals belong to the orthorhombic system (Table 1), and the [110] and [$\bar{1}$10] directions are equivalent, polymer chains grow in both directions, and a twinned crystal is formed. High exposures lead to the appearance of new, considerably weaker and diffuse polyoxymethylene reflections on the X-ray diffraction patterns, which indicates other directions of growth of the polymer crystals (main crystal and subcrystals). The *c* axes of the subcrystals lie in the equivalent directions [101] and [$\bar{1}$01], while the *a* axes are located in the *ac* plane of pentoxecan, forming angles of 46°51′ with its *a* axis. Columns of molecules can formally be distinguished along the *c* axis in the pentoxecan crystal (Fig. 6), but the shortest C...O distance between these molecules (6.79 Å) is too large for chemical bonding. The C...O distances in the directions of the *a* and *b* axes are also large (4.76 and 6.43 Å respectively—Table 2). Interaction of monomer molecules with the formation of chemical bonds between them can therefore be expected only in the diagonal directions [110], [101], and [011]. In the [011] direction, however, there are two kinds of distances between centres of gravity of molecules: $A...C = 5.74$ Å and $B...D = 7.48$ Å, giving an average of 6.61 Å (Fig. 6). Only between the molecules *B* and *D* are the C...O distances sufficiently short; such close contacts are absent between molecules *A* and *C*, so that polymerisation in the [011] direction is impossible. Growth of main crystal and subcrystals in the [110] and [101] directions respectively is probably explained by the smaller difference between the distances per monomer unit in polyoxymethylene (1.93 Å) and in these directions in pentoxecan (1.35 and 1.12 Å—Table 2).

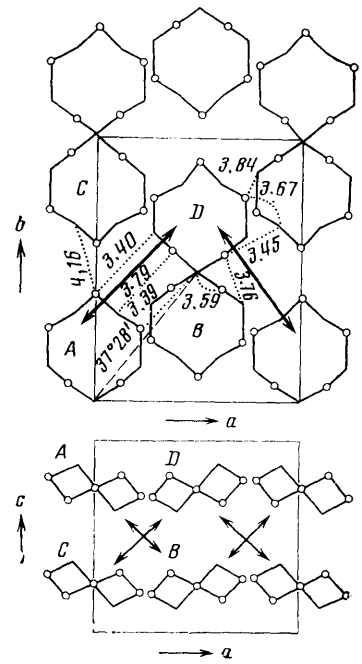



Figure 6. Packing of molecules in a crystal of pentoxecan. Thick and thin double arrows show the directions of the polymer chains in the main crystal and the subcrystals respectively.

X-Ray diffraction has revealed three orientations of the trigonal polyoxymethylene crystals formed by the polymerisation of hexoxodan. These crystals are denoted POM-1, POM-2, and POM-3 in order of their diminishing content in the specimen determined by X-ray diffraction[15]. The POM-1 crystals are elongated (the *c* axis) in the equivalent directions [100], [010], and [1$\bar{1}$0] of the trigonal hexoxodan crystal (Fig. 2*d*). The POM-3 crystals are elongated in the three equivalent directions [210], [$\bar{3}$20], and [1$\bar{3}$0]. The axis of the chain in the POM-2 crystal is parallel to the *c* axis of the monomer, so that POM-2 grows only in one direction. The powdery character of the polyoxymethylene obtained from hexoxodan is a consequence of the variety of its growth orientations. It must be pointed out that Fig. 2 shows only the directions of the crystallographic axes, and bears no relation to the actual

morphology of polyoxymethylene crystals observed e.g. by electron microscopy. In addition, an orthorhombic modification of polyoxymethylene (POM-orh.) is also formed in the polymerisation of hexoxodan. This is the first observed case of an oriented orthorhombic modification of polyoxymethylene. The axis of the chain (the *c* axis) is parallel to that of POM-1 (Fig. 2*e*). The polyoxymethylene chain forms a 9/5 helix in a trigonal crystal and a 2/1 helix in an orthorhombic crystal: i.e. the helices differ little in structure and especially in their radii. The [110] direction of POM-orh. is parallel to the *a* axis of POM-1, with very similar arrangements of the molecules in the two modifications. The reasons why two different modifications of polyoxymethylene grow in the same crystallographic direction in hexoxodan are obscure.

Table 3. Intermolecular distances *d* in the structure of hexoxodan*.

| Direction | *d*, Å | Direction | *d*, Å |
|---|---|---|---|
| C(3) I...O(1) II and equiv. pairs | | C(4) I...C(1) III | 3.77 |
| ные пары | 3.51 | C(4) I...C(1) II | 3.87 |
| C(4) I...O(1) II | 3.56 | C(4) I...C(2) III | 3.93 |
| C(4) I...O(5) II | 3.84 | C(4) I...C(6) II | 4.08 |
| C(4) I...O(1) III | 3.94 | | |

*Contacts I...II and I...III correspond to the [211] and [100] directions respectively (see Fig. 7).

The normal amplitudes of the thermal vibrations of atoms in a partly polymerised specimen of hexoxodan at room temperature, when polymerisation is fairly rapid, show that polymerisation is not accompanied by disorientation of monomer molecules that have not reacted. The twelve-membered rings that open and then combine into polymer chains should be in direct contact, at least in the initial stages of polymerisation.

It is significant that in many cases such characteristics of polymerisation as the limiting conversion, activation energy, etc. are not reproducible. Furthermore, reflections due to polyoxymethylene crystals are observed on X-ray diffraction patterns even below 5% conversion. This suggests that polymerisation is not a microscopically homogeneous process, but occurs at a multitude of individual foci, which may be for instance crystal defects.

With respect to intermolecular distances the [211] and [100] directions appear to be the most advantageous for the polymerisation of hexoxodan (Fig. 7 and Table 3). However, the initial molecule contains six oxymethylene groups, although the distance between the centres of molecules in the [211] direction is only 5.93 Å. The molecules are obviously arranged too close together in this direction for unstressed polymerisation. The formation of polymer chains not only in the [100] but also in the [210] and [001] directions, in which close C...O contacts are absent, may well be possible for monomers that polymerise by a non-topochemical mechanism, although no other such examples are known. Fig. 8, illustrating the mutual orientation of monomer and polymer molecules, shows that the arrangement of centres of gravity of each of the polymers—POM-1, POM-2, and POM-3—mimics quite well the initial lattice, which has not always been observed in trioxan and tetroxocan crystals. Perhaps study of the role of dislocations will produce clearer ideas on the mechanism of the polymerisation of hexoxodan.

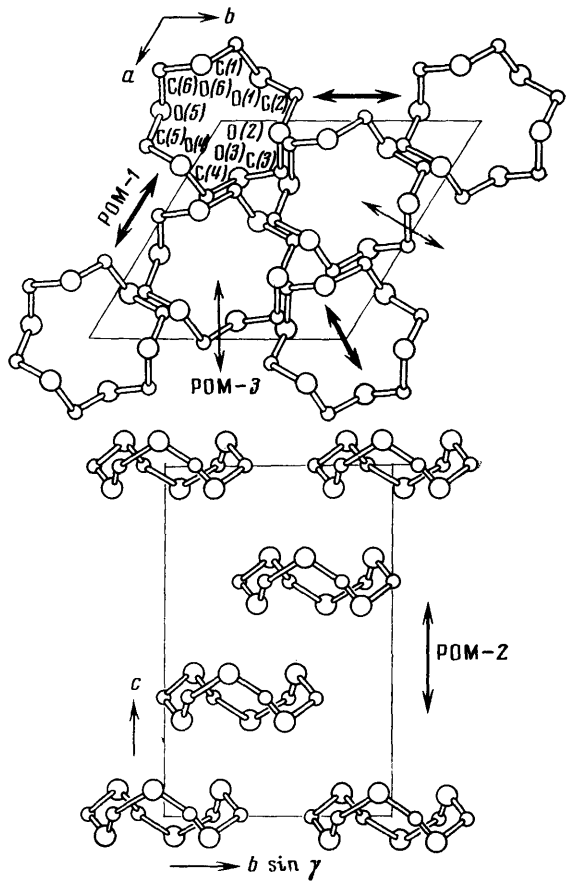



Figure 7. Two projections of the packing of molecules in a crystal of hexoxodan. The arrows show possible directions of the polymer chains.

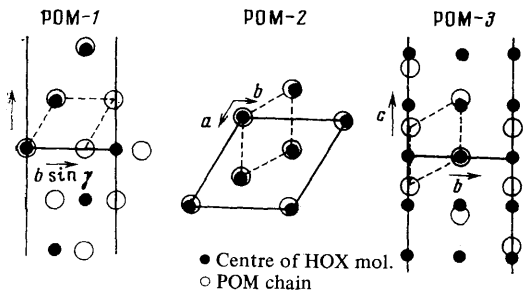



Figure 8. Diagram of distribution of HOX, POM-1, POM-2, and POM-3 molecules in projections along the axes of the polymer chains. Full and broken lines show the unit cells of hexoxodan and polyoxymethylene respectively.

In conclusion we note that the orientation and the structure of polymer crystals is determined by many factors, that transition from the initial monomer crystal to the polymer crystal involves many stages, and that it is quite difficult to establish precisely the role of the structure of the initial crystal in each stage, even if the overall process is topotactic [15].

## 2. Other Cyclic Monomers

Introduction of an initiator—potassium trimethylsilanoxide—enables hexamethylcyclotrisiloxane, as well as the *cis*- and *trans*-isomers of trimethyltriphenylcyclotrisiloxane, to be polymerised in the solid phase at room temperature or above [34]. Recent X-ray structural studies on hexaphenylcyclotrisiloxane [35], the above *cis*- and *trans*-isomers [36,37], and hexamethylcyclotrisiloxane [38] have led to several interesting conclusions on the possibilities and the mechanism of the solid-phase polymerisation of cyclotrisiloxanes. The organic derivatives have a characteristic layer structure (Fig. 9), with large interlayer spacings in trimethyltriphenylcyclotrisiloxane (9.48 and 9.52 Å in the *cis*- and *trans*-isomers). This completely eliminates the possibility of initiation of polymerisation between the layers, so that the polymer chain must develop in the plane of a layer, in which intermolecular Si...O contacts are sufficiently close (e.g. 4.28 and 4.51 Å in the *trans*-isomer). Thus the above "stacking" scheme of the polymerisation of cyclic monomers (suggested in particular even for hexamethylcyclotrisiloxane), according to which monomer molecules are arranged in piles in the crystal and polymerisation leads to the formation of elongated polymer helices, cannot be applied to these trisiloxanes [8].

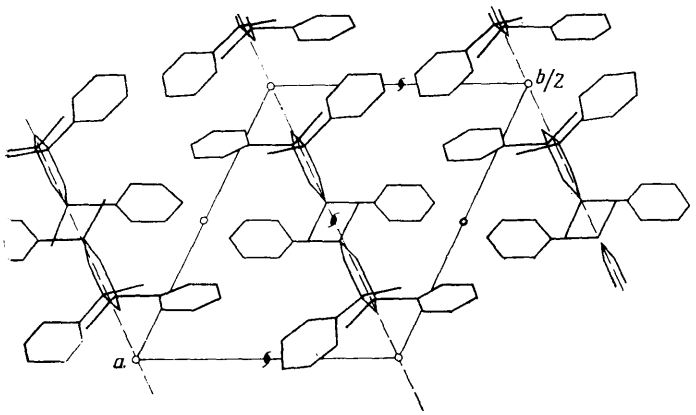



Figure 9. Packing of molecules in a crystal of *trans*-trimethyltriphenylcyclotrisiloxane. The broken lines show the direction of the layers of molecules.

Topochemical polymerisation by a single crystal of cyclic bithiazyl $S_2N_2$ has recently yielded an analytically pure single crystal of polythiazyl $(SN)_x$ (Fig. 10), which acts as a unidimensional metallic conductor [39-42]. The macromolecules have a completely planar structure, which with a topochemical mechanism can be achieved only by polymerisation in the layer. This evidently provides experimental confirmation of solid-phase polymerisation with ring cleavage occurring in layers of molecules.

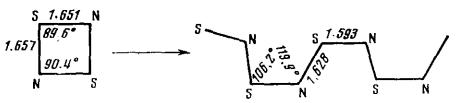
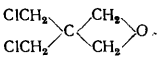



Figure 10. Polymerisation of bithiazyl. Bond lengths and angles obtained from X-ray examination of monomer and polymer crystals.

A thorough study has been made also of the polymerisation of 3,3-bischloromethyloxetan




and its analogues. It was suggested that this polymerisation is rigidly controlled by the lattice, since a highly crystalline and oriented polymer is formed [43,44]. But the formation of polymers when oxetans are exposed to X-rays leads neither to shifts in the reflections from the monomer crystals nor to the appearance of additional reflections, in contrast to for example the polymerisation of solid oligomers of formaldehyde [45] (above). X-Ray examination of the structures of bisiodomethyloxetan [46,47] and also of polybischloromethyloxetan [48] has shown that polymerisation should entail considerable displacement of the halogenomethyl groups. Such a transition must involve intermediate formation of amorphous zones. Hence the morphology and the orientation of products of the solid-phase polymerisation of oxetans are governed not by the actual mechanism of polymerisation but by secondary processes.

## III. POLYMERISATION OF MONOMERS WITH MULTIPLE BONDS

The solid-phase polymerisation of molecules containing double and triple bonds differs in many respect from that of heterocyclic monomers. Transition from a cyclic molecule to a linear unit in a polymer chain involves no change in the valency configuration of the atoms, whereas the polymerisation of unsaturated compounds is accompanied by rehybridisation of the interacting atoms of the initial molecules. The mechanics of growth of the polymer chain is also fundamentally different in the solid-phase polymerisation of cyclic and of unsaturated monomers: in the former case the gap between adjacent molecules in the crystal, joining together to form the polymer chain, is filled as a result of cleavage of the cyclic molecules and straightening-out of the monomer unit in the direction of chain growth; in the case of unsaturated monomers the distance between adjacent monomer molecules forming the polymer chain should contract by ~2 Å (the difference between the intermolecular distance and the interatomic bond length in the macromolecule [4]). The "lever" mechanism of the polymerisation of rigid rodlike molecules suggested by

Wegner[5] (Fig. 11) can be applied in the latter case. The molecules, in the form of small sticks with reactive functional groups at their ends, are stacked in the crystal in such a way that two reactive groups in adjacent molecules are ~3 Å apart. Polymerisation takes place without displacement of the centres of gravity of the molecules in the lattice, either by their gradual rotation proceeding from molecule to molecule or by simultaneous rotation throughout a stack. Reactions occurring in this way are termed *topochemical* in the narrow sense.

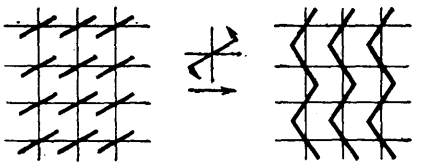


Figure 11. Simplified scheme of topochemical solid-phase polymerisation by the lever mechanism.

The solid-phase polymerisation of dienes (termed "four-centre polymerisation"), monomers containing triple bonds, and also certain other linear monomers with multiple bonds takes place by such a "lever" mechanism.

## 1. Four-centre Polymerisation

Molecules such as distyrylpyrazine (DSP) and derivatives of *p*-phenylenediacrylic acid§, packed "head to tail" in the crystal, yield polymers containing cyclobutane rings in the main chain and a completely ordered arrangement of substituents[49-54] (Fig. 12). Solid-phase polymerisation gives a product of exceptionally high crystallinity[55], but in solution an amorphous polymer is obtained.

Distyrylpyrazine molecules are arranged in the crystal in such a way that the relative positions and mutual orientation of the reactive double bonds are favourable for the formation of a cyclobutane ring; but crystals of another polymorphic modification (of undetermined structure) do not polymerise in the solid phase. Fig. 13*a* shows that the approximately planar distyrylpyrazine molecules are stacked along the *c* axis, which favours polymerisation in this direction. The shortest distance between the centres of double bonds in adjacent molecules is 3.94 Å (I*a*...II*b*, II*a*...III*b*, etc.). The next shortest distance, between double bonds of molecules in different stacks (5.42 Å), is too large for interaction[11]. It is therefore most probable that double bonds related by centres of symmetry react on irradiation (with the formation of cyclobutane rings), so that the polymer chains should grow in the direction of the *c* axis.

During polymerisation the X-ray diffraction pattern of distyrylpyrazine gradually changes into that of the polymer[51]. The mutual orientation of crystals of monomer and polymer has been established from the rotation photographs and the Weissenberg patterns of a partly polymerised crystal: the *a*, *b*, and *c* axes of the polymer are parallel to the corresponding axes of the monomer, but the characteristic elongation of spots on the X-ray patterns indicates some disordering of the polymer in the (001) plane. Since a single crystal of the monomer is converted by polymerisation into a polycrystal consisting of slightly disoriented fine blocks (crystallites), no X-ray structural analysis of the polymer has yet been made. Electron-microscopic study of polydistyrylpyrazine crystals has shown[56] that they consist of rodlike crystallites of square cross-sections about 1 μm thick, elongated in the direction of the *c* axis.

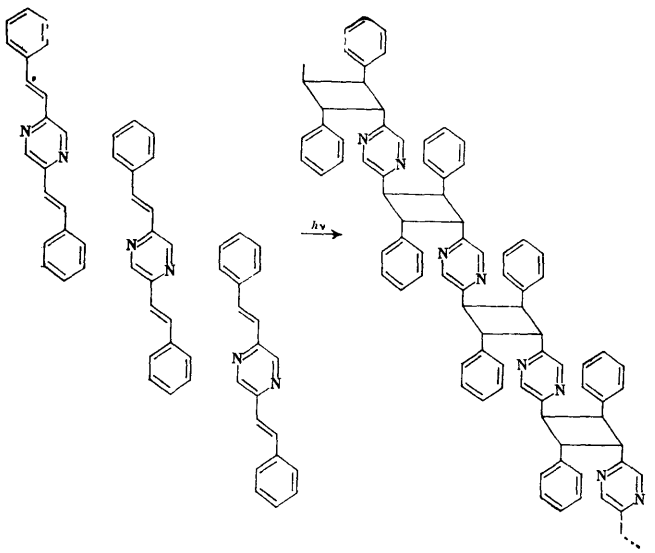


Figure 12. Four-centre photopolymerisation of dienes exemplified by that of distyrylpyrazine.

When crystals of distyrylpyrazine are exposed to light of wavelength exceeding 400 nm, polymerisation ceases at an intermediate stage: an oligomer having a mean degree of polymerisation of 5 is formed[57]. Comparison of the X-ray patterns of monomer and oligomer indicates that the latter, like the polymer, is well oriented, with its axes parallel to the corresponding axes of the monomer. The oligomer can be converted into the polymer by exposure to light of shorter wavelength. The degree of orientation of the polymer obtained from the oligomer is almost the same as that of the polymer obtained from the monomer. On conversion of the monomer into the polymer the *a* axis contracts by 11%, the *b* axis becomes 13% longer, and the *c* axis decreases by <2%. Thus the centre of gravity of the unit cell of the monomer is only slightly displaced in the direction of chain growth (the *c* axis), which is important for obtaining polymers in good yield.

The source of lattice deformations is the change in the distance between the double bonds I*a* and II*b* from the van der Waals value to the length of the σ bond in cyclobutane (1.56 Å).[58] Since the repeat distance along the *c* axis remains almost unchanged on polymerisation, the interaction of these double bonds leads to close contact of the

§ Dienes that polymerise by this mechanism are listed in Refs. 5 and 49.

second double bond II*a* with the double bond III*b*, as a result of which the excited molecule III reacts more readily with a double bond in II than in the next molecule IV. Fig. 13*b* shows how the polymer chain is superposed on the (010) projection of the monomer crystal; despite rotation of the central segment, displacement of the phenyl side-chains is insignificant.

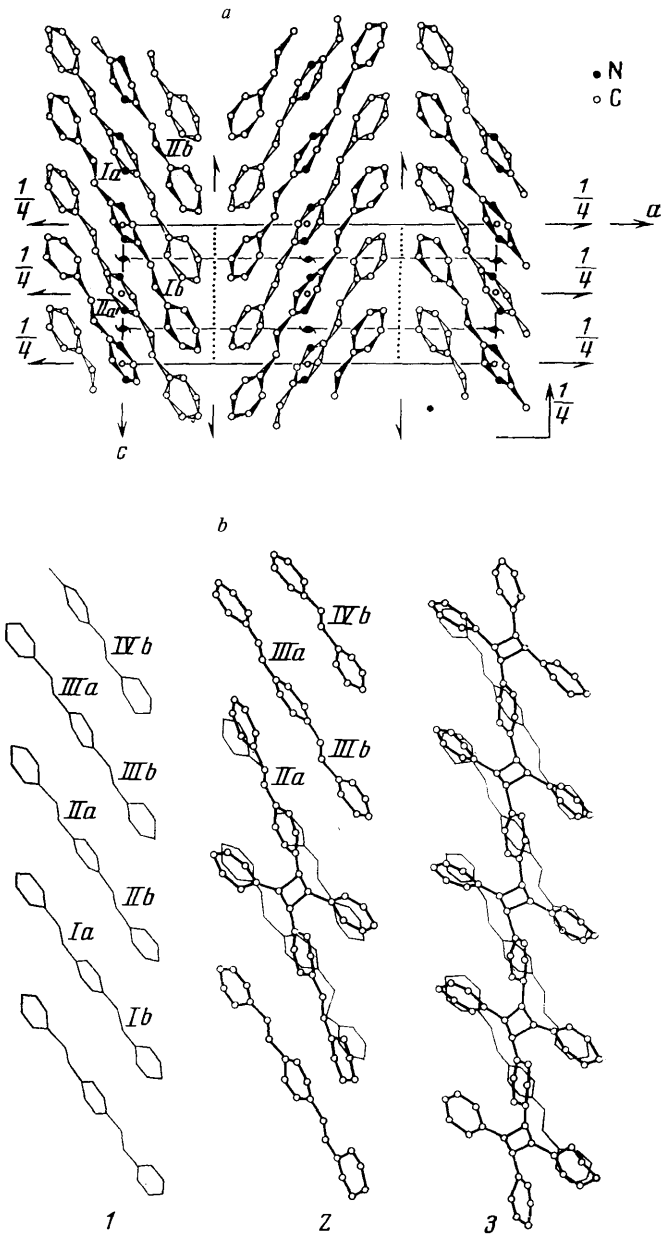



Figure 13. (*a*) Packing of molecules in a crystal of distyrylpyrazine. (*b*) Scheme of polymerisation of distyrylpyrazine shown by projections of the monomer: 1) alone; 2) combined with molecular model of dimer; 3) combined with molecular model of polymer.

Important results are obtained from a study of the behaviour of polydistyrylpyrazine on recrystallisation. The difference between the X-ray patterns of recrystallised and initial polymers[59] shows that the latter is formed under the control of the crystal lattice of the monomer and is not in the thermodynamically most stable form. It is extremely interesting that polydistyrylpyrazine undergoes thermal depolymerisation in high yield[53]. The scheme in Fig. 14 for the reversible interconversion of monomer and polymer is based[7] on thermodynamic and spectral investigations of the polymerisation–depolymerisation and a comparison of X-ray patterns obtained at various stages in these processes. Crystalline polydistyrylpyrazine is thermally more stable than the amorphous polymer, probably because the crystal lattice of the polymer protects the cyclobutane groups from thermal degradation by restricting local movement of the polymer chain.

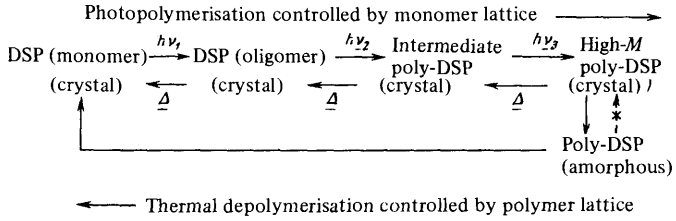



Figure 14. Scheme of reversible polymerisation of distyrylpyrazine (DSP).

In connection with the growing interest in asymmetric synthesis by topochemically controlled reactions in a chiral crystal[5,60–64] a series of 1,4-photodimerising monomers has been obtained containing as substituents "chiral handles" promoting crystallisation of these monomers into asymmetric structures[65,66]. Dimers and polymers obtained from the monomers (Fig. 15) are in fact chiral, with optical rotation of opposite sign to that of the monomer. A racemic crystal of structure similar to that of one of the enantiomers A or B (Fig. 15)¶, but containing (in equal quantities) substituents X of opposite chirality, also yields an optically active polymer on exposure. On the other hand, replacement of the chiral groups in an optically active monomer by methyl groups enhances the optical activity of the polymer. Thus optical induction accompanying polymerisation is caused by the chiral influence of the environment of the reaction centre in the crystal, not by the chiral influence of the "chiral handles".

## 2. Polymerisation of Monomers with Conjugated Triple Bonds

The solid-phase polymerisation of monomers containing conjugated triple bonds, discovered by Wegner in 1968, is a classic example of topochemical polymerisation by a

¶ The optically active monomer (Fig. 15) and its racemate crystallise in the $P1$ space group with closely similar cell parameters.

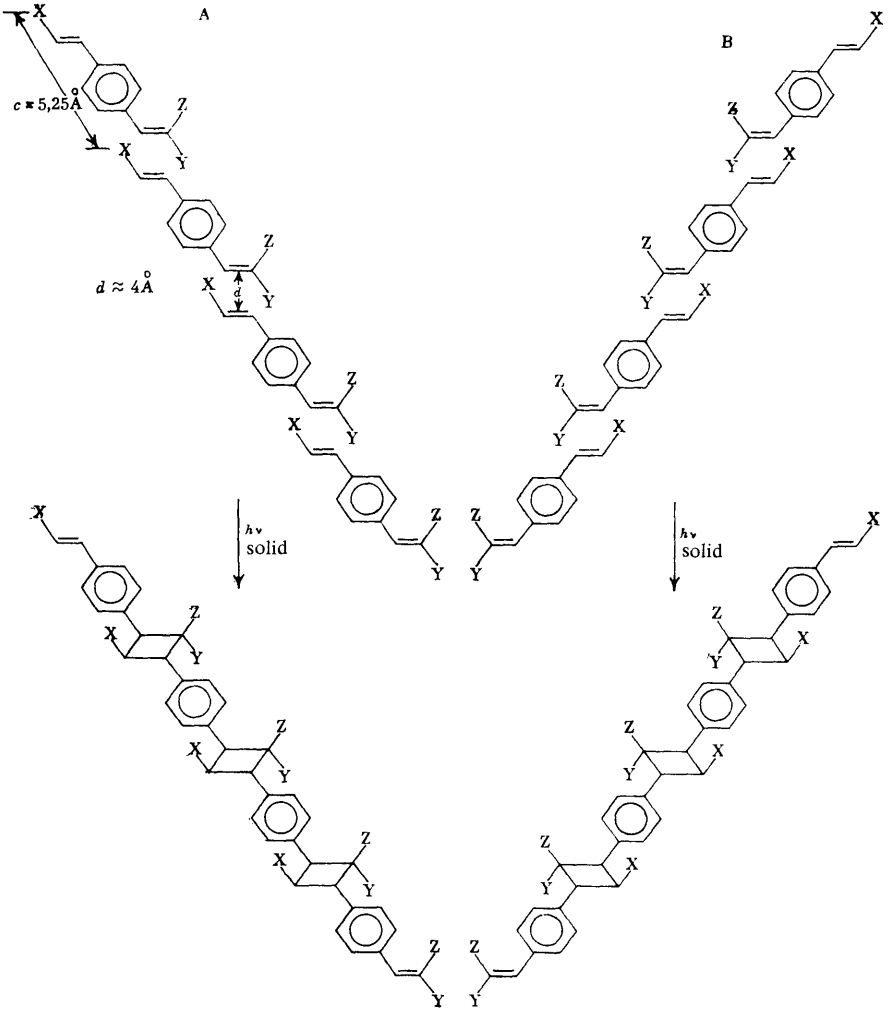
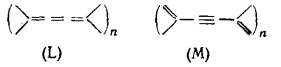



Figure 15. Structure and polymerisation in enantiomorphous crystals A and B. The suggested structure of the monomer is based on the parameters of the unit cell (molecular plane in the *ab* plane), and that of the polymer from n.m.r. data for the dimer and data for polydistyrylpyrazine.

lever mechanism [6,67-69]. The process is shown diagrammatically in Fig. 16. Equation (1) represents the formation of a polymer whose main chain, according to X-ray examination [70,71], is a planar conjugated system with a *trans*-arrangement of the substituents:

$$n\mathrm{R{-}C{\equiv}C{-}C{\equiv}R{-}R \rightarrow {-}\underset{\mathrm{R}}{\mathrm{C}}\left[=\underset{\mathrm{R}}{\mathrm{C}}{-}\mathrm{C}{\equiv}\mathrm{C}{-}\mathrm{C}\right]_n=\underset{\mathrm{R}}{\mathrm{C}}{-} \quad (1)$$

The distribution of bond lengths in the main chain (Fig. 17) is described better by M of the two possible structures



(L) (M)

for 1,4-addition products. The same distribution of bond lengths is suggested also by spectral investigation [72].

The polymerisation of diynes yields a completely ordered three-dimensional macroscopic single crystal of the polymer, in many cases of the same size as the single crystal of the monomer. For example, a polymeric single crystal weighing >1 g can easily be obtained from hexa-2,4-diynylene ditoluene-*p*-sulphonate [5]†. The polymerisation of colourless single crystals of diynes is usually accomplished by ultraviolet irradiation or by heating below the melting point, although other methods of initiation are possible, and is accompanied by a marked change in colour. Polymerisation does not take place in the melt or in solution [67].

Only imperfect microcrystalline aggregates of the polymers, often possessing a fibrous structure, are

† A list of diynes that polymerise in the solid phase will be found in Ref. 5.

obtained in the previous cases of the solid-phase polymerisation of trioxan and tetroxocan [13,14,16-18] and in four-centre photopolymerisation [55,56]. In these cases polymerisation is accompanied by breakdown of the initial monomer single crystal. This is due to the mechanism of polymerisation, which may be described as a phase transition characterised by stages of nucleation and growth of nuclei of the new (polymer) phase in a matrix of the initial crystal. This is known as heterogeneous solid-phase polymerisation. In homogeneous solid-phase polymerisation the polymer chains are "dissolved" in the matrix of the monomer crystal, and phase separation does not occur. The polymerisation of monomers containing conjugated triple bonds is such a homogeneous process [73].

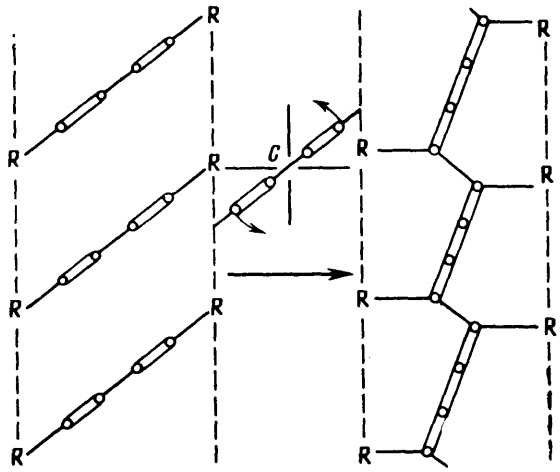



Figure 16. Polymerisation of conjugated diynes. Reaction involves rotation of monomer molecules about the centres of gravity *C*.

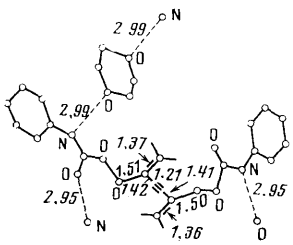



Figure 17. Structure of polymer obtained from hexa-2,4-diynylene bisphenylcarbamate. The broken lines show hydrogen bonds with neighbouring polymer chains and with molecules of dioxan of crystallisation.

In the polymerisation of certain diynes no change in density takes place, and no appreciable quantity of amorphous polymer is formed, but monomer and polymer are completely isomorphous. Such isomorphism has been noted e.g. with hexa-2,4-diynylene ditoluene-*p*-sulphonate [74]. However, other diynes, e.g. hexa-2,4-diynylene bis-stearoylcarbamate, give polymers possessing only two-dimensional orientation. These phenomena can be related and explained by means of the simple scheme [8] shown in Fig. 18. We suppose that a monomer passes into a polymer topochemically, by lever polymerisation, the solid product being in a modification that is not in general the energetically most advantageous, since the molecules are in an unfavourable stressed conformation. This is the transition $A \rightarrow B$. State *D* is thermodynamically stable for the polymer. If the monomer lattice is disturbed sufficiently, e.g. because of the difference between its density and that of the polymer, or if unchanged monomer is removed, the macromolecules relax and pass into state *D*. This state is not usually achieved, for the mobility of molecules is limited at the usual temperatures of polymerisation or extraction. The polymer therefore passes into a vitreous state *C*. Clearly, lowering the temperature of polymerisation may result in fixation of state *B*. This may explain the observations that, when diethynyl *p*-phenylenediacrylate undergoes polymerisation below 5°C, the polymer modification corresponding to state *B* is "frozen in", whereas at about 30°C relaxation ensues with the appearance of an amorphous structure corresponding to state *C*. In the polymerisation of hexa-2,4-diynylene bisphenylcarbamate and ditoluene-*p*-sulphonate, however, the polymer formed topochemically corresponds to the thermodynamically stable modification. Polymerisation of the bis-stearoylcarbamate follows a different course, with the resulting polymer modification stable only in the presence of the monomer lattice. This involves "forced" isomorphism of monomer and polymer, in which the monomer structure is kinetically (but not thermodynamically) preferable, for the resulting polymer, to the polymer structure possessing minimum free energy. Therefore the lattice changes accompanying polymerisation are minimal.

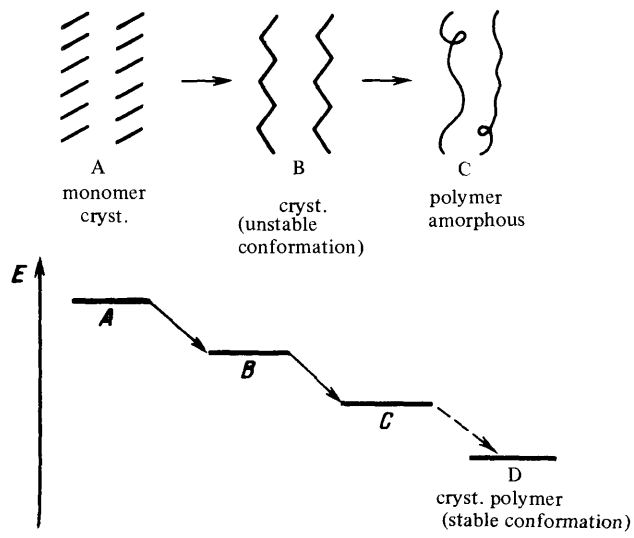
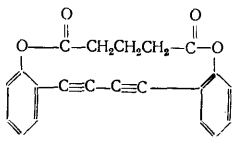


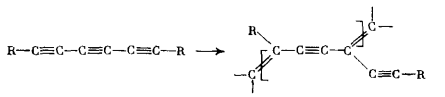

Figure 18. Relative stability of polymer chains in crystalline and amorphous polymer.

The possible isomerism of polymers obtained from cyclic diynes has been discussed[5]. If the monomer molecules are linked in the crystal only by translations, they should yield the chiral polymer shown diagrammatically in Fig. 19*a*. If, however, neighbouring molecules are linked in the direction of polymerisation by a reflecting glide plane, the achiral polymer of Fig. 19*b* should be formed, in which the side loops (rings) are alternately above and below the plane defined by the conjugated main chain. Crystals of the cyclic diyne



readily undergo photopolymerisation, but thermal polymerisation is very slow. X-Ray examination has shown that the polymer has the structure indicated in Fig. 19*b*. Unfortunately, it has not yet proved possible to select a crystalline modification of a cyclic diyne having translational symmetry only in the direction of polymerisation, although a fairly large number of reactive modifications of cyclic diynes have been described[5,75].

The solid-phase polymerisation of triynes is well known, and is easily detected from the spontaneous coloration of the monomer crystals[5,69]:



As with diynes, polymerisation is a consequence of 1,4-addition, with an acetylenic side-chain present in the monomer unit.

However, not all diynes and triynes undergo solid-phase polymerisation. The reactivity of monomers is largely determined by their packing, not by e.g. mesomeric or inductive effects. If a monomer can be obtained in different modifications, the latter usually exhibit different tendencies to undergo solid-phase polymerisation. Frequently only one modification polymerises in the solid phase, and the others do not. It is significant, for example, that crystals of hexa-2,4-diynylene bisphenylcarbamate polymerise only if they contain dioxan of crystallisation, which probably ensures that the packing of the molecules in a crystal is favourable for polymerisation[71]. Hexa-2,4-diynylene dibenzoate crystallises in two forms, one of which (S) can polymerise under the influence of high pressures, but the other (T) cannot[76]. Molecules are located at centres of symmetry and have the same conformation in both forms of crystals. However, whereas the C...C distances between triply-bonded atoms in adjacent molecules in the S form of crystal (4.02 Å) can be shortened by high pressures to the critical value at which covalent bonds are formed, the corresponding shortest C...C distance in the T form of crystal is 5.37 Å, which could not be shortened by pressure to the critical value.

Solid-phase polymerisation is possible when adjacent molecules in a crystal are arranged as shown in Fig. 20. The angle $\alpha$ between the translation relating the centres of gravity of adjacent reactant molecules and the direction of their conjugated bond system should be ~40°. The distance between the centres of gravity of neighbouring molecules is 4.7–5.2 Å, with an optimum of 4.9 Å for polymerisation: i.e. polymerisation is accompanied by minimal changes in the parameters of the unit cell.

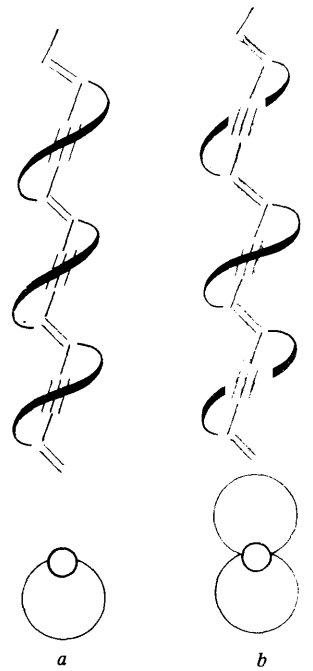



**Figure 19.** Structure of polymers obtained by the solid-phase polymerisation of cyclic diynes: *a*) chiral; *b*) achiral. Projections along the axes of the macromolecules shown at foot of diagrams.

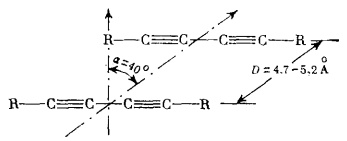



**Figure 20.** Arrangement of adjacent molecules in a stack in a diyne crstal undergoing solid-phase polymerisation, where $D$ is the distance between the centres of gravity of the molecules and $\alpha$ the angle between the axis of the molecule and the direction of translation relating neighbouring molecules in a stack.

In this connection it is very interesting to study the difference in reactivity between two substituted diacetylenes[77]: hexa-2,4-diynediol polymerises slowly in the solid phase, but diphenylbutadiyne hardly polymerises at all. Reactant molecules in a crystal of the former are related by the diagonal translation *ac*. The molecules are joined by hydrogen bonding in the direction of the *c* axis, but no hydrogen bonds are formed in the *ac* direction. The geometrical parameters $\alpha$ and $D$ (Fig. 20) are 5.34 Å and 41.4° in hexa-2,4-diynediol, and 6.04 Å and 50.9° in diphenylbutadiyne. Polymerisation of the first monomer should involve a contraction of 0.44 Å in the distance between the centres of adjacent reactant molecules, while the axes of the molecules should turn through 28°. The relative inactivity of the second monomer in the solid phase is attributed to the considerable displacement and

rotation of molecules necessary for polymerisation by 1,4-addition (respectively 1.14 Å and 37.5°). The distances between the terminal atoms of the reactive butadiyne groups are also different: 3.54 Å in the first monomer, and 4.69 Å in the second.

The relative arrangement of diyne molecules is dictated by the packing of lateral substituents. Reactive modifications should obviously be formed by diynes substituted by polar groups—hydroxyl, carboxyl, amide, and urethane—able to promote suitable orientation of the molecules in the crystal by dipole–dipole interaction or hydrogen bonding. A system of hydrogen bonds interconnecting neighbouring monomer units has been found[71] in a crystal of polymeric hexa-2,4-diynylene bisphenylcarbamate.

The parallel packing of adjacent benzene rings in the direction of the polymer chain in the crystal of poly-1,2-di(toluene-*p*-sulphonyloxymethyl)but-1-en-3-ynylene[70], which fixes the relative arrangement of neighbouring monomer units, is probably also a consequence of the dipole–dipole interaction of polar side-groups. Nevertheless, the presence of such groups is neither a necessary nor a sufficient condition for the solid-phase polymerisation of diynes. For example, octacosadiyne containing purely aliphatic substituents has a low-temperature modification which undergoes photopolymerisation exceptionally readily, whereas its high-temperature modification is inactive from 15°C up to the melting point[5]. Thus the orientation of adjacent molecules necessary for polymerisation can be ensured also by the packing of non-polar groups. On the other hand, among diphenylbutadiyne derivatives disubstituted with polar groups only the *ortho* and *meta* isomers are active in the solid phase, whereas the corresponding *para*-disubstituted compounds do not polymerise[57].

The best test of the above ideas of Wegner[5], of course, would have been a structural investigation both ot the monomer and of the polymer formed from it, but this has not yet been done. With many diynes, e.g. bisphenylcarbamates, X-ray examination is difficult because of the extreme rapidity of polymerisation on exposure. With diynes that polymerise slowly in the solid phase (hexa-2,4-diynediol, etc.) the crystalline structure of the monomers is known[74,78], but the structure of the polymer has not been investigated. On the application of large radiation doses with the aim of achieving high degrees of conversion the polymeric hexadiynediol becomes amorphous[78]. The structure of diphenylbutadiyne is known[79], but it is almost inactive in the solid phase.

Successive determination of the Raman spectra during the polymerisation of diynes[72] revealed spectral bands due to states intermediate between the initial monomer and the final polymer. The intensity of the bands due to the intermediate states increased initially, and then diminished. However, the vibration frequencies of the intermediate states were independent of the degree of polymerisation. Investigation of the ultraviolet spectra during the polymerisation of hexa-2,4-diyne-1,6-ylene revealed two intermediate spectral states differing both from the monomer, from the polymer, and from combinations thereof. However, lower intermediate products could not be identified by thin-layer chromatography[67]. The infrared spectra of partly polymerised hexa-2,4-diyne-1,6-diol show that the intermediates, present in considerable quantities, are completely hydrogen-bonded both in the monomer crystal and in the extracted polymer[72].

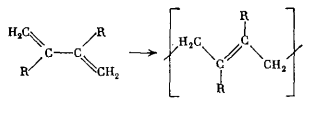
Thus spectral methods clearly establish the stepwise character of the solid-phase polymerisation of diynes, but the nature of the intermediates is obscure and requires further investigation.

## 3. Polymerisation of Monoethylenic Monomers

The above lever mechanism is impossible for the polymerisation of alkenes‡, and growth of the polymer chain requires considerable displacement of the molecules. Therefore topochemical polymerisation is not usually observed with these compounds[5]. The solid-phase polymerisation of vinyl monomers generally yields amorphous polymers, and the actual process takes place in "amorphous zones" or "local melts" arising from the absence of geometrical correspondence between monomer and polymer lattices.

Only the polymerisation of vinyl stearate and other quasi-crystalline long-chain vinyl and acrylic monomers takes place under definite structural control[81–83], occurring preferentially in monolayers, apart from the channel polymerisation of dienes in the form of inclusion compounds[84,85]. Polymerisation of ethylenic monomers in a quasi-crystalline state is possible if their molecules contain suitable substituents capable of being densely packed, while the ethylenic groups are situated in quasi-liquid regions and hence are highly mobile. This phenomenon is termed the "crystallinity of side-chains"[86,87]. A typical case is the polymerisation of *N*-*p*-vinylphenylbenzamide[88] or vinyl stearate, when the packing of the side-chains is largely preserved during polymerisation, but the linking of the double bonds is not specific and an atactic polymer is formed. The solid-phase polymerisation of long-chain unsaturated compounds has recently aroused especial interest, since it may occur in monolayers or in multilayer structures formed from them[82,83].

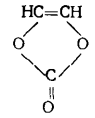
In channel inclusion compounds the "host" molecules, e.g. urea or thiourea, form an open structure, in the channels in which the molecules of a suitable monomer may be distributed. The polymerisation of alkenes in the form of inclusion compounds in urea or thiourea has been known for a long time[34,89]. Direct X-ray structural investigation of butadiene and its 2,3-disubstituted derivatives in the lattice of perhydrotriphenylene or urea as host has recently shown[62,85,90] that such derivatives are tightly packed "head to tail" in the channels. Powerful irradiation yields *trans*-1,4-polybutadiene by 1,4-addition:




The host lattice does not disintegrate during polymerisation, and an isolated stressed macromolecule is formed in each channel. After the host lattice has been cautiously dissolved, a highly crystalline fibrous product remains, comprising stressed chains[85]. The specific character of these reactions consists in the mutual isolation of the channels and the greatly restricted mobility of the monomer molecules. In a channel a monomer molecule is unable to rotate about its long axis, its mobility being reduced to the possibility of translational diffusion, which creates the necessary conditions for the formation of an ordered polymer.

‡ Because no rotation of such molecules is able to bring the ends of the double bonds within the distance necessary for polymerisation.

Crystals of vinylene carbonate



which polymerise on exposure to $\gamma$-rays, comprise layers perpendicular to the [$\bar{2}$01] direction[91]. The shortest intermolecular C...C distance between vinyl groups lies in the plane of the ($\bar{2}$01) layer (Fig. 21). But the formation of chemical bonds in this plane would have required large molecular rotations both in and perpendicular to the plane, which would have results in local stresses in the lattice. Polymerisation develops preferentially along surfaces parallel to the axes of the polymer to form a heterogeneous phase[92]. Weissenberg diagrams obtained after irradiation for 48 h established that the *a* and *b* axes of the polymer were parallel to those of the monomer. Thus polymerisation proceeds in the (110) plane. The polymer chain is a 3/1 helix extending along the *b* axis of the monomer crystal. At 10% conversion a signal due to the amorphous polymer appears on the diffractograms, at 35% only two peaks corresponding to a crystalline substance remain, and at 67% conversion the polymer is completely amorphous. The initially formed polymer probably has a thermodynamically unstable conformation and is able to exist only when a considerable crystalline environment is preserved by the monomer[92].

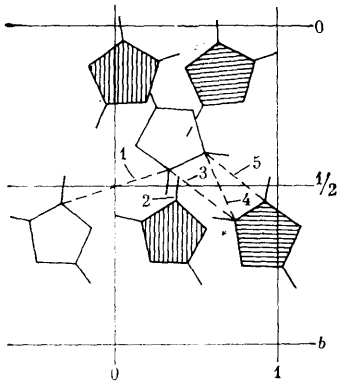



Figure 21. Packing of molecules in a crystal of vinylene carbonate projected on the ($\bar{2}$01) face (plane of layer). Molecules lying above and below this plane are shown by vertical and horizontal hatching respectively. Intermolecular vinyl–vinyl distances < 4 Å are indicated (Å): 1) 3.776; 2) 3.778; 3) 3.902; 4) 3.864; 5) 3.902.

The initial stage in the polymerisation of crystalline acenaphthylene is also a topotactic process[93,94], which, like that of vinylene carbonate, takes place not in the plane of the separating layers but in planes having $z = 0.25$ and 0.75. The polyacenaphthylene chains are oriented along the *a* and *b* axes of the monomer crystal. From the size of the identity period along the chain axis a *threo*-diisotactic structure was suggested for the polymer chain.

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The above survey has shown that solid-phase polymerisation is not necessarily controlled by the lattice and does not necessarily give a stereoregular crystalline polymer. The crystal structure of the monomer may be destroyed by the growing polymer chains, so that only the initial stages of oligomerisation take place under the control of the lattice. This yields an amorphous polymer, which in some cases (oxetans) is able to crystallise. On the other hand, the product of solid-phase polymerisation frequently does not possess the expected morphological properties, because relaxation processes, which are so characteristic of other polymer reactions, may occur in structures obtained topochemically.

Two general types of lattice-controlled solid-phase polymerisations can be distinguished. (i) Polymerisation with ring cleavage is characteristic of cyclic monomers whose molecules are arranged in stacks or layers in the crystal. Polymerisation in stacks involves the opening of rings with formation of helical polymer molecules (trioxan, tetroxocan, etc.). Monomers having a stressed-ring structure (cyclotrisiloxanes and probably bithiazyl), in contrast, undergo polymerisation in layers. (ii) Lever polymerisation is accomplished by the concerted displacement and rotation of rigid rodlike molecules. A clear example of the lever mechanism is provided by monomers having conjugated triple bonds, which on polymerisation give units with alternating double, triple, and single bonds. The polymerisation of these monomers completely satisfies Schmidt's conditions[9,10] and is topochemical in the narrow sense.

The next important step in the study of solid-phase polymerisation should be to obtain quantitative structural–chemical criteria of the process, in particular to investigate potential barriers to motion, the geometry, and the dynamics of molecular groups during the process by the method of interatomic potentials.

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# The Applications of Lewis Acids in Carbohydrate Chemistry

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The review gives a systematic account of the results of studies on the use of Lewis acids as catalysts of the chemical reactions of carbohydrates including polysaccharides. The data concerning the effect of Lewis acids have been grouped. in terms of the types of chemical reactions characteristic of the given class. The scope and certain limitations of their practical applications are indicated.
The bibliography includes 167 references.

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## I. INTRODUCTION

Catalysis by acids and bases of the Brønsted type is widely used in carbohydrate chemistry[1-3]. Systematic studies on the kinetics of reactions under the conditions of homogeneous acid–base catalysis established many qualitative and quantitative rules governing the influence of the acidity of the medium on the kinetic and activation parameters, the equilibrium, and the mechanisms of many reactions of simple sugars (see, for example, Refs. 4–10). The study of the mechanisms of these reactions promoted in its turn the determination of the fundamental rules of acid–base catalysis and the development of physical organic chemistry[11-14].

The situation is somewhat different as regards the applications of Lewis acids (LA) in carbohydrate chemistry. One cannot say that agents of this type have been altogether disregarded by chemists specialising in the field of carbohydrates. Thus, as early as 1892 Stockhausen and Gatterman[15,16], and then in 1926 Kunz and Hudson[17], drew attention to the formation of the disaccharide chloroderivative when lactose octa-acetate is treated with a solution of aluminium chloride in chloroform. It was shown that the acetyl group at the glycosidic centre ($C_{(1)}$) had been substituted by chlorine. The crystalline product isolated from the reaction mixture was called neolactose. In subsequent years, research workers frequently used Lewis acids in order to elucidate the scope of their applications in preparative sugar chemistry. In many instances, these studies led to a significant development of the methods in carbohydrate chemistry. As regards the theoretical aspect of catalysis by Lewis acids, the problem has not been the subject of any kind of systematic investigation. It is useful to survey the available literature data and to outline the principal trends of the development of Lewis acid catalysis as a method in carbohydrate chemistry.

In the vast majority of studies, compounds of the type $MX_n$, where X is a halogen and M the central atom functioning as an acceptor of electron pairs, have been used as Lewis acids. Attempts have been frequently made to arrange systematically compounds of this type in terms of their acid and catalytic functions[18-20], but they did not lead to the development of a universal acidity scale. The relative acidity scale of $MX_n$, obtained on the basis of the valence interactions of the Lewis acid with a base in terms of measurements of the equilibrium constants for these reactions[19], is the most successful:

$$MX_n + yB \rightleftarrows MX_nB_y \quad .$$

This scale in general agrees well with experimental data (for example with the chemical shifts of the $\alpha$-protons in the $^1$H NMR spectra of a series of oxygen compounds coordinated to Lewis acids)[20]. By analogy with the Hammett function $H_0$, Moiseev[21] proposed for variable-valence metal ions an aprotic acidity function $\theta M$, which may be used to interpret processes involving the $\pi$-complexes of ions and unsaturated compounds.

Quantum-chemical calculations have shown that, in estimating the Lewis acidity, one must take into account not only the electronic structure of the central atom but also the steric configuration of the Lewis acid complex with the base[22,23]. On the whole, the problem of the acidity spectrum of Lewis acids is still far from being fully solved, which is a serious obstacle to the development of a quantitative theory.

As in protic catalysis, the mechanisms of the Lewis catalysis of reactions can be represented by schemes providing for the interaction of the central atom of the Lewis acid with the heteroatoms of the carbohydrate molecule, involving the formation of a coordinate of covalent bond. However, with the exception of isolated individual studies[24-28], the experimental research devoted to problems of the formation of complexes by carbohydrates with Lewis acids is still insufficient to infer with any certainty the role of coordination compounds in the catalysis of the reactions of sugars. The problem of the possible activation of molecules by the protic acid produced at the stage in which the Lewis acid is coordinated to the heteroatom (for example $HB + MX_4 \rightarrow HB.MX_4 \rightarrow B - MX_3 + HX$) has not been considered in the literature at all. Nevertheless such a possibility must be taken into account in the analysis of the mechanisms of Lewis catalysis, particularly when the reactions are carried out in the presence of traces of water. In the present review, the literature data have been grouped in terms of their relevance to the characteristic reactions of simple sugars and polysaccharides.

## II. ISOMERIC TRANSFORMATIONS OF *O*-GLYCOSIDES

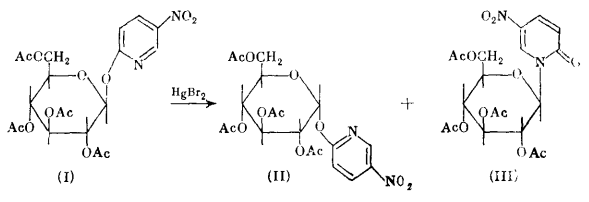
In contrast to monosaccharides and *N*-glycosides, *O*-glycosides are known[1] not to undergo anomerisation in moderately acidic aqueous solutions. Within the framework of general ideas on catalysis by Brønsted acids[6,13], the stability of the *O*-glycoside system can be accounted for by the low basicity of the proton acceptors—the ring and glycosidic oxygen atoms—responsible for the acid activation of the molecule. Appreciable protonation of these centres can be observed only in concentrated acid solutions, but in this case the anomerisation phenomenon is masked by the rapid acid hydrolysis of the *O*-glycosidic linkage. Anomerisation uncomplicated by the hydrolysis of the *O*-glycoside system can be observed in non-aqueous media, for example, in an acid methanolic solution of methyl β-D-glucopyranoside[29] or in inert organic solvents containing added Lewis acids.

This phenomenon was first observed by Pacsu[30-32] on refluxing briefly methyl tetra-*O*-acetyl-β-glucoside, cyclohexyl tetra-*O*-acetyl-β-glucoside, and methyl hepta-*O*-acetyl-β-cellobioside in the presence of $TiCl_4$ or $SnCl_4$ in dry chloroform. Fully acetylated and benzoylated sugars are also anomerised under the influence of $BF_3$ in chloroform, $HgBr_2$ in benzene, and many other Lewis acids in non-aqueous media[33-39]. In contrast to alkyl derivatives, glycosides with aromatic *O*-aglycones do not anomerise appreciably under analogous conditions[40]. The introduction of an electron-accepting aglycone suppresses to a large extent the anomerisation and at the same time increases the probability of the dissociation of the glycosidic linkage and the halogenation of the glycosidic atom. Anomerisation under the influence of non-aqueous $TiCl_4$ solutions is used nowadays in the preparative chemistry of carbohydrates in order to obtain anomeric forms of *O*-glycosides, which are otherwise difficult to synthesise (see, for example, Refs. 39 and 41).

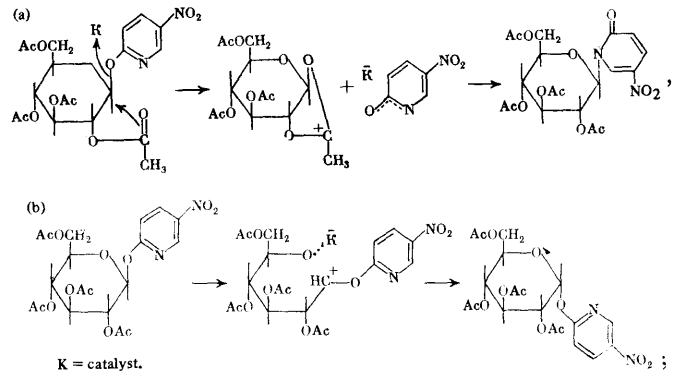
There exist contradictory views concerning the anomerisation mechanism which, incidentally, may be said also of other reactions of the glycosidic centre[5]. The problem of the detailed mechanisms of the catalysis of carbohydrate reactions is one of the most obscure in sugar chemistry. This does not involve the kinetic description of the reaction systems but is concerned with the selection of the most probable scheme for the coordination of the catalytic agent to the active centres and the mechanism of the subsequent reaction of the activated molecules.

According to Lindberg[34], anomerisation involves the opening of the carbohydrate ring with formation and subsequent cyclisation of an intermediate. The scheme of Lemieux and Shyluk[40] provides for the coordination of the catalyst to both ring and glycosidic oxygen atoms and for the possibility of reaction with heterolysis of the glycosidic or inner hemiacetal linkage, but without the formation of kinetically detectable ions.

The anomerisation of the *O*-glycoside (I) in the presence of $HgBr_2$ is accompanied by an intramolecular rearrangement (*ON*-transglycosylation), which results in the formation of the β-anomer of the *N*-glycoside (III)[42]:




The above rearrangement under the influence of Lewis acids has been studied in a number of investigations[38,42-44]. The proposed mechanisms of the catalysis presuppose two possible types of coordination of the Lewis acid—with the glycosidic (a) or ring (b) oxygen atoms, the first of which leads to intramolecular *ON*-trans glycosylation and the second to the anomerisation of the initial *O*-glycoside:



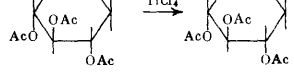

The activities of Lewis acids in the anomerisation reaction (b) increase in the following sequence: $TiCl_4 < SbCl_5 < SnCl_4 < CdCl_2 < ZnBr_2 < HgBr_2$.[38]

Lewis acids are apparently capable of inducing the epimerisation reaction in carbohydrates. For example, D-mannose-6-phosphate epimerises in an acetate buffer at pH 6 and 50°C in the presence of $Fe^{3+}$, $Cr^{3+}$, $Al^{3+}$, etc. to D-fructose-6-phosphate and D-glucose-6-phosphate[45]. The authors suggest that the ability of metal ions to catalyse the isomerisation reaction is determined by their properties as Lewis acids; the selectivity of the reaction does not in essence depend on the catalyst: D-fructose-6-phosphate is formed in all cases.

Another type of isomerisation occurring under the influence of Lewis acids is the Amadori reaction, the kinetics of which have been investigated in the presence of $ZnCl_2$ in anhydrous dioxan[46].

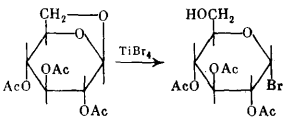
## III. THE FORMATION OF GLYCOSYL HALIDES

The halides of Group IV elements behave in relation to carbohydrates not only as catalysts but also as effective halogenating agents—a factor which must be always borne in mind in the analysis of the mechanisms of Lewis catalysis. When fully or partly acetylated sugars are introduced into the reaction in non-polar or weakly polar media, mainly the substituent at $C_{(1)}$ is replaced by the halogen[15-17]. A method for the synthesis of glycosyl halides, whereby one can obtain unstable anomeric forms of glycosyl halides, has been developed on this basis[47,48]. For example, tetra-*O*-acetyl-β-D-glucopyranosyl chloride can be obtained in a satisfactory yield after a brief treatment of β-D-glucose with a benzene solution of $TiCl_4$:

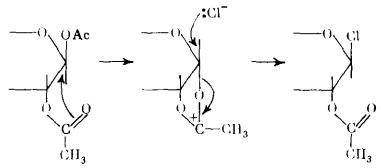



On further treatment of the β-anomer with $TiCl_4$, the former undergoes anomerisation with formation of the α-anomer, which is thermodynamically more stable under the conditions of Lewis catalysis. Anhydrous $AlCl_3$ in

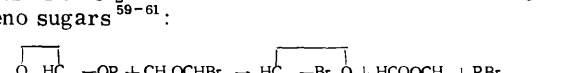
chloroform has a similar effect[47,49-51]. Treatment of tri-*O*-acetyl-laevoglucosan with a $TiBr_4$ solution causes the formation of **2,3,4**-tri-*O*-acetyl-α-glucosyl bromide[52]:



$TiCl_4$ has a similar effect on the hexa-*O*-acetyl derivatives of 1,6-anhydrocellobiose[53] and 1,6-anhydromaltose[54]. When hydrogen halides are used as the halogenating agents, the reaction is completed by the formation of a mixture of anomeric forms of the glycosyl halides in which the more stable α-anomer predominates. In contrast to this, the halogenation reaction involving the halides of Group III and IV elements is controlled by kinetic factors and may be arrested at the stage involving the formation of the β-anomers. The mechanism of the substitution of the aglycone for a halogen in acetyl derivatives of sugars may be represented by a scheme involving the participation of the neighbouring acetyl group[55,56]:



The effect of neighbouring group participation plays an important role in the stereochemical pathways of the reactions of the glycosidic centre[1] and its investigation is essential for the development of methods of stereospecific synthesis of sugar derivatives. For example, it has been established that, in the mercaptanolysis of the penta-*O*-acetyl derivatives of glucose and mannose in the presence of $ZnCl_2$, the reactivity of the β-anomers is much greater than that of the α-anomeric forms[57]. Measurements of the rates of exchange of the acetoxy-group at $C_{(1)}$ in the penta-*O*-acetyl derivatives of glucose and mannose with tin trichloride acetate in the presence of $SnCl_4$ in chloroform showed that the 1,2-*trans*-anomeric forms react much faster than the 1,2-*cis*-anomers[58]. These observations permit the conclusion that there is an intramolecular nucleophilic attack by the acetyl group at $C_{(2)}$ on the glycosidic centre, which weakens the glycosidic linkage (intramolecular nucleophilic catalysis). Acetylated derivatives of pentoses, hexoses, and disaccharides as well as partly acetylated sugars with a free glycosidic hydroxyl readily react with α-halogenoethers in the presence of catalytic amounts of $ZnCl_2$ in chloroform with formation of acetohalogeno sugars[59-61]:

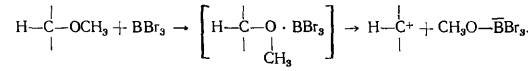


The yields of α-bromo-derivatives of tetra- and penta-*O*-acetylmonosaccharides vary in the range 50–60%.[59]

## IV. THE DISSOCIATION AND FORMATION OF CARBON–OXYGEN BONDS

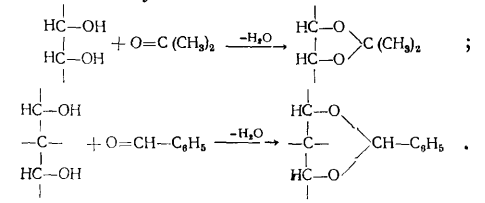
### 1. Chemical Reactions involving the Hydroxy-Groups

An effective low-temperature method for the demethylation of sugar derivatives under the influence of boron halides has been developed[62-66]. The same catalysts may also be used for deacetylation and the removal of the acetal group. For example, for the exhaustive demethylation of 2,3,4,6-tetra-*O*-methylglucopyranose, it is sufficient to keep the ether in methylene chloride in the presence of $BBr_3$ for 30 min at −80°C.[49] The use of $BCl_3$ under the same conditions leads to only partial demethylation (while hydrogen chloride dissociates only the glycosidic linkage and does not affect the ether linkages[65]) and the elimination of the methyl group may be accompanied by epimerisation at the carbon atom undergoing *O*-demethylation[67]. Monosaccharides are fully resistant to the action of $BCl_3$, with the exception of D-fructose and L-sorbose, the demethylation of which is accompanied by the formation of appreciable amounts of 5-hydroxymethylfurfural[66]. It has been noted that, in contrast to $BBr_3$, $BCl_3$ does not cleave the glycosidic linkages in disaccharides. Polycondensation with formation of di- and oligo-saccharides is also possible in the demethylation process[63]. There is no information in the literature about the mechanism of the demethylation reactions. It is suggested that the first stage involves the heterolysis of the carbon–oxygen bond in accordance with the scheme[64]

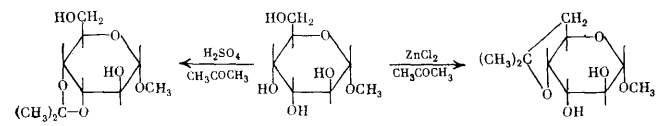


Lewis acids are widely used in the chemistry of carbohydrates, including polysaccharides, in order to synthesise ethers, including the selective protection of hydroxy-groups. $CH_2N_2 + BF_3$ (or $BF_3$ etherate) is a convenient methylating system for the synthesis of methyl ethers of sugars[68-72]. For example, a method has been developed on this basis for the synthesis of 2-*O*-methyl-D-galactose, involving the treatment of 4,6-*O*-benzylidene-3-*O*-benzoyl-β-benzyl-D-galactopyranoside with an excess of $CH_2N_2$ in solution in methylene chloride in the presence of $BF_3$ etherate, followed by debenzoylation under the influence of lithium tetrahydro-aluminate and hydrogenolysis over palladised charcoal[69].

Much attention has been devoted in carbohydrate chemistry to anhydrous zinc chloride as the catalyst of the selective protection of glycol OH groups by the formation of isopropylidene and benzylidene derivatives[73-75]:



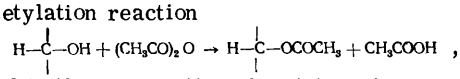
Both strong inorganic acids and $ZnCl_2$ can be used in the synthesis of the isopropylidene derivatives (1)[75-77]. On the other hand, in order to obtain benzylidene derivatives (2), mainly $ZnCl_2$ is used[74,78-82]. When the isopropylidene protecting group is introduced in the presence of $ZnCl_2$, the six-membered *m*-dioxan ring is formed preferentially. It is less stable than the five-membered dioxolan ring formed in the reaction catalysed by protic acids[83]:



A similar tendency has been observed also in catalysis by zinc chloride of the reaction involving the formation of benzylidene derivatives[74,78,84]. Incidentally, this rule is

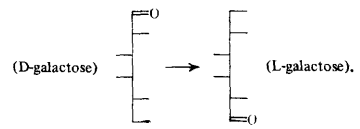
not entirely rigorous. The structure of the cyclic protecting group depends not only on the nature of the catalyst, but also on the form in which the initial monosaccharide participates in the reaction—open-chain or cyclic. In particular, when *O*-glycosides with the cyclic structure are substituted by acetone, the isopropylidene protecting group gives rise to *m*-dioxan and dioxolan rings. On the other hand, the isopropylidene protecting group enters into the open-chain forms of monosaccharides mainly as the dioxolan fragment.

The acetylation reaction



widely used in the preparative chemistry of sugars, is catalysed by both acid and basic catalysts. Among the Lewis acids used in this reaction, $ZnCl_2$ is most common. Fructose[85,86], salts of aldonic acids[87], cellulose[88], and other derivatives have been successfully acetylated in the presence of $ZnCl_2$. The addition of $BF_3$ accelerates the acetylation of uronic acids by acetic anhydride[51,89]. As in other reactions of sugars, the anomerisation of partly or fully acetylated forms is a complicating factor. In the presence of acid catalysts, the equilibrium shifts towards the preferential accumulation of the $\alpha$-anomer as the temperature is raised. $ZnCl_2$ can therefore be used to obtain the $\alpha$-anomer directly during acetylation with a mixture of acetic anhydride and acetic acid. For example, in order to obtain the $\alpha$-anomer of penta-*O*-acetylgalactopyranose, it is sufficient to treat the $\beta$-anomer with the acetylating mixture in the presence of $ZnCl_2$.[90,91]

We may note that the D–L isomerisation of a galactose derivative has been achieved by Micheel and coworkers[92,93] on the basis of the acetylation reaction in the presence of $ZnCl_2$ via the mechanism

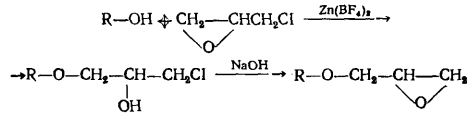



i.e. by converting the 6-hydroxy-group into a formyl group and the glycosidic centre into a primary alcohol fragment. They showed that treatment of 2,3,4,5-tetra-*O*-acetyl-6-tosyl-*al*-D-galactose with zinc chloride in acetic anhydride leads to the formation of a racemic mixture of the D- and L-forms of hepta-*O*-acetylgalactose. After 30 years, Micheel returned to the study of this reaction and confirmed with the aid of $C_{(1)}$-labelled galactose the validity of the fundamental isomerisation mechanism[94].

It has been shown that $BF_3$ in anhydrous dioxan catalyses the formation of methyl 4,6-*O*-methylene-D-glycopyranosides on reaction of methyl glycopyranosides with formaldehyde[95]. Furthermore, $BF_3$ and $SbCl_5$ in methylene chloride catalyse the addition of glycosidic fragments to the free OH groups of acetylcellulose when the latter reacts with *O*-protected thio-, *O*-, and *N*-glycosides[96]. The degree of substitution varies in the range 0.1–0.47 depending on the nature of the glycosylating agent. Compared with $BF_3$ and $SbCl_5$, Lewis acids such as $AlCl_3$, $AlBr_3$, $TiCl_4$, and $ZnCl_2$ proved to be less effective agents in the substitution reaction.

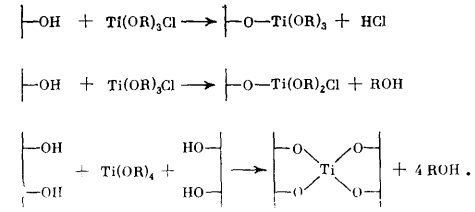
Lewis acids are also used in the chemistry of polysaccharides, particularly cellulose, in order to synthesise its alkyl and acyl derivatives. Comparative studies have shown that the Lewis acids can be arranged in the following sequence in terms of their catalytic activity in the formation of cellulose ethers and esters[97]: $FeCl_3 > SbCl_5 > AlCl_3 > TiCl_4 > SnCl_4 > ZnCl_2 > BF_3.O(C_2H_5)_2 > HgCl_2$.

The influence of Lewis acids on the reactions of cellulose, acetylcellulose cellulosedialdehyde, and carboxymethylcellulose with the epoxy-derivative of butadiene has been studied[98]. It has been shown that the reaction of cellulose with chloromethyloxiran in the presence of zinc tetrafluoroborate followed by treatment of the product with a dilute solution of NaOH leads to the formation of a cellulose ether containing a free epoxy-group[99]:



However, comparative studies of the influence of the addition of acids and bases on the interaction of cellulose with various aromatic mono- and bi-functional epoxy-derivatives have shown that Lewis acids are nevertheless less suitable than alkaline agents for the preparation of cellulose ethers, since they initiate many side reactions arising owing to the degradation of the macromolecules[100].

The interaction of $TiCl_4$, alkoxytitanates, and titanate orthoesters with polyols, unsubstituted sugars, and cellulose leads to the partial or complete substitution of the chlorine atoms and alkoxy-groups and the formation of Ti–O–C linkages as a result of the exchange interaction with the free OH groups of the carbohydrate chains[101,102] for example:



Ammonia, pyridine, formamide, or dimethylformamide are used as the hydrogen chloride acceptors. In contrast to $TiCl_4$ complexes with acetylated sugars, titanium-containing sugar and cellulose ethers [and esters?] are resistant to hydrolysis in weakly alkaline and neutral media.

Lewis acids exhibit a catalytic effect in the transesterification of cellulose nitrates by carboxylic acid chlorides[103–106]. The nitrogen content in the substitution product varies approximately exponentially with catalyst concentration at a fixed instant. For example, in the reaction of cellulose nitrate and acetyl chloride at 20°C, the dependence of the nitrogen content on the $AlCl_3$ concentration is of the following form 60 min after the start of the reaction[106]:

$$\ln [N],\ (\%) = 2.50 - 0.25\,[AlCl_3],\quad r = 0.98.$$

The possible mechanisms of this reaction have been analysed[103].

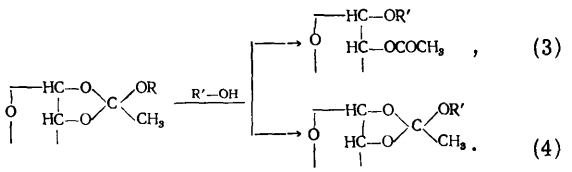
## 2. The Formation and Dissociation of Glycosidic Linkages

The synthesis of *N*-glycosides with strongly and moderately basic aglycones does not as a rule present special difficulties[107]. The problem of finding effective (particularly stereoselective) methods for the synthesis of glycosides with weakly basic aglycones (in particular *O*-glycosides[1]) constitutes a more urgent problem. In the search for these methods, the influence of Lewis acids has been frequently studied. Thus it has been suggested[108] that $ZnCl_2$ be used to synthesise thioglycosides, while in another

study[109] anhydrous $AlCl_3$ was proposed for the synthesis of O-arylglycosides by the Helferich method. However, the greatest success has been achieved in the employment of mercury salts as initiators of the formation of glycosidic linkages[50,56,110-112].

The Zemplen–Helferich version[113,114] of the Koenigs–Knorr O-glycosylation method, according to which mercury acetate or cyanide is added to the organic solvent (benzene, chloroform, nitromethane, acetonitrile) in order to obtain O-alkyl glycosides, has been widely used in laboratory practice. These additives are believed to play the role of acceptors of hydrogen chloride, which is eliminated from the initial acyl halides, although one cannot rule out the possibility that they also exhibit the catalytic functions characteristic of Lewis acids. Among individual reports, one may mention the catalysis by mercury chloride of the formation of O-glycosidic linkages in 2-deoxysugar derivatives[115-117].

Kochetkov and coworkers[118,119] proposed and subsequently developed significantly[120,124] a method for the synthesis of O-glycosides as a result of the interaction of catalytic amounts of $HgBr_2$:



(3)

(4)

The mode of reaction depends significantly on the nature of the solvent and the amount of catalyst. Thus, the transesterification [reaction (4)] takes place preferentially in dichloroethane with formation of a new orthoester. On the other hand, when nitromethane is used and at $HgBr_2$ concentrations not exceeding $8 \times 10^{-3}$ mole per mole of the initial orthoester, the reaction is directed towards glycosylation [reaction (3)].[125] Certain disaccharides and polysaccharides have been obtained by this method[126-128].

One of the highly promising trends in carbohydrate chemistry involves studies on the development of specific methods for the synthesis of polysaccharides[1,129]. The vigorous development of research on this problem is associated with the task of finding new biopolymers—blood plasma substitutes, anticoagulants, etc. As a rule the acid-catalysed polycondensation of simple sugars with unsubstituted OH groups leads to the formation of oligo- and poly-saccharides with different sets of hemiacetal and ether linkages between the monosaccharide units and a disordered branched structure. Lewis acids have been used to accelerate the synthesis of polysaccharides only in very few investigations. One may mention the polymerisation of 1,6-anhydroglucose in the presence of boron, aluminium, and iron halides[130], the polymerisation of 1,4-anhydro-2,3,6-tri-O-benzylglucopyranoside in the presence of boron trifluoride etherate and antimony and phosphorous pentafluorides[131], and the copolymerisation of O-substituted derivatives of 1,6-anhydroglucose and 1,6-anhydromaltose under the influence of $PF_5$ in methylene chloride at low temperatures[132]. Tetra-O-acetyl-β-D-mannopyranoside polymerises under the influence of $ZnCl_2$ with formation of oligomers[133]. An approximately 10% yield of a linear polymer with a regular structure has been obtained by treating 2,3,4,2′,3′,4′-hexa-O-acetyl-6-t-butylmelibiosyl chloride with mercury cyanide in boiling nitromethane and subsequent Zemplen deacetylation[134].

The orthoester method of forming O-glycosidic linkages is promising for the specific synthesis of oligo- and polysaccharides[126,127]. Prolonged treatment of partly substituted sugar orthoesters (having one free OH group) with small amounts of $HgBr_2$ in boiling nitromethane leads to the formation of regular polysaccharides. In particular, a galactoglucan—a heteropolysaccharide consisting of alternating α-galactopyranose and α-glucopyranose units linked by 1,6-bonds (molecular weight approximately 1500)—and an arabinan—a polysaccharide made up of α-L-arabinofuranose with α-glycosidic linkages (molecular weight approximately 8000)—have been obtained in this way[126].

There is comparatively little information about the catalytic activity of Lewis acids in reactions involving the dissociation of O-glycosidic linkages. Kinetic studies[135-137] demonstrated a pronounced destructive action of $AlCl_3$, $TiCl_4$, and $SnCl_4$ in non-polar solvents in relation to the acetal linkages of cellulose. During the first 5–10 min from the start of the reaction, the average degree of polymerisation ($DP_{av}$) already reaches its lowest value (150–200) and remains constant virtually without change even after 10 days of treatment with the degrading agent. Under these conditions, temperature does not have a significant influence on the process kinetics. Thus, when cotton cellulose is kept in 0.1% $AlCl_3$ solution in dry carbon tetrachloride for 5 min, $DP_{av}$ falls from 2200 to 200 and in the resulting specimen there are no macromolecules with $DP > 200$ whatsoever. X-Ray diffraction analysis of the degraded specimens showed that the positions and relative intensities of the diffraction reflections remain the same as in the initial cellulose. This result can be explained by the fact that mainly the glycosidic linkages in the structurally disordered regions, which do not give rise to an intrinsic diffraction pattern, are degraded. On the other hand, the ordered part of the cellulose fibre retains its supermolecular structure during treatment with the degrading agent. There is virtually no decomposition from the ends of the chains.

The solvent in which the process is carried out has a marked influence on the degradation kinetics[138]. It has been shown that the degree of degradation of cellulose with 0.1 and 1% solutions of Lewis acids at 20°C diminishes regularly over a period of 5–60 min with increase of the dielectric constant $\epsilon$ of the non-aqueous solvent. The nature of the change of the average degree of polymerisation as a function of $\epsilon$ shows that the subsequent electrostatic interaction plays a significant role together with the donor–acceptor interaction via the lone electron pair of the solvent molecule and the vacant orbital of the central atom of the Lewis acid. For example, the influence of organic solvents with low dielectric constants ($\epsilon < 12$) on the degree of degradation of cellulose specimens by 1% $TiCl_4$ solutions in 60 min can be represented by a relation of the type

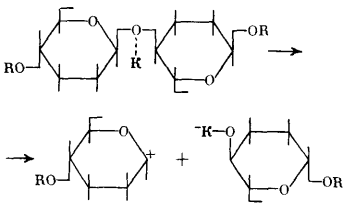
$$DP_{av} = 259.05\varepsilon - 432, \quad r = 0.995.$$

The shape of the curve relating the content of carbonyl groups in the degraded specimens to the dielectric constant, the number of carbonyl groups being determined by the Szabolcs method, makes it possible to reiterate with a greater degree of certainty the conclusion reached above: the degree of degradation of cellulose decreases monotonically with increase of $\epsilon$, which is described quantitatively by the equation

$$[CO] = \frac{1.345}{\varepsilon} + 0.043, \quad r = 0.940.$$

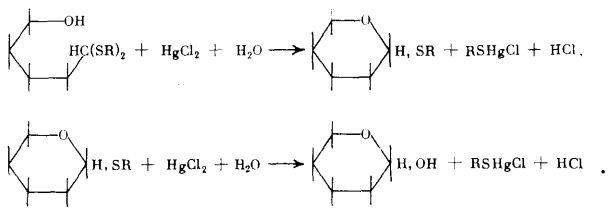
The differential molecular weight distribution curves for the specimens subjected to brief treatment with Lewis acid solutions in dry organic solvents in most cases have a shape close to that of the Gaussian distribution and indicate the formation of specimens homogeneous as regards the degree of polymerisation[139-141], in which the water-soluble fraction does not exceed 2% and there are no macromolecules with a degree of polymerisation exceeding 1000.

The mechanism of the decomposition of the cellulose chain may be represented by a scheme providing for the coordination of the Lewis acid molecule to the ring or glycosidic oxygen atoms and for subsequent heterolysis of the $C_{(1)}$–O bond with formation of a $C_{(1)}$ carbonium ion:



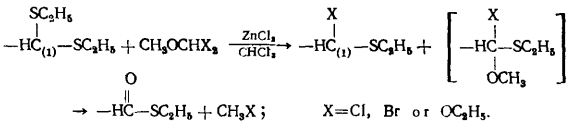
## V. REACTIONS OF SUGAR THIOACETALS

The formation of thioglycosides in the decomposition of dithioacetals in the presence of mercury(II) chloride, established by Schneider and Sepp[142-144] and then by Pacsu and coworkers[145,146] is of great importance for the development of the chemistry of sugar thio-derivatives. The composition of the products of the decomposition of the dithioacetals depends on the reaction conditions and the $HgCl_2$ concentration. In the presence of an excess of $HgCl_2$, stable and readily separated complexes of the dithioacetals with $HgCl_2$, which have been proposed for the identification of sugars[147,148], are formed. The degree of decomposition of the dithioacetals depends on the ratios of the rate constants for the successive stages of the formation of the thioglycoside and its decomposition to the monosaccharide:

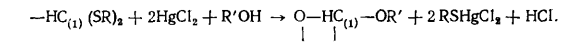


The highest yield has been observed for glucose and ribose thioacetals; the rate of the second stage for mannose and xylose thioacetals is higher than that of the first and it is in practice impossible to isolate the thioglycoside from the reaction mixture[149,150]. It is important to note that thioglycosides in the furanose form may be synthesised by this method. This is favoured by carrying out the reaction at low temperatures and by adding mercury(II) oxide in order to bind hydrogen chloride[151]. The corresponding thioglycopyranosides are produced together with the furanose forms[152].

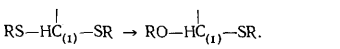
The cleavage of the monosaccharide mercaptals in the presence of catalytic amounts of $ZnCl_2$ and $\alpha$-halogenoethers is accompanied by the formation of products of the substitution of one of the mercapto-groups by a halogen atom and an alkoxy-residue[59]:



In absolute alcohol in the presence of $HgCl_2$, the decomposition of dithioacetals leads to the formation of the corresponding *O*-alkyl glycoside in the furanose or pyranose form[147,151]:



At room temperature in the presence of added mercury(II) oxide, glycofuranosides are formed in high yields[149,153,154]; on the other hand, the formation of glycopyranosides is promoted by an increase of temperature and an acidic pH of the medium[155]. According to Pacsu[156], the formation of *O*-alkyl glycosides under the conditions of the alcoholysis of dithioacetals is preceded by the formation of a mixed acetal:

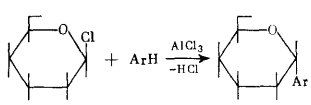


The latter is an intermediate in the *O*-glycosylation reaction. The formation of acetal forms of this kind has been confirmed experimentally[157,158].

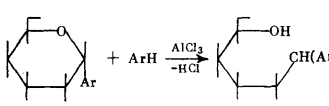
A change in the reaction conditions can lead to the formation of dialkyl acetals, as shown[159] for the diethyl dithioacetal of L-rhamnose. The highest yield of the acetal is observed on low-temperature treatment of the diethyl dithioacetal of fructose in methanol with mercury(II) chloride in the presence of an excess of mercury(II) oxide[156]. When the reaction is carried out in aqueous solution in the presence of $HgCl_2$, the thioacetal protecting groups are fully removed[160,161]. This method is used widely in carbohydrate chemistry, particularly in the synthesis of acetylated *al*-forms of monosaccharides[160] sugars with nitrogen atoms in the carbohydrate ring[162,163], and oligosaccharides[164].

## VI. THE FORMATION OF CARBON–CARBON BONDS

The formation of *C*-glycosides as a result of arylation at $C_{(1)}$ of acetylglucosyl chloride in the presence of anhydrous aluminium chloride, observed by Hurd and Bonner[165,166], may serve as an analogue of the Friedel–Crafts reaction in carbohydrate chemistry:



With increase of $AlCl_3$ concentration, an acyclic disubstituted arylation product is formed:



This reaction is complicated by a number of side processes and for this reason has not found applications in the synthesis of *C*-glycosides[167].

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Summarising the data described, we may note that, although Lewis acids have found fairly extensive applications in the synthesis of various derivatives of simple sugars, nevertheless their possibilities have been by no means fully exhausted. It is already clear that the range of their activity is much wider than that of Brønsted acids, which are extensively used in carbohydrate chemistry. The interaction of Lewis acids with polysaccharides has been investigated to a much lesser extent and the studies have been concerned only with cellulose, without involving other polysaccharides. With rare exceptions, this has been basically applied research. The results which have already been obtained urgently require a further profound development of research in this field.

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# Oxidative Dehydrogenation of Hydrocarbons

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Experimental data are examined and the present state of the theory of the oxidative dehydrogenation reactions of hydrocarbons is discussed. Fundamental varieties of oxidative dehydrogenation have been considered as a function of dehydrogenating agent and the involvement of the solid surface in the process. Attention is concentrated on the elucidation of the process characteristics, the reaction mechanisms, and the nature of the active surface.
The bibliography includes 196 references.

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## I. INTRODUCTION

The abstraction of a hydrogen atom from the dehydrogenated molecule in the oxidative dehydrogenation reaction proceeds under the influence of an oxidant which binds hydrogen into a chemical compound. The most thoroughly investigated dehydrogenating agents (oxidants) are oxygen and iodine, under the influence of which hydrogen is removed from the hydrocarbon molecule with formation of water and hydrogen iodide respectively. Hydrocarbons belonging to different homologous series, namely paraffins, naphthenes, aromatic alkyl-substituted compounds, etc., undergo oxidative dehydrogenation. This process arises from a comparatively recently established and successfully developing series of studies. It makes it possible to synthesise very effectively olefins and diene monomers from more saturated hydrocarbons. The study of the oxidative dehydrogenation reactions as a new and unusual variety of partial oxidation of organic compounds is also of independent theoretical interest.

Various data concerning the oxidative dehydrogenation have been published in a number of reviews [1-8]. Oxidative dehydrogenation reactions are exothermic. The equilibrium yields of lower olefins are higher compared with the usual dehydrogenation of the same hydrocarbons. The dehydrogenation of olefins and aromatic alkyl-substituted hydrocarbons is achieved with high yields of products and selectivity in the presence of oxygen and solid catalysts, while the dehydrogenation of paraffins can be carried out similarly in the presence of iodine and oxygen or solid acceptors of hydrogen iodide.

The oxidative dehydrogenation of butenes to butadiene (or the similar dehydrogenation of isopentenes to isoprenes),

$$C_nH_{2n} + {}^1/_2O_2 \rightarrow C_nH_{2n-2} + H_2O\,, \qquad (1)$$

is a heterogeneous-catalytic reaction. Paraffinic hydrocarbons are oxidised by oxygen in the gas phase by a radical-chain mechanism with low yields of olefins in accordance with the overall equation

$$C_nH_{2n+2} + {}^1/_2O_2 \rightarrow C_nH_{2n} + H_2O\,. \qquad (2)$$

The use of iodine-containing substances makes it possible to achieve fairly readily the dehydrogenation of $C_4$–$C_5$ paraffins to diolefins. Iodine, reduced via the reaction

$$C_nH_{2n+2} + I_2 \rightarrow C_nH_{2n} + 2HI \qquad (3)$$

or

$$C_nH_{2n+2} + 2I_2 \rightarrow C_nH_{2n-2} + 4HI \quad (n \geqslant 4)\,, \qquad (4)$$

can be regenerated by oxidising with oxygen the hydrogen iodide formed:

$$2HI + {}^1/_2O_2 \rightarrow I_2 + H_2O\,, \qquad (5)$$

or by binding it to solid acceptors, for example constant-valence metal oxides:

$$MeO + 2HI \rightarrow H_2O + MeI_2\,, \qquad (6)$$

or variable-valence oxides:

$$Me_2O_3 + 6HI \rightarrow 2MeI_3 + 3H_2O + I_2\,. \qquad (7)$$

In the last case the oxide is partly reduced with liberation of iodine. The iodine sorbed by the acceptor can be regenerated by atmospheric oxygen via the reaction

$$MeI_3 + {}^1/_2O_2 \rightarrow MeO + I_2\,. \qquad (8)$$

Solid catalysts which are not HI acceptors but which are capable of greatly accelerating the oxidative dehydrogenation reactions of paraffins in the presence of iodine and oxygen are also known. The nature of the activity of these catalysts differs significantly from that of the usual heterogeneous catalysts.

Industiral processes for the synthesis of butadiene by the oxidative dehydrogenation of butenes in the presence of oxygen and solid catalysts and of n-butane in the presence of iodine, oxygen, and solid HI acceptors are being developed at the present time. A number of other unsaturated hydrocarbons can also be obtained in high yields with the aid of oxidative dehydrogenation.

## II. DEHYDROGENATION OF PARAFFINIC HYDROCARBONS IN THE GAS PHASE

### 1. THE REACTIONS OF HYDROCARBONS IN THE PRESENCE OF INDIVIDUAL RADICAL-FORMING SUBSTANCES

#### (a) The Nature of the Additive and the Selectivity of the Decomposition Reaction

The reactions of hydrocarbons are influenced significantly by the addition of substances which decompose into radicals or facilitate the formation of free radicals in the reaction system. The acceleration of the decomposition of paraffins by the addition of oxygen, iodine, epoxyethane, nitrogen oxides, hydrogen sulphide, bromine, azomethane, tetramethylethylene, metal alkyls, peroxides, etc.[9-22] and the retardation of the decomposition following the addition of nitric oxide, olefins, oxygen, hydrogen sulphide, hydrogen bromide, amides, hydrides, alkali metal hydroborates, and certain other substances[12,14,17,23-31] have been noted in the literature.

According to modern ideas, the addition of substances promoting the formation of free radicals has a dual effect (accelerating and retarding) on the reaction. The acceleration of the reaction is attributed to the replacement of the step involving chain generation or propagation by faster steps involving a molecule of the additive or the radicals (atoms) formed on its decomposition, while the retardation of the reaction is attributed to the replacement of the more active radical by a less active one or by the involvement of the additive in the chain termination stages[17,32-34]. Depending on the nature of the radical-forming additives and the experimental conditions, the mode of decomposition of hydrocarbons can vary significantly. The change in selectivity may be attributed to the acceleration or retardation of the individual stages of the overall process, leading to the formation of a particular product. In the presence of certain substances (iodine, bromine, chlorine, hydrogen sulphide, oxygen, and nitrous oxide), the ratio of the dehydrogenation and cracking products increases† [10,15,21,35-37].

The influence of the addition of iodine, oxygen, nitric acid, and epoxyethane on the reactions of butane has been investigated[13] under the conditions usually employed in oxidative dehydrogenation: 530°C and dilution with an inert gas at an overall pressure of 1 atm. Under these conditions, the addition of oxygen, iodine, epoxyethane, and nitric acid accelerates the decomposition of n-butane: in the absence of these substances, there is no change in n-butane. Cracking is the principal mode of reaction in the presence of all the above radical-forming additives in amounts up to approximately 8%.

The available information about the additives investigated suggests that the reaction of n-butane is initiated via the following process:

$$C_4H_{10} + R \rightarrow \dot{C}_4H_9 + RH\,, \qquad (9)$$

where $R = \dot{I}$, $O_2$, $\dot{N}O_2$ or $\dot{C}H_3$, and the activation energies $\epsilon$ are respectively ~25, 40, 23, and 10 kcal mole$^{-1}$.[17,19,38,39]

The mechanism of the decomposition of the butyl radical with formation of cracking products in the presence of small amounts of additives is apparently the same as in the absence of additives, as shown by the similarity of the composition of the decomposition products. The cracking products are formed via the unimolecular decomposition of the butyl radical and the interaction of lower alkyl radicals with the initial molecule:

$$\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6 \quad \varepsilon = 23\text{—}27 \text{ kcal mole}^{-1}, \qquad (10)$$

$$\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4\,, \qquad (11)$$

$$C_4H_{10} + \dot{C}H_3 \rightarrow \dot{C}_4H_9 + CH_4 \quad \varepsilon \simeq 9 \text{ kcal mole}^{-1}, \qquad (12)$$

$$C_4H_{10} + \dot{C}_2H_5 \rightarrow \dot{C}_4H_9 + C_2H_6\,. \qquad (13)$$

When much greater amounts of the additives are introduced (up to 15–30%), differences are observed in the mode of reaction depending on the nature of the radical-forming substance, which indicates the interaction of the butyl radical with the additive. In the presence of iodine, dehydrogenation takes place and in the presence of the same amount of the other compounds cracking products are formed.

The activation energies quoted for reaction (9) in which hydrogen atoms are abstracted show that the dehydrogenating action of the additives is not related to their activity with respect to the abstraction of hydrogen atoms. Evidently the formation of large amounts of olefins does not involve the abstraction of hydrogen atoms by the active species from the alkyl radical, i.e.

$$\dot{C}_4H_9 + R \rightarrow C_4H_8 + HR\,,$$

and takes place via addition reactions between them.

Thus the dehydrogenating action of iodine is associated with the properties of the intermediates formed during the interaction between the alkyl radical and the additive. The interaction of the butyl radical with iodine

$$\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_9I$$

or

$$\dot{C}_4H_9 + I_2 \rightarrow C_4H_9I + \dot{I}$$

leads to the formation of alkyl iodides, which readily decompose at temperatures below 300° with formation of an olefin and HI or an olefin, a paraffin, and iodine[40,41].

One principle of the action of effective dehydrogenating agents (radical-forming substances), which is apparently general, follows from the data presented: the dehydrogenating effect of radical-forming substances is due to their inability to form compounds with alkyl radicals, which readily decompose into olefins.

#### (b) Dehydrogenation in the Presence of Iodine.

The conversion of paraffinic hydrocarbons into olefins by reaction (3) at approximately 300°C proceeds according to Benson's data via the interaction of the alkyl radical with an iodine molecule and the decomposition of the iodide thus produced. For example, the following equations may be formulated for the dehydrogenation of propane to propene[38]:

$$\begin{gathered} I_2 + M \rightleftarrows 2\dot{I} + M \quad \varepsilon = 35{,}5 \text{ kcal mole}, \\ C_3H_8 + \dot{I} \rightleftarrows \text{iso-}\dot{C}_3C_7 + HI \quad \varepsilon \simeq 25 \text{ kcal mole}^{-1}, \\ \text{iso-}\dot{C}_3H_7 + I_2 \rightleftarrows \text{iso-}C_3H_7I + \dot{I}\,, \\ \text{iso-}C_3H_7I \rightleftarrows C_3H_6 + HI\,. \end{gathered} \qquad (I)$$

The mechanism of the dehydrogenation of paraffins having a long chain with $C \geqslant 4$ [reaction (4)] has been examined by Raley et al.[15] According to their data,

†Cracking is understood in the present review as the decomposition of the hydrocarbon with rupture of the C–C bond.

paraffins are dehydrogenated to mono-olefins at approximately 300°C via the formation and decomposition of intermediate iodine compounds, as in Benson's mechanism. At higher temperaturss (500°C), the concentration of atomic iodine increases markedly and, according to the authors [15], the preferred pathway involves the formation of olefins via the direct abstraction of a second hydrogen atom by an iodine atom:

$$\dot{C}_nH_{2n+1} + \dot{I} \rightarrow C_nH_{2n} + HI .$$

According to Raley et al. [15], the dehydrogenation of a mono-olefin to a di-olefin proceeds similarly to the dehydrogenation of a paraffin to a mono-olefin. The reaction mechanism for n-butane is as follows:

$$\begin{gathered} I_2 + M \rightleftarrows 2\dot{I} + M , \\ C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI, \varepsilon = 25 - 27 \text{ kcal mole}^{-1} , \\ \dot{C}_4H_9 + \dot{I} \rightarrow C_4H_8 + HI , \\ C_4H_8 + \dot{I} \rightarrow \dot{C}_4H_7 + HI, \varepsilon \simeq 10 \text{ kcal mole}^{-1} , \\ \dot{C}_4H_7 + \dot{I} \rightarrow C_4H_6 + HI . \end{gathered} \qquad (II)$$

However, comparison of the above data for the reaction of n-butane in the presence of iodine and other radical-forming substances is inconsistent with the hypothesis that olefins are formed without an intermediate iodide. The intermediate formation of iodides has also been confirmed by experiments on the decomposition of the latter under dehydrogenation conditions [41].

A more complete mechanism of the dehydrogenation of n-butane has been proposed by Chekhov et al. [42]:

$$\begin{gathered} I_2 + M \rightleftarrows 2\dot{I} + M , \\ C_4H_{10} + I \rightleftarrows \dot{C}_4H_9 + HI , \\ \dot{C}_4H_9 + I_2 \rightleftarrows C_4H_9I + \dot{I} , \\ C_4H_9I + \dot{I} \rightleftarrows C_4H_9 + HI + \dot{I} , \\ C_4H_9I \rightleftarrows C_4H_8 + HI , \\ C_4H_8\text{-}1 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI , \\ C_4H_8\text{-}2 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI , \\ \dot{C}_4H_7 + I_2 \rightleftarrows C_4H_7I + \dot{I} , \\ C_4H_7I + \dot{I} \rightleftarrows C_4H_6 + HI + \dot{I} , \\ C_4H_7I \rightleftarrows C_4H_6 + HI , \end{gathered} \qquad (III)$$

which involves, in conformity with scheme (I), stages in which iodides are formed and, in conformity with scheme (II), stages in which intermediate butenes are formed. Scheme (III) leads to the following equation for the rate of consumption of b-butane, which is close to the experimental equation:

$$w = k\,[C_4H_{10}]\,[I_2]^{1/2}/(1 + \beta),$$

where $\beta$ characterises the reversibility of the reaction. The activation energy for the reaction at 380–535°C is 43 kcal mole$^{-1}$. [43]

The dominant products of the reactions of higher paraffins with iodine are aromatic hydrocarbons:

$$C_nH_{2n+2} + 4I_2 \rightleftarrows C_nH_{2n-6} + 8\,HI \;(n \geqslant 6) .$$

By analogy with catalytic dehydrocyclisation and oxidative dehydrogenation of lower paraffins to diolefins, the aromatisation of $C \geqslant 6$ paraffins presumably proceeds via the following consecutive stages: paraffin → mono-olefin → diene → triene → cyclohexadiene → aromatic hydrocarbon [44].

(c) Reactions of Paraffinic Hydrocarbons in the Presence of Oxygen

One of the products of the high-temperature oxidation of paraffins by oxygen is an olefin with the same number of carbon atoms. However, the yields of dehydrogenation products are small. The main reaction pathway is cracking and, in the presence of high oxygen concentrations, also complete oxidation.

Most workers have adopted nowadays the mechanism of the formation of olefins by reaction (2) involving the successive abstraction of two hydrogen atoms from the paraffin molecule [45-51]:

$$C_nH_{2n+2} + O_2 \rightarrow \dot{C}_nH_{2n+1} + H\dot{O}_2 \; \varepsilon \simeq 40 \text{ kcal mole}^{-1} .$$
$$\dot{C}_nH_{2n+1} + O_2 \rightarrow C_nH_{2n} + H\dot{O}_2 .$$

Appleby et al. [10] proposed a mechanism for the conversion of n-butane in the presence of oxygen, according to which cracking products are formed via the unimolecular decomposition of the butyl radical [reactions (10)–(13)]. The mechanism involves stages in which butene is formed and also chain propagation and termination stages with participation of the $H\dot{O}_2$ radical:

$$\begin{gathered} C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2 , \\ \dot{C}_4H_9 + O_2 \rightarrow C_4H_8 + H\dot{O}_2 , \\ H\dot{O}_2 + C_4H_{10} \rightarrow H_2O_2 + \dot{C}_4H_9 , \\ 2\,H\dot{O}_2 \rightarrow H_2O_2 + O_2 , \\ H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/_2O_2 , \\ 2\,H\dot{O}_2 \xrightarrow{\text{wall}} H_2O + 1{,}5\,O_2 , \\ \dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6 , \\ \dot{C}H_3 + C_4H_{10} \rightarrow CH_4 + \dot{C}_4H_9 , \\ \dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4 , \\ \dot{C}_2H_5 + C_4H_{10} \rightarrow C_2H_6 + \dot{C}_4H_9 . \end{gathered} \qquad (IV)$$

Scheme (IV) leads to a kinetic equation whose order is 1.5 with respect to butane and 0.5 with respect to oxygen, in agreement with experimental data in the presence of small amounts of added oxygen. However, this scheme does not agree with the kinetic equations for oxygen : butane ratios greater than 0.08–0.1, which involve higher orders with respect to butane and oxygen under these conditions [51]. Furthermore, scheme (IV) does not include reactions with participation of reactive $\dot{O}H$ radicals present in the hydrocarbon–oxygen reaction system (the activation energy for the abstraction of a hydrogen atom by the $\dot{O}H$ radical from the n-butane molecule should be not more than 8 kcal mole$^{-1}$) nor does it include reactions involving the formation of extensive oxidation products. With increase of the concentration of oxygen, its interaction with butyl radicals becomes more significant. We have proposed [51] a mechanism for the formation of cracking and far-reaching oxidation products of n-butane, which includes, in contrast to scheme (IV), reactions involving the formation, isomerisation, and decomposition of peroxy-radicals, a chain propagation stage with participation of the $\dot{O}H$ radical and unimolecular $\dot{O}H$ termination, as well as the overall formaldehyde oxidation reaction:

$$\begin{gathered} C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2 , \\ \dot{C}_4H_9 + O_2 \rightarrow C_4H_8 + H\dot{O}_2 , \\ C_4H_{10} + H\dot{O}_2 \rightarrow \dot{C}_4H_9 + H_2O_2 , \\ H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/_2O_2 , \\ \dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6 , \\ \dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4 , \\ C_4H_{10} + \dot{C}H_3 \rightarrow \dot{C}_4H_9 + CH_4 , \end{gathered}$$

$$
\begin{gathered}
C_4H_{10} + \dot{C}_2H_5 \rightarrow \dot{C}_4H_9 + C_2H_6 , \\
\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2 , \\
n\text{-}C_4H_9\dot{O}_2 \rightarrow \dot{C}_4H_8O_2H , \\
\dot{C}_4H_8O_2H \rightarrow C_3H_6 + CH_2O + \dot{O}H , \\
C_4H_{10} + \dot{O}H \rightarrow \dot{C}_4H_9 + H_2O , \\
CH_2O + O_2 \rightarrow CO_2 + H_2O , \\
iso\text{-}C_4H_9\dot{O}_2 \rightarrow \dot{C}_3H_4CH(O_2H)CH_3 , \\
\dot{C}_3H_4CH(O_2H)CH_3 \rightarrow C_3H_4 + CO + \dot{O}H + CH_4 , \\
\dot{O}H \xrightarrow{wall} \text{termination} .
\end{gathered}
\qquad (V)
$$

Scheme (V) leads to kinetic equations for cracking and extensive oxidation, which are of second order with respect to butane and of third order with respect to oxygen, in agreement with experimental data.

## 2. DEHYDROGENATION OF PARAFFINIC HYDROCARBONS IN THE PRESENCE OF IODINE AND OXYGEN

The dehydrogenation of paraffins in the joint presence of iodine and oxygen was first investigated by Raley et al.[15], who concluded that the role of oxygen consists in regenerating iodine via reaction (5). They proposed a reaction mechanism for 500°C:

$$
\begin{gathered}
I_2 + M \rightleftarrows 2\dot{I} + M , \\
C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI , \\
\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_8 + HI , \\
C_4H_8 + \dot{I} \rightarrow \dot{C}_4H_7 + HI , \\
\dot{C}_4H_7 + \dot{I} \rightarrow C_4H_6 + HI , \\
2HI + {}^1/_2O_2 \rightarrow I_2 + H_2O , \\
\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2 ,
\end{gathered}
\qquad (VI)
$$

$C_4H_9\dot{O}_2$ – cracking and extensive oxidation products.

However, further investigations showed that the role of oxygen is not limited to its participation in the oxidation of hydrogen iodide [reaction 5].[1,52,53] The role of oxygen and iodine depends on the reactant concentration ratios. At concentrations close to those employed by Raley et al. (equimolar iodine/hydrocarbon ratio, amount of oxygen much less than that of iodine), oxygen reacts mainly with hydrogen iodide, since the dissociation energy of the H–I bond (71.3 kcal mole$^{-1}$) is much smaller than that of the C–H bond in the paraffin (89–95 kcal mole$^{-1}$).

With decrease of the amount of iodine in the system and increase of the concentration of oxygen, one of the functions of the latter becomes the generation of the active radicals $\dot{O}H$, $\dot{C}H_3$, etc., as happens in the reaction of n-butane in the absence of iodine (see above). Calculation based on the kinetic equation of the collision theory assuming that the pre-exponential factors are the same showed that the rates of abstraction of a hydrogen atom by an oxygen molecule,

$$C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2 , \qquad (O)$$

and an iodine atom,

$$C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI , \qquad (i)$$

are comparable at approximately 500°C, provided that the concentration of atomic iodine is approximately $10^4$ times smaller than that of molecular oxygen:

$$\frac{w_0}{w_i} = \frac{a_0\, e^{-40/RT}\,[C_4H_{10}]\,[O_2]}{a_i\, e^{-25/RT}\,[C_4H_{10}]\,[\dot{I}]} \simeq 10^{-4}\,\frac{[O_2]}{[\dot{I}]} .$$

This ratio of $w_0$ and $w_i$ can obtain in the presence of an excess of oxygen by one or two orders of magnitude relative to molecular iodine, since the equilibrium degree of dissociation of iodine molecules into atoms is approximately $10^{-2}$ at 530°C, while under the conditions of the reacting system the equilibrium is apparently not attained.

The fact that $w_0$ and $w_i$ are comparable implies the dominant role of oxygen in the formation of alkyl radicals, since the reactions of oxygen with a hydrocarbon involve the formation of considerable amounts of species more active than iodine and oxygen ($\dot{O}H$, $H\dot{O}_2$, $\dot{C}H_3$, etc.). This conclusion is confirmed by kinetic data for the conversion of n-butane in the presence of equimolar amounts of oxygen and small amounts of iodine[52-54].

The role of iodine introduced in small amounts consists mainly in its participation in the stages determining the selectivity of the reaction, i.e. in the stages of further transformation of butyl radicals and not their generation. This is indicated, in particular, by the fact that the addition of iodine up to approximately 7% relative to butane increases the fraction of dehydration products, but has little influence on the degree of conversion of the hydrocarbon[53,55]. Apart from its participation in the formation of dehydrogenation products, the role of iodine consists in inhibiting cracking, which may occur in consequence of the replacement of active radicals by less active species, for example as a result of the replacement of alkyl or hydroxy-radicals by iodine atoms[18]. When larger amounts of iodine are introduced into the system, the reaction of atomic iodine with the initial butane begins to play an increasing role:

$$C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI ,$$

as a result of which the rate of conversion of butane increases.

The above considerations may be applicable also to the subsequent two hydrogen abstraction stages: its abstraction from the butene molecule and from the butenyl radical. Butene is known to be oxidised in the presence of oxygen at high temperatures with high degrees of conversion, the first stage of the reaction consisting of the formation of the butenyl radical[9], and in the absence of iodine or special catalysts, for example bismuth molybdate (see below), appreciable amounts of butadiene are not formed.

Until recently, there have been few data on the mechanism of the regeneration of iodine by oxygen [reaction (5)]. In the development of the mechanism of the dehydrogenation of butane in the presence of iodine and oxygen (see below), the present author proposed a radical HI oxidation stage:

$$HI + O_2 \rightarrow \dot{I} + H\dot{O}_2 , \qquad (14)$$

the activation energy of which was estimated as approximately equal to the heat of reaction (approximately 20 kcal mole$^{-1}$).

The following mechanism has been proposed recently for the oxidation of hydrogen iodide at temperatures in the range 100–200°C[56]:

$$
\begin{gathered}
HI + O_2 \rightleftarrows \dot{I} + H\dot{O}_2 , \\
HI + H\dot{O}_2 \rightleftarrows \dot{I} + H_2O_2 , \\
2\dot{I} + M \rightleftarrows I_2 + M .
\end{gathered}
$$

The activation energy was found to be close to 20 kcal mole$^{-1}$. The reaction is inhibited by the product (iodine).

On the basis of the conclusions reached concerning the role of the individual reactants and about the intermediate formation of iodides and butenes[13,41], the present author

proposed a mechanism for the dehydrogenation of n-butane to butadiene in the presence of oxygen and iodine for small iodine/oxygen ratios [52,53]:

$$
\begin{aligned}
&I_2 + M \rightarrow 2\dot{I} + M\,,\\
&C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2\,,\\
&C_4H_{10} + H\dot{O}_2 \rightarrow \dot{C}_4H_9 + H_2O_2\,,\\
&C_4H_{10} + \dot{O}H \rightarrow \dot{C}_4H_9 + H_2O\,,\\
&C_4H_{10} + \dot{C}H_3 \rightarrow \dot{C}_4H_9 + CH_4\,,\\
&C_4H_{10} + \dot{C}_2H_5 \rightarrow \dot{C}_4H_9 + C_2H_6\,,\\
&\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_9I\,,\\
&\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2\,,\\
&\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6\,,\\
&\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4\,,\\
&C_4H_9I \rightarrow C_4H_8 + HI\,,\\
&C_4H_9\dot{O}_2 \rightarrow \dot{O}H + \text{cracking and extensive oxidation products,}\\
&C_4H_8 + H\dot{O}_2 \rightarrow \dot{C}_4H_7 + H_2O_2\,,\\
&C_4H_8 + \dot{O}H \rightarrow \dot{C}_4H_7 + H_2O\,,\\
&C_4H_8 + \dot{C}H_3 \rightarrow \dot{C}_4H_7 + CH_4\,,\\
&C_4H_8 + \dot{C}_2H_5 \rightarrow \dot{C}_4H_7 + C_2H_6\,,\\
&\dot{C}_4H_7 + \dot{I} \rightarrow C_4H_7I\,,\\
&C_4H_7I \rightarrow C_4H_8 + HI\,,\\
&HI + O_2 \rightarrow \dot{I} + H\dot{O}_2\,,\\
&2\dot{I} + M \rightarrow I_2 + M\,,\\
&2\dot{C}_4H_7 \rightarrow \text{termination,}\\
&H_2O_2 \rightarrow H_2O + {}^1/_2O_2\,.
\end{aligned}
\qquad \text{(VII)}
$$

On the assumption of a steady state, scheme (VII) leads to an equation for the rate of dehydrogenation of n-butane to butadiene which is close to that obtained experimentally for low degrees of conversion:

$$w = k\,[C_4H_{10}]^{0.4}\,[I_2]^{0.6}\,[O_2]^{0.4}$$

and to an activation energy which is close to the experimental value (approximately 35 kcal mole$^{-1}$).

A mechanism for the dehydrogenation of n-butane in the presence of iodine and oxygen was also proposed[42,57] by Chekhov and coworkers. It includes, apart from the stages comprised in scheme (III) in the absence of oxygen, also a stage with its participation:

$$
\begin{aligned}
&I_2 + M \rightleftarrows 2\dot{I} + M\\
&C_4H_{10} + \dot{I} \rightleftarrows \dot{C}_4H_9 + HI\,,\\
&\dot{C}_4H_9 + I_2 \rightleftarrows C_4H_9I + \dot{I}\,,\\
&C_4H_9I + \dot{I} \rightleftarrows C_4H_8 + HI + \dot{I}\,,\\
&C_4H_9I \rightleftarrows C_4H_8 + HI\,,\\
&C_4H_8\text{-}1 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI\,,\\
&C_4H_8\text{-}2 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI\,,\\
&\dot{C}_4H_7 + I_2 \rightleftarrows C_4H_7I + \dot{I}\,,\\
&C_4H_7I + \dot{I} \rightleftarrows C_4H_6 + HI + \dot{I}\,,\\
&C_4H_7I \rightleftarrows C_4H_6 + HI\,,\\
&2\,HI + {}^1/_2O_2 \rightarrow I_2 + H_2O\,, \qquad (a)\\
&\dot{C}_4H_9 + O_2 \rightarrow C_4H_8 + H\dot{O}_2\,, \qquad (b)\\
&\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2\,, \qquad (c)\\
&C_4H_9\dot{O}_2 \rightarrow \text{cracking and extensive oxidation products}\,. \qquad (d)
\end{aligned}
\qquad \text{(VIII)}
$$

According to scheme (VIII), the role of oxygen consists, apart from stages (*b*), (*c*), and (*d*) in scheme (VI), in abstracting a hydrogen atom from the butyl radical [reaction (*b*)].

Adel'son et al.[58] proposed the following mechanism for the conversion of isopentane in the presence of iodine and oxygen:

$$
\begin{aligned}
&I_2 + M \rightleftarrows 2\dot{I} + M\,, && (a)\\
&\text{iso-}C_5H_{12} + \dot{I} \rightleftarrows \text{iso-}\dot{C}_5H_{11} + HI\,, && (b)\\
&\text{iso-}\dot{C}_5H_{11} + I_2 \rightleftarrows \text{iso-}C_5H_{11}I + \dot{I}\,, && (c)\\
&\text{iso-}C_5H_{11}I \rightleftarrows \text{iso-}C_5H_{10} + HI\,, && (d)\\
&\text{iso-}C_5H_{10} + \dot{I} \rightleftarrows \text{iso-}\dot{C}_5H_9 + HI\,, && (e)\\
&\text{iso-}\dot{C}_5H_9 + I_2 \rightleftarrows \text{iso-}C_5H_9I + \dot{I}\,, && (f)\\
&\text{iso-}C_5H_9I \rightleftarrows \text{iso-}C_5H_8 + HI\,, && (g)\\
&\text{iso-}C_5H_{12} + H\dot{O}_2 \rightarrow \text{iso-}\dot{C}_5H_{11} + H_2O_2\,, && (h)\ (\text{IX})\\
&\text{iso-}\dot{C}_5H_{11} \rightarrow \dot{C}H_3 + C_4H_8\,,\\
&\text{iso-}\dot{C}_5H_{11} \rightarrow \dot{C}_2H_5 + C_3H_6\,,\\
&2\,H\dot{O}_2 \rightarrow H_2O_2 + O_2\,,\\
&2\,HI + {}^1/_2O_2 \rightarrow I_2 + H_2O\,, && (p)\\
&\text{iso-}\dot{C}_5H_{11} + O_2 \rightarrow \text{iso-}C_5H_{10} + H\dot{O}_2\,, && (r)\\
&\text{iso-}\dot{C}_5H_{11} + O_2 \rightarrow \text{iso-}C_5H_{11}\dot{O}_2\,, && (s)\\
&\text{iso-}C_5H_{11}\dot{O}_2 \rightarrow CO + H_2O + \text{decomposition products.} && (t)
\end{aligned}
$$

The stages in which isopentane is dehydrogenated to isopentenes [reactions (*a*)–(*d*)] are analogous to those in the dehydrogenation of propane via Benson's mechanism (I), while the stages involving the dehydrogenation of isopentenes to isoprene [reactions (*e*)–(*g*)] are analogous to those in the dehydrogenation of isopentane to isopentene. Apart from the reactions included in the previous scheme or processes analogous to them [reactions (*p*)–(*t*)], the role of oxygen consists in the participation of the oxygen-containing radical $H\dot{O}_2$ in the formation of butyl radicals [reaction (*h*)].

Each of the last three mechanisms of the oxidative dehydrogenation of $C_4$–$C_5$ paraffins in the presence of iodine and oxygen [mechanisms (VII)–(IX)] can give a satisfactory quantitative agreement with experimental reaction rates for a reasonable choice of constants for the fundamental stages[54,57,58]. Nevertheless, none of them can claim to be complete. Thus the only reaction of oxygen in scheme (VIII), apart from the regeneration of iodine and the formation of side products, is abstraction of a hydrogen atom from the butyl radical. However, in the presence of iodine, which is much more selective in relation to dehydrogenation than oxygen, this stage hardly plays a significant role. On the other hand, the reactions of the most active radicals ($\dot{O}H$, $\dot{C}H_3$, $\dot{C}_2H_5$, and $H\dot{O}_2$) were not taken into account in this mechanism. For this reason, the applicability of scheme (VIII) to the reaction in the presence of large amounts of oxygen is unlikely. In scheme (IX) for the dehydrogenation of isopentane, the involvement of oxygen is represented by a large number of reactions. However, this scheme also does not include chain propagation reactions with participation of lower alkyl or hydroxy-radicals. In the present author's mechanism (VII) published previously, the reactions of butane in the presence of oxygen and comparatively small amounts of added iodine are represented by the reactions of oxygen-containing lower alkyl radicals with hydrocarbon molecules. However, it does not include certain reactions with participation of iodine, which are present in other schemes: the interaction of atomic iodine with hydrocarbon molecules and of hydrocarbon radicals with molecular iodine.

In later studies, Adel'son and coworkers[59,60] introduced a further series of reactions into scheme (IX), in particular the interaction of hydrocarbon molecules with the methyl radical:

$$\dot{C}H_3 + \text{iso-}C_5H_{12} \rightarrow CH_4 + \text{t-}\dot{C}_5H_{11},$$

$$\dot{C}H_3 + \text{iso-}C_5H_{10} \rightarrow CH_4 + \text{iso-}\dot{C}_5H_9,$$

and of isopentane with the hydroxy-radical:

$$\dot{O}H + \text{iso-}C_5H_{12} \rightarrow H_2O + \text{t-}\dot{C}_5H_{11}.$$

However, in order to devise a sufficiently complete detailed mechanism for the reaction in this extremely complex system, which is subject in addition to the influence of the surface (this will be discussed below), further studies are necessary and it is first essential to revise the kinetic data for the fundamental stages of the dehydrogenation process and concomitant reactions.

## III. DEHYDROGENATION REACTIONS IN THE PRESENCE OF SOLID CATALYSTS

### 1. DEHYDROGENATION OF OLEFINS IN THE PRESENCE OF OXYGEN

#### (a) Certain Experimental Data

The available information about the chemical compositions of the catalysts of the oxidative dehydrogenation of olefins in the presence of oxygen [reaction (1)] and the yields of products is given in the reviews published previously[1,8,61]. High yields of butadiene and isoprene were obtained in the presence of many catalysts having different compositions. Most of them (bismuth–molybdenum, antimony–tin, etc.) were known previously as catalysts of incomplete oxidation. However, certain catalysts of the oxidative dehydrogenation of olefins are similar in composition to the catalysts of ordinary dehydrogenation (for example, the mixed nickel, calcium, and chromium phosphate).

Aromatic alkyl-substituted hydrocarbons also undergo heterogeneous-catalytic oxidative dehydrogenation in the presence of oxygen; however, the optimum catalysts for these substances have a composition different from that of the catalysts for the dehydrogenation of olefins. The high yields of styrene in the dehydrogenation of ethylbenzene in the presence of aluminium oxide are striking[62].

Among binary systems of the type $MoO_3$–oxide of a Group V element (bismuth, arsenic, phosphorus, and antimony) deposited on $\alpha$-$Al_2O_3$, the molybdenum–bismuth catalyst is the most active[63]. Its optimum composition without a carrier or on carriers for the dehydrogenation of $C_4$–$C_5$ olefins lies within the limits of the ratio Bi : Mo = 0.5–2.[64-69]. Among catalysts having the composition $M_mO_n$–$Sb_2O_4$ (where M = Fe, Sn, Mn, V, Cr, Ni, Co, or Cu), the $Fe_2O_3$–$Sb_2O_4$ catalyst (atomic ratio in the range $1/16 \leq Fe/Sb \leq 1/4$) has the best parameters for the dehydrogenation of butene[70] and is followed in this respect by $SnO_2$–$Sb_2O_4$ (optimum composition $1/4 \leq Sn/Sb \leq 4/1$).[71-73] In the presence of the bismuth–molybdenum catalyst, the rate of dehydrogenation of but-1-ene is higher than that of but-2-ene [74,75] and the rate of dehydrogenation of 3-methylbut-1-ene is higher than those of the dehydrogenation of the remaining two isopentene isomers[76,77]. The rates of dehydrogenation of 3-methylbut-1-ene, 2-methylbut-2-ene, and 2-methylbut-1-ene at 386° in the presence of the catalyst with the atomic ratio Mo : Bi = 1 are in the proportions 4.3 : 1.2 : 1.[77]

The dependence of the reactivity of olefins on their molecular structure in the presence of other catalysts has been investigated comparatively little, but it is clear that it can differ significantly from that in the presence of the bismuth–molybdenum catalyst. Thus the yields of isoprene in the presence of the iron–zinc–chromium catalyst in the dehydrogenation of isopentenes decrease in the sequence 2-methylbut-2-ene > 2-methylbut-1-ene > 3-methylbut-1-ene.[78] The reactivities of the isopentene isomers decrease in the same sequence in the presence of phosphoric acid deposited on silica gel[79].

In the presence of the bismuth–molybdenum catalyst, a zero reaction order with respect to oxygen and a nearly first order with respect to mono-olefins is observed over a fairly wide range of concentrations and experimental conditions[80-82]. A zero order with respect to oxygen obtains also with increase of oxygen concentration above a limiting value, which is usually much lower than the concentration of the hydrocarbon. A zero reaction order with respect to oxygen has likewise been observed in the presence of the iron–chromium–zinc and phosphoric acid catalysts[83,84], but has not been found in the presence of the iron–antimony and antimony–tin catalysts even at oxygen concentrations exceeding by several factors of ten the concentration of the olefin. In the presence of low product concentrations, reaction orders close to 1/2 with respect to mono-olefins and oxygen have been found for these catalysts[85].

With decrease of temperature from 420° to 350°C, the apparent activation energy for the dehydrogenation of but-1-ene in the presence of the bismuth–molybdenum catalyst in a stirred reactor increases from 11 to 36 kcal mole$^{-1}$,[86] which has attributed to the inhibition of the reaction by butadiene[87]. Dehydrogenation in the presence of these catalysts may be inhibited by added water and unsaturated carbonyl compounds[88,89], which can be attributed, like the poisoning by butadienes, to the blocking of active centres.

#### (b) The Dehydrogenation Mechanism

Oxidative dehydrogenation of mono-olefins has nowadays come to be regarded as a reaction analogous to allylic oxidation: the oxidation of propene to acrolein and oxidative ammonolysis[66,87,90-92]. According to the mechanism of Adams and Jennings[93], the oxidative dehydrogenation in the presence of the bismuth–molybdenum catalyst proceeds via an intermediate allyl complex, for example:

$$CH_2=CH-CH_2-CH_3 \quad \text{or} \quad CH_3-CH=CH-CH_3 \xrightarrow{(a)} \rightarrow \underbrace{H_2C=CH=CH-CH_3}_{Z} \xrightarrow[+Z_1-O]{(b)} \underbrace{H_2C=CH=CH-CH_2}_{Z} \rightarrow$$

$$\xrightarrow{(c)} Z\,(H_2C=CH-CH=CH_2) \xrightarrow{(d)} H_2C=CH-CH=CH_2. \qquad (X)$$

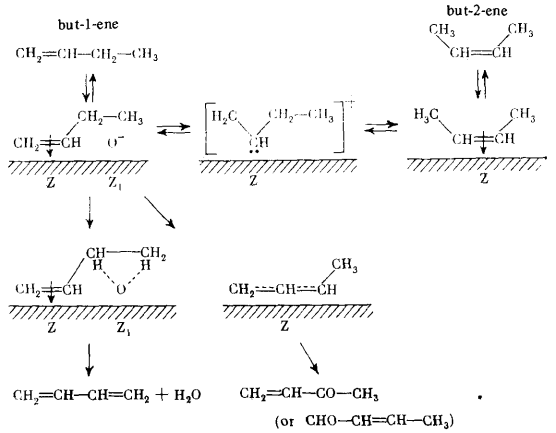
The rate limiting stage is believed to be the dissociative adsorption of the initial olefin.

According to the data of Margolis and Krylov[92,94], who also treat oxidative dehydrogenation as a reaction analogous to allylic oxidation, the stage involving the interaction between the surface hydrocarbon radical and the adsorbed oxygen [reaction (*b*)] is more complex than shown in scheme (X) and includes the formation of an intermediate positively charged hydrocarbon–oxygen complex containing an excess of carbon atoms relative to

oxygen atoms. The rate-limiting stage of the dehydrogenation process is believed to be the formation of the hydrocarbon–oxygen complex.

However, the analogy between the oxidation of propene to acrolein and the oxidative dehydrogenation of butenes is not observed in all cases. This is shown by a number of facts. There are catalysts in the presence of which the oxidation of propene to acrolein and oxidative ammonolysis proceed satisfactorily, while oxidative dehydrogenation takes place to only a slight extent [for example copper (I) oxide[95] and the vanadium–molybdenum catalyst[96]]. On the other hand, other catalysts are more or less active in oxidative dehydrogenation, but allylic oxidation does not take place in their presence [the iron–zinc–chromium, antimony–chromium[97], copper (II) oxide, manganese–molybdenum, vanadium–bismuth, and other[96] catalysts]. However, only partial specificity of catalytic activity to oxidative dehydrogenation reactions and reactions involving oxidation to acrolein is observed even in the presence of bismuth–molybdenum catalysts. Thus the $\beta$-phase is most active in the former reactions while the $\alpha$- and $\gamma$-phases are most active in the latter[99]. In the oxidative dehydrogenation of butenes, the products contain small amounts of methyl vinyl ketone and crotonaldehyde, which must be regarded as very close analogues of acrolein formed via the allylic mechanism. However, the relative yields of butadiene and unsaturated carbonyl products in the presence of the same catalyst differ appreciably for different butene isomers[100]. In the oxidation of isopentene isomers, the reactivity series with respect to unsaturated carbonyl compounds and isoprene do not agree. For example, the rate of partial oxidation in the presence of $Cu_2O$ decreases in the sequence 2-methylbut-1-ene > 2-methylbut-2-ene ≥ 3-methylbut-1-ene, while the rate of oxidative dehydrogenation in the presence of the same catalyst decreases in the sequence 3-methylbut-1-ene > 2-methylbut-1-ene > 2-methylbut-2-ene.[95]

Alkhazov et al.[101] proposed a mechanism for the oxidative dehydrogenation of butenes with the intermediate formation of the surface butene $\pi$-complex; the allyl complex is regarded as an intermediate in the formation of products containing the carbonyl group:




(XI)

According to scheme (XI), the dehydrogenation of but-2-ene can occur only after its preliminary isomerisation to but-1-ene. Scheme (XI) is therefore difficult to apply to the catalysts (iron–antimony[102] and uranium–antimony[103]) in the presence of which but-2-ene is dehydrogenated, but butenes are not isomerised.

The available data suggest that the oxidative dehydrogenation of mono-olefins can proceed via different mechanisms. One of the manifestations of these features is probably the dependence of the relative reactivity of isopentene isomers on the chemical composition of the catalyst. The differences in the mechanisms can consist in the formation of different surface intermediates. Thus in the presence of CuO the rate of oxidative dehydrogenation of 2-methylbut-1-ene and 2-methylbut-2-ene is almost independent of the addition of other mono-olefins (pent-1-ene or 3-methylbut-1-ene), i.e. there is no competition between the hydrocarbons as regards adsorption[98]. This shows that the dehydrogenation reaction on CuO bypasses the isopentene chemisorption stage. The pre-catalytic effect involving an enhancement of the adsorption of butenes under the influence of the adsorption of oxygen has not been observed in the presence of the iron–zinc–chromium catalyst. This effect, indicating the formation of an oxygen–hydrocarbon complex, has been observed in the presence of other catalysts of the oxidative dehydrogenation of butenes (molybdenum–bismuth, antimony–tin, and antimony–chromium). The above findings imply, according to the authors[97], that, in contrast to other catalysts, oxygen does not react with the butene molecule in the presence of the iron–zinc–chromium catalyst and its role consists in oxidising the hydrogen split off from the butene. This may also be the mechanism of the oxidative dehydrogenation of butenes on palladium[104].

During the oxidative dehydrogenation reaction in the presence of the bismuth–molybdenum catalyst, oxygen in the catalyst lattice is consumed. This involves partial reduction of the higher oxides of bismuth and molybdenum to lower oxides. The active oxidised form of the catalyst is maintained by the supply of oxygen from the gas phase. The catalyst dehydrogenation and reduction reactions proceed at comparable rates[105]. Thus the rate of the overall oxidative dehydrogenation process is determined within certain concentration limits by the rate of reduction, which is of first order with respect to butene and of zero order with respect to oxygen. Analogous results, indicating the oxidative dehydrogenation of but-1-ene via alternate oxidation and reduction, have been obtained in the presence of the antimony–tin[106] and iron–antimony[107] catalysts. With increase of the degree of reduction, its rate decreases rapidly, while the rate of oxidation rises. The steady state in the process corresponds to the surface of the iron–antimony catalyst being reduced approximately to the extent of 55%.[107]

The oxidation-reduction mechanism for the reactions of butenes, including side and secondary reactions, can be represented schematically as follows (Boreskov et al.[102]):

$$
\begin{gathered}
K(O) + C_4H_8 \rightleftarrows K(OC_4H_8)\,, \\
K(OC_4H_8) \rightarrow K(C_4H_8) + H_2O \xrightarrow[\text{fast}]{} C_4H_8 + K(r)\,, \\
K(OC_4H_8) \xrightarrow{+x_1K(O)} \nu_1CO_2 + \nu_1H_2O + (x_1+1)K(r)\,, \\
K(O) + C_4H_8 \rightleftarrows K(OC_4H_8)\,, \\
K(OC_4H_8) \xrightarrow{+x_2K(O)} \nu_2CO_2 + 3/4\nu_2H_2O + (x_2+1)K(r)\,, \\
K(r) + O_2 \rightarrow K(O_2^-) \xrightarrow[\text{fast}]{+K(r)} 2K(O)\,,
\end{gathered}
\qquad \text{(XII)}
$$

where K(O) and K($r$) are respectively the oxidation and reduction sites on the catalyst surface, $x_1$ and $x_2$ are coefficients, and $\nu_1$ and $\nu_2$ are stoichiometric coefficients. An interaction of the hydrocarbon molecule with the catalyst surface more extensive than the formation of the intermediate surface butene is not taken into account in scheme (XII). On the assumption that the surface is homogeneous and that there is no mutual influence of the

adsorbed species, but without the postulate that adsorption equilibrium is reached and that a rate-limiting stage is present, scheme (XII) leads to a kinetic equation for the overall conversion of butene with a reaction order of 1/2 with respect to butene and oxygen, in agreement with experimental results. The oxidation-reduction mechanism with alternate oxidation and reduction evidently cannot occur in the presence of catalysts such as $Al_2O_3$ by virtue of the very nature of this catalyst.

In the presence of the spinel zinc–chromium ferrite catalyst, oxidative dehydrogenation also occurs without the involvement of lattice oxygen. The catalyst is not reduced during the reaction. This is suggested by the finding that, in the absence of oxygen, the yield of butadiene is very low. It amounts to not more than several per cent of the yield in the presence of oxygen and falls to zero after the consumption of 1–2 oxygen monolayers [108]. According to the mechanism proposed by the authors [108] for the converson of butene in the presence of the zinc–chromium ferrite catalyst, the first hydrogen atom is abstracted at an active centre consisting of an iron(III) cation with participation of adsorbed oxygen:

$$[A] + C_4H_8 + Fe^{3+} + O_a^- \rightarrow (C_4H_7Fe)^{3+} + OH^- ,$$

while lattice oxygen is involved in the abstraction of the next hydrogen atom:

$$(C_4H_7Fe)^{3+} + O_L^{2-} \rightarrow C_4H_6 + Fe^{2+} + OH .$$

Here [A] is an anionic vacancy associated with $Fe^{3+}$, $O_a^-$ is an adsorbed oxygen radical, and $O_L^{2-}$ is the lattice oxygen. The oxygen involved in the reaction is regenerated by the following processs:

$$2OH^- \rightarrow H_2O + O_L^{2-} + [A] ,$$

$$Fe^{2+} + 1/2O_2 \rightarrow Fe^{3+} + O_a^- .$$

Boreskov et al. [109] observed in the presence of the same specimens of the iron(III) oxide catalyst the occurrence of the dehydrogenation reaction via different mechanisms, one of which was the oxidation-reduction mechanism. Depending on the oxygen content in the reaction mixture, the catalyst operating in the steady state consists of magnetite on which the oxidation-reduction reaction takes place or $\alpha$-$Fe_2O_3$ on which the hydrogenation mechanism is different from the oxidation-reduction mechanism.

### (c) The Nature of the Active Surface of the Catalyst

In many cases, the catalytic activities in the oxidation of propene to acrolein, oxidative ammonolysis, and oxidative dehydrogenation of olefins are found to vary in parallel. For example, all three reactions proceed satisfactorily in the presence of bismuth–molybdenum or antimony–tin catalysts. The optimum compositions of the bismuth–molybdenum catalyst for these reactions are similar. However, as noted above, the specificities of the catalysts in relation to the above reactions are frequently not the same.

Data concerning the influence of chemical composition on catalytic properties agree with the hypothesis that the oxidative dehydrogenation of olefins can proceed via different mechanisms, one of which is analogous to allylic oxidation. In this case, the oxidative dehydrogenation reactions can probably proceed both on active centres for partial oxidation and on other centres.

A correlation is observed between the catalytic properties and the physicochemical characteristics associated with the mobility of the lattice oxygen and the strength with which the hydrocarbon adsorbed on the surface is retained. In order to characterise the mobility of oxygen, parameters such as the susceptibility of the catalysts to reduction [105,110], the diffusion of the bulk-phase lattice oxygen to the catalyst surface [111], the activation energy for the isotope exchange of the lattice oxygen with labelled molecular oxygen [66], and finally the energies of the bonds between oxygen and the catalyst surface, calculated from the heats of oxidation and reduction of the catalyst [112] or from data for the thermal desorption of oxygen from the catalyst surface [113], have been used. The most important conclusion reached in these studies is that the mobility of oxygen must have a definite optimum value for selective oxidation. When the mobility of oxygen is low, the catalyst is inactive, while an excessively high mobility entails the formation of products of the complete oxidation of the hydrocarbon.

The oxygen on the catalyst surface is as a rule inhomogeneous as regards the strength of its binding to the surface; the activity and selectivity of the catalytic action depend on the strength of this binding [112,114]. Thus the removal of 10–12% of the oxygen monolayer from the surface of the calcium-nickel phosphate catalyst leads to a decrease of the degree of conversion of butene and an increase in the selectivity with respect to butadiene [115].

According to Marshneva's data [113], weakly bound oxygen, involved in the complete oxidation reaction, has binding energies of 4–9 kcal $mole^{-1}$ on different catalysts. On the other hand, the energy spectrum of the surface oxygen on the bismuth–molybdenum and iron–antimony catalysts for oxidative dehydrogenation lies in the region above 61 kcal $mole^{-1}$.

The relation between the catalytic properties and the strength of binding of the hydrocarbon to the surface is manifested by the correlations between the reactivity and ionisation potentials [77,78]. Since the adsorbed hydrocarbon species are charged, the ionisation potentials can be regarded as a measure of the capacity of the hydrocarbons for adsorption on the catalyst surface. On the bismuth–molybdenum and antimony–tin catalysis, the reactivity increases, while on the catalysts with iron oxides it diminishes with increase of the ionisation potential [78].

The catalytic properties of individual oxides in mixed catalysts based on them have been compared [101]. Systems comprising mixtures of oxides, one of which is moderately active in relation to extensive oxidation (bismuth, tin, manganese, and indium oxides) and the other is active with respect to the isomerisation of but-1-ene to but-2-ene (molybdenum, tungsten, antimony, and phosphorus oxides), are active in the oxidative dehydrogenation of butenes. The ability of the catalysts to promote isomerisation apparently reflects in a definite manner the optimum energy of binding of the olefin to the catalyst.

There are still few data concerning the nature of the active centres responsible for chemisorption and catalysis in oxidative hydrogenation reactions. The most active incomplete oxidation catalysts are mixed oxides with a definite ratio of the cations (for example Bi : Mo = 2 : 1–1 : 2). Hence follows the hypothesis that allylic oxidation requires the obligatory presence in the catalyst of a doublet consisting of two ions of different kinds on which the hydrocarbon and oxygen are adsorbed respectively [95,116–118]. The presence of paired centres in oxidation catalysts is indicated by the finding that, at high dilutions of the transition metal oxide by a non-transition metal oxide (down to transition metal concentrations of the order

of 1% and less), the catalytic activity diminishes, in contrast, for example, to the catalyst of the usual dehydrogenation, whose activity increases under the conditions of such dilution[94].

Various hypotheses have been put forward concerning the site of adsorption and the nature of the bond between the hydrocarbon and the surface of the catalyst of allylic oxidation. According to Sachtler and de Boer[110,119], the allyl group is retained on the surface as a result of the formation of a carbon–oxygen σ bond between one of the carbon atoms and a surface oxygen ion. Other workers[105] believe it to be more likely that the allyl group is bound to a transition metal ion as a result of the formation of a π-complex, while the hydrogen atom is linked to an oxygen atom. If the hydrocarbon is adsorbed on metal ions, the cations retaining the hydrocarbon in bismuth–molybdenum catalysts may be $Mo^{6+}$ [94,105] or $Bi^{3+}$.[116,120]

In the general case, the presence of cations of different kinds is not an obligatory condition for the oxidative dehydrogenation of olefins. This is demonstrated by the occurrence of dehydrogenation in the presence of catalysts such as silica gel or phosphoric acid on carriers[79,121] and also by the possible occurrence of reactions via an impact mechanism between the adsorbed oxygen and gas-phase olefin molecules (CuO, see above).

The optimum strength of the binding of oxygen to the surface is attained for a definite lattice structure. It is suggested that such a structure may be formed by oxygen ions bound to cations by double bonds[122–125]. This hypothesis is supported by the correlation between the selectivity and the number or strength of the Mo=O double bonds in molybdate catalysts[126,127]. The strength of binding of the complexes to the surface, the degree of deformation of the C–H bonds, and the mobility of oxygen depend on the nature of the positive lattice ions, which is probably the cause of the differences between the reaction mechanisms on catalysts of different chemical compositions. For example, in the presence of the iron–zinc–chromium catalyst, on which there is no interaction between the adsorbed hydrocarbon and oxygen according to Krylova et al.[97], dissociative adsorption apparently takes place on the catalyst cations, similar to the behaviour in the usual catalytic dehydrogenation.

In the presence of catalysts such as phosphoric acid or alumina, the yields of oxidative dehydrogenation products are correlated with their acidic properties[128,129], which probably play a significant role in the nature of their acidity. The phosphoric acid catalyst contains protic and aprotic centres and is poisoned by butylamine. Alumina is a strong aprotic acid. The acid centres of the catalysts can serve as the adsorption sites for the reactant and for the formation of intermediate surface compounds[128,130].

## 2. DEHYDROGENATION OF PARAFFINIC HYDROCARBONS IN THE PRESENCE OF OXYGEN, HALOGENS, AND SULPHUR COMPOUNDS

### (a) Reaction in the Presence of Oxygen

Table 1 presents certain typical data for the formation of the dehydrogenation products of paraffinic hydrocarbons in the presence of oxygen and solid catalysts. Compared with the reaction under similar conditions but in the absence of catalysts (see, for example, Skarchenko[1]), there is a sharp increase of the yields of diolefins.

The overall conversion into dehydrogenation products increases to a lesser extent, although in some cases (n-butane) it may exceed severalfold the yields of these products in the empty reactor. The difference between the reaction in the presence and absence of the catalyst is nevertheless not large enough to rule out the occurrence in the presence of the catalyst of gas-phase reactions, which apparently make a significant contribution to the overall conversion of the hydrocarbon.

Table 1. The formation of dehydrogenation products from paraffinic hydrocarbons in the presence of oxygen and solid catalysts.

| Initial hydrocarbon | Catalyst | Molar ratio $C_nH_{2n+2}$:$O_2$:$N_2$(or $H_2O$) | Temp., °C | Yields of products*, mole % | | Selectivity w.r.t. dehydrogenation products, mole % | Refs. |
|---|---|---|---|---|---|---|---|
| | | | | monoolefins | diolefins | | |
| Ethane | mixed Zn, Pb, and Na oxides | 1:0.4:0 | 770 | 30 | — | 85 | 131 |
| Propane | mixed Na, V, and Al oxides | 1:0.3:1.2 | 490 | 17 | — | 79 | 132 |
| n-Butane | Na phosphomolybdate | 1:1:0 | 600 | 5 | 17 | 78 | 133 |
| n-Butane | nickel–molybdenum | 1:1:8 | 560 | 4 | 11 | 66 | 134 |
| n-Butane | mixed Ni, Mg, and P oxides | 1:1:14 | 593 | 4 | 14 | 44 | 135 |
| n-Butane | mixed Ni, Sn, P, and K oxides | 1:1:10 | 595 | 7 | 20 | 65 | 136 |
| Isopentane | mixed Fe, Ni, and Sb oxides | 1:1:20 | 538 | 1 | 7 | 44 | 137 |

*The yields of products are expressed in mole % relative to the initial hydrocarbon.

The surface of the reactor walls has a significant influence on the oxidation of paraffinic hydrocarbons regardless of whether complete or incomplete oxidation, dehydrogenation, or cracking predominates[1,11,12,41,138–141]. The influence of the solid surface on radical-chain reactions is usually attributed to its involvement in chain initiation and termination processes[11,12,17]. The termination of oxidation chains on the surface may involve the capture of $\dot{O}H$, $\dot{H}O_2$, $\dot{C}H_3$ etc. radicals. The conversion may be initiated on an active surface centre via the reaction[11]

$$C_nH_{2n+2} \xrightarrow{+(O_2)_{ads}} \dot{C}_nH_{2n+1}\,. \qquad (15)$$

However, the initiation and termination of chains on the surface is apparently only the simplest instance of the influence of the surface on the rate of radical-chain reactions. The influence of the surface may be attributed also to its involvement in chain branching of propagation. For example, according to Norikov et al.[139], in the oxidation of n-butane the surface of quartz catalyses the isomerisation of an unstable intermediate (s-butylperoxy-radical), which leads to the formation of one of the products of incomplete oxidation–acetaldehyde.

One of the functions of the catalyst in the oxidative dehydrogenation of paraffins is evidently the inhibition of oxidative cracking and of far-reaching oxidation, which has been observed on the surface of quartz[12,41]. All this does not of course rule out the possibility of the simultaneous occurrence in the system of definite heterogeneous-catalytic oxidative and other reactions with formation of dehydrogenation products. One of the possible mechanisms of the heterogeneous-catalytic oxidative

dehydrogenation of n-butane (in the presence of cobalt molybdate) has been proposed by Boutry et al.[142] The dehydrogenation of paraffins cannot proceed via a mechanism analogous to the dehydrogenation of olefins in the presence of bismuth molybdate, since the latter does not catalyse the dehydrogenation of paraffins[74]. Dieolefins may be formed from the intermediate mono-olefins via the usual heterogeneous-catalytic mechanism. Indeed substances such as phosphates or molybdates dehydrogenate mono-olefins with high yields of dienes. This probably explains the finding that the yields of butadiene in the presence of catalysts become higher than the yields of butenes (Table 1).

Mono-olefins may be formed to some extent via the usual dehydrogenation mechanism: mixed oxides containing substances such as chromium, vanadium, nickel, zinc, etc. are dehydrogenation catalysts[143]. Jouy and Balaceanu[144] indicate the possible role of the interaction of oxygen with the hydrogen removed from the hydrocarbon molecule. Thus all the catalysts which they tested (platinum, aluminium–chromium, etc.) readily oxidised hydrogen and there was no dehydrogenation of paraffin in the absence of oxygen under these conditions.

(b) Dehydrogenation in the Presence of Iodine and Oxygen

The characteristics of the dehydrogenation of n-butane in the presence of solid catalysts were investigated by the present author[1,145,146]. The experiments were performed mainly at 530°C in the presence of small (up to 3–4% relative to the hydrocarbon and oxygen) amounts of iodine. The dehydrogenation reaction is accelerated by the reactor walls, broken quartz, and to a particularly large extent in the presence of certain metal oxides and halides and other compounds on a porous carrier. An analogy is observed between the occurrence of dehydrogenation in the presence of solid catalysts and in the empty reactor. Changes in process parameters such as temperature, contact time, and reactant ratio had approximately the same influence on the conversion of n-butane in the presence of solid catalysts as in the empty reactor. A marked influence, comparable to that of the chemical composition of the catalyst, is shown by factors which determine the surface/volume ratio and the distribution of the surface in the reaction zone.

These studies led to the conclusion[1,146] that oxidative dehydrogenation in the presence of oxygen and iodine is not a heterogeneous-catalytic reaction. The increase of the yield of dehydrogenation products under the influence of solid catalysts cannot be accounted for by the inhibition of a side or secondary reaction, since the catalytic effect of the surface is not necessarily accompanied by a significant change in the distribution of products and the rate of conversion of butadiene in the presence of catalysts is actually higher than in the empty reactor. The characteristics of the action of a solid surface can be explained in terms of the hypothesis that the active surface accelerates a slow stage occurring in the bulk-phase reaction without altering significantly its mechanism. The oxidation of hydrogen iodide and the activation of oxygen and iodine by the surface have been considered to be stages of this kind.

The oxidation of hydrogen iodide [reaction (5)] is accelerated by oxidative dehydrogenation catalysts, but this cannot explain the increase of the yield of butadiene, since the rate of reaction (5) under the experimental conditions greatly exceeded the rate of dehydrogenation[1,147]. To test the possibility of heterogeneous initiation via the reaction of the hydrocarbons with oxygen [reaction (15)], a study was made[41] of the influence of broken quartz packing on the conversion of n-butane in the presence of oxygen. It was found that, under conditions close to those in the dehydrogenation reaction (but without iodine), the quartz surface strongly inhibits the conversion of butane and this is incompatible with the hypothesis of heterogeneous initiation [reaction (15)] with participation of oxygen. The data obtained can be explained if it is assumed that iodine may be activated on the catalyst surface, for example as a result of an increase of the concentration of atomic iodine in the system (analogously to the assumption made by Semenov for the chlorination reaction[18]):

$$I_2 + L \rightarrow L - I + \dot{I}$$

or by the formation of a reactive chemisorbed iodine molecule.

The role of the catalyst consists in accelerating the reactions of hydrocarbon molecules and radicals with iodine. At the same time the solid catalyst may also have a negative influence on the process, accelerating the secondary reactions of the dehydrogenation products.

Oxidative dehydrogenation in the presence of oxygen, iodine, and solid catalysts has also been investigated by Adel'son and coworkers. In the majority of experiments isopentane (and in addition also isopentenes and isobutane) were dehydrogenated and iodine was taken in an amount of 10% relative to carbon and oxygen. The observed characteristics proved to be in many respects analogous to those described above for the dehydrogenation of n-butane. Thus the dehydrogenation of those catalysts is accelerated by the addition of broken quartz[148–150]. The catalytic effect of the surface has been explained by the acceleration of a slow stage of the process[150,151]. The role of the catalyst does not consist in activating oxygen, since the quartz surface inhibits the conversion of hydrocarbons in the absence of iodine[152,153]. However, in contrast to the results quoted above for the dehydrogenation of n-butane, the authors[150,151] concluded that, under the conditions of their experiments, the slowest reaction stage is the oxidation of hydrogen iodide [reaction (5)] and that the role of the catalyst is to accelerate it. It is noteworthy that unduly high activation energies for reaction (14), involving the abstraction of the hydrogen atom from the hydrogen iodide molecule (29 kcal mole$^{-1}$ [150] and 25 kcal mole$^{-1}$ [151]) were used in a comparative estimate of the rates of oxidation of hydrogen iodide and dehydrogenation[150,151] instead of the more reliable value of 20 kcal mole$^{-1}$ (see above). This must have led to unduly low rates of oxidation of HI.

The ratio of the rate of oxidation of HI and dehydrogenation depends in general on the reactivity of the hydrocarbons and the reactant concentration ratios. With increase in the reactivity of the hydrocarbon and the concentration of iodine, which accelerates dehydrogenation and inhibits the oxidation of hydrogen iodide (see Section II), the above rate ratio can change significantly towards a reduced rate of reaction (5) and the acceleration of this reaction by the catalyst then becomes one of the causes of the increase of the yields of dehydrogenation products.

The dehydrogenation of n-hexane in the presence of iodine and oxygen is also accelerated by broken quartz and other active solid catalysts[145]. The main product of the iodine-induced dehydrogenation of n-hexane is benzene regardless of the presence of oxygen or solid catalysts. The preferential formation of the aromatic product takes place not only for appreciable degrees of conversion (above 30–40%) into dehydrocyclisation

products, as in the usual heterogeneous-catalytic processes [143], but also for low degrees of conversion (less than 10%). [145] If the aromatisation of paraffins in the presence of iodine proceeds via intermediate olefins (see above), the implication is that the difference between the reactivity of hexenes and hexane in iodine-induced dehydrogenation is very large.

(c) Dehydrogenation in the Presence of Chlorine- and Bromine-Containing Substances

Considerable advances have been made in recent years in the dehydrogenation of paraffins under the influence of chlorine, bromine, their compounds, and oxygen (Table 2). For the same halogen/hydrocarbon ratio, the yields of dehydrogenation products decrease in the sequence iodine > bromine > chlorine compounds. Mixtures of halogens are extremely effective. Juding from the available data[162,163], more effective dehydrogenation parameters are achieved in the presence of a mixture of iodine, bromine, and chlorine than when only one of the halogens is used. It follows from other patents [164-167] that higher yields of dienes and styrene were achieved in the dehydrogenation of olefins and ethylbenzene respectively than in the dehydrogenation of paraffins in the presence of the same amounts of the halogen. The main products of the dehydrogenation of n-hexane in the presence of HCl and oxygen for degrees of conversion up to 30% were hexenes (Table 2).

Table 2. The yields of products in the presence of HCl or bromine compounds, oxygen, and solid catalysts.

| Initial hydrocarbon | Catalyst | Halogen-containing substance (X) | Molar ratio $C_nH_{2n+2}:X:O_2$ | Temp., °C | Yields of products, mole %: mono-olefins | diolefins | benzene | Selectivity w.r.t. dehydrogenation products, mole % | Refs. |
|---|---|---|---|---|---|---|---|---|---|
| Ethane | Fe, Li, Ln chlorides-$Al_2O_3$ | HCl | 1:1:1 | 575 | 79 | — | — | 87 | 154 |
| n-Butane | $CeCl_3$-$SiO_3$ | HCl | 1:2:1,5 | 560 | 30 | 32 | — | 80 | 155 |
| n-Butane | $Fe_2O_3$-RbCl-$SiO_2$ | HCl | 1:2.3:1.3 | 585 | 28 | 33 | — | 76 | 156 |
| n-Pentane | $Fe_2O_3$-KCl-$SiO_2$ | HCl | 1:1.7:1 | 525 | 32 | 11 | — | 87 | 157 |
| Isopentane | mixed oxides and chlorides | HCl | 1:1.4:1 | 500 | 27 | 20 | — | 79 | 158 |
| n-Hexane | $Fe_2O_3$-CsCl-$SiO_2$ gel | HCl | 1:0.6:0.7 | 521 | 23 | 4 | 2 | 50 | 159 |
| n-Butane | Mg ferrite | HBr | 1:0.16:1.2 | 525 | 3 | 51 | — | 80 | 160 |
| Isopentane | $CoCl_2$-LiCl-$MgCl_2$-pumice | $Br_2$ | 1:0.1:1.9 | 500 | 21 | 17 | — | 71 | 161 |

In the presence of HCl and oxygen but without a catalyst, there is virtually no dehydrogenation. Thus at 550°C and for the butane : HCl : $O_2$ = 1 : 0.8 : 1 ratios, 38% of butenes and butadiene is formed in the presence of the $FeCl_3$–KCl–$SiO_2$ catalyst; in the absence of the catalyst, dehydrogenation products were not detected [168]. Dehydrogenation in the presence of HCl and $O_2$ apparently proceeds via a mechanism different than in the presence of chlorine, which is capable, in contrast to HCl, of interacting directly under the dehydrogenation conditions with the hydrocarbon in the gas phase via a radical-chain mechanism [169]. The role of the catalyst in the dehydrogenation of paraffins in the presence of chlorine may be to generate chlorine atoms by the cleavage of molecular chlorine, as has been assumed for the chlorination of hydrocarbons [18,169]. On the other hand, dehydrogenation in the presence of HCl and oxygen should probably be regarded as a heterogeneous-catalytic reaction.

Both in the presence of chlorine and in the presence of HCl and oxygen, hydrocarbons are probably dehydrogenated via intermediate organic chlorides. These products are formed on direct interaction of the hydrocarbons with chlorine [169]. In the presence of HCl, oxygen, and metal chloride as catalysts, methane and ethane undergo oxidative chlorination with formation of alkyl chlorides in accordance with the overall equation [170]

$$HCl + 1/2O_2 + RH \rightarrow RCl + H_2O .$$

It is also known that $C_3$–$C_4$ alkyl chlorides readily decompose above 300–400°C into olefins and HCl. [169]

There is a correlation between the activity of catalysts in relation to oxidative dehydrogenation and oxidation of HCl:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O . \qquad (16)$$

The activity increases for both reactions in the following series of metal compounds: Nb < Ce < Bi < (Mn, Fe, Co, Ni, Pd) < V < Cu. [171]

Ioffe and Kikot' [155] proposed a multistage mechanism for the dehydrogenation of n-butane to butadiene via the intermediate formation of alkyl and alkenyl chlorides, chlorine, and butenes:

$$\begin{aligned} &4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O , \\ &C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl , \\ &C_4H_9Cl \rightarrow C_4H_8 + HCl , \\ &C_4H_8 + Cl_2 \rightarrow C_4H_7Cl + HCl , \\ &C_4H_7Cl \rightarrow C_4H_6 + HCl , \end{aligned} \qquad (XIII)$$

where the rate-limiting stage is the oxidation of HCl [reaction (16)]. According to scheme (XIII), the hydrocarbon reacts with chlorine alone and the role of oxygen is limited to its involvement in the formation of chlorine [reaction (16)]. According to scheme (XIII), chlorine should be a much more active dehydrogenation agent than HCl, which has not been confirmed experimentally [168].

Tarasova and Solomatina [168] proposed mechanisms for the dehydrogenation of butane to butenes:

$$C_4H_{10} + 1/2O_2 + HCl \rightarrow [C_4H_9Cl] + H_2O \qquad (XIV)$$
$$\downarrow$$
$$C_4H_8 + HCl$$

and to butadiene:

$$C_4H_{10} + 2HCl + O_2 \rightarrow [C_4H_8Cl_2] + 2H_2O \qquad (XV)$$
$$\downarrow$$
$$C_4H_6 + 2HCl ,$$

According to these mechanisms, the reaction proceeds without the formation of intermediate chlorine. These mechanisms reflect to a greater extent the specific features of the process than mechanism (XIII). However, when butadiene is formed [mechanism (XV)], the absence of intermediate butene is doubtful. There are few experimental data concerning the conversion of paraffins into mono- and di-olefins in the absence of chlorine compounds. However, it is known that the dehydrogenation of butane in the presence of HCl and oxygen involves the formation of an appreciable amount of butenes, whose capacity for conversion into butadiene in the presence of the same catalyst is greater than that of butane [172]. At least a significant fraction of butadiene should therefore be formed via butenes.

Bromine compounds behave more like iodine compounds in oxidative dehydrogenation reactions than like chlorine compounds. In the presence of oxygen and HBr (in contrast to HCl and similarly to HI), dehydrogenation occurs also in the empty reactor [147,173]. Thus at 500°C and for the isopentane : oxygen : HBr = 1 : 1 : 2.1 ratios, 13% of isoprene is formed in the absence of the catalyst [173].

When the catalyst ($CoCl_2$, LiCl, and $MgCl_2$ on pumice) was introduced, the yield of isoprene rose to 26%.

In the joint presence of iodine and chlorine or bromine, the dehydrogenation of hydrocarbons apparently proceeds via a radical-chain mechanism. The acceleration of the reaction under the influence of the addition of the second halogen may be associated with the interaction between the halogens, which leads to the replacement of the slow reaction stages by faster stages. For example, when chlorine is added to the paraffin–iodine system, the comparatively slow formation of the alkyl radical on interaction with iodine

$$C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI, \quad \varepsilon \simeq 25 \text{ kcal mole}^{-1}$$

is replaced by the rapid reaction [39]

$$C_4H_{10} + \dot{Cl} \rightarrow \dot{C}_4H_9 + HCl, \quad \varepsilon \simeq 1 \text{ kcal mole}^{-1}.$$

On the other hand, the formation of atomic chlorine in the presence of iodine is facilitated by the fact that it may not involve the dissociation of a chlorine molecule:

$$Cl_2 + M \rightarrow 2\dot{Cl} + M, \quad \varepsilon \simeq 57 \text{ kcal mole}^{-1}$$

but may proceed, for example, via the reaction

$$Cl_2 + \dot{I} \rightarrow ClI + \dot{Cl},$$

whose rate should be much higher.

### (d) The Reaction of Hydrocarbons in the Presence of Sulphur Compounds

Appreciable yields of dehydrogenation products are reached in the presence of sulphur or sulphur compounds ($H_2S$, $SO_2$, COS, etc.) and solid catalysts [174–178]. In the dehydrogenation of ethane in the presence of $H_2S$ and oxygen (with $C_2H_6 : H_2S : O_2 = 1 : 1.5 : 0.75$) and cadmium oxide on $Al_2O_3$ with a specific surface less than 1 $m^2\ g^{-1}$, the yield of ethylene was 77% for a selectivity of about 90%. [174] In the dehydrogenation of butane in a mixture with $SO_2$ on a bismuth–iron phosphate catalyst, the sum of butenes and butadiene formed was 38% for a selectivity of 38%, while in the dehydrogenation of isobutane on molybdenum sulphide the yield of isobutenes was 30% for a selectivity of 61%. [175]

Olefins with long $C_4$–$C_5$ chains are dehydrogenated with higher yields of products than the corresponding paraffins [175]. In the presence of sulphur (0.5 mole) and oxygen (1 mole per mole of hydrocarbon), ethylbenzene is converted into styrene with a yield exceeding 80% for a selectivity above 90%. [178,179] The degree of conversion of n-hexane in the presence of various catalysts and $SO_2$ reached 44–93%. [175] The dominant product for highest degrees of conversion was benzene (in a yield up to 54%). For moderate degrees of conversion, a considerable proportion of the products consisted of olefins, whose yields (up to 23–24%) exceeded those which are reached in the usual catalytic dehydrogenation [143,180]. Thus higher yields are reached in many instances in the dehydrogenation of hydrocarbons in the presence of sulphur compounds than in oxidation by oxygen or in the usual catalytic dehydrogenation.

There are reasons why dehydrogenation in the presence of sulphur compounds should be regarded as a process involving heterogeneous-catalytic reactions [178,185]. In the absence of the catalyst, the reaction proceeds to only a slight extent. Thus the dehydrogenation of n-hexane and cyclohexane (500°C, space velocity 0.5 $h^{-1}$) in a 1 : 1 mixture with $SO_2$ on alumina leads to the formation of up to 15 and 35% of benzene respectively. When alumina is replaced by quartz, the reaction hardly occurs. In the absence of sulphur dioxide, there is also no dehydrogenation on $Al_2O_3$. [182] During the reaction, $SO_2$ interacts directly with the hydrocarbon but not with the hydrogen evolved, since dehydrogenation ceases immediately after the removal of $SO_2$. Here $SO_2$ behaves as a hydrogen acceptor, being converted in the dehydrogenation reaction into hydrogen sulphide, for example:

$$C_4H_{10} + 1/3SO_2 \rightarrow C_4H_8 + 1/3H_2S + 2/3H_2O.$$

By accepting hydrogen, sulphur is similarly converted into hydrogen sulphide, for example via the reaction

$$C_4H_{10} + 1/2S_2 \rightarrow C_4H_8 + H_2S.$$

According to Pasternak and Vadekar [183], mixtures of $H_2S$ and oxygen are more effective. During the oxidation of $H_2S$, which occurs simultaneously with the dehydrogenation reaction, the $S_2$ biradical as well as other active species ($H\dot{S}$, $S_2^+$) are formed and are probably involved in the intermediate dehydrogenation stages.

## IV. DEHYDROGENATION IN THE PRESENCE OF SOLID ACCEPTORS OF HYDROGEN IODIDE

### 1. THE INFLUENCE OF THE CHEMICAL COMPOSITION OF THE HYDROGEN IODIDE ACCEPTOR

The influence of the chemical composition of the acceptor on the yield of n-butane, propane, and isopentane dehydrogenation products in the presence of iodine (but without oxygen) has been investigated [145]. The specimens were prepared by mixing ground oxide powders with a binder. In terms of the yields of the n-butane dehydrogenation products, the constant-valence metal oxides investigated can be arranged in the following sequence:

$$SrO \simeq CaO > ZnO > MgO. \qquad (17)$$

In the presence of variable-valence metal oxides, which are reduced on interaction with HI, the yields of butadiene decrease in the sequence

$$Mn_3O_4 \simeq Fe_2O_3 > Co_3O_4 > Ni_2O_3 > CuO > Cu_2O. \qquad (18)$$

Fairly high yields of butadiene were obtained only in the presence of $Mn_3O_4$ and $Fe_2O_3$. In the presence of the remaining variable-valence metal oxides, the main process is oxidation by the oxygen evolved from the lattices of the oxides as a result of their partial reduction by the hydrocarbon. In the dehydrogenation of propane and isopentane, the oxide acceptors investigated can be arranged, with slight deviations, in the same sequences in terms of the yields of products as in the dehydrogenation of n-butane.

The influence of the chemical composition of HI acceptors on the dehydrogenation of paraffinic hydrocarbons by oxygen supplied to the system has been investigated in a number of studies. The highest yields of isoprene in the presence of calcium, barium, strontium, zinc, nickel, iron, cobalt, copper, and manganese oxides have been obtained when alkaline earth metal and manganese oxides were used [184]. Alkali metal hydroxides deposited on carriers are extremely effective acceptors. In the dehydrogenation of isopentane in the presence of iodine and oxygen, the yield of isoprene decreases in the sequence [185]

$$NaOH > KOH > BaO > CaO > CuO \qquad (19)$$

(the oxides and hydroxides were deposited on $Al_2O_3$).

NaOH, KOH, and $MnO_2$ acceptors deposited on $Al_2O_3$ were investigated[186]. On sodium acceptors, it is possible to achieve higher yields of butadiene and a much smaller loss of iodine from the reactor than in the presence of the manganese acceptor[186]. However, a disadvantage of the sodium acceptor is the appreciable corrosion of the reaction apparatus. In the presence of the potassium acceptor, the loss of iodine from the reactor is smaller, but the yields of butadiene for the same amount of iodine are lower than in the presence of the sodium acceptor[187].

The influence of the chemical composition of HI acceptors in the dehydrocyclisation of n-hexane has been investigated[188]. The metal oxides were prepared by pressing their powders with added binder and potassium iodide. Tor the ratios $C_6H_{14}:I_2:O_2 = 1:{\sim}0.9:1$, the yields of benzene decreased in the sequence

$$Fe_2O_3 > Mn_2O_3 > CaO > ZnO > CuO > Co_3O_4 > Ni_2O_3 \qquad (20)$$

and in the presence of the last four oxides they were lower than in the reaction in the empty reactor.

Under optimum conditions, yields of benzene exceeding 60% were achieved in the dehydrocyclisation of n-hexane in the presence of an acceptor[189], but they do not exceed the yield of this product in the usual catalytic aromatisation. The yields of hexene in the presence of HI acceptors are even lower than in the empty reactor or in the presence of non-accepting solid catalysts. Considerable amounts of coke-like and tarry side products are formed.

The distribution of acceptors in sequences (17)–(20) apparently depends to a definite extent on the method of preparation of the specimens, the additives present, and the experimental conditions. For low amounts of iodine supplied (iodine/hydrocarbon = 0.1) and an equimolar amount of oxygen, the yields of butadiene obtained in the presence of active HI acceptors such as sodium hydroxide on $Al_2O_3$ are lower than in the presence of ground quartz[190] and only a mixture of the acceptor and quartz makes it possible to obtain higher yields of butadiene than on quartz. A similar effect has been observed in the dehydrogenation of isopentane. The fact that the replacement of quartz by an active HI acceptor for low amounts of iodine supplied leads to a decreased yield of diolefins can be accounted for, on the one hand, by the catalytic influence of quartz and, on the other hand, by the fact that the acceptor binds HI and removes a definite proportion of the iodine from the reaction sphere. The study of the time variation of the yield of diolefins showed that, after complete iodination, the acceptor has approximately the same influence on the reaction as the quartz packing.

## 2. THE BINDING OF HYDROGEN IODIDE BY SOLID ACCEPTORS

Reactions involving the absorption of HI [reactions (6) and (7)] belong to the class of exchange topochemical reactions:

$$\text{solid}_{(1)} + \text{gas}_{(1)} \rightarrow \text{solid}_{(2)} + \text{gas}_{(2)}$$

and exhibit properties characteristic of reactions of this type.

The comparative reactivities of a number of metal oxides in relation to HI have been investigated[191,192]. The oxides were prepared in two ways: by deposition in a thin layer on quartz plates and by the granulation of commercial preparations. The oxide grains (approximately 2 mm in size) were the same as those employed in experiments on oxidative dehydrogenation in the presence of iodine (see above). The average thickness of the layer of oxide deposited on plates was approximately 1–2 μm. The specific surfaces of the finished specimens did not exceed several $m^2\ g^{-1}$ and their pore volumes were in the range 0.1–0.3 $cm^3\ g^{-1}$. The experimental data for the oxides investigated are described by the kinetic equation

$$\alpha = kt^n \qquad (21)$$

or

$$1 - \sqrt[3]{1-\alpha} = kt^m\,, \qquad (22)$$

where $\alpha$ is the degree of conversion and $n$ and $m$ are constants. The reactions of the metal oxides with HI are retarded up to a complete arrest for degrees of conversion departing widely from equilibrium. The granulated constant-valence metal oxides can be arranged in the following sequence in terms of their reactivity for low (up to 1–2%) degrees of conversion:

$$SrO > BaO > CaO > ZnO > MgO\,, \qquad (23)$$

while variable-valence metal oxides can be arranged in the following sequence:

$$Mn_3O_4 > Co_3O_4 > CuO > Fe_2O_3 > Ni_2O_3\,. \qquad (24)$$

The rate of reaction of the granulated metal oxides with HI is much lower than that of the oxides deposited on plates. For all the oxides in the grains, except zinc oxide, the reaction virtually ceases under the conditions investigated when the degree of conversion is less than 5%. The degree of conversion reached for the same oxide on plates is between 10 and 95%. Thus the dependence of the reactivity of the oxides on their particle size is so great that it is manifested even more markedly than its dependence on the chemical nature of the oxide. The arrest of the reaction of the oxide with hydrogen iodide under conditions remote from equilibrium has been explained[192] in terms of the theory of impedance in topochemical reactions[193]. The ionic radius of $I^-$ (2.2 Å) greatly exceeds that of $O^{2-}$ (1.4 Å). The molar volume of the iodide formed is therefore much greater than that of the initial oxide, i.e. the volume of the reaction system greatly increases during the reaction. The molar volumes of the iodides of the metals investigated (calcium, magnesium, strontium, barium, manganese, nickel, and copper) are greater by a factor of 2.7–5.8 than those of the corresponding metal oxides. As a consequence of the increased volume of the system, the conversion of the oxide into the iodide entails an increase in the compactness of the outer layer of the specimen, which inhibits the diffusion of HI into the bulk of the oxide and the removal of water vapour, and, in the case of variable-valence oxides, also the removal of iodine from the reaction zone.

In the majority of experiments with oxides deposited on plates and with granulated oxides in all cases, the observed values of $n$ and $m$ in Eqns. (21) and (22) were smaller than unity and the apparent activation energies above 400°C did not exceed 10–11 kcal $mole^{-1}$,[194] which is characteristic of reactions occurring under conditions with diffusion-induced inhibition. The only exception (with respect to the values of $m$ and activation energies) is ZnO on plates. The product of the reaction of ZnO with HI (zinc iodide) sublimes under the experimental conditions. The removal of the iodide from catalyst sites containing ZnO which has not reacted should lead to an increase with time

of the proportion of defects in the surface layer of the oxide and to the formation of transport pores, which is probably the cause of the pronounced S-shape of the kinetic curves for reactions involving the absorption of HI by zinc oxide and also the comparatively small extent of the diffusion-induced inhibition of this reaction [192]. The impedance phenomenon has a significant influence on the dehydrogenation process in the presence of oxides which are HI acceptors. The acceptor is rapidly exhausted, so that its large excess relative to the hydrocarbon is required.

### 3. FACTORS DETERMINING THE EFFICIENCY OF HYDROGEN IODIDE ACCEPTORS IN THE OXIDATIVE DEHYDROGENATION PROCESS

In order to elucidate the factors which determine the efficiency of HI acceptors, the yields of dehydrogenation products were compared with the rates and equilibria of the reactions of metal oxides with hydrogen iodide [41,145]. At temperatures in the range 300–530°C, the equilibrium degree of conversion of all the oxides investigated (BaO, SrO, CaO, ZnO, $Cu_2O$, etc.), except magnesium oxide, into the iodides is close to 100%, while for MgO it is not more than 10%. [145,194] The yields of diolefins in the oxidative dehydrogenation of n-butane and isopentane in the presence of magnesium oxide are also lower than on the remaining constant-valence metal oxides. However, no relation is observed for the latter oxides between the degree of approach to equilibrium in the reaction with HI and the yields of dehydrogenation products, since the equilibrium in the reaction involving the absorption of HI is almost completely displaced towards the formation of the iodide on virtually all the oxides‡.

Under the conditions of the dehydrogenation experiments, the acceptor : hydrocarbon weight ratio was 140 to 150. For low degrees of conversion (up to 1–2%), the rate of sorption of HI by the granulated metal oxides decreases in sequences (23) and (24) and the yield of butadiene decreases as a function of the chemical composition of the acceptor in sequences (17) and (18). Thus, for constant-valence metal oxides, there is a correlation between the reactivity in relation to HI and the yields of butadiene in the dehydrogenation of n-butane [sequences (17) and (23)]. In the presence of $Mn_3O_4$, the highest yields of butadiene are observed and the rates of binding of HI by this oxide are a maximum. However, for the remaining variable-valence metal oxides, no correspondence is observed between sequences (18) and (24). This can probably be accounted for by the catalytic influence of some of the above oxides, promoting the dehydrogenation and complete oxidation of the hydrocarbons [41].

The correspondence between the yields of dehydrogenation products and the reactivities of the acceptor in relation to HI is associated with the fact that the reaction involving the absorption of HI is not sufficiently fast under the dehydrogenation conditions to influence the rate and equilibrium of the dehydrogenation reaction, and the efficiency of the acceptor is determined by the rate of its reaction with HI. The observed impedance phenomenon and other experimental findings, in which a pronounced diffusion-induced inhibition of the reaction of the oxides with HI is manifested, demonstrates the particular importance of ensuring a sufficient degree of dispersion of the acceptor in order to improve its efficiency. Indeed, under the conditions usually employed in oxidative dehydrogenation (in the presence of a large excess of the acceptor relative to HI), the yield of dehydrogenation products begins to fall for degrees of conversion of the oxides into the iodides not exceeding several per cent [194,195].

When dehydrogenation with an HI acceptor proceeds in the presence of oxygen, the binding of HI is accompanied by the oxidation of the metal iodide by oxygen—reaction (8), involving the regeneration of iodine and the acceptor, takes place. The rate of dehydrogenation is therefore also important for the yields of the products of this reaction. According to Kolobikhin [187], the yields of butadiene on the potassium acceptor (KOH deposited on $Al_2O_3$) are much lower than on the sodium acceptor for the same content of iodine. At the same time, the rate of binding of hydrogen iodide on the potassium acceptor is apparently higher than on the sodium acceptor, as can be inferred from the loss of HI from the reactor. However, the rate of regeneration of the potassium acceptor is much lower than that of the sodium acceptor: under the conditions tested, the sodium acceptor is regenerated to the extent of 52% after 20 min, while the potassium acceptor is regenerated to the extent of only 8.7%. Thus the yields of the dehydrogenation products decrease with increase of the rate of regeneration of the acceptor.

In the study of granulated HI acceptors, a dependence of either the rate of absorption of HI or of the rate of dehydrogenation on their porous structure was not observed (although one must bear in mind that the pore volumes and the specific surfaces of the acceptors were small [192,194]). This can be explained by the fact that the increased compactness of the outer layer of the grain as a result of impedance is so great that the inner surface is blocked and hardly participates in the reaction. However, the dependence on the porous structure of the acceptor is manifested when a granulated acceptor is compared with one deposited on a carrier with a well developed porous structure (for example CaO on the KSK silica gel with a specific surface of about 100 $m^2 g^{-1}$). [1,196]

The influence of the inner surface of the acceptor on the conversion of the hydrocarbon is caused, on the one hand, by the increased rate of binding of HI and of the regeneration of the acceptor and, on the other, by the increased extent of the secondary reactions of the dehydrogenation products. In the presence of porous catalysts, isoprene undergoes a particularly extensive conversion. The yields of isoprene in the dehydrogenation of isopentane in the presence of porous acceptors as well as in the presence of porous non-accepting catalysts are therefore low.

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Studies in the field of the oxidative dehydrogenation of hydrocarbons have been carried out during the last decade mainly on the following lines.

1. The development of the theory and technology of industrial processes (iodine dehydrogenation of butane, oxygen dehydrogenation of butenes). The technological aspects of the problem were not considered in the present review.

‡For this reason, it is difficult to justify theoretically the hypothesis [184] of a relation between the yields of isoprene and the decrease of the free energy of binding of HI for the oxides of metals such as barium, strontium, zinc, manganese, etc.

2. The accumulation of data (mainly empirical data) on the yields of products and the selection of catalysts and process conditions for other oxidative dehydrogenation procedures, which are of clear practical interest and are likely to be applied on an industrial scale in the near future (dehydrogenation in the presence of chlorine and sulphur compounds, dehydrogenation of paraffinic hydrocarbons in the presence of oxygen and solid catalysts).

3. The search for new, previously unknown dehydrogenating agents and the associated development of ideas about the general principles of the action of dehydrogenating agents.

There is an extremely large variety of types of oxidative dehydrogenation processes. Those which have been most thoroughly investigated can be subdivided into two types to a first approximation: heterogeneous-catalytic reactions and radical-chain reactions catalysed by the surface. The dehydrogenation of olefins in the presence of oxygen belongs to the first variety, which may also include the dehydrogenation of paraffins in the presence of HCl or sulphur compounds and oxygen. Iodine dehydrogenation (in the presence or absence of oxygen) belongs to the second variety.

The accumulated experimental data show that, in dehydrogenation involving halogen compounds, there are analogies between the reactions of hydrocarbons belonging to different homologous series, the reactivity increasing with increased degree of unsaturation of the hydrocarbon. The influence of unsaturation in iodine dehydrogenation is so great that the dehydrogenation of $C_4$–$C_5$ paraffins leads to the almost exclusive formation of diolefins, while the dehydrogenation of $C_6$ paraffins yields aromatic products. The dehydrocyclisation of higher paraffins in the presence of chlorine and sulphur compounds and oxygen as well lead, like ordinary catalytic dehydrocyclisation, to the formation of a considerable amount of mono-olefins. In dehydration in the presence of oxygen, there is as a rule no similarity in the behaviour of paraffins and olefins.

Iodine dehydrogenation is employed in practice in an extremely complex system with gaseous and solid regenerators (acceptors); solid acceptors also exhibit a catalytic activity. The mechanism of iodine dehydrogenation in the presence of oxygen and an HI acceptor has been elucidated mainly by the separate investigation of the reaction in simplified and model systems (dehydrogenation in the presence of individual radical-forming substances, the influence of non-accepting catalysts, the reactions of acceptors with HI, etc.). The results can be regarded as a first approximation to the reaction mechanism involving the simultaneous occurrence of these processes in a real system.

Iodine dehydrogenation can be regarded merely as a first advance in the field of oxidative dehydrogenation of paraffins. Further development of methods for oxidative dehydrogenation should probably lead to the development of additional processes with more readily available and cheaper dehydrogenating agents, particularly agents based on chlorine or sulphur compounds. There already exists a definite theoretical basis, which makes it possible to direct the search for new systems of dehydrogenating agents (mixtures of radical-forming substances) along a rational pathway.

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# Chemical Transformations of Aminoglycoside Antibiotics

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Aminoglycoside antibiotics belong to the class of pseudo-oligosaccharides, which is a chemotherapeutically important group of antibiotics with a broad spectrum of antimicrobial activity. The review surveys and gives a systematic account of the literature data relevant to the chemical properties of aminoglycosides. Particular attention has been devoted to the chemical transformations of natural antibiotics.
The bibliography includes 323 references.

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## I. INTRODUCTION

Aminoglycoside antibiotics have changed in recent years from a very narrow and specific group of preparations into a large family with many members, including antibiotics such as streptomycin, neomycin, kanamycins, gentamicins, etc. This class of antibiotics has aroused interest of representatives of a wide variety of disciplines—experts in therapy, selection [of drugs ?], chemical synthesis, and biochemists: the broad search for Actinomycite strains producing aminoglycosides and the vigorous development of biosynthesis is due to the chemotherapeutic properties of the aminoglycoside antibiotics used to fight the most dangerous types of infection.

At the same time the appearance of new antibiotics is accompanied by an increase of the number of bacterial strains with multiple resistance to therapeutic agents. One of the main forms of bacterial resistance to aminoglycosides consists in their inactivation by enzymes produced by micro-organisms. Chemists were faced with the acute problem of specific modification of aminoglycosides in order to create preparations active in relation to multiply resistant forms of bacteria. The determination of the mechanisms of the enzymatic inactivation of aminoglycoside antibiotics, the study of the mechanisms of their action, and the elucidation of the dependence of the biological activity of a compound on its structure made it possible to establish promising trends in chemical transformations. Progress in the study of chemical properties was achieved with the aid of the latest techniques in physicochemical methods of research such as NMR, infrared spectroscopy, mass spectrometry, X-ray diffraction analysis, gas–liquid chromatography, high-pressure liquid chromatography, and electrophoresis.

Natural aminoglycoside antibiotics have become the richest source of a wide variety of monosaccharides, have enriched carbohydrate chemistry in unusual previously unknown aminosugars, and have exerted a significant influence on its development.

The present review surveys and gives a systematic account of the literature data relevant solely to the chemical properties of aminoglycosides, since examination of important problems such as biosynthetic pathways, methods for the determination of structures, the mechanism of action, the dependence of biological properties on structure, etc., would have greatly increased the size of the review. Particular attention is devoted to methods for the specific chemical transformations of natural antibiotics.

The stereochemistry of aminoglycosides has been examined in detail in Umezawa[1,2] and Daniels'[3] reviews. The methods for the determination of the structures of the products of the enzymatic inactivation of aminoglycoside antibiotics have been discussed in Umezawa's reviews[4,5]. †

## II. CLASSIFICATION OF AMINOGLYCOSIDE ANTIBIOTICS

Chemically, aminoglycoside antibiotics are pseudo-oligosaccharides. Their molecules consist of two fundamentally different components. One component is a carbohydrate containing at least one amino-group, and the other is the aglycone. The aminosugar is linked to the aglycone by the glycosidic $C_{(1)}$–O bond. The number of carbohydrate rings in the molecule varies from one to four and at least two carbohydrate substituents are linked to the aglycone. The aglycone is a cyclitol or an aminocyclitol. Antibiotics with the most valuable antibacterial properties contain aminocyclitols, mainly streptidine or deoxystreptamine. Thus, aminoglycoside antibiotics belong to the class of aminoglycosidic aminocyclitols.

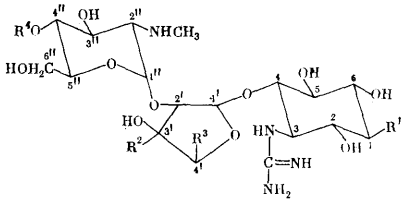
Since aminoglycoside antibiotics are pharmaceutical preparations, it is quite natural that their classification should be based on molecular properties which have the greatest influence on their biological activity. Analysis of the literature data has shown that the biological activity of aminoglycosides depends significantly on their structure (the number, nature, and relative positions of the carbohydrate rings linked to the aglycone and the nature of the

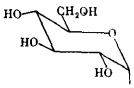
† The problems of biosynthesis have been analysed by Rhinehart and Stroshane[310].

aglycone), functional groups, and molecular configuration and conformation. It is most useful to base the classification on the structural properties of aminoglycoside molecules.

Depending on the nature of the aglycone, aminoglycosides are divided into two important subclasses: one of them includes antibiotics containing streptidine and the other includes those containing deoxystreptamine. The subclass of aminoglycosides containing streptamine has very few members, but includes therapeutically important antibiotics—streptomycin, dihydrostreptomycin, and mannosidostreptomycin. Bleunsomycin, differing from the other streptomycin antibiotics by the structure of the aglycone, has come to be included in the same subclass.

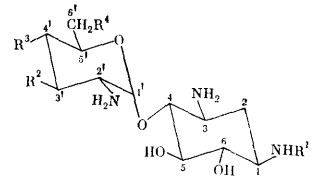
Aminoglycosides containing deoxystreptamine are distinguished by their wide variety, and their characteristic feature is the large number of members of each antibiotic family. Thus two neomycins, four hybrimycins, two lividomycins, four butirosins, the isomeric ribostamycin and xylostasin, seven kanamycins, at least fifteen gentamicins, and several antibiotics of the type of sisomicin are known at the present time. The deoxystreptamine antibiotics can be subdivided into several groups depending on the nature and number of carbohydrate substituents in the molecule and their distribution relative to the carbon atoms of the deoxystreptamine ring.



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| Streptomycin | $-NHC(=NH)NH_2$ | CHO | $CH_3$ | H |
| Dihydrostreptomycin | $-NHC(=NH)NH_2$ | $CH_2OH$ | $CH_3$ | H |
| Mannosidostreptomycin | $-NHC(=NH)NH_2$ | CHO | $CH_3$ |  |
| Oxystreptomycin | $-NHC(=NH)NH_2$ | CHO | $CH_2OH$ | H |
| Bluensomycin | $-OCONH_2$ | CHO | $CH_3$ | H |

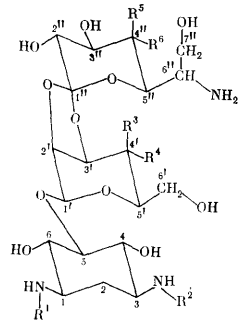
Depending on the number of substituents in the aglycone, aminoglycoside antibiotics containing deoxystreptamine can be divided into two types. The first includes antibiotics in which deoxystreptamine has one carbohydrate substituent, and the second includes those which have two carbohydrate substituents in the deoxystreptamine ring. In aminoglycosides which are monosubstituted 2-deoxystreptamines, the pyranosyl substituent is attached to the carbon atom either in the 4- or 5-position.

Neamine[6], paromamine[9,11], and their semisynthetic derivatives such as 4′-deoxyneamine[12], 3′,4′-dideoxyneamine[13,14], 3′,4′,5,6-tetradeoxyneamine[15], 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]neamine[16,17], 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-4′-deoxyneamine[12], and 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-3′,4′-dideoxyneamine[18–21] form a group of antibiotics which are pseudodisaccharides, in which the 2-deoxystreptamine ring has a pyranosyl substituent at the carbon atom in the 4-position:



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| Neamin | H | OH | OH | $NH_2$ |
| Paromamine | H | OH | OH | OH |
| 3′,4′-Dideoxyneamine | H | H | H | $NH_2$ |
| 1-*N*-[(*s*)-4-Amino-2-hydroxybutyryl]neamine | $-CO-\underset{OH}{CH}-CH_2-\underset{NH_2}{CH_2}$ | | OH | OH | $NH_2$ |
| 1-*N*-[(*s*)-4-Amino-2-hydroxybutyryl]-3′,4′-dideoxyneamine | $-CO-\underset{OH}{CH}-CH_2-\underset{NH_2}{CH_2}$ | | H | H | $NH_2$ |

The antibiotics characterised by the presence of only one substituent in the aglycone also include antibiotics of the destomycin series. In contrast to neamine and paromamine, the carbohydrate substituent in the molecules of these antibiotics is at the $C_{(5)}$ carbon atoms of the deoxystreptamine ring and the pyranose ring also has a substituent—destomic acid. This group includes hygromycin B,[22–25] the antibiotic A-396-1 (SS-56-D),[26,27] destomycins A, B, and C,[28–33] and the antibiotics SS-56-C,[27] and A-16316-C.[34]

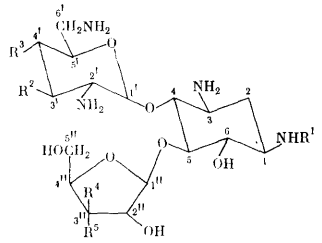


| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ |
|---|---|---|---|---|---|---|
| Destomycin A | $CH_3$ | H | $CH_3$ | H | OH | H |
| Destomycin B | $CH_3$ | $CH_3$ | H | OH | H | OH |
| Destomycin C | $CH_3$ | $CH_3$ | OH | H | OH | H |
| Hygromycin B | H | $CH_3$ | OH | H | OH | H |
| A-396-1 | H | H | OH | H | OH | H |
| A-16316-C‡ | $CH_3$ | $CH_3$ | H | OH | OH | H |

A characteristic feature of the aminoglycosides belonging to the group of disubstituted 2-deoxystreptamines is the presence of a pyranosyl substituent at $C_{(4)}$. The second substituent is either at $C_{(5)}$ or $C_{(6)}$. A pyranosyl substituent is located at $C_{(6)}$, while only the furanosyl substituent is at $C_{(5)}$ in all known instances. Accordingly, aminoglycoside antibiotics of this type can be subdivided into two varieties. The first includes aminoglycosides whose deoxystreptamine ring has pyranosyl and furanosyl substituents at the carbon atoms in the 4- and 5-positions respectively, while the second variety combines antibiotics having paranosyl substituents at $C_{(4)}$ and $C_{(6)}$.

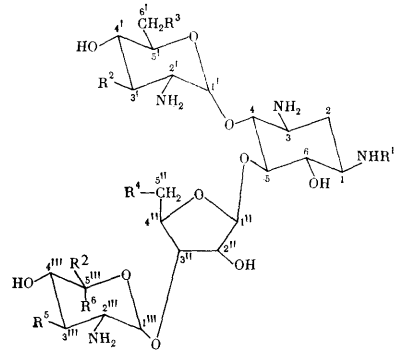
‡ The structure of this antibiotic has not been established exactly.

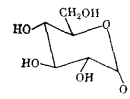
Aminoglycosides containing a furanosyl substituent (D-ribose or D-xylose) can be divided in their turn into two groups. The first includes antibiotics containing unsubstituted D-ribose or D-xylose. Its representatives are ribostamycin[16,35-38], xylostasin[16,37,39], butirosins A and B[16,37,40-47], and the antibiotics Bu-1709 $E_1$ and $E_2$ [46] as well as their semisynthetic derivatives 3′-deoxyribostamycin[48], 4′-deoxyxylostasin[12], 3′,4′-dideoxyribostamycin[20,49], 3′,4′,5″-trideoxyribostamycin[20,49], 1-*N*-methylribostamycin[50], 4′-deoxybutirosins A and B,[12,37] 3′,4′-dideoxybutirosin B,[51] and 5″-amino-5″-deoxybutirosin[52].

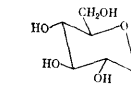
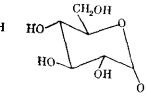


| | $R^1$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ |
|---|---|---|---|---|---|
| Ribostamycin | H | OH | OH | H | OH |
| Xylostasin | H | OH | OH | OH | H |
| Butirosin A | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | OH | OH | OH | H |
| Butirosin B | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | OH | OH | H | OH |
| 3′,4′-dideoxyribostamycin | H | H | H | H | OH |
| 3′,4′-dideoxybutirosin B | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | H | H | H | OH |

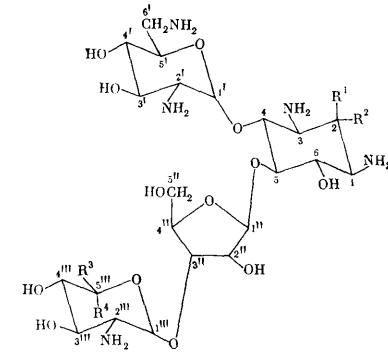
The second group includes antibiotics having an additional pyranosyl substituent at the $C_{(3'')}$ atom of the D-ribose ring: neomycins B and C,[6,53] paromomycins I and II,[54-56], and lividomycin B.[57] Lividomycin A[58-62] and mannosylparomomycin[63], which are 4″-*C*-mannosyl derivatives of lividomycin B and paromomycin respectively, can be usefully combined into a separate subgroup together with 5″-deoxylividomycin A[64] and 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-lividomycin A.[65] A characteristic feature of these antibiotics is the presence of four carbohydrate rings in the molecule.



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | $R^7$ |
|---|---|---|---|---|---|---|---|
| Neomycin B | H | OH | $NH_2$ | OH | OH | $CH_2NH_2$ | H |
| Neomycin C | H | OH | $NH_2$ | OH | OH | H | $CH_2NH_2$ |
| Paromomycin I | H | OH | OH | OH | OH | $CH_2NH_2$ | H |
| Paromomycin II | H | OH | OH | OH | OH | H | $CH_2NH_2$ |
| Lividomycin B | H | H | OH | OH | OH | $CH_2NH_2$ | H |
| Lividomycin A | H | H | OH | OH |  | $CH_2NH_2$ | H |

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | $R^7$ |
|---|---|---|---|---|---|---|---|
| 5″-Deoxylividomycin A | H | H | OH | H |  | $CH_2NH_2$ | H |
| 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-lividomycin A | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | H | OH | OH |  | $CH_2NH_2$ | H |

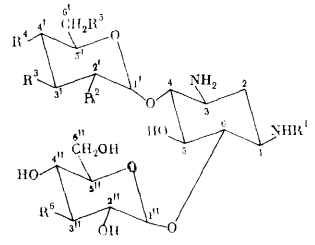
The neomycin group of antibiotics also includes hybrimycins A1, A2, B1, and B2,[66,67] in which the aglycones are streptamine (hybrimycins A) and epistreptamine (hybrimycins B).



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| Hybrimycin A1 | H | OH | H | $CH_2NH_2$ |
| Hybrimycin A2 | H | OH | $CH_2NH_2$ | H |
| Hybrimycin B1 | OH | H | H | $CH_2NH_2$ |
| Hybrimycin B2 | OH | H | $CH_2NH_2$ | H |

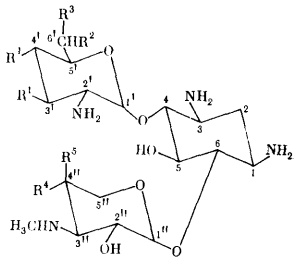
The aminoglycoside antibiotics whose deoxystreptamine ring has two pyranosyl substituents at the $C_{(4)}$ and $C_{(6)}$ atoms are the most important chemotherapeutically. Depending on the nature of the carbohydrate substituent at the $C_{(6)}$ atoms, they can be divided into two groups with numerous members. The first comprises the family of kanamycin antibiotics, a characteristic feature of which is the presence of 3-amino-3-deoxy-$\alpha$-D-glucose at the $C_{(6)}$ atom of the deoxystreptamine ring. The second group consists of the gentamicin antibiotics, whose deoxystreptamine ring has either garosamine[68] or 3-methyl-amino-3-deoxypentapyranose at the $C_{(6)}$ atom.

The family of kanamycin antibiotics includes kanamycins A, B, and C,[69-74] the antibiotics NK-1001, NK-1012-1, NK-1013-1, and NK-1013-2,[75] tobramycin (nebramycin, factor 6),[76-82] nebramycins, and factors 2,4,5, and 5′,[76,80-83] as well as their semisynthetic derivatives 3′-deoxykanamycin A,[84] 4′-deoxykanamycin A,[85] 6″-deoxykanamycin A,[86-88] 6′-*N*-methylkanamycin B,[89] 3′,4′-dideoxykanamycin B,[90-91] 3′,4′-dideoxy-6′-*N*-methylkanamycin B,[89] amikacin (BB-K8),[92-94] 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]kanamycin B,[95] 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-3′,4′-dideoxykanamycin B,[95] etc.



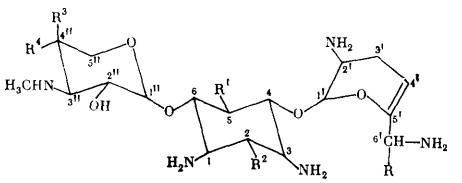
| | R¹ | R² | R³ | R⁴ | R⁵ | R⁶ |
|---|---|---|---|---|---|---|
| Kanamycin A | H | OH | OH | OH | $NH_2$ | $NH_2$ |
| Kanamycin B (nebramycin, factor 5) | H | $NH_2$ | OH | OH | $NH_2$ | $NH_2$ |
| Kanamycin C | H | $NH_2$ | OH | OH | OH | $NH_2$ |
| NK-1001 | H | OH | OH | OH | $NH_2$ | OH |
| NK-1012-1 | H | $NH_2$ | OH | OH | $NH_2$ | OH |
| 3'-Deoxykanamycin A | H | OH | H | OH | $NH_2$ | $NH_2$ |
| 4'-Deoxykanamycin A | H | OH | OH | H | $NH_2$ | $NH_2$ |
| Tobramycin (Nebramycin, factor 6) | H | $NH_2$ | H | OH | $NH_2$ | $NH_2$ |
| 3',4'-Dideoxykanamycin B | H | $NH_2$ | H | H | $NH_2$ | $NH_2$ |
| 6'-*N*-Methylkanamycin A | H | OH | OH | OH | $NHCH_3$ | $NH_2$ |
| 3',4'-Dideoxy-6'-*N*-methylkanamycin B | H | $NH_2$ | H | H | $NHCH_3$ | $NH_2$ |
| Amikacin | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | OH | OH | OH | $NH_2$ | $NH_2$ |
| 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]kanamycin B | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | $NH_2$ | OH | OH | $NH_2$ | $NH_2$ |
| 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-3',4'-dideoxykanamycin B | —CO—CH(OH)—$CH_2$—$CH_2$—$NH_2$ | $NH_2$ | H | H | $NH_2$ | $NH_2$ |

The family of gentamicin antibiotics includes the gentamicin complex C [3,68] (the gentamicins $C_1$, $C_2$, and $C_{1a}$ [96-110]), the gentamicins, A, [111-113] $A_1$, [113] $A_2$, [113] $X_2$, [113-118], B (the antibiotic Sch 14 342), [113-118] and $B_1$, [113] the antibiotics JI-20 A and JI-20 B, [113] G-418, [113,119-121], and sagamicin [122-125].



| | R¹ | R² | R³ | R⁴ | R⁵ |
|---|---|---|---|---|---|
| Gentamicin $C_{1a}$ | H | $NH_2$ | H | $CH_3$ | OH |
| Gentamicin $C_1$ | H | $NHCH_3$ | $CH_3$ | $CH_3$ | OH |
| Gentamicin $C_2$ | H | $NH_2$ | $CH_3$ | $CH_3$ | OH |
| Gentamicin A | OH | H | OH | OH | H |
| Sagamicin | H | $NHCH_3$ | H | $CH_3$ | OH |

The gentamicin antibiotics also comprise sisomicin [126-134], mutamicins [135], verdamicin [113,136], and the antibiotics 66-40B and 66-40D. [113,137] A characteristic feature of these antibiotics is the presence of an unsaturated carbohydrate substituent (dehydropurpurosamine) at the $C_{(4)}$ carbon atom of the deoxystreptamine ring §.



| | R | R¹ | R² | R³ | R⁴ |
|---|---|---|---|---|---|
| Sisomicin | H | OH | H | OH | $CH_3$ |
| Mutamicin-1 | H | OH | OH | OH | $CH_3$ |
| Mutamicin-2 | H | H | H | OH | $CH_3$ |
| Verdamicin | $CH_3$ | OH | H | OH | $CH_3$ |
| 66-40B | H | OH | H | H | OH |
| 66-40D | H | OH | H | OH | H |

The following principles have been adopted in the numbering of the carbon atoms of different fragments of the molecules of aminoglycoside antibiotics.

1. Each cyclic fragment of the molecule (carbohydrate, aminocyclitol) has its own independent numbering of the carbon atoms.
2. The numbering in aminocyclitol begins with the carbon atom linked to the amino-group; the numbering proceeds in the direction such that the second amino-group is attached to the carbon atom with the smallest number.
3. The numbering of the carbon atoms in the carbohydrate substituents corresponds to the numbering adopted in carbohydrate chemistry: it begins with the carbon atom linked to the hemiacetal hydroxyl.
4. The carbon atoms of the carbohydrate substituent at the $C_{(4)}$ atom of the aminocyclitol are designated by primed numbers.
5. The carbon atoms of the carbohydrate substituent at the $C_{(5)}$ or $C_{(6)}$ carbon atom of the aminocyclitol are designated by doubly primed numbers.
6. The carbon atoms in the carbohydrate rings attached to the carbohydrate substituents of the aminocyclitol are designated by triply primed numbers.

## III. THE MAIN PHYSICOCHEMICAL PROPERTIES OF AMINOGLYCOSIDES

Since aminoglycoside antibiotics are pseudo-oligosaccharides, it follows naturally that they possess many physicochemical properties and undergo many of the reactions characteristic of oligosaccharides. For example, aminoglycosides do not absorb between 220 and 360 nm in the ultraviolet. In most cases, their infrared spectra have no characteristic absorption bands and resemble those of oligosaccharides.

It has been shown for kanamycin monosulphate [73,74] and streptomycin [138] that the wavelengths corresponding to the bonds in the aminoglycoside antibiotics have values characteristic of ordinary covalent bonds. The interatomic distances in kanamycin are as follows: 1.48 Å for S = O (four bonds), 1.55 Å for C–C (sixteen bonds), 1.45 Å for C–N (four bonds), and 1.45 Å for C–O (fifteen bonds). The lengths of the intramolecular hydrogen bonds in the kanamycin molecule show that the oxygen of the hydroxy-groups at the $C_{(5)}$ atom of the deoxystreptamine ring is linked by a strong hydrogen bond to the hydroxy-group at the $C_{(2)}$ atom of the 6-amino-6-deoxy-$\alpha$-D-glucose ring, i.e. the stereochemical structure of the 4-O-[6'-amino-6'-deoxy-$\alpha$-D-glucopyranosyl]-2-deoxystreptamine molecule is rigid and determines the stability of the compound even in aqueous solutions.

The $^1$H NMR spectra of aminoglycoside antibiotics are extremely complex and require the use of model compounds for their interpretation [313]. The $^{13}$C NMR spectroscopy has come to be widely used in the study of the stereochemistry of aminoglycosides in recent years [23,38,314-317]. The employment of $^{13}$C NMR spectroscopy made it possible to elucidate the nature of $\alpha$- and $\beta$-streptomycins [318]. $^{13}$N NMR spectroscopy has been used in the study of nebramycin antibiotics [319].

Crystalline aminoglycosides strongly retain water and carbon dioxide [103]. The gentamicin antibiotics retain water so tenaciously that it cannot be removed completely even on heating the specimens *in vacuo* for seven days at 50°C. [109]

Aminoglycoside antibiotics are readily adsorbed by cellulose, celite, and other filter materials [139], and the total initial amount of the antibiotic cannot be recovered even on acidification.

Aminoglycosides are extremely stable on prolonged storage in both powdered and crystalline state as well as in

§ Reports of the isolation of new antibiotics of the sisomicin series have appeared recently [311,312].

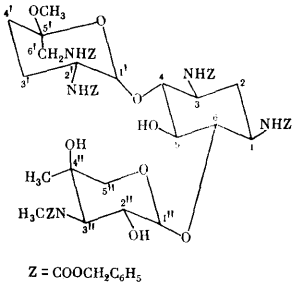
aqueous solutions[140,141,301]. There is no change in the activity of aqueous kanamycin solutions when they are heated in an autoclave for 30 min at 120°C in the pH range 2–9.[141] The gentamicin complex C also withstands heating in an autoclave for 20 min.[142]

## IV. REACTIONS INVOLVING GLYCOSIDIC LINKAGES. HYDROLYSIS OF AMINOGLYCOSIDES

Aminoglycoside antibiotics are as a rule stable in solution at pH ≥ 7.0, but are relatively readily hydrolysed in acidic media. An exception is streptomycin, which is unstable in alkaline solutions; at pH 8.5, rapid inactivation takes place[143,144]. Kanamycin is more stable in the pH range 6–8 than at pH 2.0.[71,145] The gentamicin complex C is stable in the pH range between 2.0 and 14.[142]

Hydrolysis of aminoglycoside antibiotics by hydrochloric acid solutions under various conditions leads to the rupture of the glycosidic linkages and the formation of compounds which correspond to fragments of the aminoglycoside molecules in different combinations[146]. It has been shown for kanamycin that hydrolysis involves initially the glycosidic linkage between 6-amino-6-deoxy-α-D-glucose and 2-deoxystreptamine[147–149]. The acid hydrolysis of antibiotics of the gentamicin and sisomicin series does not entail the rupture of the glycosidic linkage between the purpurosamine rings and garamine, which is evidently due to the presence of the 2′-*C*-$NH_2$ group[302]. The main hydrolysis product is gentamine. On the other hand, *N*-substituted sisomicins are extremely sensitive to hydrolysis [they can be hydrolysed by treatment with the Amberlite IR-120 ($H^+$) resin]. The main hydrolysis product is garamine[303] and further hydrolysis of the latter is not observed.

It should also be noted that the methanolysis of pentakis-*N*-benzyloxycarbonyl-sisomicin results in the formation, together with garamine, of a methanol adduct having the following structure:




Z = $COOCH_2C_6H_5$

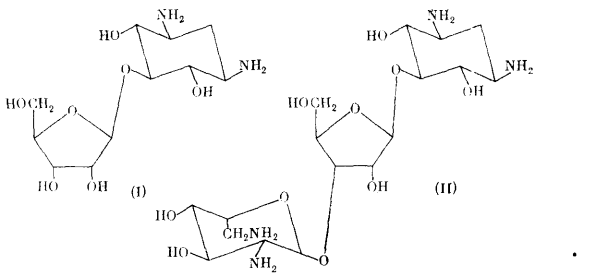
Acid hydrolysis of aminoglycoside antibiotics combined with the periodate oxidation of the *N*-acylated hydrolysis products is the basis of studies designed to determine their structure. For example, the method has been used successfully for kanamycins A,[150–155] B[156] and C,[7,10] lividomycin A,[58,60] and the antibiotic G-418. Analysis of the products of the mild acid hydrolysis of destomycin A and hygromycin B showed that these antibiotics differ in the structure of the main glycoside, but also have a component in common—destomic acid[23,28–31].

However, it is better to use acid methanolysis in the determination of the structures of antibiotics. The combination of acid methanolysis with the periodate oxidation of the hydrolysis products and the simultaneous acid hydrolysis of per-*N*-acetyl-per-*O*-methyl derivatives makes it possible to determine the detailed structure of the aminoglycoside. The method has been used in the determination of the structures of kanamycin[157–164], gentamicin[180,112,165,166], sisomicin[167], ribostamycin[36], Bu-1975 $C_1$ and $C_2$,[12] and many other aminoglycoside antibiotics. Methanolysis of the gentamicin complex C yields gentamicin and an anomeric mixture of methylgarosamides. The degradation of purpurosamine under these conditions is not observed, since the rupture of the glycosidic linkage is apparently prevented by the protonation of the 2′-*C*-amino group.

The rupture of the glycosidic linkage in acid hydrolysis has been used successfully not only for the determination of the structures of new antibiotics, but also for synthetic purposes. For example, in the synthesis of 1-*N*-[(*S*)-4-amino-2-hydroxybutyryl]neamine, the furanosyl linkage in butirosins A and B is hydrolysed by a solution of hydrochloric acid in methanol[16,19,20]. It is noteworthy that the amide bond between the aminoacyl group and the 1-*C*-amino-group in the deoxystreptamine ring is retained on acid hydrolysis. The rupture of the amide bond is observed during moderate alkaline hydrolysis. Ribostamycin is then formed from butirosin B,[16] while the alkaline hydrolysis of 4′-deoxybutirosin yields the corresponding 4′-deoxyribostamycin[19].

The selective cleavage of the glycosidic linkage in the elimination of the mannose component in the synthesis of lividomycin B from the lividomycin A is achieved by Barry's method (treatment with sodium periodate in the dark with subsequent removal of iodate, hydrolysis, and treatment with phenylhydrazine)[61,168].

The periodate oxidation of per-*N*-benzyloxycarbonyl derivatives of paromomycin and neomycin leads to the elimination of one or two diaminosugar rings, depending on the reaction conditions. After the removal of protecting groups, either a pseudodisaccharide (I) or a pseudotrisaccharide (II) is obtained[169]:

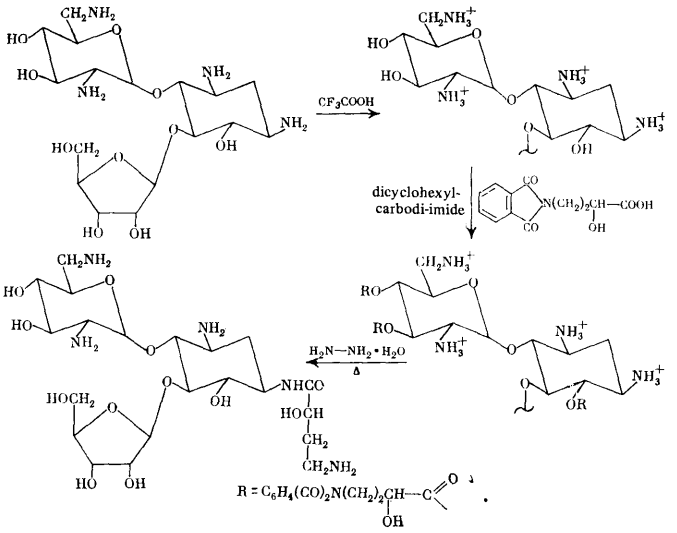



In conclusion one should note the possibility of the acid hydrolysis of paromomycin (I), neomycin, and kanamycin with the aid of ion-exchange resins[170].

## V. REACTIONS INVOLVING AMINO-GROUPS

Aminoglycoside antibiotics readily form salts with inorganic acids. The ability of aminoglycosides to form salts has been used for the selective protection of the amino-groups in an elegant synthesis of butirosin B from ribostamycin[171]. The amino-groups of ribostamycin were

protected by preliminary treatment with trifluoroacetic acid. The scheme of the synthesis is presented below.




Aminoglycoside antibiotics readily form Schiff bases with aldehydes in aqueous alcoholic media[69,172-175]. Streptomycin, which contains the formyl group, forms Schiff bases on reaction with amines[176]. In contrast to other aminoglycosides, when gentamicin antibiotics give rise to Schiff bases, a cyclic oxazolidine is formed via the $NH_2$ group at the $C_{(3'')}$ atom and the OH group at the $C_{(4'')}$ atom in the garosamine component of the molecule[175,177].

Salicylidene derivatives of aminoglycosides are used in mass-spectrometric studies[178-180] and in the investigation of the dispersion of the optical rotation of aminoglycoside aminocyclitols[181].

The reduction of the Schiff bases with sodium tetrahydroborate leads to the formation of *N*-alkyl- and *N*-aryl-kanamycins and other basic antibiotics[174,176,182-184]. It is interesting to note that the possibility of obtaining monoalkylate products has been demonstrated for neomycins and paromomycin[182]. *N*-Alkyl derivatives of aminoglycosides can be obtained also without the preliminary synthesis of the corresponding Schiff bases—by reductive alkylation[174]. The ability of 1-fluoro-2,4-dinitrobenzene to partially dinitrophenylate kanamycin, neomycin, and paromomycin constitutes a method for the determination of the number of free amino-groups and the molecular weights of basic antibiotics[185].

The antibiotics react with formaldehyde to form products corresponding to different degrees of substitution, depending on the reaction conditions[183,186]. It has been shown that the hydrogenolysis of kanamycin in water in the presence of formaldehyde leads to the formation of *N*-octamethylkanamycin. On the other hand, when the reaction is carried out in an acidic medium (acetic acid), the formation of *N*-tetramethylkanamycin is promoted[187]. Various methods for the synthesis of *N*-methanesulphonate and *N*-methanesulphinate derivatives of aminoglycoside antibiotics have been developed[188]. The corresponding "Mannich bases" have been obtained from kanamycin and tetracycline[189-191].

The kanamycin Schiff bases react with carbon disulphide in an alkaline alcoholic medium, forming compounds having the general formula $KM(CSSA)_n$, where KM is kanamycin and A is an alkali metal atom[192]. In an aqueous alkaline solution, kanamycin reacts with trichloromethanesulphenyl chloride, forming *N*-trichloromethylthiokanamycin. Other basic antibiotics behave similarly[193,194]. Derivatives of basic antibiotics having antibacterial properties can be obtained by the reaction of the aminoglycoside bases with trichloromethanesulphenyl chloride and 2-amino-1-(*p*-nitrophenyl)propane-1,3-diol[193].

The aminoacid derivatives of aminoglycosides formed via the $NH_2$ group at the $C_{(1)}$ atom of the deoxystreptamine ring have continuously attracted the attention of chemists, biochemists, and specialists in chemotherapy in recent years. This interest was aroused by the antibacterial properties of the derivatives, particularly by their high activity against species of micro-organisms exhibiting multiple drug resistance. The problem of the synthesis of aminoacid derivatives reduces intrinsically to the problem of the selective protection of the amino-groups exhibiting a higher reactivity than the 1-*C*-amino-group.

The amino-groups of aminoglycoside antibiotics are known to be located in molecular fragments of different types and have different environments; nevertheless, in most cases they are hardly distinguishable as regards their reactivity, and the chemical reaction involves all the groups simultaneously. For example, the amino-groups are readily acetylated by acetic anhydride in methanol at room temperature[111,142,148,172,195-197] and react with ethyl[198] and benzyl[88,199] chlorocarbonate esters and dimedone[200]. Differences between the reactivities of the amino-groups can be detected in reactions of aminoglycosides with mild acylating agents such as *N*-benzyloxycarbonylhydroxysuccinimide or benzyl *p*-nitrophenyl carbonate and t-butoxycarbonyl azide.

In a series of studies devoted to the synthesis of amikacin (BB-K8) and its positional isomers and analogues, *N*-benzyloxycarbonylhydroxysuccinimide was used successfully for the selective protection of the amino-groups[92,93,201]. Aminoacid derivatives of tobramycin were obtained using a similar scheme[202]. The sequence in which the positional isomers of amikacin are synthesised and their structures make it possible to arrange the kanamycin amino-groups in order of their decreasing activity in the acylation reaction (sequence based on the positions in the molecule):

$$C(6') > C(1) > C(3) > C(3'').$$

It is interesting to note that, in the series of gentamicin antibiotics, the selectivity in the mode of acylation depends on the pH of the medium and the mode of reaction changes almost completely if the amino-groups of the antibiotics are protonated. Under these conditions, the 1-*C*-$NH_2$ group is the most reactive in relation to acylating agents, while the primary $-CH_2NH_2$ group exhibits the lowest reactivity. This phenomenon, noticed for the first time by Wright[304], has been used to obtain 1-*N*-acyl derivatives of gentamicin $C_{1a}$, sisomicin, and verdamicin[305]. The acylation of kanamycin is usually carried out with *N*-substituted aminoacids subjected to preliminary activation with *N*-hydroxysuccinimide[16,93,203].

It has been shown in relation to the synthesis of amikacin and 1-*N*-[(*S*)-4-amino-2-hydroxybutyryl]kamamycin B that benzyloxycarbonyl chloride can also be recommended for the selective blocking of the $NH_2$ group at $C_{(6)}$.[204] Evidently, t-butoxycarbonyl azide[205] is the most suitable agent for the selective protection of the $NH_2$ group at the $C_{(2')}$ atom in the synthesis of aminoacid derivatives of kanamycin B and 3′,4′-dideoxykanamycin B.[95,206,207] The t-butoxycarbonyl protecting group has valuable advantages over

other types of protecting groups—it can be removed selectively in the presence of *N*-benzyloxycarbonyl groups by means of trifluoroacetic acid, which permits the subsequent modification of only one amino-group. 6′-*N*-Alkyl derivatives of amikacin have been obtained by this method[184].

The $NH_2$ groups at the $C_{(2')}$ and $C_{(3)}$ atoms have been successfully protected with the trifluoroacetyl group in the synthesis of 1-*N*-[(*S*)-4-amino-2-hydroxybutyryl]- and 1-*N*-[(*S*)-3-amino-2-hydroxypropionyl]-gentamicins $C_1$ by treating the gentamicin with an equivalent amount of ethyl trifluorothioacetate in methanol solution[208,209]. The sequence in which the trifluoroacetyl protecting group is introduced makes it possible to arrange the amino-groups of gentamicin $C_1$ in the following sequence in terms of their activity with respect to this reagent (sequence based on the positions in the molecule):

$$C(2') > C(3) > C(1) > C(6') > C(3').$$

It is noteworthy that the selective acylation of the $NH_2$ group at the $C_{(1)}$ atom of gentamicin $C_{(1)}$ by γ-amino-α-hydroxybutyric acid can be carried out also without the preliminary blocking of the 2′-*C*- and 3-*C*- amino groups[210].

In the synthesis of the isomers of the aminoacid derivatives of butirosin from natural butirosin, it was necessary to select for the protection of the free amino-group a substituent having extremely specific properties: its bond with the amino-group must be stable in an alkaline medium and must be readily ruptured under conditions ensuring the retention of the amide linkage. It was shown that the most suitable protecting group is produced by forming a conjugated enamine in the reaction with dimedone[200]. The advantages of the products thus obtained are their high solubility, intense absorption in the ultraviolet, and ready purification by ion-exchange chromatography. The dimedone groups are removed with the aid of gaseous chlorine.

A new approach to the selective protection of the amino-groups, based on the formation of a cyclic carbamate or oxazolidone via the $NH_2$ group at the $C_{(1)}$ atom and the OH group at the $C_{(6)}$ atom of the deoxystreptamine ring, was introduced into the chemistry of aminosugars and aminocyclitols by Umezawa and coworkers[211]. This approach has been employed successfully in synthesis of butirosin B,[47,212] 3′-deoxybutirosin B,[213] and the aminoacid derivatives of 3′,4′-dideoxyneamine[18,21], 3′,4′-dideoxyribostamycin[212], lividomycin A,[65,214] and 6′-amino-6′-deoxylividomycin A.[215]

Carbamates or oxazolidinones are usually obtained by treating *N*-per(benzyloxycarbonyl)aminoglycosides with sodium hydride in dimethylformamide at room temperature. The formation of the cyclic carbamate can be explained by the initial attack by sodium hydride on the OH group at $C_{(6)}$ with subsequent anchimeric attack by the resulting alkoxide ion on the urethane carbonyl at $C_{(1)}$. The use of cyclic carbamates for the protection of groups in the *trans*-positions has been described for the first time in connection with the synthesis of *D*-glucopyranosido[2,3 : 4,5]-2′-oxazolidinones[216] with the aid of *NN*′-carbonyldi-imidazole. When the resulting carbamate is heated with barium hydroxide in aqueous dioxan, selective hydrolysis with liberation of the $NH_2$ group at $C_{(1)}$ and the OH group at $C_{(6)}$ takes place. Subsequent acylation at the amino-group and elimination of all the protecting groups lead to the aminoacid derivatives of aminoglycosides formed via the $NH_2$ group at $C_{(1)}$.

Weinstein and coworkers[177] showed in relation to the gentamicin complex C that simultaneous selective protection of the amino- and hydroxy-groups of the garosamine ring can be achieved as a result of the formation of oxazolidine when the gentamicin complex reacts with aldehydes in ethanol.

It has been shown for the synthesis of butirosin that the aminoacid derivatives of aminoglycoside antibiotics having a free hydroxy-group at the $C_{(6)}$ atom of the deoxystreptamine ring can be obtained by the elegant reaction involving the O→N acyl migration of the aminoacid group from the $C_{(6)}$ atom to the amino group at $C_{(1)}$[171] (see the reaction scheme at the beginning of this Section).

*N*-Benzyloxycarbonyl derivatives of aminoglycoside antibiotics are reduced to the corresponding *N*-methylaminoglycosides on heating with lithium tetrahydroaluminate in tetrahydrofuran. The reaction has been used in the preparative synthesis of 6′-*N*-methylkanamycin and 3′,4′-dideoxy-6′-*N*-methylkanamycin B.[89] The selective 6′-*N*-benzyloxycarbonylation of aminoglycosides has been carried out successfully with the aid of benzyl *p*-nitrophenyl carbonate[217] in aqueous dioxan at 0–5°C.

*N*-Glycoside derivatives of aminoglycoside antibiotics, exhibiting antibacterial activity, are obtained by Pan's enzymatic transglycosylation reaction[218–221].

## VI. REACTION INVOLVING HYDROXY-GROUPS

The most characteristic reactions of the hydroxy-groups of aminoglycoside antibiotics are those involving the formation of esters[222–225] and ethers[14,88,155,198,226]. They are used widely in the protection of hydroxy-groups in the synthesis of various derivatives of antibiotics.

Like the amino-groups, the hydroxy-groups of aminoglycosides have different reactivities. The primary alcoholic OH groups at $C_{(6'')}$ and $C_{(6')}$ are chemically the most reactive, the hydroxy-groups and $C_{(2')}$ and $C_{(2'')}$ are somewhat less reactive, and the hydroxy-group at the $C_{(5)}$ atom of the deoxystreptamine ring is least reactive. The reactivities of the remaining hydroxy-groups are virtually the same. The only known instance of reaction involving the hydroxy-group at $C_{(5)}$ is the synthesis of esters of gentamicin $C_{1a}$.[227]

The interaction of kanamycin with concentrated sulphuric acid at a reduced temperature leads to the formation of kanamycin sulphonate esters, the number of ester groups corresponding to the number of hydroxy-groups in the molecule of the antibiotic. This property of basic antibiotics has been used to develop a method for the determination of the number of free hydroxy-groups in biological preparations[222]. Kanamycin Schiff bases are readily *O*-acylated by benzoyl chloride, benzoic acid anhydride, and benzoate esters with formation of the corresponding *O*-benzoate esters after acid hydrolysis[223]. Kanamycin esters having the general formula $(RCO_2)_nC_{18}H_{21}O_4(OH)_{7-n}(NH_2)_4$, where R is an alkyl group, an alkoxy-group, a *p*-substituted phenyl group, an aryl group, etc, are formed by the reaction of sodium alkoxides derived from the kanamycin Schiff bases with acid chlorides[224].

On reaction with alkane- and arene-sulphonyl chlorides, aminoglycosides readily form sulphonates, which are used to introduce various functional groups into the molecule of the antibiotic (halogen, H, $N_3$, COOH, $NH_2$, etc,) via an exchange reaction of the sulphonyloxy-groups with a particular nucleophile. Trifluorophenyl derivatives of aminoglycosides can also be used for such purposes instead of the sulphonate derivatives[88,198].

*O*-Methyl derivatives are usually obtained by treating aminoglycosides with dimethyl sulphate in the presence of alkali by the method of West and Holden[228] modified by Umezawa et al.[155] This reaction has been used in the synthesis of 3′- and 4′-*O*-methylneamines[14,226]. Diazomethane has been used a methylating agent in the synthesis of 4′,6′-*O*-methyl-lividomycin A;[215] the reaction was catalysed by boron trifluoride etherate.

The differences between the reactivities of the hydroxy-groups have been used in the synthesis of many derivatives of aminoglycosides formed via the most reactive OH group at the $C_{(6'')}$ or $C_{(6')}$ atom; the syntheses are based on the exchange reactions of aminoglycos-6″-*O*-ylalkane(arene)-sulphonates with nucleophiles. 6″-Deoxykanamycin[86-88,229], kanamycin-6″-uronic acid, its methyl ester and amide[198], 6″-hydrazinokanamycin[230,231], 6″-halogenokanamycins[88,231], kanamycin-6″-phosphate[232,233], and 6′-amino-6′-deoxygentamicin A[234] have been obtained in accordance with this scheme. Among aminoglycoside antibiotics containing a furanosyl substituent, the most reactive hydroxy-group is at the $C_{(5'')}$ atom. The following derivatives of these antibiotics have been obtained: ribostamycin-5″-uronic acid, its methyl ester and hydrazide[235], lividomycin A-5″-phosphate and 5″-deoxylividomycins B[236,237] and A,[64] 6′-amino-5″,6′-dideoxylividomycin A,[64] 5″-amino-5″-deoxybutirosin[52], and 5″-amino-3′,4′,5″-trideoxybutirosin[238]. Apart from the OH groups at the $C_{(5'')}$ atom, lividomycins A and B have a further hydroxy-group with a high reactivity—the groups at the $C_{(6')}$ atom. A number of derivatives have also been obtained via this hydroxy-group: 6′-amino-6′-deoxylividomycins A[215] and B[239] and 6′-deoxy-6′-methylamino- and 6′-deoxy-6′-(2-hydroxyethylamino)lividomycins B.[239]

Derivatives of aminoglycoside antibiotics readily epimerise at the 2″-*C*-hydroxy-group in solutions in the presence of bases or simply on heating in dimethylformamide. Thus, such treatment of kanamycin derivatives leads to the formation of the corresponding mannosyl derivatives[240-243]. It has been shown for gentamicin $C_1$ that epimerisation is also observed on solvolysis of the 2″-C-methanesulphonate in 10% aqueous dimethylformamide[244]. The epimerisation of paromamine in the 3′-*C*-position has been achieved by reduction with sodium tetrahydroborate of the corresponding glycos-3′-yl derivative obtained by oxidising tri-*N*-(benzyloxycarbonyl)-di-4′,6′-*O*-isopropylideneparomamine in the methyl sulphoxide–acetic anhydride system in the dark at room temperature for three days[245]. The epimerisation at the 2′-*C*-hydroxy-group has been observed in the synthesis of 3′-amino-3′-deoxykanamycin via a mechanism which is based on the cyclisation of the dialdehyde obtained by the periodate oxidation of tetra-*N*-acetylkanamycin with nitromethane followed by the reduction and hydrazinolysis[242]. Direct treatment of the intermediate 3′-deoxy-3′-nitro-derivative with hydrazine leads to the decomposition of the nitrosugar component of the compound.

In contrast to the modification of amonoglycosides via the chemically most reactive hydroxy-group at $C_{(6'')}$, the problem of transformations via the 3′-*C*- and 4′-*C*-hydroxy-groups is much more complex, since such reactions necessitate the blocking of all the hydroxy-groups of the antibiotics except those at $C_{(3')}$ and $C_{(4')}$. This is very difficult to achieve in view of the virtually identical reactivities of the hydroxy-groups (except those at $C_{(6'')}$ or $C_{(5'')}$). On the other hand, the synthesis of 3′- and 4′-deoxy and 3′,4′-dideoxy-derivatives of aminoglycosides in one of the tasks of primary importance, since these semisynthetic antibiotics are in fact highly active in relation to bacterial strains inactivating aminoglycosides via the commonest mechanism of enzymatic inactivation—*O*-phosphorylation at $C_{(3')}$. This task can be carried out readily only when there exists a simple method for the selective protection of the functional groups of the antibiotic. At the present time such a method has not been developed yet, and, for example, 3′-deoxykanamycin A has not so far been obtained from the natural antibiotic. The situation is simpler in the case of aminoglycosides incorporating a non-amino-fragment. Nevertheless, the synthesis of 3′- and 4′-deoxy-derivatives of these antibiotics are extremely complex multistage processes, with very low yields of the required product.

Antibiotics containing a non-amino-component give rise to a 3′-deoxy derivative as a result of the selective tosylation of the OH group at $C_{(3')}$ with subsequent exchange for the halogen atom and reduction. A typical scheme for the synthesis of 3′-deoxykanamycin B[79] is as follows. After protecting the amino-groups, the hydroxy-groups at $C_{(3')}$, $C_{(4')}$, $C_{(4'')}$, and $C_{(6'')}$ are blocked with the aid of the isopropylidene or cyclohexylidene groups and the 2″-*C*-hydroxy-group is benzolated; the protecting groups are removed from the 3′- and 4′-*C* positions under mild conditions, the toluenesulphonate group is introduced selectively at $C_{(3')}$ and is exchanged for the halogen atom, and 3′-deoxykanamycin B is obtained after reduction and elimination of protecting groups. A virtually similar scheme constitutes the basis of the synthesis of 3′-deoxy-derivatives of ribostamycin[48] and butirosin B.[213] It has been shown for the synthesis of 3′-deoxybutirosin B that the 2-nitrobenzene-1-sulphonate group is exchanged for a halogen atom more readily than the tosyl group[213].

In the synthesis of 3′,4′-dideoxy-derivatives of aminoglycosides, after the methanesulphonation of the hydroxy-groups at $C_{(3')}$ and $C_{(4')}$ a double bond is introduced by the Tipson–Cohen method[246,247] and hydrogenated, and, after the removal of the blocking groups, the required compound is obtained. This scheme is the basis of the synthesis of aminoglycoside derivatives such as 3′,4′-dideoxykanamycin B,[51,90,91,248] 3′,4′-dideoxy- and 3′,4′,5″-trideoxy-ribostamycin[20], 3′,4′-dideoxybutirosins B[51,212] and A,[249] 5″-amino-3′,4′,5″-trideoxybutirosin A,[238,250] 3′,4′-dideoxyneamine[13], and 1-*N*-[(*s*)-4-amino-2-hydroxybutyryl]-3′,4′-dideoxyneamine[19].

An unexpected synthesis of 4′-deoxykanamycin A of kanamycin A has been discovered. It has been shown that the hydrogenolysis of nona-*NO*-acetyl-6′-*N*-benzyloxycarbonylkanamycin A over palladium on charcoal at room temperature results in the migration of the *O*-acetyl group from the 4′-*C*-position to the 6′-*C*-amino-group. Thus a simple method has been found for protecting all the amino- and hydroxy-groups except the hydroxy-group at $C_{(4')}$.[251] In this synthesis, the 4′-*C*-hydroxy-group is removed by exchanging the methanesulphonyl group for the thioloacetate group with subsequent reduction over Raney nickel at atmospheric pressure.

A second method for the synthesis of 4′-deoxykanamycin, based on the formation of a 4′,6′-cyclic carbamate by the reaction of the tri-*N*-ethoxycarbonyl derivative of kanamycin with phenyl chloroformate[211], was described at the same time[251]. However, this method is complex, it is sufficient to say that it consists of thirteen stages.

The synthesis of deoxy-derivatives of gentamicin is complicated by a series of cyclisations and rearrangements in the garosamine ring[244]. The attempt to obtain 2″-deoxygentamicin $C_1$ was unsuccessful owing to epimerisation. The 2″-*C*-hydroxy-group was removed from gentamicin $C_2$. Methanesulphonation of the pentabenzylidene derivative of gentamicin $C_2$ led to the formation of the 2″-*O*-methanesulphonyl derivative, which cyclises to an epimine after the removal of the benzylidene groups. The

epimine was acetylated with acetic anhydride in methanol and the acetyl derivative was reduced over Raney nickel at 140°C and 176 atm in 30 h. After the removal of the protecting groups, two products were obtained—2″-deoxygentamicin $C_2$ and its rearrangement product—2″-deoxy-3″-desmethylamino-2″-methylaminogentamicin $C_2$, the second substance being the main reaction product.

The reduction of penta-*N*-benzyloxycarbonylper-*O*-acetylgentamicin $C_1$ with sodium in liquid ammonia leads to 4″-deoxygentamicin $C_1$.[252] It has been shown for garamine that the reaction cannot be extended to the synthesis of 2″-deoxyderivatives by reducing the 2″-acetyl- or 2″-thiobenzoyl-garamine[252].

## VII. COMPLEXES OF AMINOGLYCOSIDES

Owing to the large number of their hydroxy- and amino-groups, aminoglycoside antibiotics readily form complexes with heavy metal salts. The formation of aminoglycoside complexes with water-soluble inorganic copper, nickel, cobalt, zinc, magnesium, and iron salts has been described[253-258]. The metal content in the complex varies in the range 0.5–3.0 atoms per mole of the antibiotic[320].

The study of the infrared spectra of chelates of kanamycin, deoxystreptamine, and ethylenediamine with copper(I) chloride, led Yamabe[255] to the conclusion that kanamycin forms a chelate with $Cu^{2+}$ via the propylidenediamine component of deoxystreptamycin. On the other hand, comparison of the polarograms of the chelates of kanamycin and deoxystreptamine shows that these complexes are of different types[255] Thus the problem of the particular amino-groups of kanamycin involved in the formation of chelates with heavy metal ions remains open. The structure of the chelates must undoubtedly depend on the nature of the amino-groups participating in the formation of the complex and on their reactivity.

It has been shown that $Ca^{2+}$ and $Mg^{2+}$ salts decrease the degree of binding of gentamicin and other deoxystreptamine-containing antibiotics to bacterial and blood serum proteins. The maximum binding (70%) is observed in the absence of metal cations, the degree of binding decreasing with increase of the metal ion concentration[259]. There is no doubt that this phenomenon is based on the ability of the aminoglycoside antibiotics to form complexes with metal salts. Under conditions involving competition between the binding of aminoglycosides by metal salts or proteins, the preferred process is apparently the formation of complexes of metal ions.

The capacity of aminoglycoside antibiotics for complex formation is used in the analysis of drugs[260,261]. Kanamycin forms anisotropic monoaxial crystals with the Reinecke salt[262]. The reaction makes it possible to determine kanamycin in solutions at the minimum concentration of 1 : 100 000.

The most important application of the ability of aminoglycosides to form complexes of the Reeves cuprammonium method for the determination of structures[263]. The method has been used to determine the structures of virtually all aminoglycoside antibiotics[54,264-268].

Aminoglycoside antibiotics are known to form carbonates readily by reaction with carbon dioxide. However, the study of the $^{13}C$ NMR spectra of the products resulting from the absorption of carbon dioxide by gentamicins $C_1$, $C_2$, and $C_{1a}$ showed that carbon dioxide is bound by these substances without the formation of carbonates. The structure of the resulting complexes is unknown[103].

## VIII. THE FORMATION OF *O*-GLYCOSIDIC LINKAGES. DIRECT SYNTHESIS OF AMINOGLYCOSIDES

The so called "total" synthesis of aminoglycosides, involving the condensation of mono- and pseudodi-saccharides by the Koenigs–Knorr reaction, is very important in the chemistry of aminoglycoside antibiotics. Despite its complexity, the method retains its importance, because it makes it possible to decide finally the validity of the determination of the structure of the aminoglycoside antibiotic and also to obtain derivatives of aminoglycosides which cannot so far be synthesised by the transformation of existing antibiotics.

After the preliminary synthesis of the initial monosaccharides and aminocyclitols[269-281], the method has been used to synthesise streptomycin[282], dihydrostreptomycin[283,321], kanamycins A,[284-287] B,[288,289] and C,[290-292] ribostamycin[293,294,322], xylostasin[39], 3′-*O*-methylkanamycin A,[295] 3-amino-2,3-dideoxy-$\alpha$-arabinohexapyranosylgentamine $C_1$,[296] the isomeric di-*O*-($\alpha$-D-glucopyranosyl)-2-deoxystreptamines[297], as well as a number of glycosides containing 6′-amino-6′-deoxy-$\alpha$-D-glucopyranosyl-2-deoxystreptamine[271], etc.,[323].

It is noteworthy that the classical method of glycoside synthesis (the Koenigs–Knorr reaction) is unsuitable on an industrial scale not only because of the low yields of the final product, but also because of the formation of large amounts of the $\beta$-isomer. A new method of synthesis of $\alpha$-D-glucopyranosyldeoxystreptamines, developed by the Lemieux–Nagabhushan group and based on the reaction of dimeric tri-*O*-acetyl-2-deoxy-2-nitroso-$\alpha$-D-glucopyranosyl chloride with alcohols[298-306], is therefore of definite interest. The Lemieux–Nagabhushan reaction has been used successfully to obtain various derivatives of gentamicin $X_2$,[307] gentamicin B,[308] and pentosyl derivatives of garamine[309].

In conclusion one should note that, in the absence of a suitable method for the selective protection of hydroxy-groups, the method of "total" synthesis is so far the only available procedure for obtaining 3′-deoxykanamycin[84,299,300]. The method is also important for the synthesis of various isomers of aminoglycosides required for the elucidation of the role of the structural components of the aminoglycoside molecules in their antibacterial activity.

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# Chitin and Its Chemical Transformations

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The present state of research in the field of the natural polysaccharide chitin and chitosan is described. The bibliography includes 225 references.

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## I. INTRODUCTION

Despite the fact that chitin has been known for a long time[1,2] and occurs widely in nature, it has still been little investigated. There has been an increase of interest in chitin owing to the general development of the chemistry of polysaccharides and synthetic polymers. A number of studies have been published recently on chitin derivatives which are of practical value. There has been a considerable expansion of research also on the properties of deacetylated chitin (chitosan). A survey of the literature data is therefore of definite value, particularly since the available reviews[3-7] do not reflect fully the advances achieved in this field.

## II. THE STRUCTURE AND PROPERTIES OF CHITIN

Chitin occurs in nature in the organisms of certain lower animals and plants, predominantly in crustacea[8-11], insects[12], and fungi[11-15]. It is always present in combination with other substances[16], such as proteins, inorganic salts, or polysaccharides. During its isolation in a pure form, the chitin-containing material is therefore treated with appropriate reagents[13,17-19], which decompose the secondary substances but do not affect the chitin macromolecule. Plant and animal chitins are identical, which has been confirmed by their chemical composition[20], specific gravity[21], specific optical rotation[22], and the repeat period obtained by X-ray diffraction[23].

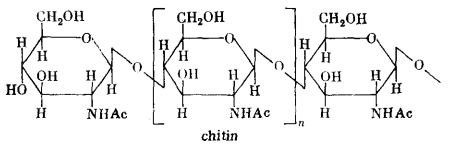
Chitin is one of the commonest polysaccharides in nature; marine crustacea alone yield thousands of millions of tons of chitin annually[24]. However, the industrial utilisation of chitin is difficult owing to its even distribution in nature.

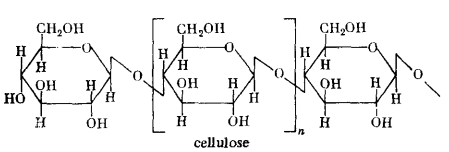
### 1. The Hydrolysis of Chitin

The complete acid hydrolysis of chitin leads to the formation of glucosamine and an equimolar amount of acetic acid[25]. After the hydrolysis of chitin with 70–72% sulphuric acid at room temperature for 2–3 days, monoacetylglucosamine was isolated[26]. This important discovery made it possible to determine the position of the acetyl group in monoacetylglucosamine. By hydrolysing chitin with highly concentrated hydrochloric acid, Zechmeister and coworkers[27,28] obtained not only the final chitin hydrolysis product (acetylglucosamine) but also a number of intermediate fractions, the acetylation of which gave a biose octa-acetate and chitotriose acetate[29]. They noted that the biose octa-acetate is identical with the chitobiose octa-acetate isolated in other investigations[30,31] by the acetolysis of chitin. Partial hydrolysis of chitin by concentrated hydrochloric acid in later studies[32-36] gave *N*-acetylchito-oligosaccharides. The chito-oligosaccharides were separated by thin-layer[37-39] and ion-exchange chromatography[40] as well as other methods[41-43]. Acetolysis of plant and animal chitins yielded chitobiose octa-acetate and chitotriose undeca-acetate, which are identical regardless of whether they are obtained from plant or animal chitin[35,36,44,45].

Chitin is very resistant to the action of bacteria[46], but micro-organisms decomposing it do exist[47-49]. It has been shown[50,51] that chitin is hydrolysed by the enzyme chitinase with formation of up to 80% of acetylglucosamine. A similar yield of acetylglucosamine has been obtained on cleavage of plant chitin with chitinase[52]. The above data suggests that chitin is a homogeneous linear polymer.

Comparison of the activation energies for the hydrolysis of chitin by nitric acid[53] and of cellulose by sulphuric acid[54] and of their repeat periods obtained by X-ray diffraction[23,55-57] as well as the formation of chitobiose octa-acetate by the acetolysis of chitin and the specificity of the action of chitinase show that the *N*-acetylglucosamine residues are joined via oxygen with the $\beta$-glucosidic 1,4-linkage and are alternately rotated by 180°, i.e. the chitin macromolecule has a structure similar to that of cellulose, but differs from it by the fact that there is an acetamide group at $C_{(2)}$ instead of a hydroxyl:




The oxidation of chitin by periodate also confirmed the above structure[58].

## 2. The Supermolecular Structure of Chitin

Many studies on the structure of chitin [59-71] led to the conclusion that chitin has a highly ordered stereoregular structure. Its X-ray diffraction pattern reveals a well-defined orthorhombic lattice [66]. The macromolecular chains of chitin are involved in strong hydrogen bonds both via the NH and CO group and via hydroxy-groups [68, 69, 72]. The crystal structure proposed by Carlström [68] has been confirmed by data obtained in a study [72] of the infrared spectrum of chitin. Detailed analysis of this spectrum confirmed the presence of the intermolecular C=O...N–H hydrogen bond along the fibre axis and the absence from the chitin crystals of free OH, NH, and C=O groups not involved in the hydrogen bond. The authors believe that the OH group at $C_{(6)}$, which exhibits free rotation, may be linked by an intramolecular hydrogen bond to the bridge oxygen and the nitrogen atom in a neighbouring glucosamine unit.

Recent X-ray diffraction studies [4,69,73] indicate the existence of chitin in three crystalline forms ($\alpha$, $\beta$, and $\gamma$), differing in the size of the crystal lattice. It has been shown [74] that $\alpha$-chitin is orthorhombic and its unit cell contains fragments of two chains only, arranged in opposite directions. All the forms are stable in boiling 5% KOH or NaOH solution [75], but their treatment with 6 *N* HCl leads to the conversion of the $\beta$- and $\gamma$-forms into the $\alpha$-form [75]. Similar conversions have been observed also by other workers [11,73].

## 3. The Properties of Chitin

Despite the similarities of the structures of chitin and cellulose, they differ significantly. In contrast to cellulose, chitin swells only slightly in solutions of alkalis and does not dissolve in the solvents used for cellulose (solutions of the amminecopper complex, the iron–tartrate–sodium complex, benzyltriethylammonium hydroxide, and the cadmium–ethylenediamine complex), probably due to the absence from chitin of two adjacent hydroxyls, which in the case of cellulose are responsible for the formation of molecular compounds [76,77].

At the same time, chitin dissolves comparatively readily in concentrated hydrochloric and sulphuric acids [78,79], from which it can be isolated almost unaltered [80]. Nitric and phosphoric acids also dissolve chitin [81,82]. When chitin is dissolved in acids, gradual hydrolysis takes place, as a result of which a glucosamine salt is formed. Chitin solutions are laevorotatory; in hydrochloric acid with a specific gravity of 1.16, the initial specific rotation is $-14.7°$ and the final rotation is $+56°$ (which corresponds to the rotation of the glucosamine hydrochloride formed [22]). In view of this, chitin solutions in acids are unstable, their viscosity varying with time, so that it is impossible to determine the true molecular weight by viscometric, osmometric, light scattering, or sedimentation methods. An attempt has been made to estimate the molecular weight of chitin by measuring its viscosity in 50% nitric acid [81] and by extrapolating the viscosity to zero dissolution time. By comparing the values obtained with the analogous viscosities of wood cellulose in amminecopper solution, the authors [81] concluded that chitin and wood cellulose have similar molecular weights; this method is only approximate.

The method of copper numbers (determination of the content of terminal aldehyde groups) was used by Iterson [83] to estimate the degree of polymerisation (DP) of chitin. According to his data, the degree of polymerisation of chitin corresponds to 103 units. However, in another study [84] this method gave DP = 66. The method is comparatively rapid and can be used to characterise the variation of the degree of polymerisation of chitin. However, it does not yield unambiguous results owing to the polydispersity of the specimen and the possible oxidation of the terminal aldehyde groups to carboxy-groups. According to the data of other investigators [85-87], the degree of polymerisation of chitin varies from several hundreds to thousands of *N*-acetylglucosamine residues.

Chitin dissolves on heating in concentrated solutions of certain salts [87,88] and the latter can be arranged in the following sequence in terms of their dispersing capacity [38]:

$$LiSCN > Ca(SCN)_2 > CaI_2 > CaBr_2 > CaCl_2.$$

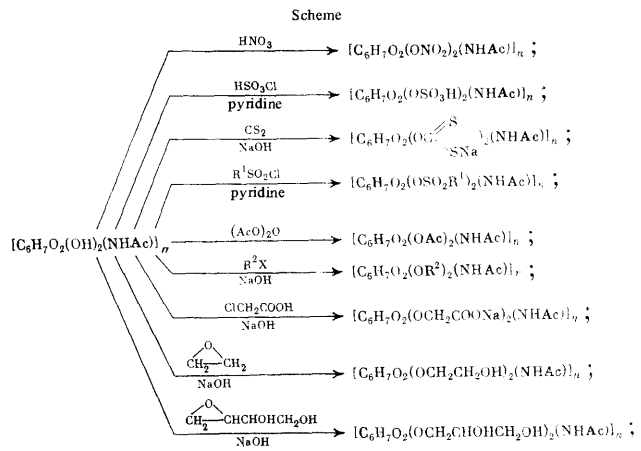
Partial dissolution of chitin has been observed in mixtures of dimethylformamide and nitrogen dioxide [89].

## III. REACTIONS IN THE CHAINS OF THE CHITIN MACROMOLECULE

Chitin is less reactive than cellulose when an attempt is made to modify it chemically, because of the characteristics of its supermolecular structure—the presence in chitin of stronger hydrogen bonds and a small active surface area, which follows from the determination of the amount of non-freezing water [90] and the measurements of the heats of swelling of chitin and cellulose [90].

In contrast to cellulose, there are only two hydroxy-groups in chitin, which can be involved in chemical reactions and can form disubstituted chitin derivatives. However, owing to their low reactivity, complete substitution is not usually achieved. The known reactions of chitin modifications are indicated schematically below:

Scheme




$R^1 = CH_3$ or $CH_3C_6H_4$; $R^2 = CH_3$ or $C_2H_5$.

### 1. The Synthesis of Esters

Chitin acetates cannot be obtained by the method [91] involving the use of perchloric acid as the catalyst. Chitin has been acetylated [92] with acetic anhydride and dry hydrogen chloride in the course of 120 h at room temperature; an overall degree of substitution of 2.99 (taking into account the acetyls group in the initial chitin) was

achieved. Chitin acetate substituted to this extent dissolves in formic acid and in 50% aqueous resorcinol solution. When water is added to the solution, acetylchitin is precipitated. Concentrated inorganic acids (sulphuric and hydrochloric) slowly dissolve acetylchitin, but it cannot be isolated from the solutions, since hydrolysis takes place. Concentrated nitric acid (specific gravity 1.50) dissolves acetylchitin very rapidly and the latter can be isolated from the solution by the addition of water, nitroacetylchitin, containing 2.14% of nitro-nitrogen, being precipitated.

Chitin has been acetylated[53] for three months with a mixture of acetic acid and acetic anhydride in the presence of zinc chloride; this yielded chitin acetate containing 2.5 acetyl groups per residue. The preparation was highly destructured.

Chitin dissolved in phosphoric acid has been acetylated[93] both in the presence and absence of perchloric acid as the catalyst. In the presence of 1% $HClO_4$, 27.5% of acetyl groups were introduced in 4 h at 75°C, which corresponded to a degree of substitution of 1.80; in the absence of the catalyst, a maximum degree of substitution of 1.70 was attained at 80°C. It is seen from these data that the limiting degree of substitution is not reached under homogeneous conditions. The esters obtained dissolved in 50% aqueous resorcinol solution and phenol and partially in *m*-cresol.

Chitin nitrates were obtained for the first time[94] by nitrating chitin with fuming nitric acid. Schorigin and Hait[95] investigated this process in detail and established that, during nitration with nitric acid alone (specific gravity 1.50), the maximum yield of chitin nitrate containing 7.51% of nitro-nitrogen, which corresponds to the substitution of 1.5 hydroxy-groups, is attained. The chitin nitrate obtained ignites at 163°C and is denitrated by sodium hydrogen sulphide in 3 h at 16°C. Its X-ray diffraction pattern indicates a fibrous structure with the same repeat period as that of chitin[81].

Among organic solvents, nitrochitin dissolves partly only in formic acid and can be isolated from solution by the addition of water. It also dissolves in sulphuric and hydrochloric acids but is not reprecipitated by the addition of water.

Chitin xanthate was described for the first time by Thor and Henderson[96-98], who impregnated chitin with a 43% solution of NaOH at 25°C for 2 h and then mixed it with crushed ice and added carbon disulphide; this resulted in the conversion of chitin into a gel and then its dissolution. The solution is unstable, chitin is deacetylated at room temperature, and chitosan xanthate is precipitated from solution. To avoid coagulation, the solution must be stored below 0°C. Chitin xanthate solutions are suitable for the formation of filaments and films[98].

Chitin sulphate esters have been described[99,100] and the authors obtained them by treating chitin with chlorosulphonic acid in different media. In pyridine[99] the sulphate formation reaction was carried out over a period of 7 h during which 14.4% of sulphur was introduced. When the reaction was carried out in dichloroethane[100] for 2 h, a sulphate ester containing 13–15% of sulphur, depending on temperature, was obtained. Chitin with this sulphur content dissolves in water. The molecular weights of all the esters were determined by the osmometric method and were found to be 14 000–17 000, depending on the conditions of synthesis[100]. In order to avoid the possible degradation of the chitin macromolecule, it has been suggested that formamide be used as a solvent for chlorosulphonic acid[101].

Methanesulphonate and toluene-*p*-sulphonate esters[102] have been obtained by treating with methanesulphonyl and toluene-*p*-sulphonyl chlorides chitin which had been subjected to preliminary activation by reprecipitation from solution in phosphoric acid in the presence of dry pyridine. The optimum conditions under which the maximum sulphur content is achieved (10.22%) during tosylation obtain in the presence of the chitin : tosyl chloride : pyridine = 1 : 10 : 50 ratios and when the reaction is carried out at room temperature for 10 days. The mono(toluene-*p*-sulphonate) ester[102] contains 8.98% of sulphur. In the preparation of the monomethanesulphonyl derivative of chitin, the optimum conditions obtain in the presence of the chitin : methanesulphonyl chloride : pyridine = 1 : 10 : 40 ratios at room temperature and when the synthesis is carried out over a period of 7 days[102], whereupon up to 12.57% of sulphur can be introduced (the monomethanesulphonate chitin ester should contain 11.4% of sulphur).

## 2. The Synthesis of Ethers

Methyl ethers containing 9.34% of $OCH_3$ group have been obtained[103] after 45 methylations of alkali-treated chitin with dimethyl sulphate. Preliminary activation of chitin with hydrochloric acid and subsequent 15 methylations in the presence of alkali made it possible to increase the content of methoxy-groups to 16.07%, which corresponds to monomethylchitin. Monomethylchitin dissolves in formic acid, swells strongly, and partly dissolves in glacial acetic acid.

Ethyl ethers containing 33.83% of $OC_2H_5$ groups, which correspond to a degree of substitution of 1.59, were obtained for the first time[104] by treating alkylchitin with ethyl chloride for 10 h with stepwise heating of the reaction mixture to 130°C. During the synthesis of the ether, the acetyl groups of chitin are hydrolysed. The ether contained 2.04% of free amino-groups, 2.75% of hydroxy-groups, and 4.53% of acetyl groups, which corresponds to the composition $[C_6H_7O_2(OH)_{0.34}(NH_2)_{0.70}(NHCOCH_3)_{0.21}.(OC_2H_5)_{1.59}]_n$. The molecular weight of the ether thus obtained[103], determined in ethyl methyl ketone by the method of sedimentation in an ultracentrifuge, was 66 000. Ethylated chitin forms films with a strength of 6.8–7.3 kgf mm$^2$ and an elongation of 15–23%.

Hydroxyethyl ethers are obtained by treating alkali-treated chitin with epoxyethane under heterogeneous[104] or homogeneous conditions[16,105]. More severe heterogeneous conditions are required for the reaction than in the case where homogeneous conditions are employed. In both cases the formation of water-soluble ethers requires a considerable excess of epoxyethane. A nitroxyethyl ether of chitin[104], containing 5.71% of nitro-nitrogen, has been obtained from the hydroxyethyl ether.

Glyceryl ethers[106] have been synthesised by treating alkali-treated chitin with glycerol monochlorohydrin or with glycidol. Treatment of chitin with glycerol monochlorohydrin did not give rise to a water-soluble ether, despite the high content of glycerol residues (up to 49%). In contrast to the initial chitin, the ether obtained

did not dissolve even in hydrochloric or phosphoric acids, which indicated the cross-linking of the ether with traces of the glycerol dichlorohydrin present in the monochlorohydrin. When glycidol was used to alkylate chitin, ethers soluble in 4 and 8% sodium hydroxide were obtained.

Carboxymethyl ethers in the form of sodium salts (Na-CMC) have been described[107-110]. The kinetics of the carboxymethylation of chitin dissolved in solutions of alkali have been investigated[108] and it has been shown that, with increase of the concentration of sodium hydrodide to 15–20% and of temperature to 20° to 30°C, the rate of reaction increases sharply. However, an increase of the reaction temperature entails the formation of a precipitate from the alkaline solution owing to the elimination of the acetyl groups and the formation of chitosan. For this reason, at the end of the carboxymethylation reaction the reaction mixture is sometimes subjected to additional acetylation with acetic anhydride at pH 10 for 2 h at room temperature[116]. In order to determine the structure of Na-CMC, it was subjected to periodate oxidation and acid hydrolysis[111]. Chromatographic analysis of the hydrolysis product showed that substitution takes place mainly at $C_{(6)}$, which is indicated also by the susceptibility of Na-CMC to periodate oxidation. During carboxymethylation[108] under heterogeneous conditions, the acetyl groups are not hydrolysed. At room temperature, the reaction proceeds most completely and a degree of substitution of 0.8–1.0 is attained. An increase of reaction temperature to 40–60°C accelerates the hydrolysis of monochloroacetic acid, so that the main reaction requires a smaller amount of the alkylating agent.

A new method has been described[110] for the preparation of carboxymethylchitin involving the preliminary activation of chitin with dimethyl sulphoxide. Carboxymethylchitin with a degree of substitution of 0.99, which is readily soluble in water, has been synthesised in this way. Acidification of Na-CMC with a dilute hydrochloric acid solution[109] yielded a chitino-glycolic acid, which swells strongly and partly dissolves in water, in contrast to celluloso-glycolic acid[112]. Na-CMC containing 6% Na and more readily dissolves in water. Aqueous solutions of Na-CMC and H-CMC exhibit polyelectrolytic properties, i.e. the intrinsic viscosity increases on diluting the solution[113].

## IV. THE PREPARATION OF CHITOSAN AND ITS PROPERTIES

The preparation of chitosan from chitin has been described in numerous articles[34,84,114-117] and patents[118,119]. Gilson[114] was the first to obtain chitosan by fusing chitin with potassium hydroxide at 180–190°C; this treatment results in the hydrolysis of the *N*-acetyl groups. A patent[118] proposes milder conditions for the preparation of chitosan, involving the heating of chitin with a 40% solution of sodium hydroxide at 110°C for 4 h. The methods of preparation of chitosan have been studied in detail[116]. The author notes that the deacetylation of chitin in 40% sodium hydroxide at 135–140°C is slow; 60% of the acetyl groups are hydrolysed after 24 h. The deacetylation of chitin at 120°C in an anhydrous medium consisting of potassium hydroxide (50%), ethanol (25%), and monoethylene glycol (25%) has been described[115]. In order to achieve the required degree of deacetylation and the corresponding viscosity, the reaction is carried out for a specified time, which yields satisfactorily reproducible data[115]. The deacetylation of chitin with a mixture of potassium hydroxide and hydroxylamine is more difficult[120]. At 100°C and pH 13 approximately 70% of the acetyl groups are removed in the course of 10–20 h.

Darmon and Rudall[67] followed the changes in the infrared spectra during the deacetylation of chitin. The intensity of the carbonyl (1625 $cm^{-1}$) and amide (3265 and 3100 $cm^{-1}$) bands diminishes during the formation of chitosan, while that of the 3365 and 3445 $cm^{-1}$ bands increases, which indicates the appearance of the $NH_2$ group. X-Ray diffraction studies on chitosan have shown that it has the same crystal lattice as chitin, but the degree of order in its macromolecules is smaller[64,67]. Chitosan, regenerated in the form of a film in a salt or basic form[121], gives rise to X-ray diffraction patterns characteristic of amorphous substances.

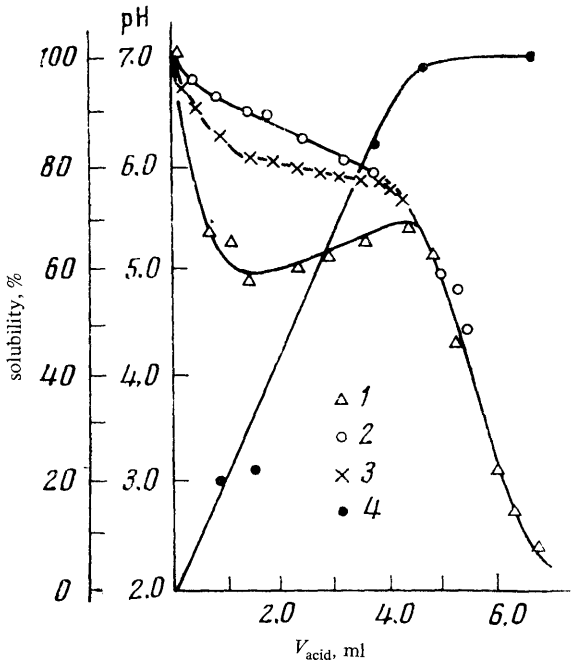



Figure 1. Potentiometric titration curves for chitosan: 1) direct titration of the initial chitosan; 2) back titration; 3) direct titration of reprecipitated chitosan; 4) solubility.

We established that the changes in the supermolecular structure during the dissolution of chitosan may be followed by its potentiometric titration. Direct potentiometric titration of the initial chitosan with acid by the individual sample method (Fig. 1, curve *1*) yields a titration curve with two extrema. The minimum at pH 4.9 corresponds to the neutralisation of the accessible amino-groups, after which further addition of acid leads to a gradual increase of pH to 5.5 (the maximum on the curve) as a result of the liberation of the amino-groups which had been previously involved in hydrogen bonding. The maximum corresponds to the complete dissolution of chitosan (Fig. 1, curve *4*); under these conditions, the supermolecular structure has been disrupted and all the

amino-groups become accessible to titration. The back-titration curve (Fig. 1, curve 2) forms a hysteresis loop with curve 1, from the area of which it is possible to estimate the energy consumed in the disruption of the structure [when $pH - \lg\alpha/(1-\alpha)$ is plotted against $\alpha$, where $\alpha$ is the degree of dissociation]. This energy, amounting to 2.8 kcal mole$^{-1}$, corresponds to the dissociation energy of the hydrogen bonds. In the direct titration of reprecipitated chitosan (Fig. 1, curve 3), the area of the hysteresis loop is much smaller, which indicates the incomplete restoration of the intermolecular hydrogen bonds on reprecipitation.

The viscosity and hence the molecular weight of chitosan are greatly influenced by the conditions used in the deacetylation of chitin: in an atmosphere of an inert gas (nitrogen, argon), chitosan with a higher molecular weight is obtained[122,123]. In contrast to chitin, chitosan dissolves in dilute acid solutions from which it can be isolated without alteration. Chitosan can be therefore readily characterised on the basis of its viscosity and polydispersity. A study of the flow of aqueous solutions of chitosan hydrochloride in a capillary showed[124] that its solutions do not exhibit structural viscosity.

The amino-group imparts polyelectrolytic properties to chitosan, as shown by a study of the viscosity of chitosan hydrochloride [solutions][124,125]. It was found that, at a fairly high ionic strength, the intrinsic viscosity becomes a linear function of concentration. In order to suppress completely the polyelectrolytic effect of chitosan solutions in acetic acid, it is necessary to add sodium chloride to a concentration of 0.5 M; in hydrochloric acid, this is achieved at an acid concentration of 0.3 M.

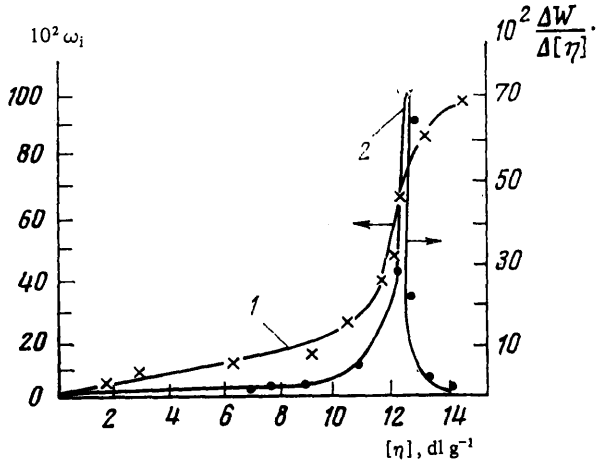



Figure 2. The integral (curve 1) and differential (curve 2) curves for the distribution of chitosan with respect to molecular weight; $w_i$ is the proportion by weight of the given fraction, $W$ the overall proportion by weight, and $[\eta]$ the intrinsic viscosity.

The polydispersity of chitosan has been demonstrated qualitatively in the extraction of chitosan lyophilised with alcohol[122], which resulted in a decrease of the relative viscosity. The molecular weight distribution has been studied by the fractional precipitation of chitosan from solution in 2% acetic acid[123] with acetone. The integral and differential distribution curves with respect to molecular weight (Fig. 2) indicate a comparative homogeneity of chitosan.

## V. REACTIONS IN THE CHITOSAN CHAINS

The presence of two hydroxyls and of a primary amino-group in chitosan extends the scope of its possible modification. In the synthesis of chitosan derivatives, the preparation of specifically substituted compounds (the synthesis of *O*- or *N*-derivatives) is of special interest. The method developed previously for the specific synthesis of chitosan esters (*O*- and *N*-sulphochitosans)[126] has been recently supplemented by a method for the specific synthesis of ethers (*O*-sulphoethyl- and *O*-carboxymethyl-chitosans)[127]. The synthesis of selectively substituted chitosan derivatives ensures the formation of compounds with specified properties, required in various applications.

### 1. The Synthesis of Esters

The sulphonation of chitosan was achieved for the first time[128] by treatment with a mixture of sulphur trioxide and dioxide at the boiling point of the mixture. The resulting ester contained 14.8% of sulphur and exhibited anticoagulation activity *in vivo* and *in vitro*. Subsequently chlorosulphonic acid in pyridine[129], the sulphur trioxide–pyridine complex[130], and sulphuric acid[131,132] were used to sulphonate chitosan. In the last case, the formation of fully *N*-sulphonated chitosan was noted[132].

A method has been developed for the selective sulphonation of chitosan by altering the reagent and media[126]. Using the pyridine–sulphur trioxide complex as the sulphonating agent in an aqueous alkaline medium at pH 9–10, the authors obtained *N*-sulphochitosan containing one sulphamate group per glucosamine unit. Subsequent treatment of *N*-sulphochitosan with a mixture of sulphur dioxide and trioxide in the cold yielded the *O*-sulphonated derivative (75% of the hydroxy-groups were substituted). The authors note the absence of anticoagulation activity of the *N*-derivative and the high activity of this kind of the *ON*-derivative of chitosan.

The phosphorylation of chitosan has been carried out by treatment with phosphoryl chloride at 40°C for 5 h.[99] The authors do not state either the degree or site of phosphorylation.

The acetylation of chitosan with acetic anhydride at 100–135°C in a sealed tube yields a highly destructured preparation, whose properties resemble those of chitin[133,134].

The acylation of chitosan by treatment with formic acid and propionic and butyric anhydrides at 110° to 125°C leads to the formation of the corresponding *N*-derivatives of chitosan[135]. A similar type of reaction occurs when alkali-treated chitosan is treated with benzoic anhydride, as shown by the insolubility of the specimens in dilute hydrochloric acid.

The arenesulphonation of chitosan has been achieved by the reaction of benzene- and naphthalene-sulphonyl chloride with alkali-treated chitosan[135]. The derivatives contained approximately one substituent per

glucosamine unit. Benzenesulphonylchitosan is partly soluble in dilute hydrochloric acid and readily soluble in solutions of alkali in contrast to naphthalenesulphonylchitosan, which is sparingly soluble in alkali.

### 2. The Synthesis of Ethers

The synthesis of chitin ethers in an alkaline medium in the absence of special precautions entails a smaller or greater degree of deacetylation. For this reason, the final products are sometimes the corresponding chitosan ethers. Thus, in the synthesis of ethyl[103], carboxymethyl[107], and glyceryl[108] ethers of chitin, the degree of deacetylation is 60% and more, as a result of which the final product was called in one instance[107] carboxymethylchitosan. In view of the simultaneous occurrence of the deacetylation and alkylation processes, the resulting compound cannot be regarded as solely an *O*-derivative.

The formation of chitosan ethers with substituents located in specified positions requires the introduction of *N*-protecting groups.

The sulphoethylation of chitosan[136] has been carried out by treatment with sodium β-chloroethanesulphonate in the presence of alkali in isopropyl alcohol and in mixtures of *o*-xylene with propyl and isopropyl alcohols. The highest degree of substitution reached 0.35. Determination of the position of the substituent by the analysis of the amino-nitrogen and conductimetric titration showed that both *O*- and *N*-sulphoethylation take place.

For specific *O*-alkylation of chitosan, the amino-group was protected by reaction with an aromatic aldehyde, which results in the formation of a Schiff base[127,137]:

$$[C_6H_7O_2(OH)_2NH_2]_n + nR^1C_6H_4CHO \rightarrow [C_6H_7O_2(OH)_2N=CHC_6H_4R^1]_n ;$$
(I) (II) (III)

$$(III) \xrightarrow{ClR^2ONa} [C_6H_7O_2(OH)_{2-x}(OR^2ONa)_xN=CHC_6H_4R^1]_n ;$$
(IV)

$$(IV) \xrightarrow{CH_3COOH} [C_6H_7O_2(OH)_{2-x}(OR^2OH)_xNH_2 \cdot CH_3COOH]_n + R^1C_6H_4CHO ;$$
(V)

$$(V) \xrightarrow{NaOH} [C_6H_7O_2(OH)_{2-x}(OR^2ONa)_xNH_2]_n ;$$
(VI)

$R^1 = H, OH, OCH_3$ or $NO_2$; $R^2 = C_2H_4SO_2$ or $CH_2CO$;

$x$ is the degree of substitution. Chitosan was treated in a neutral medium with the corresponding aromatic aldehyde at room temperature for 3 h. In contrast to benzaldehyde, anisaldehyde, and *o*-nitrobenzaldehyde, salicylaldehyde reacts fully with the amino-groups of chitosan. Salicylidenechitosan is stable in an alkaline medium but decomposes in an acidic medium into the initial components. The sulphoethylation of salicylidenechitosan has been carried out under the conditions used for the sulphoethylation of chitosan[136]. The resulting sulphoethylsalicylidenechitosan was decomposed with 50% acetic acid and then treated with a 2% solution of sodium hydroxide in order to convert it into the basic form. The final product was *O*-sulphoethylchitosan, which was confirmed by the Van Slyke analysis of the amino-nitrogen and conductimetric titration; the highest degree of substitution was 0.31. Such sulphoethylchitosan is soluble in water and in 2% acetic acid solution; when the degree of substitution is lower, the product is soluble only in dilute acids.

*O*-Carboxylation of chitosan has also been achieved via salicylidenechitosan[127] by treating the latter with sodium monochloroacetate; using 9 moles of the reagent per mole of the chitosan, a monosubstituted carboxymethylchitosan with free amino-groups was obtained.

Cyanoethylchitosan was obtained by the reaction of alkali-treated chitosan with acrylonitrile at different temperatures[138]. It was shown that it is desirable to carry out the reaction at 20°C for 24 h, since this entails the complete substitution of both hydroxy-groups without the hydrolysis of the cyanoethyl groups. An increase of temperature causes the hydrolysis of the cyanoethyl groups, so that one obtains derivatives with a lower degree of substitution. Cyanoethylation does not take place in a neutral medium, while in an acidic medium 0.31 of a cyanoethyl group per glucosamine unit is introduced at 20°C over a period of 24 h.

### 3. *N*-Alkylation of Chitosan

The *N*-methylation of chitosan has been carried out[135] by heating powdered chitosan with a tenfold excess of methyl iodide at 100°C for 6 h. A single treatment yielded mono-*N*-methylchitosan and subsequent treatment did not increase the degree of *N*-methylation. The hydriodide of mono-*N*-methylchitosan has been obtained by treating the doubly methylated chitosan with methyl iodide at 50°C for 3 h.

*N*-Methoxyethylchitosan has been obtained by the reaction of hydroxyethylchitosan with methyl iodide[139].

*NNN*-Trimethyl- and *NNN*-triethylchitosans have been synthesised by heating chitosan up to the boiling point of the corresponding alkyl iodide in absolute ethanol in the presence of organic bases[140]. Treatment with an organic base under these conditions is more effective the higher its p$K_a$. In the presence of triethylamine, almost fully *NNN*-trimethylated chitosan was obtained in a single treatment, which was confirmed by NMR.[140] The NMR spectrum of the resulting *NNN*-trimethylchitosan contains a signal at 6.80 p.p.m., confirming the presence of nitrogen in the tetra-substituted state. Signals corresponding to protons attached to secondary and tertiary nitrogen are absent.

*NNN*-Trimethyl- and *NNN*-triethyl-chitosans in salt-forms are readily soluble in water, while in the basic forms they are soluble in benzyltriethylammonium hydroxide solutions. The iodides of the quaternary bases are unstable, evolving iodine on storage. *N*-derivatives of chitosan are polyelectrolytes and their basicity increases with the degree of substitution.

## VI. THE APPLICATIONS OF CHITIN, CHITOSAN, AND THEIR DERIVATIVES

There are numerous data concerning the attempts to use chitin, chitosan, and their derivatives in various branches of industry and medicine. A wide variety of the properties of the above compounds are used: their ability to form fibres and films, their capacity for ion exchange and complex formation, and their physiological activity in the absence of toxicity. The above wide

variety of properties of the chitin and chitosan compounds make it useful to synthesis new derivatives and to employ them in practice.

## 1. Films and Fibres Based on Chitin and Chitosan

The possibility of forming films and fibres from chitin dispersions was demonstrated as early as 1926.[10,141] However, a more thorough development of this process was achieved later in a study[97] whose authors obtained films by depositing dispersions of chitin xanthate onto a glass support with subsequent regeneration of chitin in a coagulation bath containing 40% of ammonium sulphate and 5% of sulphuric acid in water. The resulting film has a tensile strength of 9.49 kgf $mm^{-2}$ in the dry state and 1.75 kgf $mm^{-2}$ in the moist state. The films did not swell in water, dilute acids and alkalis, and organic solvents. This method constitutes the basis of the formation of mixed chitin-cellulose fibres via chitin and cellulose xanthates[142]. The fibres exhibit increased dyeability and have ramielike properties. The fibre obtained from partly hydrolysed chitin by the method of Thor and Henderson[97] exhibits ion-exchange properties and can be used to regenerate and purify antibiotics, aminoacids, and other organic acids[116].

Films made of chitosan and its salts are obtained from solutions in acids or water[143-145]. The films are distinguished by a high strength, resistance to alkalis, and possess effective electrotechnical properties[121,146]. When such films were acetylated by treatment with acetic acid and dicyclohexylcarbodi-imide in solutions of alkali or in water containing an organic base, chitin films were obtained with a high mechanical strength, rigidity, and transparency[147]. The regenerated chitin films retain their properties for 30 years[148].

In order to obtain chitosan fibres, Chi-Ming Pao used a solution of chitosan in acetic acid with added lead acetate, glycerol, and alcohol and a precipitation bath containing alkali, glycerol, and sodium sulphate[116,149]. The strength of this fibre corresponds to 9–10.8 dissociative km [? (Ed. of Translation)] and the elongation on rupture is 30%. A method is also available for the preparation of fibres from a mixture of aqueous solutions of chitosan and poly(vinyl alcohol)[150]. The resulting fibres can be dyed with direct acid dyes and show a low capacity for the acquisition of an electrical charge. The use of chitosan in textile industry as a finishing[151], sizing[152], and anti-shrinking agent[153], which improves at the same time the capacity of fabrics for being dyed[154], is based on its film-forming properties. Chitosan can also be used as a thickening agent in pastes for pigment printing on fabrics[155-157]. In the paper industry, chitosan is used as an adhesive[158-160]. The graft-copolymer of chitosan with 2-acrylamido-2-methylpropanesulphonic acid, acrylamide, or acrylic acid is added to paper pulp in order to improve the printing and mechanical properties of the paper[161,162]. When a chitosan coating is applied to the surface of lithographic paper[163] and photographic paper[164,165], the sensitivity of the paper to the formation of an image and the stability of the latter are improved. When chitosan is added to paper pulp and when paper is subjected to a surface treatment with chitosan solutions, many of its properties are improved: the tensile strength, breaking strength, the resistance to breaking and puncturing, and also wet strength[166]. The same effect is achieved when cyanoethylchitosan is introduced into paper or when paper is subjected to a surface treatment with cyanoethylchitosan solutions; papers of this kind also exhibit improved dielectric properties[167].

## 2. Anion Exchangers Based on Chitosan

The anion-exchange properties of chitosan due to the presence of the primary amino-group have aroused interest in this substance as a basis for the preparation of anion-exchange resins. Such resins have been obtained by treating chitosan with formaldehyde[168] and epichlorohydrin[169,170] or by treating chitin with epichlorohydrin and subsequent deacetylation[171,172]. The resins based on chitosan are resistant to alkalis and have an exchange capacity of approximately $4 \times 10^{-3}$ mole $g^{-1}$ (with respect to a neutral salt). These resins have been used to separate DL-mandelic acid into its optical isomers[171]. Cellulose impregnated with chitosan formate[173] and paper impregnated with chitosan[174] are used in the ion-exchange chromatography of nucleic acids. The separation on ion-exchangers of this kind is more effective than on paper impregnated with diethylaminoethylcellulose.

## 3. Analytical Applications of Chitin and Chitosan

Chitin and chitosan have been recently used in various types of chromatography for the separation of nucleic acid derivatives[175,176], for the isolation of egg albumen lysozyme[177,178], and for the separation of the tobacco mosaic virus[179]. Using chitin or chitosan, agar has been fractionated with respect to the degree of sulphonation[180] as a result of the formation of a complex with the highly sulphonated component of agar.

Colloidal titration of chitosan[139] and glycol-chitosan[181] has been used to determine pectin and pectic acid and colloidal titration of hydroxyethyl- and methoxyethyl-chitosan has been used to determine lignosulphonic acid[182].

The use of chitosan for the determination of heavy metals in sewage, sea water, and aqueous brines, is based on its capacity to form polymeric complexes with such metals[183-195]. Chitosan has been used as a chromatographic solid carrier for the selective extraction and accumulation of mercury, cobalt, gold, antimony, silver, chromium, iron, zinc, iridium, palladium, copper, cadmium, nickel, and lead ions[183,184,187-189,192]. The resistance of chitosan to radiation with retention of chelating properties suggested its use for the concentration of waste from nuclear fuel[185,190,191]. These studies have been reviewed in detail in a monograph[7].

## 4. The Applications of Chitosan and Its Derivatives in Medicine

There are numerous data concerning the usefulness of chitosan for the treatment and diagnosis of various diseases. This is promoted by the low toxicity of chitosan and its derivatives even in large doses[196].

Studies on these lines were begun by the investigation of the use of sulphochitin and sulphochitosan as blood anticoagulants. In terms of their activity, the above compounds are comparable to the natural anticoagulent heparin[197-200]. The study of the influence of the structure of sulphochitosan (*O*- and *N*-sulpho-derivatives) on its anticoagulation activity revealed that it is manifested only when all the amino-groups are sulphonated and increases rapidly with increase of the degree of *O*-sulphonation[201]. The introduction of carboxy-groups by oxidising chitosan sulphate increases its activity. In the intravenous administration of chitosan, its molecular weight is important: a decrease of the latter increases the toxicity of the

preparation[129]. By sulphonating chitosan films, antithrombogenic surfaces, retarding the coagulation of blood, have been obtained[202]. Complexes of chitosan with heparin and dextran sulphate also exhibit anticoagulation activity[203,204].

Studies of another type involve the use of chitosan for the treatment of the gastric ulcer based on its antacid activity[205] and the ability to suppress the activity of pepsin[206]. A composition containing chitosan has been proposed and has been recommended under conditions of increased acidity[207]. Chitin-based compositions accelerate the healing of wounds when applied to the affected surface[208,209]. In one study[210], the antisclerocic activity of chitosan due to the activation of lipoprotein lipase[211], was noted. The influence of chitosan on the activities of certain enzymes has been observed in a number of studies: inhibition of deoxyribonuclease[212], activation of hyaluronidase[213], and $\beta$-glucuronidase[214]. The complex salt of chitosan with the 1,4-lactone of D-glucaric acid also exhibits physiological activity[215].

Reports have appeared recently on studies of the use of chitosan for the inhibition of cell growth[212] and the decomposition of cells[216] in certain types of malignant tumours. The complex of chitosan with iododeoxycytidylic acid penetrates cancer cells selectively, which facilitates the diagnosis of cancer[217]. Chitosan causes the selective aggregation of the cells of L 1210 leukaemia *in vitro*[218].

## 5. Other Applications of Chitin and Chitosan

Individual reports indicate the usefulness of chitin, chitosan, and their derivatives in a wide variety of branches of the national economy. In the mining industry, chitin sulphate, carboxymethylchitin, and carboxyethylchitin are used for the preparation of drilling compositions[219] and the water-soluble salts of these derivatives are suitable for the formation of cementing materials[220]. Partly deacetylated chitin is used in the dye industry for the improvement of the susceptibility of glass[221] and synthetic[222] fibres to dyeing. Finely ground chitin is added in the cosmetic industry as an additive to creams, gels, and other cosmetic agents[223]. In the food industry, chitosan is used to clarify plant juices and extracts[224]. Chitosan has also been proposed for the coagulation of turbidity in various aqueous media[225].

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# The Chemistry of the Surfaces of the Acid Forms of Natural Layer Silicates

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Modern ideas about the nature of the exchangeable acidity of a group of layer silicates (clay minerals) are described and the results obtained during the last decade with the aid of physical and physicochemical techniques are surveyed. The dependence of the surface acidity on non-stoichiometric substitutions in the structure of the minerals, the influence of a number of factors on the spontaneous conversion of the H-forms of the silicates into Al-Fe-Mg-forms, the mechanism of this phenomenon, the ion-exchange properties and the thermal stabilities of the H- and Al-Fe-Mg-forms, and other problems are examined.
The bibliography includes 80 references.

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## I. INTRODUCTION

Natural silicates (clay minerals) have acquired considerable importance recently in scientific research and in practice[1-11]. The amounts of these minerals available in the USSR are enormous and many of their physicochemical properties permit their successful use as substitutes for expensive and scarce synthetic materials. For a more effective and purposeful utilisation of layer minerals in industry, it is necessary to have at ones disposal reliable information both about the chemistry of their surfaces and about methods for their modification. The present review deals with modern ideas about the nature of the exchangeable acidities† of the acid forms of clay minerals. The solution of this problem opens considerable prospects for the application of the above forms as catalysts, stationary phases in gas-adsorption chromatography, fillers of polymeric media, etc. The elucidation of the nature of the exchangeable acidity of clay minerals is important for geochemistry and soil science, since it promotes a correct understanding of the processes involved in the genesis of minerals and soils and also for the development and justification of practical measures undertaken to improve the fertility of acid soils.

## II. NON-STOICHIOMETRIC SUBSTITUTIONS IN THE STRUCTURE AND THE NATURE OF THE EXCHANGEABLE ACIDITY

In the study of the nature of clay minerals and of the chemical stability of their hydrogen-forms, one must take into account the crystal structures of these aluminosilicates and the causes, associated with the latter, which are responsible for the cation exchange in which such substances are involved. For this purpose, it is necessary to develop new, more accurate methods for the determination of the non-stoichiometric isomorphous substitutions or other defects in the lattices of the minerals, which cause them to behave as ion exchangers.

Table 1. The influence of the heat treatment of the Li-forms of layer silicates on their capacity ($\mu$equiv.g$^{-1}$) (duration of heat treatment of specimens 1.5 h).

| Mineral | 25° C | 100° C | 200° C | 300° C | 400° C | 500° C | Isomorphism, % | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | in octahedra | in tetrahedra |
| Pyzhevskii [Pyzhev?] montmorillonite | 1130 | 1050 | 40 | 34 | 10 | 0 | 97.0 | 0.0 |
| Gorbskii [Gorbi?] beidellite | 410 | 410 | 410 | 408 | 400 | 395 | 0.0 | 100.0 |
| Kovdorskii [Kovd?] vermiculite | 1420 | 1420 | 1420 | 1420 | 1420 | 1420 | 0.0 | 100.0 |
| Bug region nontronite | 980 | 965 | 202 | 202 | 202 | 190 | 79.0 | 21.0 |
| Glukhov kaolinite | 250 | 242 | 34 | 34 | 46 | 48 | 86.0 | 12.0 |
| Cherkassy palygorskite | 150 | 150 | 120 | 80 | 208 | 210 | 47.0 | 53.0 |

A method based on the different types of behaviour of the exchangeable $Li^+$ ions on heating layer minerals at 200 to 300°C for 1-1.5 h has been proposed[12] (Table 1). It follows from the data in the Table that, when the non-stoichiometric isomorphous substitutions in minerals with a dioctahedral structure are located in the octahedral network, then $Li^+$ ions migrate under the influence of temperature to the vacant sites of the silicate[13] or into the interstices[14]. The excess negative charge of the layer is neutralised and the mineral loses its capacity for ion exchange. When the non-stoichiometric substitutions are located in the tetrahedral network, the Li-form fully retains its ion-exchange properties after heating. The above observation holds also in the presence of isomorphous substitutions in both tetrahedral and octahedral networks.

†This implies $H^+$, $Al^{3+}$, and $Fe^{3+}$ ions capable of being exchanged for other cations.

The influence of the positions of the non-stoichiometric substitutions in the structures of layer silicates on the nature of their exchangeable acidity was examined on the basis of the above results [15]. Pyzhevskii [Pyzhev?] montmorillonite, the Bug region nontronite, Kovdorskii [Kovd?] vermiculite (particle size $< 40$ μm), Gorbskii [Gorbi?] beidellite, Cherkassy palygorskite, and Glukhov kaolinite were chosen for investigation. The acid forms of the above aluminosilicates were prepared from the Na-forms by the ion-exchange method under static conditions [16]. The content and nature of the exchangeable acid ions on the surface were determined electrochemically[17,18] and also by analysing the equilibrium solution after treating the acid forms of the minerals with 0.5 *N* $BaCl_2$ solution. A detailed analysis of other methods for the investigation of the surface acidity of solids has been described by Ovcharenko and Vasil'ev [18].

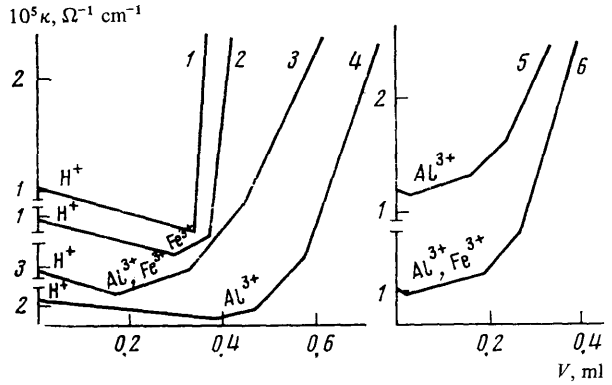



**Figure 1.** Curves for the conductimetric titration of acid forms of layer silicates with 0.095 *N* NaOH solution: 1) montmorillonite (0.027 g); 2) nontronite (0.037 g); 3) palygorskite (0.22 g); 4) kaolinite (0.19 g); 5) beidellite (0.041 g); 6) vermiculite (0.014 g).

Fig. 1 presents conductimetric titration curves for aqueous suspensions of freshly prepared acid forms of layer silicates. It follows from the data in the Figure that, after the complete or partial distribution of non-stoichiometric substitutions in the octahedral network (montmorillonite, nontronite, palygorskite, and kaolinite, see Table 1), the H-form of this type of mineral acquires strongly acid properties and contains on its surface freely mobile exchangeable hydrogen ions (Fig. 1, curves *1–4*). A completely different behaviour is observed in the titration of the acid forms of both vermiculite and beidellite in which non-stoichiometric isomorphous substitutions are almost completely distributed in the tetrahedral network. Their titration curves are analogous to the titration curves of a weak acid by a sodium hydroxide solution (Fig. 1, curves *5* and *6*). Analysis of a salt extract (0.5 *N* $BaCl_2$) showed that $Al^{3+}$ ions are present on the surface of beidellite, while the vermiculite surface contains $Al^{3+}$ and $Fe^{3+}$ ions in approximately equal amounts. These results lead to the conclusion that, after the substitution of the exchangeable $Na^+$ ions of the mineral by the $H^+$ ions of the resin [15], the exchangeable protons immediately interact with the tetrahedra where silicon has been substituted by aluminium or tervalent iron.

According to the proposed model [15] (Fig. 2), three exchangeable protons compensate the ruptured bonds (i.e. there is a conversion of $\equiv SiO^-$ into $\equiv SiOH$ groups) and the $Al^{3+}$ (or $Fe^{3+}$) ion liberated from the tetrahedron neutralises the charges of two neighbouring intact tetrahedra and one charge formed at the apex of the disrupted tetrahedron. $Al^{3+}$ (or $Fe^{3+}$) ions can also compensate the charges of the intact tetrahedra located in neighbouring basal planes. The simultaneous disruption of all the defective tetrahedra is impossible owing to the deficiency of the exchangeable $H^+$ ions, since three protons are required to transfer $Al^{3+}$ or $Fe^{3+}$ ions to a site where exchange is possible.

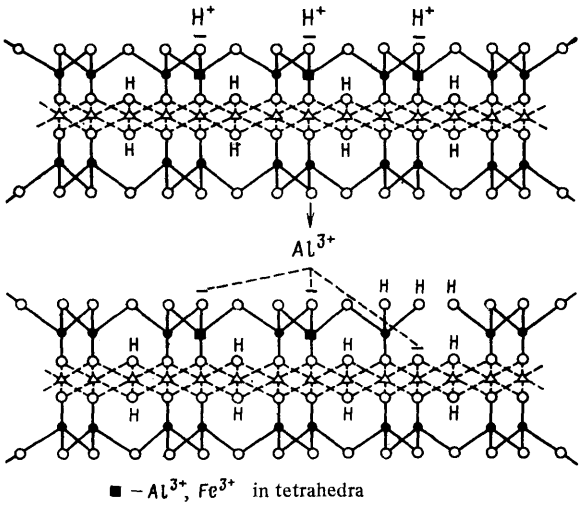



**Figure 2.** The disruption by exchangeable protons of the tetrahedra in which silicon has been substituted by aluminium or tervalent iron.

The transfer of the charge of the mineral from the tetrahedral to the octahedral network is confirmed by the constancy of the exchange capacities of the silicates before and after treatment with the KU-2 resin in the H-form [15,19]. Furthermore, it follows from Fig. 2 that, after the complete substitution of the exchangeable $Na^+$ ions of the silicate by the $H^+$ ions of the resin and rapid conversion of the H-form into the Al-Fe-form, one-third of the surface charge of the mineral is transferred from the tetrahedral to the octahedral network. After the conversion of Al-Fe-vermiculite into the Na-form and after the regeneration of the acid mineral, one-third of the exchange capacity should be due to the exchangeable $H^+$ ions. The results of these experiments are presented in Table 2, which shows that approximately one-third of the exchange capacity of vermiculite after the above operations have been carried out is indeed due to the exchangeable hydrogen ions. The H-Al-Fe-form of vermiculite obtained proved to be chemically unstable and was converted after 6 h (at 25°C) into the Al-Fe-Mg-form. The homoionic H-forms of vermiculite and beidellite could not be obtained after several (>2) treatments with the resin, since their structure was disrupted by protons [15,19].

The above considerations concerning the decomposition of defective tetrahedra by hydrogen ions have been confirmed by ESR studies [19]. The ESR spectra of the specimens were recorded in the X-range. The ESR spectrum of Kovdorskii [Kovd?] Na-vermiculite (Fig. 3, curves *1* and *2*) contains a very broad and intense band of complex shape with the absorption centre at $g \simeq 4.3$ and a relatively weak band at $g \simeq 2$. The low-field signals ($g = 4$–$6$) are usually assigned [20,21] to ions in the S-state ($Mn^{2+}$, $Fe^{3+}$) in a strong crystal field of low symmetry, for example in glasses. In vermiculite, the majority of $Fe^{3+}$ ions exist in the form of isomorphous substitutions in the tetrahedral network [22].

**Table 2.** The exchangeable acidity of Na-vermiculite after two cycles of treatment of the mineral with the KU-2 resin in the H-form ($c_{susp}$ = 0.6 wt.%; $V_{susp}$ = 200 ml; $V_{resin}$ = 200 ml).

| Time of contact with resin, h | Amount of exchangeable acid ions on surface, μequiv. $g^{-1}$ | | Amount of exchangeable ions in salt extract (0.5 *N* $BaCl_2$), μequiv. $g^{-1}$ | | | Total exchange capacity w.r.t. $Ba^{2+}$, μequiv. $g^{-1}$ |
|---|---|---|---|---|---|---|
| | $H^+$ | $Al^{3+}+Fe^{3+}$ | $H^+$ | $Al^{3+}+Fe^{3+}$ | $Mg^{2+}$ | |
| 1 | 410 | 820 | 360 | 780 | 165 | 1400 |
| 2 | 380 | 800 | 300 | 750 | 200 | 1380 |
| 4 | 340 | 760 | 300 | 700 | 260 | 1300 |
| 7 | 60 | 660 | 45 | 590 | 470 | 1210 |

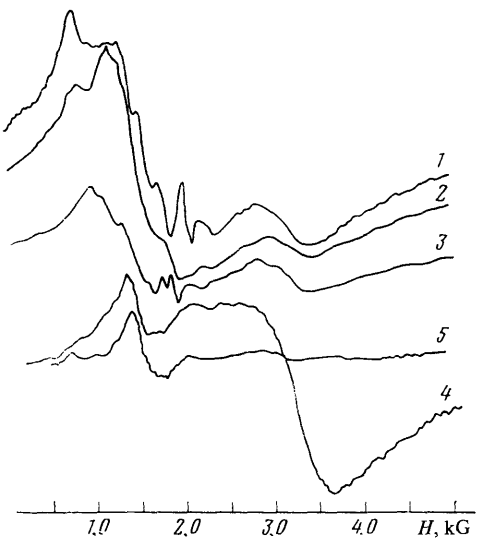



**Figure 3.** ESR spectra of Kovdorskii [Kovd?] Na-vermiculite: 1) air-dry; 2) dried at 105°C; 3) treated with 2 *N* HCl for 1 h; 4) treated with the KU-2 resin in the H-form for 6 h; 5) treated with the resin for 8 h.

The exchangeable cations, located directly at the iron–oxygen tetrahexra, greatly reduce the symmetry of the crystalline environment about the $Fe^{3+}$ ions (to orthorhombic and below). In terms of the approximation of the crystal field to orthorhombic or similar symmetry, the solution of the Hamiltonian [19] yields the ESR absorption in the region [23] of $g \simeq 4.3$. Consequently the intense band in the ESR spectrum of vermiculite must be assigned mainly to $Fe^{3+}$ ions in the tetrahedral network. The $Fe^{3+}$ ions in the octahedral layer of vermiculite involved in the exchangeable complex may contribute to this band. It follows from a comparison of spectra *1* and *2* in Fig. 3 that adsorbed water is present in the immediate environment in the $Fe^{3+}$ ions and has a significant influence on the form of the ESR spectrum. When vermiculite is treated with an acid (Fig. 3, curve *3*), the main change in the ESR spectrum consists in a decrease of the intensity of the band at $g \simeq 4.3$. This is associated with the removal of part of the tetrahedral and ion-exchange iron.

**Table 3.** The exchangeable acidity of vermiculite after its Na-form has been in contact with the KU-2 resin in the H-form ($c_{susp}$ = 0.9 wt.%; $V_{susp}$ = 200 ml; $V_{resin}$ = 200 ml).

| Time of contact with resin, h | Amount of exchangeable ions on surface, μequiv. $g^{-1}$ | | Total exchange capacity, w.r.t. $Ba^{2+}$, μequiv. $g^{-1}$ | Time of contact with resin, h | Amount of exchangeable ions on surface, μequiv. $g^{-1}$ | | Total exchange capacity, w.r.t. $Ba^{2+}$, μequiv. $g^{-1}$ |
|---|---|---|---|---|---|---|---|
| | $Al^{3+}+Fe^{3+}$ | $Mg^{2+}$ | | | $Al^{3+}+Fe^{3+}$ | $Mg^{2+}$ | |
| 0.33 | 490 | — | 1420 | 5.0 | 1200 | 180 | 1410 |
| 0.50 | 680 | — | 1420 | 6.0 | 1260 | 200 | 1410 |
| 1.0 | 850 | — | 1420 | 8.0 | 1030 | 260 | 1400 |
| 2.0 | 890 | 180 | 1410 | 9.0 | 950 | 350 | 1380 |
| 3.0 | 1120 | 280 | 1410 | 11.0 | 840 | 420 | 1260 |
| 4.0 | 1160 | 240 | 1410 | 14.0 | 480 | 740 | 1240 |

Table 3 shows that the interaction of Na-vermiculite with the KU-2 resin in the H-form leads to the complete substitution, even in the first few hours, of $Na^+$ by $Al^{3+}$ and $Fe^{3+}$ ions, which appear as a result of the disruption of the tetrahedral network of the mineral. For example, the complex band at $g \simeq 4.3$ disappears almost completely from the ESR spectrum of vermiculite treated with the cation-exchange resin for 6 h (Fig. 3, curve *4*). In this part of the spectrum, a narrow signal remains, while the broad band at $g \simeq 2$ hardly changes but diminishes appreciably on further contact with the resin (Fig. 3, curve *5*), but the narrow signals with $g \simeq 4.3$ remain unaltered. Spectra *4* and *5* (Fig. 3) are characteristic of montmorillonite [24,25]. Analysis of the infrared spectra [19] also shows that, when Na-vermiculite is treated with the ion-exchange resin for 8 h, a montmorillonite structure with the absorption bands characteristic of this mineral is formed. X-Ray diffraction analysis indicates the appearance on the diffractometer trace of the resin-treated vermiculite of distinct reflections characteristic of montmorillonite [19].

Thus, when Na-vermiculite comes into contact with the cation exchanger in the H-form, the substitution of $Na^+$ ions by $H^+$ ions is followed by the dissociation of the oxygen bridges joining the defective tetrahedra to neighbouring tetrahedra and octahedra, as a result of which structural $Al^{3+}$ and $Fe^{3+}$ ions pass to exchange sites and then to the resin. This is manifested in the ESR spectrum to the disappearance of the broad band at $g \simeq 4.3$ due to the $Fe^{3+}$ ion located initially in the tetrahedral network.

It follows from the above data that, when the non-stoichiometric isomorphous substitutions are fully or completely distributed in the octahedral network, it is possible to obtain under certain conditions [17,18] the hydrogen- or mixed H-Al-Fe-form of the layer aluminosilicate with strongly acid properties. When the non-stoichiometric substitutions are located in the tetrahedral network, the exchangeable protons rapidly decompose the defective tetrahedra, as a result of which exchangeable $Al^{3+}$ or $Fe^{3+}$ ions appear on the aluminosilicate surface.

## III. CHEMICAL STABILITY OF THE H-FORMS OF LAYER SILICATES AND THE MECHANISM OF THEIR AGEING

It was established as early as 1934 [26] that the H-forms of argillaceous minerals are chemically unstable and are converted spontaneously into the Al-Fe-Mg-forms (age). The authors of one of the earliest investigations of this problem found [27] that, after storage for one month, the exchange capacity of air-dry H-montmorillonite is virtually determined solely by hydrogen ions. In the specimen of the same mineral which had been repeatedly saturated with water and dried, a large proportion of the total exchange capacity was due to the fraction of aluminium ions. Similar data were obtained in other investigations [28-31]. In some of these, the influence of various factors on the ageing of H-clays was studied [30,31]. Our investigations showed that, with increase of temperature, the rate of ageing of the H-forms of natural aluminosilicates investigated‡ increases sharply [17,18,32-34]. Fig. 4 illustrates the temperature dependence of the ageing process of H-montmorillonite§. [33] A study of the rate of ageing of H-days in methyl, ethyl, and n-propyl alcohols and dioxan showed [17,18,32-35] that ageing is not observed in pure organic solvents, while in their mixtures with water the rate of this process depends on the content of the organic component in the mixture (Fig. 5). Fig. 5 shows that, compared with alcohols, dioxan has a stronger influence. The influence of the content of the disperse phase in the suspensions on the ageing of H-minerals was also studied. The experiments showed that, with increase of the content of the solid phase, particularly when it exists in the form of a dense deposit, the rate of ageing falls. Continuous stirring of the suspension accelerated the ageing of the specimen somewhat [17,18,36].

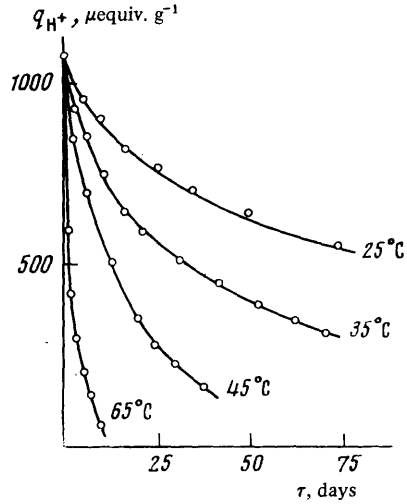



**Figure 4.** The influence of temperature on the rate of ageing of a 0.3% suspension of H-montmorillonite.

‡The kinetic experiments were performed on dilute suspensions of the H-forms with constant stirring.

§Here and henceforth data are presented only for H-montmorillonite. Similar results were obtained for other minerals.

Only a few studies have been devoted to the elucidation of the mechanism of the ageing of the hydrogen-forms of natural aluminosilicates. Miesserov believes [37,38] that the ageing of the H-form of montmorillonite involves the octahedral layer and is a result of the interaction of the hydrogen in the hydroxy-groups in the tetrahedral layer with the hydroxy-groups located at the aluminium atoms. Mitra and Singh [30] concluded that H-montmorillonite ages owing to the exchange of the hydrogen ions located in the basal planes of the clay particles for the aluminium ions on the crystal faces. As a result of the Brownian movement of the particles, the double layers formed by $H^+$ and $Al^{3+}$ ions overlap, which leads to exchange. However, if this mechanism is adopted, one cannot understand why the process ceases completely in a polar solvent such as methyl alcohol.

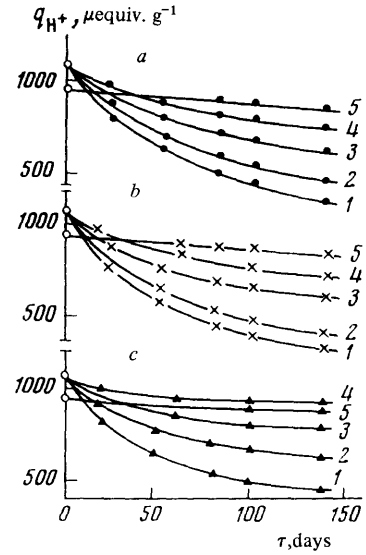



**Figure 5.** The influence of the content of organic solvent in the intermicellar medium on the rate of ageing of a 0.3% suspension of H-montmorillonite; content of solvent in the mixture (wt.%): 1) 10; 2) 30; 3) 60; 4) 60; 5) 100; *a*) ethanol; *b*) propanol; *c*) dioxan.

Eeckman and Loudelaut [31] established by a series of experiments that the rate of ageing of montmorillonite in the hydrogen-form is described empirically by the equation of a parabola. They suggested that the ageing mechanism involves the mutual diffusion of $H^+$ and $Al^{3+}$ ions. Aluminium ions diffuse along the surface of the particles from the crystal faces to the centre and there is a flux of hydrogen ions in the opposite direction. As soon as the hydrogen ions reach the crystal faces, they interact with the lattice, as a result of which a constant concentration of $Al^{3+}$ ions is maintained on the lateral surface. According to the authors, the rate of ageing is determined solely by the diffusion of $H^+$ and $Al^{3+}$ ions. To test the diffusion mechanism of ageing which they proposed, Eeckman and Loudelaut [31] used the following procedure. Assuming that the empirical parabolic equation which they derived is equivalent to Fick's Second Law, they obtained, after a

series of mathematical transformations, an expression susceptible to an experimental test. The test showed that the mutual diffusion coefficient of $H^+$ and $Al^{3+}$ ions is extremely small during the ageing of H-montomorillonite ($10^{-20}$ $cm^2$ $s^{-1}$), which is inconsistent with the observed rate of ageing and its temperature dependence [17,18]. By comparing the principal results of the application of the diffusion mechanism to the description of the ageing of H-montmorillonite, it can be easily shown that these ideas suffer from significant disadvantages [17]. In particular, the use of Fick's Second Law to characterise the mutual diffusion of $H^+$ and $Al^{3+}$ ions during ageing is completely unjustified. It is well known that Fick's Laws do not describe satisfactorily the diffusion of charged species, because in the given instance the occurrence of the process depends on many specific factors, primarily on the electric field arising during the migration of ions (the diffusional potential jump) [39,40]. The mutual diffusion coefficient calculated by the authors [31] is therefore doubtful. We may also recall that the theoretical calculations performed by Eeckman and Loudelaut are in poor agreement with their own experimental data.

Another attempt to interpret the mechanism of the ageing of the hydrogen-form of montomorillonite was undertaken recently [41,42]. To describe the ageing of the H-forms of this mineral, the authors used hyperbolic functions. This empirical approach to the process, without a definite physical basis, appears to be unjustified. The conclusion reached [41,42] about the kinetics of the ageing process (reaction order $n = 1$) is therefore unconvincing.

On the basis of the analysis of the entire set of the available literature data and our own experiments [18,33], we suggest that the ageing of the H-forms of clay minerals is a heterogeneous chemical reaction involving hydronium ions and not free protons. The involvement of water molecules in the given reaction is indicated by the results presented in Fig. 5, from which it follows that, when an organic solvent is added to the intermicellar medium, the rate of ageing of the H-form of the layer silicate falls. This is because in a water–organic solvent mixture some of the $H^+$ ions of the clay are solvated with formation of lyonium (and not hydronium) ions, for example $C_2H_5OH_2^+$, which are produced to a greater extent the higher the content of the organic component in the mixture. In non-aqueous media, where hydronium ions are altogether absent, ageing ceases completely. Together with the above factors, the rate of ageing of H-clays in water–organic solvent mixtures may be influenced by the association of the organic solvents with water, which results in a decrease of the activity of water molecules [43]. The validity of the above ideas concerning the decisive role of water in this reaction is confirmed very convincingly by the results [33] presented in Fig. 6. They show that the air-dry specimens of the H-forms of aluminosilicates, which still contained a certain amount of water, aged gradually. On the other hand, the specimens subjected to additional dehydration *in vacuo*, with simultaneous freezing out of water by liquid nitrogen, and then stored in sealed bulbs showed no signs of ageing whatever.

As shown above (Fig. 4), the rate of ageing of the H-forms of silicates increases sharply with increasing temperature, like the rate of any chemical reaction. This finding proves the chemical nature of the phenomenon investigated. We used a general kinetic equation for the mathematical description of this reaction. It was assumed [18,33] that the rate of ageing of H-minerals is determined mainly by the content of exchangeable $H^+$ ions, since the concentrations of other reactants—aluminium, iron, and magnesium present in the solid phase and the water present in the system in excess—may be regarded as constant. Therefore

$$-dq_{H^+}/d\tau = kq_{H^+}^n, \quad (1)$$

where $q_{H^+}$ is the content of exchangeable $H^+$ ions in $\mu$equiv. $g^{-1}$, $\tau$ the time in days, $k$ the reaction rate constant, and $n$ the power exponent corresponding to the order of the chemical reaction. Having plotted the dependence of the reaction rate on the concentration of exchangeable $H^+$ ions in terms of logarithmic coordinates, it is easy to determine from the slopes of the straight lines the orders of the chemical reactions [17,18,32–34]. Calculations showed that at the beginning of the ageing process is of third order, after which there is a decrease of the order to second and below. The activation energies were calculated separately for the second- and third-order reactions by plotting lg $k$ against the reciprocal of temperature. The results fit on parallel straight lines corresponding to the following activation energies: 20 kcal g-ion$^{-1}$ for the ageing of H-montmorillonite and H-nontronite; 17 kcal g-ion$^{-1}$ for the ageing of H-palygorskite; 25 kcal g-ion$^{-1}$ for the ageing of H-kaolinite. [18] Fig. 7 presents examples of the above determinations for the ageing of H-montmorillonite. These results show that the ageing of the hydrogen-forms of layer silicates is indeed a heterogeneous chemical reaction.

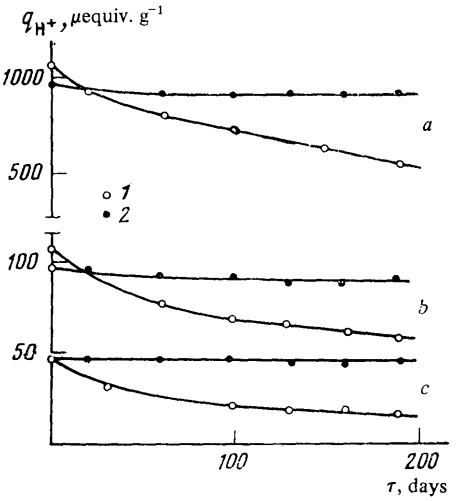



Figure 6. Kinetics of the ageing of air-dry (1) and fully dried specimens (2) of the H-forms of montmorillonite (*a*), palygorskite (*b*), and kaolinite (*c*) at 25°C.

Fig. 8 illustrates the model proposed [44] for the disruption by the exchangeable protons and water molecules of the crystal structure of montmorillonite. Evidently, three exchangeable $H^+$ ions are involved in the fundamental reaction step. One proton (Fig. 8*a*) reacts with a basic OH group (=Al–OH) and forms a water molecule. Simultaneously, two other protons attack via an electrophilic mechanism the ≡Si–O–Al= bonds, as a result of which the latter are broken with formation of two silanol groups and the liberation of an $Al^{3+}$ ion. The loss of the aluminium

ion from the octahedral network reduces the stability of the silicon–oxygen tetrahedra. The presence of a water molecule in the system and the catalytic effect of the exchangeable $H^+$ and $Al^{3+}$ ions [45,46] lead to the dissociation of the ≡Si–O–Si≡ bonds, as a result of which two molecules of silicic acid are released into the equilibrium solution¶:

$$2\left[\begin{array}{l}\equiv Si-O\\ \equiv Si-O\end{array}\!\!>Si(OH)_2\right] + 4H_2O \rightarrow 4[\equiv SiOH] + 2Si(OH)_4 . \quad (2)$$

When the next three exchangeable protons interact, the same products are obtained (Fig. 8*b*). In this case, the siloxane linkages are ruptured in accordance with the equation

$$2[\equiv Si-O-Si(OH)_3] + 2H_2O \rightarrow 2[\equiv SiOH] + 2Si(OH)_4 . \quad (3)$$

In contrast to the first reaction step (Fig. 8*a*), in this instance two exchangeable $H^+$ ions apparently rupture initially the ≡Si–O–Al≡ bond, after which one proton reacts with a hydroxy-group at an aluminium atom.

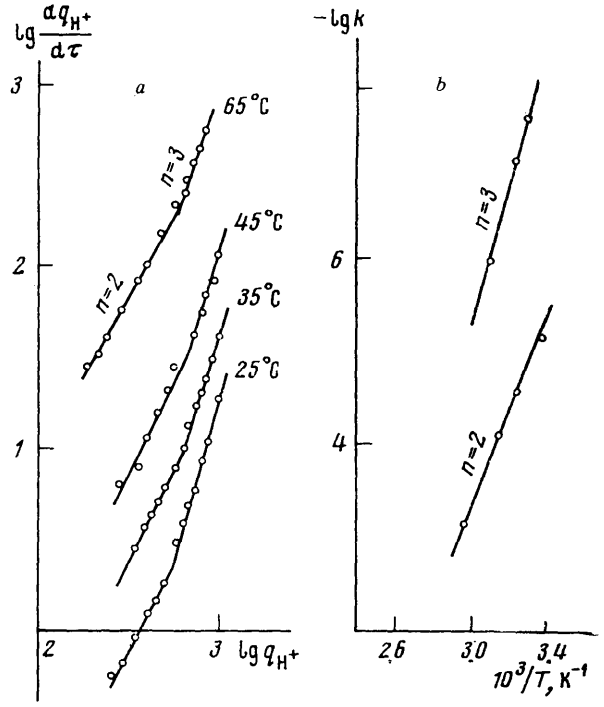



Figure 7. Dependence of the ageing of a 0.3% suspension of H-montmorillonite in water on its content of exchangeable $H^+$ ions at different temperatures (*a*) and of the logarithms of the rate constants for the second- and third-order reactions on the reciprocal of temperature (*b*).

It follows from Eqns. (2) and (3) that water is one of the reactants in the ageing of H-silicates. In is now understandable why ageing of the H-forms is not observed in non-aqueous media [17,18,33–35].

¶Silicic acid was determined in terms of $SiO_2$ by a standard method [47,48].

Subsequently the reaction under consideration proceeds analogously to those illustrated in schemes *a* and *b* in Fig. 8. After the complete conversion of the hydrogen-form of the aluminosilicate into the Al-form (the ageing cycle), its exchange capacity falls [31], because during the ageing of the H-forms of the minerals some of the $Mg^{2+}$ ions emerge from the octahedral layer (Fig. 8*c*), i.e. the number of non-stoichiometric isomorphous substitutions in this structure diminishes. The decrease of the number of isomorphous substitutions leads in its turn to a decrease of the exchange capacity of the aluminosilicate. Studies have shown [44] that the exchange capacity decreases by 130–140 mequiv. $g^{-1}$ in each ageing cycle of H-montmorillonite (five cycles in all were carried out).

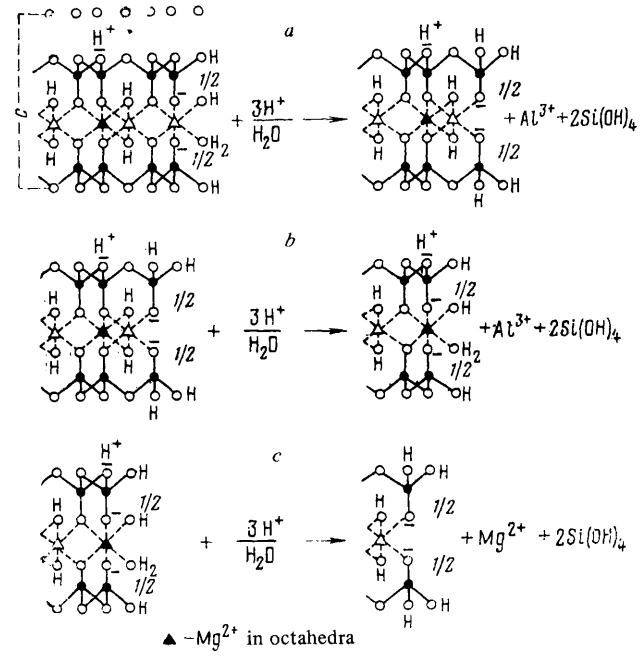



Figure 8. The disruption of the crystal structure of montmorillonite by protons.

It follows from the structure of layer silicates that the exchangeable protons, which neutralise the ruptured bonds at the crystal faces, are the first to enter into the reaction investigated. Since the exchangeable $H^+$ ions located on the basal planes are highly mobile [5,17,18,49,50], they reach the faces of the mineral and interact with the latter, liberating aluminium (iron, magnesium) ions from the lattice. The latter diffuse onto the basal plane and compensate its excess negative charge, generated after the removal of $H^+$ ions. At the same time, ions may migrate also in a different way. As a result of the Brownian movement or stirring of the suspension, the silicate particles can be oriented in such a way that the basal plane of one approaches closely to that of another. During the ion exchange between two solid phases in an aqueous medium, protons are adsorbed on the crystal faces and aluminium ions are adsorbed on the basal plane of a neighbouring particle [30]. However, it must be emphasised that neither

the mutual diffusion of $H^+$ and $Al^{3+}$ (or $Fe^{3+}$, $Mg^{2+}$) ions nor ion exchange between the aluminosilicate particles [30,31] determines the rate of reaction.

It has been shown [17,18,32-34] that the dependence of the logarithms of the rate constants for the ageing of H-silicates on the reciprocal of temperature is linear. These data as well as the high activation energies show that the process under consideration proceeds only under kinetic conditions [51]. Consequently the kinetics of the ageing of dilute suspensions of the H-forms are determined mainly by the rate of reaction of the exchangeable protons with the face of the mineral, i.e. by the rate of dissociation of the ≡Si–O–Al= and ≡Si–O–Si≡ bonds, while ion transport is of secondary importance. Basic hydroxy-groups play an important role in this process [52]. Only in the ageing of paste-like and air-dry specimens of the H-forms can the mutual diffusion of ions exert some influence on the rate of the process.

As already mentioned, the calculated activation energies for the ageing of H-silicates are the same for the second- and third-order reactions. This equality and also the observed stoichiometric amounts of $Al^{3+}$, $Fe^{3+}$, and $Mg^{2+}$ ions released from the mineral lattices suggest that the order of the reaction is in our case three, in conformity with the proposed model (Fig. 8). The observed decrease of the reaction order is caused mainly by the decrease of the concentration of the exchangeable $H^+$ ions during ageing. Only at the beginning of the process, where the surface concentration of $H^+$ ions is high, are the necessary conditions created for the occurrence of the third-order reaction. With decrease of their content, the rate of dissociation of the aluminosiloxane linkages falls. At the same time, the substitution of hydronium ions of the exchangeable $Al^{3+}$ ions located on the lateral faces of the silicates becomes more difficult. The validity of this interpretation is confirmed by a number of data [17,53]. It follows from the latter that, with decrease of the exchange capacity of montmorillonite and kaolinite†, the orders of the ageing reactions of the H-forms decreased by unity. Together with the causes described above, one cannot exclude the influence of other factors, such as the imperfection of the crystal structure of the aluminosilicate, the accumulation of silicic acid in the equilibrium solutions and its polymerisation on the surface of the particles with formation of secondary particles [54], etc.

Apart from their direct involvement in the dissolution of the aluminosilicate, water molecules play a number of additional functions. For example, owing to the considerable hydration energies of the $Al^{3+}$, $Fe^{3+}$, and $Mg^{2+}$ ions, water promotes their liberation from the octahedral layer. As a consequence of the formation of hydronium ions, it ensures a high mobility of the exchangeable protons. The addition of alcohols of dioxan to the intermicellar medium leads, as already stated above, to the appearance of lyonium ions, which are formed to a greater extent the higher the content of the organic solvent in the mixture. As a result of this, the mobility of the exchangeable protons falls with a consequent decrease of the rate of the ageing process.

It has been shown [44] that a similar pattern in the disruption of the aluminosilicate structure is observed when the aluminosilicate comes into contact with an inorganic acid. Table 4 shows that, in the interaction of the Ba-form of montmorillonite with a 0.01 *N* hydrochloric acid solution (with constant stirring of the suspension), aluminium ions and silicic acid are released into the equilibrium solution‡. As for exchangeable $H^+$ ions, the rate of reaction of the silicates with protons from the solution increases with increase of temperature. We therefore also used a general kinetic equation for the mathematical description of this process [18,33,44]. It was assumed that the rate is determined by the number of $H^+$ ions reacting, since the concentrations of the other reactants — aluminium and silicic acid present in the solid phase and the excess water in the system — can be regarded as constant. Fig. 9 shows that the dependence of the rate of reaction on the concentration of $H^+$ ions which have reacted, plotted in terms of logarithmic coordinates, consists of two linear sections. The orders of the corresponding reactions were determined from the slopes of these sections and were found to be 2 and 1. The decrease of the order of the reaction by unity compared with the ageing of the H-forms of layer silicates can be explained as follows. In contrast to the ageing reaction when Ba-montmorillonite interacts with HCl, a considerable amount of $Al^{3+}$ ions accumulates in the equilibrium solution. Since silicic acid molecules also pass to the solution, this leads to the formation of the strong aluminosilicic acid and the interaction of each aluminium ion with $Si(OH)_4$ yields one $H^+$ ion [55]. Three protons are involved in the fundamental reaction step (Fig. 8). However, after the liberation of the $Al^{3+}$ ion and two silicic acid molecules from the lattice, aluminosilicic acid is formed and one proton returns to the equilibrium solution.

Table 4. Kinetics of the interaction of Ba-montmorillonite with 0.01 *N* HCl solution at different temperatures ($V_{HCl}$ = 300 ml).

| τ, days | $[H^+]_a$, μequiv. $g^{-1}$ | $[Al^{3+}]_s$, μequiv. $g^{-1}$ | $[Al^{3+}]_{soln}$ μequiv. $g^{-1}$ | $c_{SiO_2}$, μmole $g^{-1}$ |
|---|---|---|---|---|
| 45° C, $c_{susp}$ = 0.455% | | | | |
| 5.94 | 380 | 130 | 360 | 870 |
| 9.10 | 420 | 230 | 520 | 1420 |
| 12.94 | 480 | 280 | 560 | 1710 |
| 19.94 | 540 | 350 | 610 | 2100 |
| 30.0 | 580 | 380 | 690 | 2180 |
| 41.12 | 620 | 420 | 750 | 2760 |
| 65° C, $c_{susp}$ = 0.405% | | | | |
| 0.56 | 150 | 80 | 230 | 390 |
| 1.58 | 285 | 150 | 280 | 910 |
| 2.50 | 370 | 190 | 370 | 1230 |
| 4.54 | 510 | 300 | 590 | 2110 |
| 5.54 | 570 | 340 | 680 | 2480 |
| 6.54 | 620 | 410 | 700 | 2640 |
| 98° C, $c_{susp}$ = 467% | | | | |
| 0.05 | 200 | 90 | 160 | 280 |
| 0.10 | 305 | 130 | 350 | 790 |
| 0.125 | 340 | 150 | 390 | 1120 |
| 0.167 | 390 | 190 | 480 | 1590 |
| 0.25 | 450 | 230 | 510 | 1710 |
| 0.37 | 520 | 240 | 520 | 1920 |
| 0.46 | 560 | 250 | 550 | 2030 |

Notation: $[H^+]_a$ is the amount of sorbed $H^+$ ions, $[Al^{3+}]_s$ and $[Al^{3+}]_{soln}$ are the amounts of $Al^{3+}$ liberated from the mineral onto its surface and into the equilibrium solution respectively, and $c_{SiO_2}$ is the amount of silicic acid, in terms of $SiO_2$ evolved from the mineral.

†The H-forms were prepared from specimens of these minerals subjected to preliminary activation with an inorganic acid.

‡The amount of amorphous silicic acid was determined by a standard method [48].

This is confirmed by Table 4, which shows that the amount of aluminium ions evolved from the mineral lattice is approximately one-third greater than the amount of absorbed hydrogen ions. Furthermore, the decrease of the concentration of $H^+$ ions as a result of their interaction with the montmorillonite crystals faces leads to an increase of the order of the reaction.

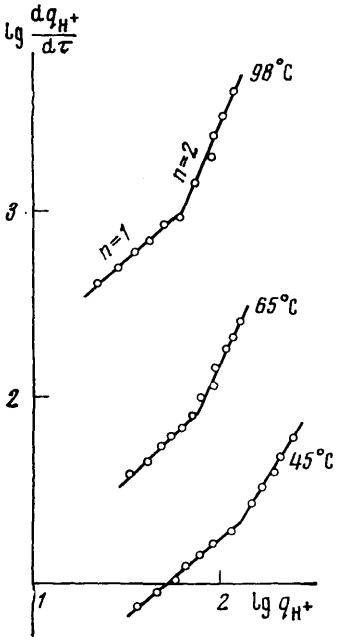



Figure 9. Dependence of the rate of interaction of $H^+$ ions with montmorillonite on the number of such ions reacting at different temperatures.

In order to calculate the activation energy for the dissolution of the mineral in an acid, we plotted[44] the logarithm of the reaction rate constant against the reciprocal of temperature. The data found for the first- and second-order reactions fit on parallel straight lines, which correspond to an activation energy of 24 kcal g-ion$^{-1}$. This value is close to that obtained earlier for the decomposition of the montmorillonite structure by exchangeable protons.

The mechanism proposed for the decomposition of natural aluminosilicates by $H^+$ ions is valid for all minerals in which non-stoichiometric substitutions or other defects, responsible for their ion-exchange capacity, are located in the octahedral network. A difference may be observed only in the quantitative release of silicic acid into the equilibrium solution (depending on the crystal-chemical type of the mineral). When layer silicates interact with inorganic acids one must bear in mind that aluminium ions exist in the intermicellar solution as cations derived from aluminosilicic acid. These cations may be adsorbed on the surface of the natural aluminosilicate instead of $Al^{3+}$ ions[56]. One should also note that, when clay minerals interacted with concentrated hydrochloric acid solutions (0.05 and 0.1 *N*), the absorption of protons was not observed[44]. This is apparently associated with the formation under certain conditions of aluminosilicic acids of different composition and the liberation of $H^+$ ions into the equilibrium solution.

## IV. THE ION-EXCHANGE PROPERTIES OF THE ACID FORMS OF NATURAL SILICATES

Extremely valuable information about the strength of binding of acid ions to the surfaces of clay minerals can be obtained from the analysis of the ion-exchange properties of the latter. At room temperature, H-silicates do not undergo appreciable changes during the first hours of ageing, which makes it possible to rule out the influence of this process when adsorption experiments are performed. The Langmuir equation has been used[17,18,57-59] to describe the ion-exchange interaction of the hydrogen- and electrodialysed (Al- and Fe-)forms of silicates with solutions of alkali and alkaline earth metal salts. The constant $b$ (adsorbability) of this equation serves as a quantitative characteristic:

$$a = a_\infty \frac{bc_e}{1+bc_e}, \qquad (4)$$

where $a$ is the degree of adsorption of the ions in $\mu$equiv. g$^{-1}$, $a_\infty$ the maximum degree of adsorption of the ions corresponding to complete coverage of the mineral surface by the latter in $\mu$equiv. g$^{-1}$, and $c_e$ the equilibrium concentration of the ions in solution in $\mu$equiv. ml$^{-1}$.

Table 5. The constants of the Langmuir equation ($a_\infty$, $\mu$equiv. g$^{-1}$; $b$, ml $\mu$equiv.$^{-1}$) characterising the adsorption of cations on the hydrogen- and aluminium-forms of the minerals.

| Cation | $Ba^{2+}$ | $Ca^{2+}$ | $Cs^+$ | $Rb^+$ | $K^+$ | $Na^+$ |
|---|---|---|---|---|---|---|
| **Montmorillonite** | | | | | | |
| $a_\infty$ (H) | 1150 | 1150 | 1170 | 1170 | 1150 | 1200 |
| $a_\infty$ (Al) | 800 | 820 | 800 | 800 | 860 | 800 |
| $b$ (H) | 1.8 | 1.8 | 1.5 | 1.5 | 0.50 | 0.10 |
| $b$ (Al) | 0.064 | 0.062 | 0.104 | 0.100 | 0.018 | 0.005 |
| **Palygorskite** | | | | | | |
| $a_\infty$ (H) | 150 | 150 | 145 | 145 | 140 | 140 |
| $a_\infty$ (Al) | 80 | 80 | 80 | 80 | 75 | 85 |
| $b$ (H) | 0.25 | 0.25 | 0.20 | 0.20 | 0.16 | 0.14 |
| $b$ (Al) | 0.035 | 0.033 | 0.048 | 0.043 | 0.017 | 0.011 |
| **Kaolinite** | | | | | | |
| $a_\infty$ (H) | 55 | 53 | 53 | 52 | 53 | 55 |
| $a_\infty$ (Al) | 47 | 48 | 46 | 47 | 47 | 48 |
| $b$ (H) | 1.5 | 1.5 | 0.36 | 0.36 | 0.12 | 0.06 |
| $b$ (Al) | 0.06 | 0.05 | 0.15 | 0.10 | 0.023 | 0.007 |

The sorption isotherms obtained for the cations on both acid forms of clay minerals are described satisfactorily by the Langmuir equation[17,18]. The experimental points fitted satisfactorily on the straight line obtained in terms of the coordinates of Eqn. (4), from which the constants $a_\infty$ and $b$ were found by a graphical method[60]; the constants are listed in Table 5. Evidently $a_\infty$ remains invariant, within the limits of experimental error, and equal to the content in the initial specimen of hydrogen

and aluminium ions§ which are exchanged for the salt cations. This indicates the independence of the exchange capacity (due to isomorphism) of clay minerals of the nature of the adsorbed cation. The constant $b$, characterising the adsorbability of the cations investigated, varies as a function of both the properties of the salt cation and the nature of the exchangeable ion in the acid form of the aluminosilicate. The latter is manifested by the fact that the adsorbability of alkali and alkaline earth metal cations on the H-forms of minerals is an order of magnitude greater than on the aluminium-forms. Consequently the bonds between the exchangeable hydrogen ions and the silicate surface of the particle are much weaker than those linking the exchangeable $Al^{3+}$ ions.

Aluminium ions are strongly hydrated in solution and their mobility is low[61], while the acid proton is not even permanently attached to a particular water molecule with which it forms a hydronium ion, migrating continuously from one water molecule to another[62]. Presumably $H^+$ and $Al^{3+}$ ions retain their properties also in the adsorbed state. This explains our observation of the greater adsorbability of cations on the hydrogen-forms of clay minerals than on the aluminium-forms. Thus it follows from the literature[57-59] that exchangeable $H^+$ ions exhibit a high mobility and behave similarly to univalent cations. The anomalous behaviour of hydrogen ions[63] can be explained by the fact that aluminium-forms of clay minerals and not hydrogen-forms were in fact investigated.

The differences in the properties of exchangeable hydrogen and aluminium ions influence also the positions of alkali and alkaline earth metal cations in the series based on their adsorbability on the acid forms of layer silicates. Whereas the cations considered can be arranged in the sequence

$$Ba^{2+} = Ca^{2+} > Cs^{+} = Rb^{+} > K^{+} > Na^{+},$$

in terms of their capacity to enter into the exchangeable complex of H-minerals, another series holds for the aluminium-forms:

$$Cs^{+} > Rb^{+} > Ba^{2+} > Ca^{2+} > K^{+} > Na^{+}.$$

The change in the cation adsorbability series as a function of the nature of the exchangeable cation of the acid form can be accounted for from the standpoint of modern ideas about the behaviour of electrolytes in solution. According to these ideas, hydrogen ions as well as alkaii and alkaline earth metal cations migrate in solution without a hydration shell[64]. Such data are lacking for aluminium ions, but, by analogy with the behaviour of beryllium ions, $Al^{3+}$ ions presumably migrate together with water molecules. In ion-exchange processes, the fundamental step in the substitution of one type of ion by another may occur, depending on the properties of the cations, both with and without the involvement of the hydration shell. This apparently leads to the fundamental difference between the ion-exchange processes on the H- and Al-forms of minerals. Whereas in the former case unhydrated cations are exchanged, in the latter the process is determined by the fact that $Al^{3+}$ ions can be displaced only together with their hydration shells. When the fundamental exchange step on the surface of a layer silicate is not complicated by the hydration of cations, their adsorption from solutions should occur more effectively the stronger their attraction to the surface of the particle. This attraction is greater the higher the charge of the ion and, for the same charge, the greater its polarisability. In the exchange of hydrogen ions for alkali and alkaline earth metal cations, doubly charged ions are therefore adsorbed more strongly than singly charged ions and, in individual groups of cations, the adsorbability increases with increasing radius of the unhydrated ion.

In the exchange processes on the aluminium-forms of clay minerals, $Al^{3+}$ ions are probably involved together with their hydration shells. Their substitution might be facilitated if their shell were disrupted in some way. This apparently actually occurs in the exchange of $Al^{3+}$ ions for $Rb^+$ and $Cs^+$ ions, which are characterised by negative hydration, consisting in the fact that, under the influence of these ions, water molecules, as it were, become more mobile than in the pure solvent[64]. This is why the adsorbability of $Rb^+$ and $Cs^+$ ions on the Al-forms of the minerals is greater than that of the remaining cations investigated, including bivalent cations. Thus the results presented show that the exchangeable $H^+$ ions of clay minerals do not exhibit any anomalous properties and retain the features characterising them in aqueous electrolyte solutions.

## V. THE INFLUENCE OF THE MOBILITY OF THE EXCHANGEABLE $H^+$ IONS ON THE NATURE OF $^1H$ NMR SPECTRA

Apart from their strongly acid properties the exchangeable $H^+$ ions manifest yet another interesting property—they influence proton magnetic resonance spectra. The $^1H$ NMR spectra of the water present in oriented preparations of the H-, Li-, and H-Li-forms of montmorillonite have been analysed[65]. The investigation showed that the shape of the $^1H$ NMR spectrum of the protons in the water molecules adsorbed by the Li-form of montmorillonite depends on the disposition of the film of the partly oriented mineral in the magnetic field. Together with a narrow line in the centre of the spectrum (Fig. 10, curve *2*), there is a distinct doublet, the distance between the peaks of which is described satisfactorily by the relation $3\cos\theta - 1$ [sic], where $\theta$ is the angle between the normal to the plane of the aluminosilicate packets and the external magnetic field $H_0$. These data indicate the anisotropic movement of $H_2O$ molecules in the interlayer space of the Li-montmorillonite obtained previously in a study of powdered specimens[66]. It is noteworthy that the maximum splitting of the doublet for the oriented preparation, when the magnetic field is applied at right angles to the plane of the film ($\theta = 0$, Fig. 10, curve *2*), amounts to approximately 4 G, which exceeds by a factor >2 the corresponding value for powdered specimens with the same moisture content[66]. The angle $\gamma_{iR}$ between the interproton vector and the normal to the plane of the packet was determined from the calculated second moment of the doublet (6 $G^2$) and was found to be ~38°. This value agrees satisfactorily with the results from a number of studies[67,68]. The $^1H$ NMR spectrum of the water in the H-form of montmorillonite shows a single narrow line, regardless of the orientation of the films in the magnetic field (Fig. 10, curve *1*). The absence of the doublet from the spectrum can be accounted for both by the different state of the water molecules in the interlayer space of H-montmorillonite and by the specific influence of the mobile exchangeable $H^+$ ions on the form of the $^1H$ NMR spectra. The nature of the mobility of the water in the Li- and H-forms should not differ significantly.

§The decrease of the content of exchangeable $Al^{3+}$ ions relative to hydrogen ions is due to the decomposition of the silicates during electrodialysis.

Studies have shown[65] that the introduction of even an insignificant amount (1–2% of the exchange capacity of the mineral) of exchangeable hydrogen ions leads to the disappearance of the doublet from the spectrum of the Li-form of the aluminosilicate. The change in the state of water under these conditions must be slight. One can therefore postulate that the introduction of small amounts of hydrogen ions into the mineral accelerates significantly only the proton exchange in the system. The role of this factor in the disappearance of the doublet structure of the $^1H$ NMR spectrum of water in the montmorillonite gels had been noted earlier[69,70] in a comparison of pulsed proton and deuteron magnetic resonance signals. It also follows from the results presented that the mechanism of "relay" proton exchange is more probable, since the formation of short-lived $H_3O^+$ ions requires a rearrangement of the electronic configuration of water molecules. Furthermore, it is difficult to suppose that all the water molecules participated in the formation of $H_3O^+$ ions in the proton exchange process in the presence of such a low concentration of $H^+$ ions on the surface of Li-montmorillonite.

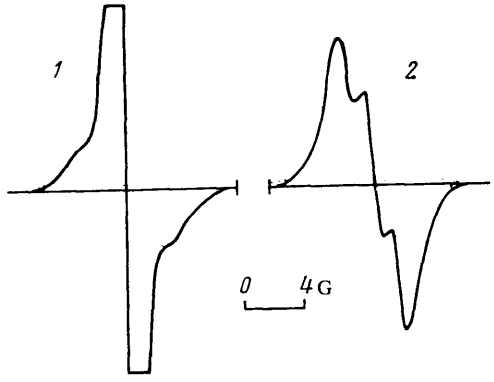



**Figure 10.** The $^1H$ NMR spectra of the oriented specimens: 1) air-dry H-montmorillonite; 2) air-dry Li-montmorillonite.

The narrow line in the centre of the $^1H$ NMR doublet spectrum of the Li-form of montmorillonite (Fig. 10, curve *2*) was assigned to the state of water whose mobility is close to that of isotropic water[66]. However, the appearance of the narrow line can also be accounted for by the influence of proton exchange, which occurs when montmorillonite is hydrated[71]. The protolytic dissociation of water molecules which takes place in this case owing to the polarising action of the cations and the surface may influence the proton exchange in the system. This effect should become more pronounced with increase of the ionic strength due to the cations. This may explain the difficulty of observing the doublet structure of the NMR spectra of the water protons when the exchangeable complex contains certain bivalent metal cations[72].

## VI. THE INFLUENCE OF TEMPERATURE ON THE STATE OF THE EXCHANGEABLE ACID IONS

The catalytic activity of natural aluminosilicates is related mainly to their surface acidity. As already stated, the hydrogen forms of layer silicates are chemically unstable and undergo the ageing process. In order to elucidate the mechanism of the chemical reactions, it is therefore necessary to take into account, under certain conditions in the catalytic process, both the composition and the state of the acid aluminosilicate ions on the surface.

Table 6. The influence of the temperature and duration ($\tau$) of heat treatment on the content of exchangeable $Al^{3+}$ and $Fe^{3+}$ ions ($\mu$equiv.g$^{-1}$) on the surface of layer silicates.

| $\tau$, h | 25–400° C | 500° C | 600° C |
|---|---|---|---|
| Al-montmorillonite | | | |
| 1.0 | 1100 | 750 | 100 |
| 2.0 | 1100 | 680 | 90 |
| 3.0–4.0 | 1100 | 600 | 90 |
| Al, Fe-palygorskite | | | |
| 1.0 | 145 | 140 | 70 |
| 2.0–4.0 | 145 | 140 | 60 |
| Al-kaolinite (Prosyanovskii [Prosyanaya?] deposit) | | | |
| 1.0–4.0 | 55 | 55 | 53 |

Tables 6 and 7 present data for the influence of the temperature and duration of the heat treatment on the content of exchangeable $Al^{3+}$, $Fe^{3+}$ and $H^+$ ions on the surface of air-dry specimens of minerals. They show that the Al-forms are chemically stable at fairly high temperatures, while the H-forms of the minerals are chemically unstable and the mechanism of their ageing changes significantly as a function of temperature.

Below 200°C, the ageing of air-dry specimens of H-clays proceeds only as far as a definite content of hydrogen ions on the surface of the aluminosilicate and then becomes sharply retarded. Such inhibition can be accounted for by the fact that the ageing process under the given conditions is determined by the rate of the spontaneous conversion of the H-form of the mineral into the Al-form and by the evaporation of water from the surface of the silicate particles[18,36]. After the removal of water, this process ceases. The proposed explanation is confirmed by the results of a study of the ageing of a completely dried H-specimens¶—even at 200°C it is hardly converted into the aluminium-form (Table 7). A completely different behaviour was observed in the ageing of the H-forms above 200°C (Table 7). In contrast to the ageing mechanism already known, the exchangeable $H^+$ ions disappear completely from the surface without the removal from the mineral structure of a stoichiometric amount of $Al^{3+}$ ions. After the heat treatment of the H-forms of clay minerals for 1 h at 300–400°C, the

¶The dry specimen of the H-mineral was prepared from the air-dry specimen by prolonged evacuation accompanied by the freezing out of moisture by liquid nitrogen, after which it was stored in a sealed bulb.

exchange capacity of the mineral decreases irreversibly by an amount equal to the number of exchangeable hydrogen ions.

The observed phenomenon is probably similar to the migration of $Li^+$ ions in the octahedral layer of the clay mineral noted earlier. The small $Li^+$ cations may be located either at vacant octahedral sites [13] or in the interstices between them [14].

Table 7. The influence of the temperature and duration ($\tau$) of heat treatment on the chemical stability of the hydrogen-forms of layer silicates (the contents of exchangeable acid ions are quoted in $\mu$equiv.g$^{-1}$).

| τ, h | 25° C | | 100° C | | 200° C | | 300° C | | 400° C | |
|---|---|---|---|---|---|---|---|---|---|---|
| | H+ | Al³+ | H+ | Al³+ | H+ | Al³+ | H+ | Al³+ | H+ | Al³+ |
| | | | | | H-montmorillonite | | | | | |
| 1.0 | 890 | 260 | 760 | 390 | 550 | 600 | 80 | 250 | 0.0 | 250 |
| 2.0 | 890 | 260 | 720 | 430 | 480 | 670 | 40 | 250 | 0.0 | 250 |
| 3.0 | 890 | 260 | 720 | 430 | 470 | 680 | 0.0 | 250 | 0.0 | 250 |
| 6.0 | 890 | 260 | 720 | 430 | 470 | 680 | 0.0 | 250 | 0.0 | 250 |
| 2.0* | 900 | 250 | 900 | 250 | 850 | 250 | 0.0 | 250 | 0.0 | 250 |
| | | | | | H-palygorskite | | | | | |
| 1.0 | 105 | 35 | 62 | 78 | 36 | 104 | 10 | 36 | 0.0 | 36 |
| 2.0 | 102 | 38 | 53 | 78 | 27 | 113 | 0.0 | 36 | 0.0 | 36 |
| 3.0 | 102 | 38 | 41 | 99 | 19 | 121 | 0.0 | 36 | 0.0 | 36 |
| 6.0 | 102 | 38 | 40 | 100 | 18 | 122 | 0.0 | 36 | 0.0 | 36 |
| 2.0* | 105 | 35 | 103 | 37 | 84 | 56 | 0.0 | 35 | 0.0 | 36 |
| | | | | | H-kaolinite | | | | | |
| 1.0 | 49 | 9 | 28 | 27 | 16 | 39 | 0.0 | 11 | 0.0 | 10 |
| 2.0 | 45 | 10 | 20 | 35 | 9 | 46 | 0.0 | 11 | 0.0 | 10 |
| 3.0 | 45 | 10 | 20 | 35 | 8 | 47 | 0.0 | 11 | 0.0 | 10 |
| 6.0 | 44 | 11 | 20 | 35 | 8 | 47 | 0.0 | 11 | 0.0 | 10 |
| 2.0* | 46 | 9 | 45 | 10 | 38 | 17 | 0.0 | 10 | 0.0 | 10 |

*In vacuo.

In order to elucidate the causes of the loss of exchange capacity by H-montmorillonite on heating to 300–400°C, a study was made of the NMR spectra of both acid forms [78]. It was observed that the NMR spectra of the initial air-dry specimens of the H- and Al-forms show an intense narrow band due to the adsorbed water molecules and hydrogen ions. The difference between the NMR spectra of the H- and Al-forms is manifested only after the removal of sorbed $H_2O$ molecules. For example, the NMR spectrum of the Al-form heated for 1 h at 200°C (Fig. 11, 1*a*) contains a broad band due to hydroxy-groups. The calculated second moment, which is approximately 4 G$^2$, agrees well with data for OH groups obtained for other cation-substituted forms of montmorillonite [14].

In contrast to the Al-form, the NMR spectrum of H-montmorillonite heated to 200°C shows a distinct narrow line with $\Delta H \simeq 0.5$ G (Fig. 11, 2*a*), against the background of the band due to hydroxy-groups, which we assigned to mobile exchangeable hydrogen ions. Quantitative study of the form of the NMR signal obtained reveals a downfield shift of the band due to $H^+$ ions relative to the signal of hydroxy-groups. Owing to the considerable width of the bands observed in the spectrum, it is difficult to estimate the shift quantitatively. If it is assumed that, on raising the temperature to 300°C, hydrogen ions become located at the ion-exchange centres on the aluminosilicate, then the NMR spectrum should exhibit a broadening of the band due to hydroxy-groups as a result of the increase in proton density. In fact, a narrow proton line is observed even at a heat treatment temperature of 500°C and the content of protons decreases (only) above this temperature, where the loss of the structural hydroxy-groups of the mineral already takes place (Fig. 11, *b*). Since at 300°C and above there are no exchangeable protons on the surfacd of montmorillonite (Table 7), it is reasonable to suppose that they migrate into its crystal structure. It also follows from the results presented that the protons captured by the lattice are not located at definite electron-donating centres, but diffuse throughout the crystal structure.

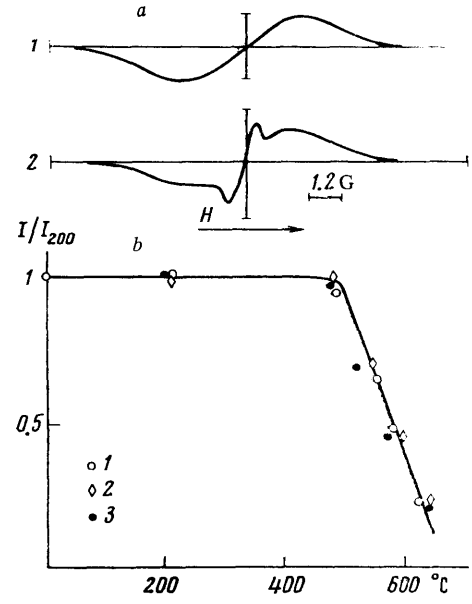



**Figure 11.** *a*) NMR spectra of the protons of the specimens of the Al-form (*1*) and the H-form (*2*) of montmorillonite dehydrated at 200°C; *b*) variation of the integral intensities in the NMR spectra of the hydroxyl protons and $H^+$ ions in the acid form of montmorillonite as a function of the temperature of the heat treatment of the specimens; 1) OH groups in the Al-form; 2) OH groups in the H-form; 3) $H^+$ ions.

X-Ray diffraction studies on the H-form of montmorillonite heated at different temperatures (25–450°C) showed that its crystal lattice does not undergo appreciable changes during the ageing processes. The non-basal reflections (4.39, 3.12, 2.48, 1.66, 1.48, and 1.27 Å, etc.) for both acid forms of the mineral are characteristic in the experimental temperature range also of other cation-substituted forms of montmorillonite [74].

Thus the available data show that the nature of the surface of the acid forms of layer silicates depends to a large extent on their heat treatment temperature. In the study of chemical transformations, it is therefore necessary to take into account the change in the chemical nature of the surface under certain conditions of catalysis. Thus, in the investigation of the catalytic process on the aluminium-form, one must bear in mind the decrease of the content of exchangeable $Al^{3+}$ ions of silicates above 500°C. The study of the mechanism of catalytic reactions on the minerals in the hydrogen-forms must be approached with

even greater caution. The elucidation of the true mechanism of the catalytic reaction is complicated in this case by the ageing processes of the H-form. Under conditions where there is no water in the system, the H-form is a chemically stable complex up to 200°C. Above this temperature exchangeable protons migrate spontaneously in the crystal structure of the mineral, which is reflected in its catalytic activity. A slight activity may be manifested under these conditions owing to the thermal dissociation of the surface hydroxy-groups [75] or other active centres in the crystals.

## VII. THE EXCHANGEABLE ACIDITY OF SILICATES ACTIVATED BY INORGANIC ACIDS AND OF ELECTRODIALYSED SILICATES

Considerable advances have been made in the study of the adsorption-structural and physicochemical properties of acid-activated minerals [1,7,76]. These investigations have established that the sorbents and catalysts obtained in this way exhibit enhanced adsorption, bleaching, and catalytic properties. The studies performed have shown[53] that both the composition of the exchangeable cations and the exchange capacity of montmorillonite depend on the activation time (Table 8). With increase of activation time, the content of hydrogen ions on the surface of the mineral falls and that of the aluminium ions increase. When the sorbent is treated with a 20% hot solution of $H_2SO_4$ for 6 h, its virtually homoionic Al-form is produced.

**Table 8.** The influence of the activation time on the amount of exchangeable $H^+$ and $Al^{3+}$ ions of montmorillonite ($\mu$equiv.$g^{-1}$) and on the concentration of $Al^{3+}$ ions in the mother liquor $[Al^{3+}]_{soln}$ (activation temperature 98°C).

| Treatment time, h | Exchange capacity, $\mu$equiv. $g^{-1}$ | Washing without cooling | | Washing after cooling | | $\frac{[Al^{3+}]_{soln}}{N}$ |
|---|---|---|---|---|---|---|
| | | $H^+$ | $Al^{3+}$ | $H^+$ | $Al^{3+}$ | |
| 1 | 960 | 350 | 615 | 500 | 465 | 0.06 |
| 2 | 880 | 300 | 580 | 390 | 490 | 0.07 |
| 3 | 790 | 190 | 605 | 310 | 485 | 0.10 |
| 4 | 780 | 80 | 710 | 180 | 610 | 0.13 |
| 5 | 700 | 50 | 655 | 100 | 605 | 0.17 |
| 6 | 650 | 40 | 660 | 40 | 660 | 0.21 |
| 8 | 630 | 30 | 640 | 30 | 640 | 0.22 |

The decrease of the number of exchangeable $H^+$ ions during the activation process can be explained as follows. When a hot solution of sulphuric acid comes into contact with the clay mineral, the mineral faces dissolve, as a result of which aluminium ions and polysilicic acid gradually accumulate in the mother liquor. On washing the specimen, the selective adsorption of tervalent aluminium (or aluminosilicate [56]) ions results in the partial or complete substitution by the latter of the hydrogen ions in the equilibrium solution depending on the concentration of the tervalent ions. At the same time, one cannot rule out also the possibility of the ageing of the H-form of the aluminosilicate during activation and particularly during the washing of the hot specimens. This is indicated by the dependence of the composition of the exchangeable cations of the activated mineral on the washing conditions: samples which were washed free of the excess electrolyte without cooling contain fewer exchangeable hydrogen ions compared with samples which had been subjected to preliminary cooling for 24 h (Table 8). This is because on cooling a suspension of the mineral in an acid solution, the $Al^{3+}$ ions cannot be distributed on the surface, since they are readily displaced by protons owing to the high concentration of the latter. During the washing of the hot specimen, the H-mineral ages after the first portion of the mother liquor has been decanted, with migration of exchangeable aluminium ions onto the surface.

The hydrogen-aluminium-form of the activated montmorillonite thus obtained is chemically unstable and is converted after a time into the homoionic Al-form. As for the homoionic H-forms of clay minerals, this process depends on the content of the disperse phase in the system, the composition of the intermicellar medium, and temperature. With increase of the concentration of the suspension and following the introduction of methanol into the dispersion medium, the rate of ageing of the activated specimens falls. In dehydrated methanol and in the dried state, the specimens investigated do not show any signs of ageing. With increase of temperature, the rate of ageing of the specimens in the aqueous suspension increases sharply. These results show that the ageing process of the activated mineral is similar to the ageing of the homoionic H-forms of layer silicates described above and is a heterogeneous chemical reaction of the exchangeable protons on the aluminosilicate faces. A necessary condition for this reaction is the presence of water molecules in the system. The calculated activation energy for the ageing of the H–Al-form (21 kcal g-ion$^{-1}$) proved to be equal to the value for the ageing of the homoionic H-form of the mineral.

Table 8 shows that the exchange capacity of the silicate after activation for 6 h changes insignificantly. This is because a large amount of aluminium ions and silicic acid accumulates in the mother liquor, as a result of which a chemical equilibrium is established in the system. At the same time, the inhibition of the dissolution of minerals may be influenced by the polymerisation processes of the above compounds. Amorphous polyaluminosilicic and polysilicic acids may be deposited on the lateral faces of silicates and prevent the interaction of hydronium ions with the latter.

It follows from the analysis of the extensive literature on the acid activation of minerals that solutions of concentrated acids (up to 20%) are used as a rule for this process [1,7,76,77]. However, in these solutions the degree of dissociation of the acid is greatly reduced and the activity of $H^+$ ions is insignificant. In order to intensify the above treatment, it is therefore desirable to use more dilute solutions of inorganic acids. One must also take into account the fact that, when unpurified minerals are used, part of the acid is consumed in the dissolution of impurities such as oxides, carbonates, organic substances, etc., which are always present in natural specimens.

Electrodialysis of aqueous suspensions of minerals is a very convenient method of obtaining their acid forms [17]. Its advantage is due to the fact that, in contrast to acid activation, it does not require additional operations involved in the removal of electrolytes from the dispersed silicate by washing, particularly since both methods frequently lead to minerals in the Al-(Fe-, Mg-)forms [17]. It has been shown in a number of studies [1,78,79] that electrodialysis of suspensions of aluminosilicates causes

the disruption of their lattices. The mechanism of the dissolution process is apparently similar to that described above and consists of the following steps. When a constant electric field is applied, the exchangeable cations in the suspension† migrate to the cathode and accumulate in the cathodic compartment. The negatively charged silicate species diffuse to the anode, becoming concentrated near the cellophane partition. During electrodialysis, water molecules are known to decompose:

$$6H_2O \rightarrow 2H_2 + O_2 + 4H^+ + 4OH^-, \quad (5)$$

$OH^-$ ions accumulating at the cathode and $H^+$ ions at the anode. When the cathodic compartment is washed with distilled water, the exchangeable cations are removed in the form of metal hydroxides. The excess negative charge of the individual mineral particles is compensated by hydrogen ions. As shown above, the H-form of the natural aluminosilicate is chemially unstable and is converted into the Al-Fe-Mg-form. Since electrodialysis is almost always accompanied by an increase of temperature, the ageing reaction proceeds under these conditions at a high rate. As a result, the mineral faces break down (Fig. 8) with liberation of silicic acid, which is always observed in the anodic compartment [17,80].

One should also note that the intensity of the given process depends both on the nature of the exchangeable cation and on the potential difference applied to the electrodes. The stronger the binding of the exchangeable cation to the surface, the greater the potential gradient required for the transfer of the exchangeable cation to the cathodic compartment. If a potential difference capable of causing the desorption of the exchangeable $Al^{3+}$ ($Fe^{3+}$) ions from the surface and of transferring them to the cathodic compartment is applied to the system, a continuous dissolution of the mineral is observed. In order to obtain the acid form of the aluminosilicate by the electrodialysis of aqueous suspensions, it is therefore necessary to monitor the process carefully. The monitoring consists in analysing the electrolyte in the cathodic and anodic chambers. As soon as the flow of exchangeable cations into the cathodic compartment ceases and silicic acid appears in the anodic compartment (in the form of $SiO_3^{2-}$ ions), electrodialysis is stopped. The composition and amount of exchangeable acid ions on the surface of the silicate are determined at the same time.

In order to obtain reliable data on the nature of the exchangeable acidity of powdered specimens, one must bear in mind the fact that the drying of their pastes must be carried out at room temperature or below. Such drying conditions inhibit the ageing of the H-forms of the minerals.

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†The suspension in the working compartment of the electrodialyser is stirred continuously [17].

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# The Photoelectron Spectroscopy of Organophosphorus Compounds

V.V.Zverev and Yu.T.Kitaev

The applications of the method of photoelectron spectroscopy in the study of the electronic and steric structures of organophosphorus compounds is examined. The spectra of two-, three-, and four-coordinated phosphorus are interpreted in terms of the approximation of Koopmans' theorem. Attention is concentrated on the elucidation of the composition of the upper occupied orbitals. The manifestations of the $n-\pi$ and $n-n$ interactions in the photo-electron spectra of these compounds are investigated.
The bibliography includes 104 references.

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## I. INTRODUCTION

The ultraviolet photoelectron spectroscopy (PES) is a unique method whereby it is possible to establish the sequence of the ionisation potentials of molecules. The first reports showing that the photoelectron spectrum contains information about the set of ionisation potentials were published by Vilesov et al.[1] and Turner and Al-Joboury[2] more than ten years ago, but the period of the most intense development of the method covers the last five years. The method of X-ray (photo)electron spectroscopy, which permits the determination of the electron binding energies in the inner non-valence levels, was developed somewhat earlier[3], but the survey of the available information about the applications of this method in the study of organophosphorus molecules is outside the scope of the present review.

This review deals with the applications of the PES method in the study of the compositions of the upper occupied molecular orbitals and of the steric structures of organophosphorus compounds. The photoelectron spectra of phosphorus compounds have been obtained by many groups of investigators and the number of compounds which have been investigated is fairly large.

The method of ultraviolet PES, described in a number of reviews and monographs (see, for example, Refs. 4–9), has become firmly established in organic chemistry. The most important results have been obtained by the PES method in the study of the $\pi-\pi$ interaction in conjugated and non-conjugated molecules with $\pi$ bonds[10,11], the $\pi-\sigma$ mixing of orbitals in non-planar molecules[12,13], the problem of the $\pi-\sigma$ separation in planar conjugated systems[14,15], the $n-n$ interaction of lone electron pairs (LEP)[16], and the $n-\pi$ interaction of LEP with an unsaturated fragment of the molecule[17-20]. The possibility of investigating by the PES method the steric structures of conjugated molecules[16-21], the steric hindrance to conjugation[17-20], and conformational equilibria[16,21] is of considerable interest. The PES method has been used in a number of studies to investigate reactivity[22-25].

The information obtained by the PES method is extensive and varied. The threshold value of the ionisation current yields the adiabatic potential $IP_m^a$, which is defined as the difference between the energies of the molecules and the ion in the zero-point vibrational state. The vertical ionisation potentials $IP_m^v$ may be determined from the maximum change in the ionisation current, which corresponds to the most probable ionisation transition.

The interpretation of the experimental data obtained by the PES method is simplest and most convenient in terms of the approximation of Koopmans' theorem[26,30], according to which the values of $IP_m^v$ are equal to the energies (with the opposite sign) of the corresponding molecular orbital:

$$IP_m^v = -\varepsilon_m. \quad (1)$$

In terms of the approximation of Koopmans' theorem, the ionisation potential $IP(\psi_m)$ may be regarded as the energy of the ionisation of an electron from the occupied orbital $(\psi_m)$. In comparing the experimental values of $IP_m^v$ with the calculated orbital energies $(-\epsilon_m)$, one also uses relations of the type

$$IP_m^v = a + b(-\varepsilon_m), \qquad (2)$$

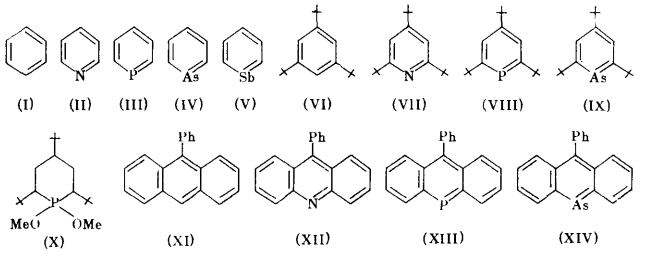
which have come to be referred to as the weakened form of Koopmans' theorem [31,32].

However, the empirical methods for the interpretation of PES data, based on the definite characteristic nature of the properties of the bands in the spectrum, are no less valuable. Thus the LEP of oxygen, sulphur, and halogen atoms contribute specific narrow bands to the photoelectronic spectra, while the delocalisation of the LEP, particularly their involvement in the $n-\pi$ interaction, leads to a broadening of the bands and a change in their shape [5]. When the LEP electrons of nitrogen [33] and phosphorus [34] are dislodged, broad bands are obtained (the difference between $IP_1^v$ and $IP_1^a$ amounts in this case to approximately 0.5 eV), which is associated both with the involvement of the LEP of these atoms in bonding and with the change in the geometry of the ion on ionisation. The upper $\pi$ orbitals of conjugated systems give rise to narrow bands with a resolved vibrational structure [5]. The intensity of the bands depends both on the nature of the atom where the corresponding orbital is predominantly localised and on the contribution to the latter by $s$ and $p$ electrons [35].

In the interpretation of PES data, relations governing series of related compounds are used, the spectra of the test compound and its perfluoro-analogue are compared [36], and account is taken of the spin–orbital and Jahn–Teller band splitting [37,39] as well as the dependence of the band intensity on the degree of degeneracy of the orbitals [37] and the energy of the ionising radiation [38]. The above procedures make it possible in many instances to interpret fairly unambiguously the photoelectron spectrum and to determine the energy of the orbitals and the nature of their interaction.

## II. $\lambda^3$-PHOSPHORINS

The photoelectron spectra of $\lambda^3$-phosphorin and its derivatives




have been obtained and interpreted by Schäfer's [40–45] and Heilbronner's [46] groups. The disposition of the molecular orbitals in $\lambda^3$-phosphorin was established by comparison with *ab initio* calculations [46] and with calculations by the method of complete neglect of differential overlapping (CNDO/2) [40,41] and was confirmed by ionisation potential data for series of related compounds [43–45] (Fig. 1 and Table 1).

**Table 1.** The vertical ionisation potentials of $\lambda^3$-phosphorins and their interpretation.

| Compound | $IP^v$, eV | | | | | Refs. |
|---|---|---|---|---|---|---|
| $\lambda^3$-Phosphorin | 9.2<br>$3b_1(\pi)$ | 9.8<br>$1a_2(\pi)$ | 10.0<br>$13a_1(\sigma, n)$ | 11.5<br>$8b_1(\sigma)$ | 12.1<br>$2b_1(\pi)$ | 46 |
| 2,4,6-Tri-t-butylphosphorin | 8.0<br>$\pi_1$ | 8.6<br>$\pi_2$ | 8.6<br>$n$ | 10.0 | | 40 |
| 9-Phenyl-10-phosphanthracene | 7.25 | 8.65 | 9.00 | 9.30 | 9.90 | 42 |
| 2-Phenyl-1-phosphanaphthalene | 7.65<br>$\pi_1$ | 8.40<br>$\pi_2$ | 8.9<br>Ph, $n$ | 9.4 | 9.8<br>$\pi_3$ | 44 |
| 2-Phenylnapthalene | 7.75<br>$\pi_1$ | 8.30<br>$\pi_2$ | 8.95<br>Ph | 9.3 | 9.95<br>$\pi_3$ | 44 |
| 10-Phenyl-9-phosphanthracene | 7.60<br>$\pi_1$ | 8.15<br>$\pi_2$ | 8.85<br>$\pi_3$ | 9.25<br>Ph, $n$ | 9.80<br>$\pi_4$ | 45 |
| 10-Phenylanthracene | 7.65<br>$\pi_1(b_1)$ | 8.05<br>$\pi_2(a_2)$ | 8.90<br>$\pi_3(a_2)$ | 9.20<br>Ph | 9.75<br>$\pi_4(b_1)$ | 45 |
| 2,4,6-Tri-t-butyl-1,1-dimethoxyphosphorin | 6.7<br>$\pi_1(b_1)$ | 8.4<br>$\pi_2(a_2)$ | | | | 43 |
| 1,1-Dibenzyl-2-phenyl-1-phosphanaphthalene | 6.0<br>$\pi_1$ | 7.90<br>$\pi_2$ | 8.8<br>Ph, $B_Z$, $\pi_3$ | 9.4 | | 44 |

When a heteroatom is introduced into the benzene molecule, the upper degenerate benzene orbital $1e_{1g}(\pi)$ splits into two orbitals of the type $b_1(\pi)$ and $a_2(\pi)$, in conformity with the $C_{2v}$ symmetry group of the substituted molecule. Since the atomic coefficient of the $a_2(\pi)$ orbital is zero at the site of substitution, the orbital should be little affected by the influence of the substituent (Fig. 2). In contrast to $a_2(\pi)$, the $b_1(\pi)$ orbital has no node at the site of substitution and its energy must depend significantly on the nature of the substituent. In terms of the approximation of the Hückel method, the change in the energy of the $b_1(\pi)$ orbital is determined by the product of the square of the atomic coefficient at the site of substitution and the Coulomb integral for the heteroatom $\Delta\alpha_X$:

$$\Delta\varepsilon(b_1(\pi)) = [C_{b_1(\pi),x}]^2 \Delta\alpha_x. \qquad (3)$$

The absence of a charge on the phosphorus atom in the $a_2(\pi)$ orbital also follows from the electron density map for the $b_1(\pi)$ and $a_2(\pi)$ orbitals of the $\lambda^3$-phosphorin molecule [47].

In the pyridine molecule, the energy of the $a_2(\pi)$ orbital is higher than that of the $b_1(\pi)$ orbital, because the nitrogen atom is more electronegative than carbon and stabilises the $b_1(\pi)$ orbital. In contrast to the pyridine molecule, in $\lambda^3$-phosphorin and in heterocyclic arsenic(IV) and antimony(V) compounds, the $b_1(\pi)$ orbital lies above the $a_2(\pi)$ orbital (Fig. 1). The reversal of the sequence of $\pi$ orbitals in $\lambda^3$-phosphorin in relation to pyridine constitutes the main problem in the interpretation of the photoelectron spectra of these compounds [40–46]. The reversal of the orbitals has been comprehensively investigated and demonstrated in several ways. The reversal of the sequence of $\pi$ orbitals can be demonstrated by quantum-chemical calculations of $\lambda^3$-phosphorin [46]. We shall also examine empirical methods for the elucidation of the reversal of levels and the conclusions concerning the electronic structure of the

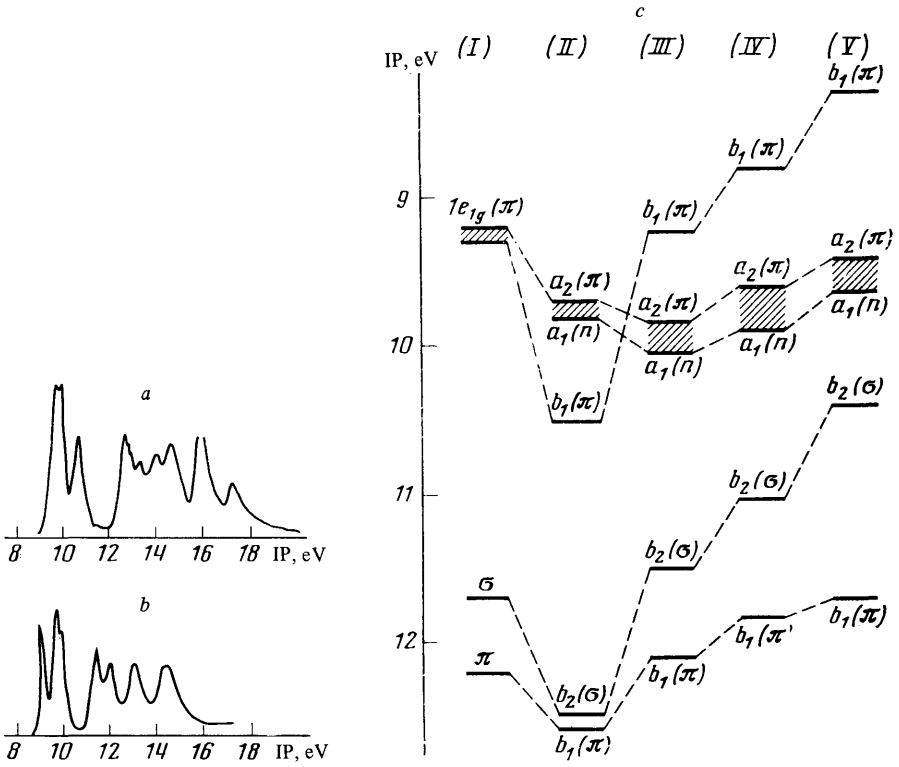



**Figure 1.** Photoelectron spectra: *a*) pyridine (II); *b*) $\lambda^3$-phosphorin (III); *c*) correlation energy level diagram for compounds (I)–(V).[46]

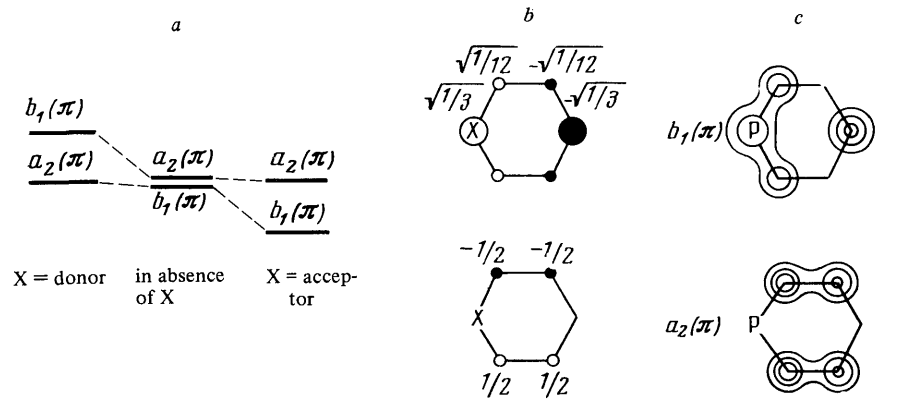



**Figure 2.** The influence of the substituents X on the relative positions of the $a_2(\pi)$ and $b_1(\pi)$ orbitals (*a*), a schematic representation of the atomic coefficients of these orbitals (*b*), and electron density maps for the $a_2(\pi)$ and $b_1(\pi)$ orbitals of $\lambda^3$-phosphorin (*c*).[47]

$\lambda^3$-phosphorin molecule which follow from this reversal. In the series of compounds (I)–(V), the ionisation potentials of the $b_1(\pi)$ orbitals are correlated with the ionisation potentials IP(X) of the atoms X:

| X | N | C | P | As | Sb |
|---|---|---|---|---|---|
| IP(X), eV | 14.53 | 11.26 | 11.0 | 9.81 | 8.64 |

when the reversal of orbitals is postulated[46]. In the derivation of the relation

$$IP^v[b, (\pi)] = 5.24 \text{ eV} + 0.362 \text{ IP(X)}, r = 0.9998 \quad (4)$$

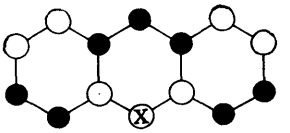
$IP_3^V[b_1(\pi)]$ was used for pyridine and $IP_1^V[b_1(\pi)]$ was used for the remaining compounds. The ionisation energy of the second occupied $\pi$ orbital of the $b_1(\pi)$ type is also correlated with IP(X):

$$IP^v[b, (\pi)] = 10.25 \text{ eV} + 0.163 \text{ IP(X)}. \quad (5)$$

In compounds (I)–(V), the potentials $IP[b_1(\pi)]$ vary less than IP(X), because the atomic coefficient $C_{b_1,X}$ of this orbital is significantly less than unity at the site of substitution. $(C_{m,x})^2 = 1/3$ is obtained for the upper $b_1(\pi)$ orbital and $(C_{m,x})^2 = 1/6$ is obtained for the second orbital of the $b_1(\pi)$ type[46]. In conformity with Eqn. (3), these squares of the atomic coefficients should determine the slopes of the linear relations between $IP[b_1(\pi)]$ and IP(X); the empirical slopes of the straight lines, described by Eqns. (4) and (5), are indeed very close to 1/3 and 1/6.

The nitrogen atom, which exhibits electron-accepting properties, stabilises the $b_1(\pi)$ orbital in pyridine [IP(N) = 14.53 eV, IP(C) = 11.26 eV]. In contrast to this, the phosphorus, arsenic, and antimony atoms destabilise the $b_1(\pi)$ component of the $1e_{1g}$ orbital of the benzene molecule, showing at the same time electron-donating properties. However, whereas the $b_1(\pi)$ orbitals in $\lambda^3$-phosphorin are destabilised compared with the corresponding benzene orbitals, the $a_2(\pi)$ orbital is additionally stabilised. It has been noted[46] that, according to *ab initio* calculations, a shift of electron density away from the phosphorus atom is observed in $\lambda_3$-phosphorin.

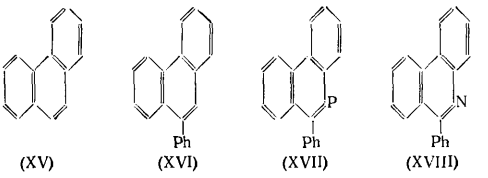
The inversion of the sequence of orbitals in compounds (I)–(V) and (VI)–(VIII) was also observed when the $IP^V[b_1(\pi)]$ of these compounds were compared with the $IP_1$ of the anthracene hetero-derivatives[42]. The problem of the degeneracy of the orbitals and of their disposition after the removal of degeneracy, which is crucial for benzene derivatives, is altogether absent for anthracene and its derivatives. In anthracene, the upper occupied $b_{2g}(\pi)$ orbital is not degenerate, its energy is much higher than that of the subsequent orbitals, and it has no node at any of the atoms:




$b_{2g}(\pi)$

Like the orbital of the $b_1(\pi)$ type, this orbital should be subject to the inductive influence of the heteroatom X (Fig. 3).

The photoelectron spectra of compounds (XI)–(XIV) show a separate band of the $\pi$ type, which unambiguously determines the value of $IP_1^V$. The inversion of the orbital sequence follows from the fact that the $IP_1^V$ of compounds (XI)–(XIV) are correlated with the values of $IP^V[b_1(\pi)]$ of compounds (I)–(V) and (VI)–(IX), selected taking into account the inversion. Since the atomic coefficient of the $b_{2g}(\pi)$ orbital at the site of substitution is smaller than the corresponding coefficient of the $b_1(\pi)$ orbital in benzene, the range of variation of $IP_1^V$ in compounds (XI)–(XIV) is also significantly narrower than in compounds (I)–(V) and (VI)–(IX) (Fig. 3). Like the correlation equations (4) and (5), these data also indicate the applicability of Eqn. (3) to the description of the dependence of the energy of the orbital without a node at the site of substitution on the electronegativity of the heterosubstituent.




(XV) (XVI) (XVII) (XVIII)

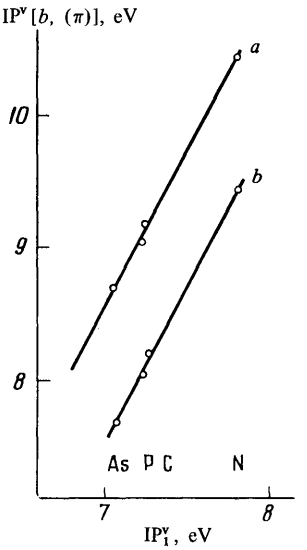



**Figure 3.** Relation between $IP^V[b_1(\pi)]$ and $IP_1^V$ of compounds (I)–(IV) and (XI)–(XIV) (*a*) and compounds (VI)–(IX) and (XI)–(XIV) (*b*).[42]

In their discussion of the photoelectron spectra of compounds (XV)–(XVIII), Schäfer et al.[45] concluded that the electronic influences of the phosphorus atom and the $sp^2$-hybridised carbon atom are identical, because, in contrast to the nitrogen-containing hetero-derivative (XVIII), the upper ionisation potentials of 9-phenyl-$\lambda^3$-phosphaphenanthrene (XVII) and 9-phenylphenanthrene (XVI) are extremely close (Fig. 4). The changes in the ionisation potentials of 2-phenylnaphthalene are just as small when the carbon atom in the 1-position is substituted by phosphorus[4] (Table 1). However the initial compounds (benzene and $\lambda^3$-phosphorin) have different photoelectron spectra; the substitution of a carbon atom by phosphorus removes the degeneracy and shifts the ionisation potentials of some of the orbitals, although to a much smaller extent than does substitution by a nitrogen atom (Fig. 4). The very significant changes in the ionisation potentials for the $\pi$ orbitals of 9-phenylphenanthrene and 2-phenylnaphthalene

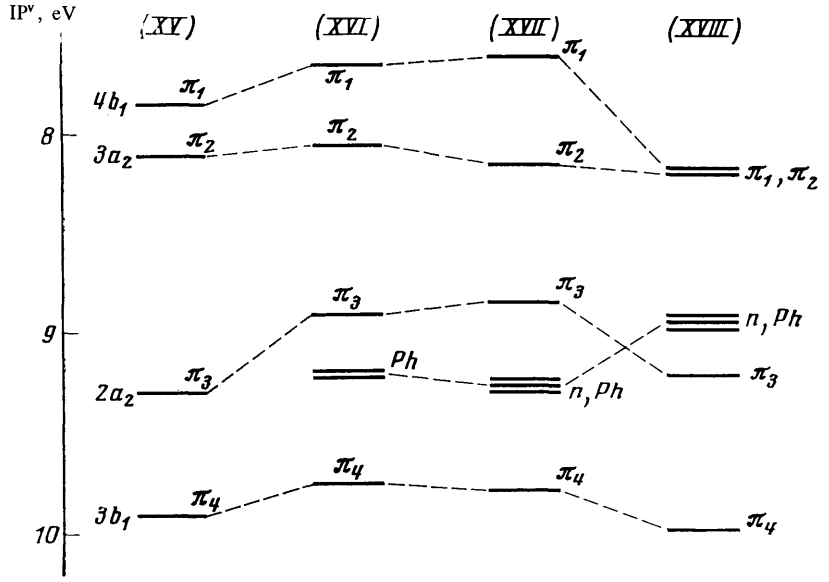



Figure 4. Correlation diagram for the ionisation potentials of compounds (XV)–(XVIII).[45]

on substitution of a carbon atom by phosphorus can be readily understood: the $\pi$ orbitals in the 9-phenylphenanthrene molecule are significantly delocalised, the atomic coefficients of the individual orbitals at the site of substitution are small and, according to Eqn. (3), the corresponding changes in the orbital energies and ionisation potentials should be insignificant.

In the discussion of the photoelectron spectrum of $\lambda^3$-phosphorin, the problem of the role of *d* orbitals was raised. On the basis of the populations of the *d* orbitals calculated by the CNDO/2 method, Schäfer and coworkers[40,41] postulated that the additional stabilisation of the $a_2(\pi)$ level as a result of the interaction with the vacant $a_2(d_{xy})$ orbital, plays a definite role in the inversion of the $b_1(\pi)$ and $a_2(\pi)$ levels. However, the excellent correlation between IP$^V[b_1(\pi)]$ and the ionisation potentials IP(X) of the heteroatoms shows that the changes in IP$^V[b_1(\pi)]$ of $\lambda^3$-phosphorin are determined solely by the electron-donating properties of phosphorus. Furthermore, *ab initio* calculations have shown[45] that the calculated sequence of $b_1(\pi)$ and $a_2(\pi)$ orbitals in $\lambda^3$-phosphorin is independent of the inclusion of *d* orbitals in the treatment. Nevertheless, if one considers only the inductive influence of the phosphorus atom, leading to the destabilisation of the $b_1(\pi)$ orbital, it is very difficult to understand the cause of the appreciable stabilisation of the $a_2(\pi)$ orbital.

We shall consider the ionisation potentials IP(n) of the LEP of phosphorus in the photoelectron spectrum of $\lambda^3$-phosphorin and its derivatives. In the range 9.5–10 eV, the spectrum of $\lambda^3$-phosphorin has two overlapping bands (Fig. 1). Since the first has a sharper peak than the second, the authors[46] suggest that $IP_2^V = 9.8$ eV corresponds to the $a_2(\pi)$ orbital and $IP_3^V(n) = 10.0$ eV corresponds to the $a_1(\sigma,n)$ orbital of the lone pair. IP$^V(n)$ is 9.25 eV for 9-phenyl-$\lambda^3$-phosphaphenanthrene[45], while IP$^V(n)$ of 1,3,5-tri-t-butyl-$\lambda^3$-phosphorin is reduced to 8.6 eV.[43] It is of interest that the ionisation potentials of the $a_2(\pi)$ and $a_1(\sigma,n)$ orbitals of all the compounds in the series (II)–(VI) (Fig. 1) are similar and vary in parallel, while in the photoelectron spectra the corresponding bands are poorly resolved.

In contrast to $\lambda^3$-phosphorin, the electronic structures of $\lambda^5$-phosphorins have been investigated by the PES method to a lesser extent. The first ionisation potential of 2,4,6-tri-t-butyl-1,1-dimethoxy-$\lambda^5$-phosphorin is reduced to 6.7 eV,[43] while that of 1,1-dibenzyl-2-phenylphosphanaphthalene is only 6.0 eV.[44] The cause of such considerable destabilisation has still not been explained. It has been noted[44] that the phosphorus atom is involved in conjugation in $\lambda^5$-phosphorins.

## III. COMPOUNDS OF THREE-COORDINATED PHOSPHORUS

The photoelectron spectra of compounds of three-coordinated phosphorus have been obtained by various groups of investigators[34,48-69]. In many cases, the first ionisation potential is attributed to the removal of an electron from the LEP of phosphorus. In a series of compounds investigated, this quantity varies over a wide range—from 12.29 eV for $PF_3$ to 7.88 eV for $Ph_3P$.[52,61] The dependence of the ionisation energy of the LEP on the charge of the phosphorus atom[7] and on the sum of the constants $\sigma_I^{ph}$[64] has been noted; the empirical ionisation potentials have been compared with the calculated orbital energies[61,70-72]. The adiabatic ionisation potentials IP$^a$ have been published for a much smaller number of compounds than have the vertical potentials IP$^V$. We may note that the adiabatic potential has been used[70,71] in a comparison with the results of *ab initio* calculations for $PH_3$ and the vertical potential has been used for other compounds. The same error has been made also in a review[7]. A handbook[73] also quotes the adiabatic potentials for some compounds and the vertical potentials for others.

The difference between the values of $IP_1^V$ and $IP_1^a$ characterises the change in the geometry of the ion compared with the isolated molecule[34,49]. The differences $IP_1^V - IP_1^a$ for phosphine, methylphosphine, trimethylphosphine, and phosphorus trifluoride molecules are 0.64, 0.58, 0.59,

and 0.70 eV respectively[34,52,62]. In the case of chloroalkylchlorophosphines, the differences are 0.47 eV for $PCl(CH_2Cl)_2$ and 0.59 eV for $PCl_2(CH_2Cl)$.[58]

The PES method has been used[34,49] to estimate quantitatively the geometrical parameters of the ions derived from the $PH_3$ and $PF_3$ molecules. The irregularity of the vibrational levels and the appreciable broadening of the first peak indicate a somewhat pyramidal structure of the $PH_3^+$ ion. The $PF_3^+$ ion has a planar structure, because the distances between its vibrational peaks are equal. Analysis of the vibrational structures of the photoelectron spectra enabled Maier and Turner[34] and Potts and Price[49] to determine the angle between the X–H bond and the axis of rotation for a number of hydrides. In the $PH_3^+$ ion, the angle is approximately 87°[40] and the barrier to inversion amounts to 0.07 eV.[34]

The reciprocal relation between the photoelectron spectra and the steric structures of the trimethyl compounds ($Me_3X$) of Group V elements has been examined[63]. The atomic ionisation potentials of the central atom X decrease on passing from nitrogen to antimony, varying in exactly the same way as the ionisation potentials of the corresponding heterocyclic compounds (I)–(VI). In contrast to these quantities, the first ionisation potentials of the compounds $Me_3X$ do not vary in parallel with the ionisation potentials of the atoms X. The same may be said also of the hydrides $H_3X$. When the heteroatom X is altered, a decrease of $IP_1^V$ is not observed in these series of compounds (Table 2).

The anomalous constancy of the $IP_1^V$ is associated with the decrease of the C–X–C valence angle in the series of compounds $Me_3X$. The C–X–C angle is 180° in trimethylamine, 99° in trimethylphosphine, and 96° in trimethylstibine. The decrease of the valence angle leads to an increase of the amount of *s* character of the LEP of the atom X on passing from nitrogen to antimony, which increases its ionisation potential. Thus the decrease of the intrinsic ionisation potential of the *p* orbital of the atom X is prevented by the increase of the amount of *s* character of the LEP, which leads to an almost constant value of the first ionisation potential.

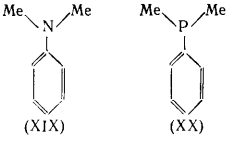
We may note that the next band in the photoelectron spectra of compounds of the type $Me_3X$ is associated with ionisation from a degenerate orbital of the *e* type, which in contrast to LEP is largely localised at the methyl groups, and should therefore be insensitive to changes in the valence angle. The ionisation potential of this orbital $IP^V(e)$ decreases correspondingly on passing from $Me_3N$ to $Me_3Sb$ (Table 2), in parallel with the ionisation potential of the atom X.

**Table 2.** The ionisation potentials (eV) of Group V elements and their trimethyl[63] and triphenyl[61] derivatives.

| $Me_3X$ | IP(X) | $IP_1^V$ (LEP) | $IP_2^V$ | $IP_3^V$ | $Ph_3X$ | $IP_1^V$ (LEP) |
|---|---|---|---|---|---|---|
| $Me_3N$ | 14.53 | 8.50 ($a_1$) | 12.3 ($a_2$) | 12.75 ($e$) | $Ph_3N$ | 10.27* |
| $Me_3P$ | 11.0 | 8.60 ($a_1$) | 11.34 ($e$) | (13.7)** | $Ph_3P$ | 7.88 |
| $Me_3As$ | 9.81 | 8.65 ($a_1$) | 10.70 ($e$) | (13.6) | $Ph_3As$ | 7.95 |
| $Me_3Sb$ | 8.64 | 8.48 ($a_1$) | 10.3 ($e$) | (13.3) | $Ph_3Sb$ | 8.18 |

*$IP_1^V(\pi) = 6.99$ eV; $IP^V(LEP) = 10.27$ eV.
**The values in brackets have been determined approximately.

We shall now examine the manifestation in the photoelectron spectra of the interaction of the LEP of phosphorus with a conjugated system. The spectra of phenylphosphines have been published by several groups of investigators[53,59–61,64], the authors conclusions about the electronic structures of phenylphosphines differing somewhat.



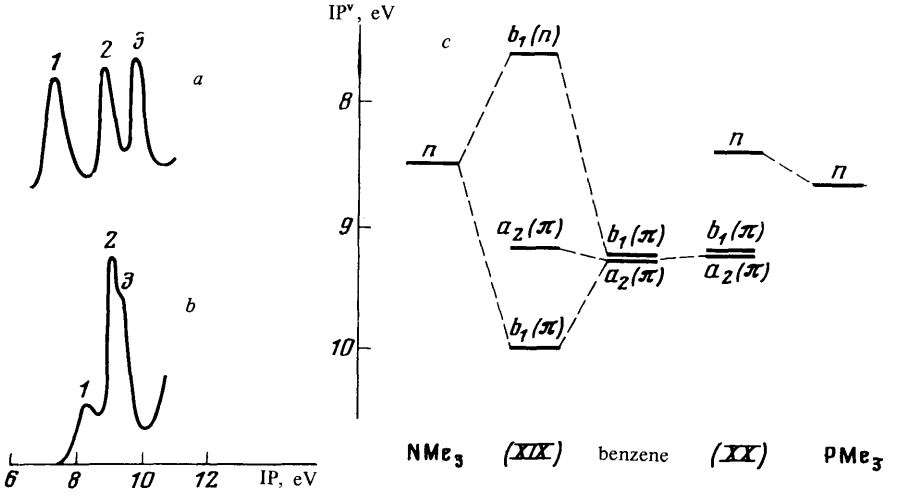



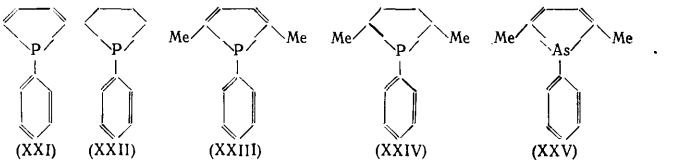

**Figure 5.** Photoelectron spectra and their interpretation[59]: *a*) *NN*-dimethylaniline (**XIX**); *b*) dimethylphosphine (**XX**).

Whereas the spectrum of *NN*-dimethylaniline has three bands of equal intensity in the region of low potentials at 7.6, 9.2, and 10.0 eV, the spectrum of dimethylphenylphosphine shows not three but two bands of different intensities, at 8.45 and 9.2 eV (Fig. 5). The second, more intense band with a maximum at 9.2 eV is not resolved into two components. The spectra of the two related molecules have been interpreted[59] in terms of the $n-\pi$ approximation, i.e. the upper occupied orbitals are represented as a combination of $n$ and $\pi$ orbitals of the heteroatom and the benzene ring. The vertical ionisation potential of the LEP of the $Me_3N$ molecule is 8.5 eV, while the ionisation potential of the degenerate $1e_{1g}$ $\pi$ orbital of benzene is 9.24 eV. As a result of the interaction with the LEP of the nitrogen atom, the degenerate $1e_{1g}$ level of benzene in dimethylaniline is split into two. The orbital of type $a_2(\pi)$, having a node at the site of substitution, does not interact with the LEP of nitrogen and its energy does not change. In contrast to it, the $b_1(\pi)$ orbital, which does not have a node at the site of substitution, interacts vigorously with the $n$ orbital of nitrogen, forming two orbitals with $b_1$ symmetry. The upper occupied $b_1(n-\pi)$ orbital receives a preferential contribution from the LEP of the nitrogen atom, while the $b_1(\pi + n)$ orbital is mainly of the $\pi$ type. The significant change in the energies of the resultant orbitals indicates an appreciable $n-\pi$ interaction in the dimethylaniline molecule (Fig. 5).

In contrast to *NN*-dimethylaniline, the energy of the highest occupied orbital in dimethylphenylphosphine is higher by only 0.15 eV compared with $Me_3P$, while the band corresponding to the degenerate benzene orbital is not split into two (Fig. 5). Hence the authors[59] conclude that there are two virtually unconnected fragments in dimethylphenylphosphine: the system of the benzene ring and the LEP of phosphorus. Accordingly $IP_1$ was assigned to the ionisation of the LEP of phosphorus and $IP_2$ to the unsplit $a_2(\pi)$ and $b_1(\pi)$ orbitals of the phenyl substituent.

We may note that the photoelectron spectra of substituted benzenes PhX, where X is a substituent containing nitrogen[17,19], sulphur[67], oxygen[17,74,75], halogens[4,75], a double bond[20], or the phenyl group[76], have been fairly well investigated. It has been shown that the splitting of the $1e_{1g}$ level depends both on the nature of the heteroatom and on the dihedral angle between the interacting fragments—the $\pi$-electron system of the benzene ring, and the $n$ or $\pi$ orbital of the substituent. Later data were obtained demonstrating the orthogonality of the plane of the benzene ring and the LEP of phosphorus[77], but no stereochemical conclusions were reached in the study by Schäfer and Schweig[59].

The next communication by the same workers[60] contains, in their view, direct proof of the non-aromatic nature of phospholes and arsoles.




(XXI) (XXII) (XXIII) (XXIV) (XXV)

The spectrum of compound (XXI) has two bands (Fig. 6), each of which refers to ionisation from two orbitals of similar energies. The appearance of the first band is interpreted as a result of ionisation from the $a_2(\pi)$ orbital of the cyclopentadiene system and the LEP of phosphorus and the second has been assigned to the $\pi$ orbitals of the phenyl substituent. Owing to hyperconjugation, the methyl substituent in the phosphole fragment increases the energy of the $a_2(\pi)$ cyclopentadiene orbital, because the energies of this orbital and the LEP of phosphorus become different. In the spectrum of the hydrogenated derivative (XXII), the component of the first band corresponding to the ionisation from the $a_2(\pi)$ cyclopentadiene orbital is absent, since the

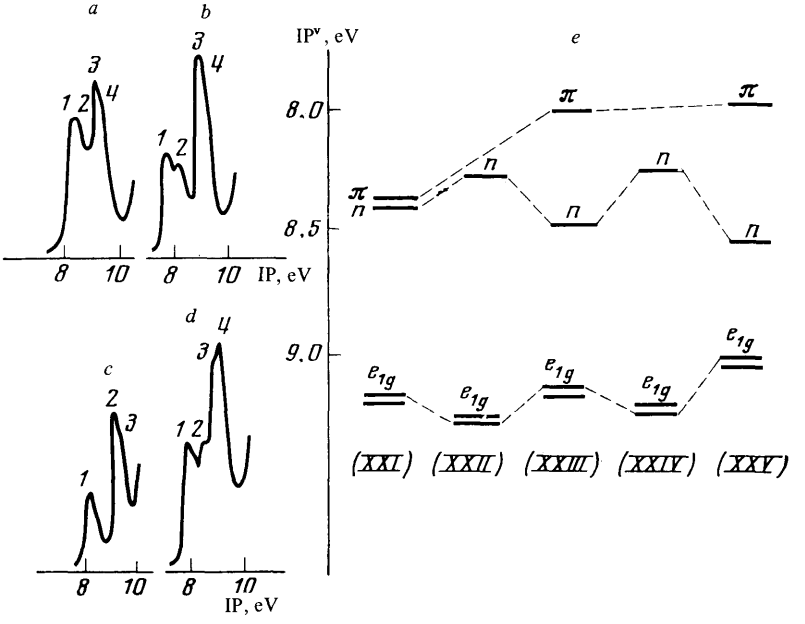



**Figure 6.** Photoelectron spectra of heterocyclic compounds: *a*) (XXI); *b*) (XXIII); *c*) (XXII); *d*) (XXV); *e*) correlation diagram for the ionisation potentials in the (XXI)–(XXV) series[60].

first band of this compound has reduced intensity and refers solely to the LEP of phosphorus. The above facts show that in the ground state the molecule of phosphole (XXI) has three non-conjugated fragments—the $\pi$-electron system of the phenyl substituent, the LEP of the phosphorus atom, and the localised diene system. The authors[59] speak of the non-aromatic nature of phosphole precisely in this sense. According to a calculation by the CNDO/2 method[72], the $C_4H_4NH$ molecule is planar, while the angle between the plane of the cyclopentadiene fragment and the P–H bond in the $C_4H_4PH$ molecule is approximately 90°.

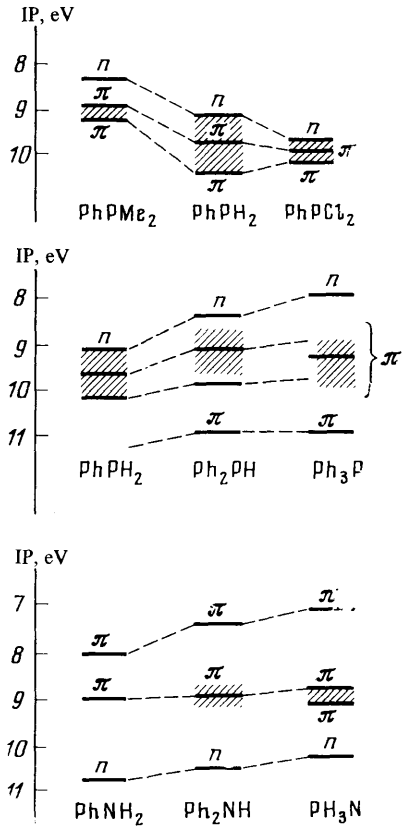



**Figure 7.** Vertical ionisation potentials and band widths (shaded regions) in the photoelectron spectra of phenyl derivatives of Group V elements[61].

Betteridge et al.[53] note the absence of the splitting of the $\pi$ level of the phenyl substituent in dichlorophenylphosphine. They suggest that the first band, with a maximum at 9.7 eV, corresponds to ionisation from three orbitals—two orbitals of the $\pi$ level of the phenyl group and the LEP of phosphorus. However, they do not indicate the absence of interaction between the LEP and the $\pi$-electron system of the phenyl substituent. They postulate that, firstly, the $PCl_2$ substituent is an electron acceptor compared with hydrogen and, secondly, that a substituent of this kind does not lead to the splitting of the upper level of benzene in other instances either. However, the authors do not quote an example confirming this conclusion, while it is known that electron-accepting substituents such as Cl,[4] F,[75] $NO_2$,[78] and CN [79] cause a very significant splitting of this level. Quantitative analysis of the spectra of $PhPCl_2$ on benzene enabled Betteridge et al. to conclude that the first band in the photoelectron spectrum of $PhPCl_2$ is compound. They also quote[53] the photoelectron spectrum of triphenylphosphine, but do not discuss this spectrum or the corresponding band assignments.

Debies and Rabalais[61] quote the photoelectron spectra of a large series of phenyl derivatives of Group V elements (Fig. 7). Thus the first ionisation potentials of phenylphosphines have been interpreted[53,59,60] as the energy required to dislodge an electron from the LEP of phosphorus. This result has been additionally confirmed by comparing the spectra of phenylphosphine and aniline obtained using two radiation sources. Compared with the experiments involving the use of the He(I) line, the use of the radiation of the He(II) line reduces the intensity of the signals due to the electrons dislodged from the 3*s* and 3*p* orbitals of phosphorus to a greater extent than the signal of the electrons dislodged from the 2*s* and 2*p* orbitals of carbon[36]. The employment of He(II) radiation in the case of phenylphosphine reduces the intensity of the shoulder on the band in the region of low energies relative to the central part of the band, which confirms the validity of the assignment of the shoulder to ionisation from the phosphorus *n* orbital and of the central band to the ionisation of the phenyl $\pi$ electrons. The fact that the intensity of the shoulder does not diminish quite as much as in other phosphorus compounds[61] shows that this orbital is delocalised to an even greater extent.

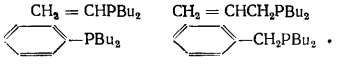
On successive substitution of the hydrogen atoms in phosphine (as well as in arsine and stibine), the intensity of the band corresponding to the phosphorus *n* orbital remains unchanged, while the intensities of the subsequent bands, corresponding to ionisation from the $\pi$ orbitals, increase owing to the increase of the number of $\pi$ electrons. This finding shows that, as in phenylphosphine, in diphenyl- and triphenyl-phosphines the first ionisation potential refers to the phosphorus *n* orbital. On the other hand, in phenylamines there is a change in intensity not in this first band but in one of the subsequent bands in the region of higher ionisation energies.

In contrast to studies[53,59,60] where it was concluded that there is no splitting of the $a_2(\pi)$ and $b_1(\pi)$ components of the $1e_{1g}$ level of benzene in phenylphosphines, the large combined bands were resolved by Debies and Rabalais[61] into their components and the $IP_V$ corresponding to the individual $a_2(\pi)$ and $b_1(\pi)$ orbitals were thus determined (Fig. 7). The splitting obtained in this way is small (0.66 eV in phenylphosphine, while the value in aniline is 1.1 eV) and can probably be partly caused by the inductive influence of the $PH_2$ group. Debies and Rabalais suggest that, in contrast to the stabilisation of the *n* orbital in phenylamines, the destabilisation of the *n* orbital in phenyl-substituted phosphorus, arsenic, and antimony compounds is a consequence of the shift of electron density from the phenyl substituent to the phosphorus, arsenic, or antimony atom via the $d_\pi$–$p_\pi$ mechanism. However, not only in phenylphosphine but also in *NN*-dimethylaniline[59], in phenylhydrazones[74], and in iodobenzene[4], i.e. in all cases where the energy of the initial *n* orbital is higher than that of the $\pi$ orbital, the upper destabilised orbital is predominantly of the *n* type when the orbitals interact (Fig. 8). In contrast to *NN*-dimethylaniline, in aniline itself the energy of

the ground $n$ orbital is below the energy of the $b_1(\pi)$ orbital and the upper orbital is predominantly of the $\pi$ type.

According to Debies and Rabalais[61], the anomalous sequence of the $IP_1^V$ of the compounds $Ph_3X$ (Sb > As > P) compared with the electronegativity series and the atomic ionisation potentials (Sb < As < P) is also a consequence of the involvement of $d$ orbitals in the interaction. It is suggested that the inversion of the sequence of ionisation potentials is caused by the reduced involvement of $d$ orbitals in the interaction when the size of the central atom increases, this being accompanied by a decrease of charge transfer to the central atom and an increase of the ionisation potential of the molecule. However, in the series of trimethyl compounds $Me_3X$ (Table 2), the same anomalous sequence of potentials, caused by the increase of the contribution of the $s$ orbital to the upper occupied $n$ orbital with increased size of the heteroatom and decreased the C–X–C valence angle, is observed.

Additional evidence showing that the interaction between the LEP of phosphorus and the $\pi$-electron system is weak was provided by a study of compounds with the methylene group[64]:




According to calculation by the CNDO/2 method, the most favoured conformation of the above compounds is one where the LEP of phosphorus lies in the plane of the $\pi$-electron system and does not interact with it[64]. The photoelectron spectra of the compounds indicate an appreciable interaction between the $\pi$ orbitals and the P–C bond.

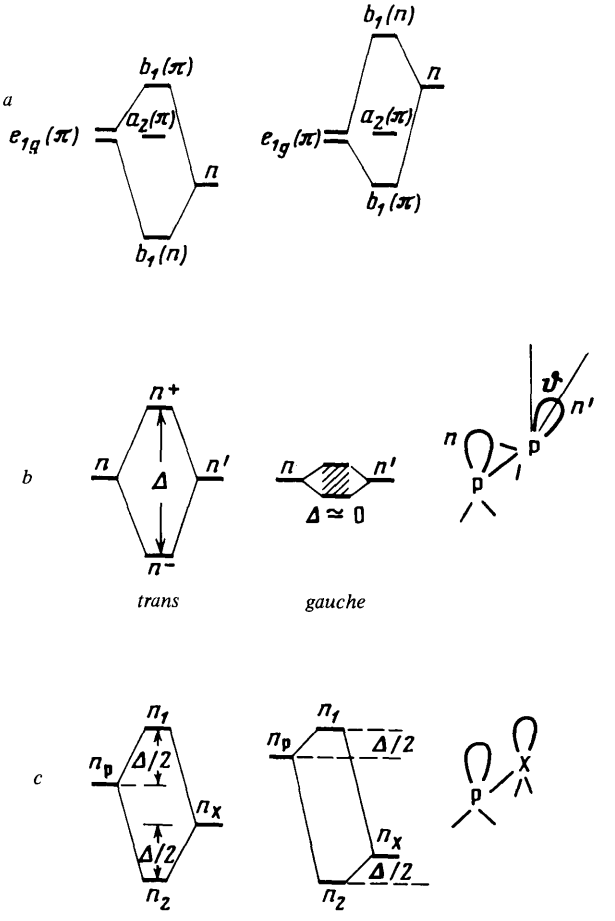
The interaction of the LEP of the phosphorus atom and that of the neighbouring atom X linked to it was also investigated by the PES method. Analysis of the $n$–$n$ interaction is one of the most important achievements of the PES method. The dependence of the $n$–$n$ interaction on stereochemical factors has been investigated in a series of compounds with N–N, O–O, and S–S bonds[16,80,82]. The two equivalent LEP $n$ and $n'$ orbitals interact through space or via a bond and form two semi-localised orbitals (Fig. 8):

$$n^+ = \frac{1}{\sqrt{2}}(n + n') \text{ and } n^- = \frac{1}{\sqrt{2}}(n - n').$$

The difference between $IP(n^+)$ and $IP(n^-)$ characterises the efficiency of the interaction and depends on the disposition of the LEP in space[18,80–82].

The photoelectron spectrum of the compound $F_2PPF_2$ has been obtained[52]. The first ionisation potential of 9.64 eV was assigned to a symmetrical combination ($n^+$) of the LEP of the phosphorus atoms, while the second ionisation potential (12.45 eV) was assigned to their antisymmetrical combination ($n^-$). The observed difference between ionisation potentials $IP_2^V - IP_1^V = 2.81$ eV indicates an extremely effective interaction between the LEP. The energy of the individual LEP in the $F_2PPF_2$ molecule, given by $\frac{1}{2}(IP_1^V + IP_2^V) = 11.04$ eV, proved to be close to the first ionisation potential of $F_2PH$ (11.0 eV), which confirms the above interpretation of the first two ionisation potentials of $F_2PPF_2$.

A lower degree of $n$–$n$ interaction of the LEP of phosphorus in the compounds $Me_2PPMe_2$ and $(CF_3)_2PP(CF_3)_2$ was later reported[56,57]; the manifestation of conformational isomerism was observed in the photoelectron spectra. In the region of low ionisation energies, the photoelectron spectra of these compounds contain three peaks. Two of these, $IP_1^V$ and $IP_3^V$, correspond to the $n^+$ and $n^-$ combinations of the LEP of the *trans*-conformer. The third low-intensity $IP_2^V$ peak indicates the presence of a certain amount of the *gauche*-conformer, for which there is no $n$–$n$ splitting (Table 3). According to the authors, the fact that the average $IP^V$ (LEP) of the *trans*-conformer is somewhat smaller than the corresponding value for the *gauche*-conformer is associated with the slight destabilisation arising when the *trans*-oriented LEP interact. However, we may note that contradictory results, obtained in a study of the conformational isomerism by the PES method[21], have also been published.




*trans* *gauche*

Figure 8. Dependence of the $n$–$\pi$ (*a*) and $n$–$n$ interactions on the relative energies of the initial orbitals: b) for equivalent $n$ orbitals; c) for non-equivalent $n$ orbitals.

For a number of molecules such as those of $(CF_3P)_m$, containing different numbers of phosphorus atoms, the average potentials are correlated with the induction constant (as a consequence of the interaction of the LEP of the phosphorus atoms). This finding indicates an insignificant role of the $d_\pi$–$p_\pi$ interaction in the above molecules[57].

The study of the $n$–$n$ interaction of non-equivalent LEP by the PES method is much more complicated. In this case, the difference between ionisation potentials $IP(n^+) - IP(n^-)$, referring to the $n$ orbitals, does not in any way

characterise the extent of the $n-n$ interaction (Fig. 8). The difference $IP(n^+) - IP(n^-)$ is determined by the difference between the LEP energies before interaction and by the $n-n$ splitting, both quantities being unknown. However, in the $Me_2PCl$ molecule one of the chlorine LEP (of the $a''$ type) is not involved in the interaction with the phosphorus LEP and thus plays the role of an internal standard, which makes it possible to estimate the extent of the $n-n$ interaction between the chlorine LEP ($a'$ type) and the phosphorus LEP.[65] The possibility of the interaction between the LEP of the phosphorus and chlorine atoms in the $PF_2Cl$ molecule was also assumed by Bassett and Lloyd[52], but they postulated that the LEP of the individual atoms in the $F_2POPF_2$ molecule do not interact with one another.

Table 3. The vertical ionisation potentials (eV) and the percentage contents of the conformers[57].

| Compound | Content of conformers, % | $IP^V$(LEP) | $IP^V$(P-P or As-As) | $IP^V$(P-P or As-C) |
|---|---|---|---|---|
| *gauche*-$Me_4P_2$ | 16 | 8.79 | 10.33 | 11.22; 11.83 |
| *trans*-$Me_4P_2$ | 84 | 7.88; 9.54 | 10.33 | 11.22; 11.83 |
| *gauche*-$Me_4As_2$ | 12 | 8.85 | 9.82 | 10.60; 11.21 |
| *trans*-$Me_4As_2$ | 88 | 7.91; 9.50 | 9.82 | 10.60; 11.21 |
| *gauche*-$(CF_3)_4P_2$ | 10 | 11.57 | 13.09 | 13.49 |
| *trans*-$(CF_3)_4P$ | 90 | 10.71; 12.11 | 13.09 | 13.49 |
| *trans*-$(CF_3)_4As_2$ | 100 | 10.39; 11.94 | 12.07 | 12.58 |

Dewar and coworkers[56] compared the photoelectron spectra of a number of compounds with the P–N bond: $(Me_2N)_mPF_{5-m}$ and $(Me_2N)_mPF_{3-m}$. The spectra were interpreted in terms of the $n$ approximation. In all cases, $IP_1$ was assigned to ionisation from the LEP of nitrogen (Table 4). If the interpretation of $IP^V$ given below is adopted, it is found that the substitution of the ethyl group at the nitrogen atom by a methyl group has a considerable influence on the phosphorus LEP[65]:

| Compound | LEP, N | LEP, P |
|---|---|---|
| $Et_2NPF_2$ | 9.45 | 10.25 |
| $Me_2NPF_2$ | 9.60 | 10.50 |

It is suggested that this is caused by a change in the valence and torsional angles. The hypothesis of the $n-n$ interaction, described by the difference $IP(n,P)-IP(n,N)$, has been used to explain the change in the torsional energy barrier to rotation about the P–N bond, which is anomalous in relation to the degree of steric hindrance[66].

Compounds of three-coordinated phosphorus $PX_3$, containing equivalent groups X = halogen, OR, $NR_2$, etc., are convenient for the investigation of the relation between PES data and the stereochemistry of the molecule. If the molecular symmetry is $C_2$ or $C_{3v}$, then the upper occupied orbitals should include degenerate orbitals of the $e$ type. The bands corresponding to these orbitals in the photoelectron spectrum should have approximately doubled intensities or should undergo spin-orbital or Jahn–Teller splitting[55,77]. When the molecule has a lower symmetry, the $e$ levels are absent under these conditions.

$P(Hal)_3$ molecules have the $C_{3v}$ symmetry and their photoelectron spectra have been interpreted in terms of ideas of this group of workers[53,55]. The first ionisation potentials are associated with ionisation from the non-bonded $a_1$, $a_2$, and $e$ orbitals. The $a_1$ orbital is preferentially localised at the phosphorus atom, while the $a_2$ and $e$ orbitals arise as a result of the interaction of the three equivalent LEP of the halogens. The band corresponding to the $e$ orbital in the spectra of $PBr_3$ and $PI_3$ undergoes spin–orbital splitting[54].

Table 4. The vertical ionisation potentials (eV) of the LEP of nitrogen [N(2$p$)] and phosphorus [P(3$p$)].

| Compound | N (2$p$) | P (3$p$) |
|---|---|---|
| $Me_2NPF_4$ | 10.35 | — |
| $(Me_2N)_2PF_3$ | 8.84; 9.95 | — |
| $(Me_2N)_3PF_2$ | 8.04; 9.03; 9.31 | — |
| $(Me_2N)PF_2$ | 9.58 | 10.48 |
| $(Me_2N)_2PF$ | 8.18; 9.14 | 10.40 |
| $(Me_2N)_3P$ | 7.61; 7.89; 8.86 | 9.98 |

Table 5. The ionisation potentials of $P(OMe)_3$, the band intensities $I$ (arbitrary units), and band assignments[53].

| $IP^V_m$, eV | $I$ | Orbital symmetry | Localisation region |
|---|---|---|---|
| 9.0 | 1 | $a$ | LEP, P |
| 10.6 | 2 | $e$ | LEP, O |
| 11.1 | 4 | $a+e+a$ | LEP, O + C–O, $\sigma$ |
| 12.4 | 2 | $e$ | P—O, $\sigma$ |
| 13.0 | 1 | $a$ | P—O, $\sigma$ |

In their interpretation of the photoelectron spectrum of $P(OMe)_3$, Betteridge et al. used data for the ionisation potentials of methanol[53]: 11.0 eV (LEP, O); 12.7 eV (C–O, $\sigma$); 15.0 eV ($CH_3$). The $C_{3v}$ symmetry was adopted for the $P(OMe)_3$ molecule and the molecular orbitals were represented by a combination of the LEP of phosphorus, the three equivalent LEP of oxygen, the C–O $\sigma$ bonds, etc. Accordingly a band corresponding to the ionisation of the LEP of phosphorus, two bands with the 1 : 2 intensity ratio associated with the $a$ and $e$ orbitals produced as a result of the $n-n$ interaction of the three LEP of the oxygen atoms ($n_O$), two bands with an intensity ratio of 1 : 2 associated with the $a$ and $e$ orbitals of the three C–O $\sigma$ bonds, etc. should accordingly be expected in the $P(OMe)_3$ spectrum. The interpretation of the photoelectron spectrum of $P(OMe)_3$ obtained in this way is illustrated in Table 5. We believe that the interpretation of this spectrum (Fig. 9) corresponds to the $C_3$ and not the $C_{3v}$ symmetry type. For the $C_3$ symmetry, where the LEP of oxygen does not undergo $\pi$-type overlapping, the degenerate $e(n_O)$ orbital should in fact be the second from above.

The mechanisms of the $n-n$ interactions of the LEP of phosphorus ($n_P$), oxygen ($n_O$), and nitrogen ($n_N$) atoms are examined in Figs. 9 and 10. In the case of $\sigma$-type overlapping[83], where the LEP ($n_X$) axes of the $X_3$ atoms are located in the $X_3$ plane, the energy of the semilocalised $e(n_X)$ orbital is also smaller than that of the $a(n_X)$ orbital. For the $\pi$-type overlapping of the LEP ($n_X$), the opposite relative positions of the $a(n_X)$ and $e(n_X)$ levels are obtained. In contrast to the $\pi$ approximation, the $n$ approximation, i.e. consideration of $n$ electrons independently of the $\sigma$ framework, is less justified[13]. The overlap integrals of the $n_X$ orbitals in the compounds $PX_3$ are small and $n-\sigma$ mixing can therefore exceed the degree of the $n-n$ interaction, leading to a different sequence of orbitals in the molecule.

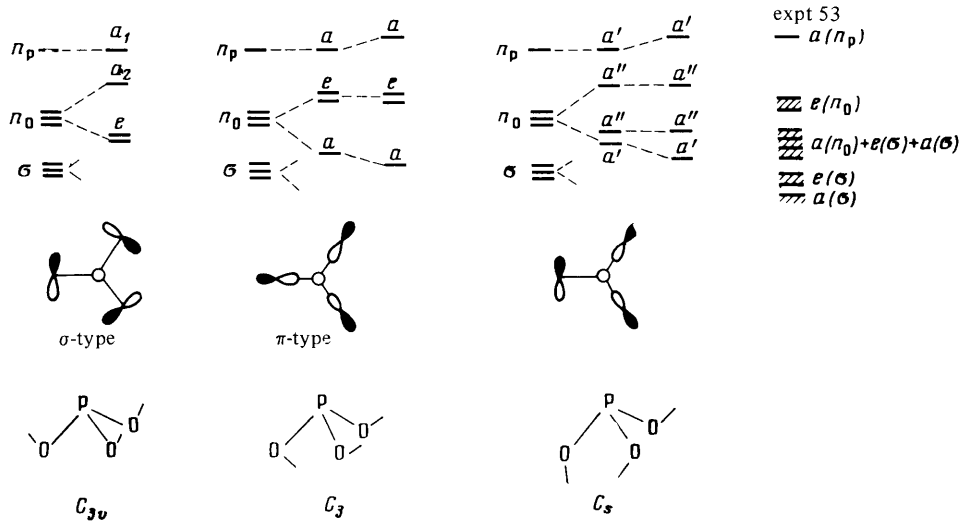



Figure 9. Schematic illustration of the $n$–$n$ interaction of the LEP of the oxygen ($n_O$) and phosphorus ($n_P$) atoms.

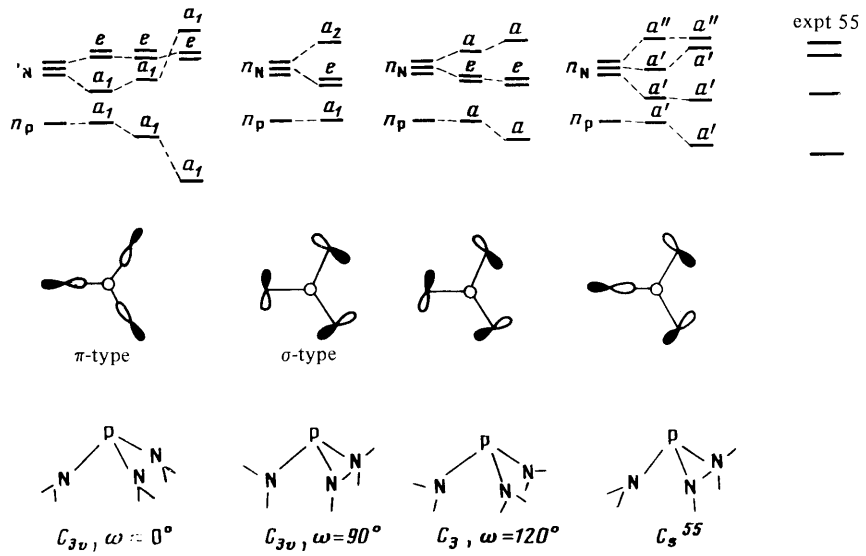



Figure 10. Schematic illustration of the $n$–$n$ interaction of the LEP of the nitrogen ($n_N$) and phosphorus ($n_P$) atoms.

Fig. 11 illustrates a correlation diagram for the $P(OH)_3$ and $P(OMe)_3$ orbital energies calculated by the CNDO/2 method[84]; the geometrical parameters were taken from Naumov and coworkers[85]. The orbital sequence obtained differs from the sequence which may be predicted in terms of the $n$ approximation (Fig. 9). The energies of the orbitals of the model compound $P(OH)_3$ reproduce in the same way the photoelectron spectrum of $P(OMe)_3$ for structures with $C_3$ and $C_S$ symmetries (Fig. 11). The intense bands with maxima at 10.6 and 11.1 eV are extremely broad and may be due to a superposition of close overlapping bands. We believe that calculations on $P(OMe)_3$ assuming the $C_S$ symmetry gives the best agreement with experiment. In the case of the $C_3$ symmetry, the two neighbouring $e$-type orbitals might have given rise to individual bands. The total energies of the structures with the $C_3$ and $C_S$ symmetries of the model compound $P(OH)_3$ proved to be similar, but the $P(OMe)_3$ structure with the $C_S$ symmetry is energetically more satisfactory. Naumov and coworkers[85] also quote qualitative evidence in support of the $C_S$ symmetry in $P(OMe)_3$ based on electron diffraction.

According to Cowley et al.,[55] the $C_S$ symmetry of the $P(NMe_2)_3$ molecule obtained by Vilkov[86] conflicts with the photoelectron spectrum of the molecule. Experimental data show that the upper occupied orbitals have similar energies, while in the case of the $C_3$ symmetry the degenerate orbital is the second highest (Fig. 10). Cowley et al.[55] proposed the $C_S$ symmetry for $P(NMe_2)_3$. In this

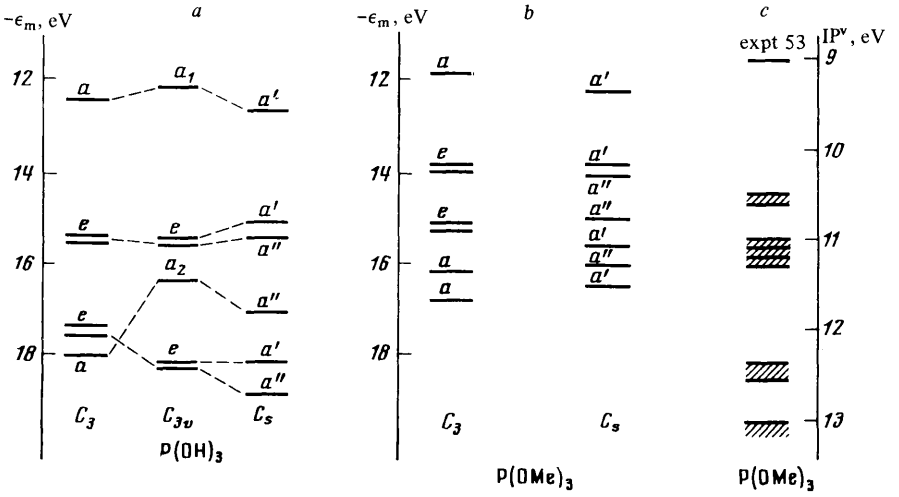



**Figure 11.** Theoretical dependence of the energies of P(OH)$_3$ (*a*) and P(OMe)$_3$ (*b*) on the steric structure of the molecules (CNDO/2 method) together with experimental data[53] (*c*).

case $IP_1$ and $IP_3$ correspond to the $n^+$ and $n^-$ combinations of the nitrogen LEP involved in σ-type overlapping, while $IP_2$ and $IP_4$ correspond to the same combinations of the phosphorus and nitrogen LEP (Fig. 10). It is suggested that the structure with the $C_S$ symmetry is stabilised owing to the smaller degree of the Coulombic repulsion of the LEP.

The compound B(NMe$_2$)$_3$, which has a similar structure, had been investigated previously by Bock and Fuss[87]. In conformity with the π-type overlapping, the second band corresponds to an *e*-type orbital ($C_3$ symmetry). The smaller difference $IP_2^V - IP_1^V$ for B(NMe$_2$)$_3$ (1.62 eV) compared with its cyclic analogue (2.2 eV) was explained by the propeller rotation of the amino-group about the B–N bond ($\omega = 33°$). In contrast to aminoborines, the $n-\sigma$ mixing and the Jahn–Teller splitting of the *e* orbital were resorted to in order to explain the photoelectron spectra of cyclohexane hetero-derivatives on the basis of $C_3$ symmetry[82].

## IV. COMPOUNDS OF FOUR-COORDINATED PHOSPHORUS

The most systematic studies on the photoelectron spectra of compounds in the series WPXYZ for W = O or S have been carried out by Vovna, Vilesov, and coworkers[58, 88–93]. The spectra of individual compounds were also obtained by other workers[37,53,71] and Bock's group studied the interaction between $X_3P$ and $BH_3$ as well as the photoelectron spectra of ylids[68,94]. The PES[58] method has been used to analyse the intramolecular interactions in compounds of four-coordinated phosphorus. Calculation by the CNDO/2 method[95] reproduces satisfactorily the changes in the ionisation potentials of the compounds WPXYZ. Thus the values of $IP_1^V$ for the compounds OPF$_3$ and OPMe$_3$ are 13.52 and 9.76 eV,[68] while the calculated values ($-\epsilon_1$) are 18.84 and 14.18 eV respectively.

The form of the photoelectron spectra of the compounds WPXYZ resembles that of the spectra of the corresponding tervalent phosphorus compounds PXYZ, but there are also significant differences (Fig. 12). The formation of the WP bonds leads to the disappearance of the band due to the ionisation of the phosphorus LEP ($n_P$) orbital. The band corresponding to the ionisation of the four $p_\pi$ electrons of W as well as a band (in the region of high ionisation energies) corresponding to the $\sigma_{PW}$ orbital of the newly formed W–P bond appear in the WPXYZ spectra. The remainder of the spectrum, characterising the ionisation of electrons from orbitals localised preferentially at the X, Y, and Z atoms, remains unchanged, being displaced towards higher ionisation energies in conformity with the electronegativity of the WP group. The first ionisation potential characterises the energy of the binding of the $p_\pi$ electrons of the W atom and the series of subsequent potentials is related to the ionisation of the LEP of the substituents. Thus, according to Zverev et al.,[58] the formation of the $\dot{O}PCl(OEt)_2$, $OPCl(\dot{O}Et)_2$, and $OP\dot{C}l(OEt)_2$ radical-cations from the OPCl(OEt)$_2$ molecule requires energies of 10.96, 11.50, and 12.28 eV respectively. In certain compounds with a P–N bond, the nitrogen atom exhibits the greatest electron-donating capacity and the first ionisation potential is determined by the nitrogen LEP. Comparison of the energies of the $n_P$, $p_{\pi,W}$, and $\sigma_{PW}$ orbitals characterises the degree of charge transfer and the amount of double-bond character of the WP linkage. The stabilisation of the $\sigma_{PW}$ orbital compared with the $n_P$ orbital indicates charge transfer from the P atom to W, while the energy of the $p_{\pi,W}$ orbital may be a measure of the reverse transfer and the amount of double bond character[68].

The band appearing on formation of the W=P bond in the region of low ionisation energies and determining the values of $IP_1$ of a large number of compounds (Table 6) is fairly characteristic of this class of compounds. In the spectra of the compounds $WPX_3$, belonging to the $C_{3v}$ or $C_3$ symmetry group, this band arises on ionisation from a degenerate *e*-type orbital localised preferentially on the $p_\pi(p_x, p_y)$ orbitals of the W atom. The broad shape of the band contour indicates the involvement of the $p_{\pi,W}$ orbital in the bonding between W and P atoms. It has been suggested on the basis of a comparison with calculations[37, 52,71,96] that this orbital is involved in $p_{\pi,W} - p_{\pi,P}$ and $p_{\pi,W} - d_{\pi,P}$ interactions. The fact that in the spectra of molecules of the type WPXYZ the band is not split into two

components is regarded as evidence for the insignificant delocalisation of the orbital over the XYZ group of atoms.

Following Zverev et al.,[58] we shall examine a series of additional factors characterising the $e(p_\pi)$ orbital of the W=P bond. In the compounds $WPX_3$ (X = Cl, Br, or OEt), the LEP of the substituents $X_3$ give rise to two semilocalised orbitals $a_2(n_X)$ and $e(n_X)$. A change in the inductive influence of the W atom should cause the same shifts of the energies of these orbitals, while conjugation, leading to mixing of the $e(n_X)$ orbital with other $e$-type orbitals, can alter the difference between the energies of the $a_2(n_X)$ and $e(n_X)$ orbitals. Experimental data (Table 7) show that in the $PCl_3$ molecule this difference is smaller (0.3 eV) than in the $OPCl_3$ (0.63 eV) and $SPCl_3$ (0.59 eV) molecules, i.e. in these molecules the $e(n_X)$ orbital interacts more effectively with $e$-type orbitals: the occupied $e(p_\pi)$ orbital or the vacant $e(d_\pi)$ orbital. However the interaction between the $e(n_X)$ and $e(p_\pi)$ orbitals cannot be significant, because the difference between the energies of the $a_2(n_X)$ and $e(n_X)$ orbitals remains constant for the compounds $OPX_3$ and $SPX_3$, despite the significant difference between the energies of the $e(p_\pi,S)$ and $e(p_\pi,O)$ orbitals[58].

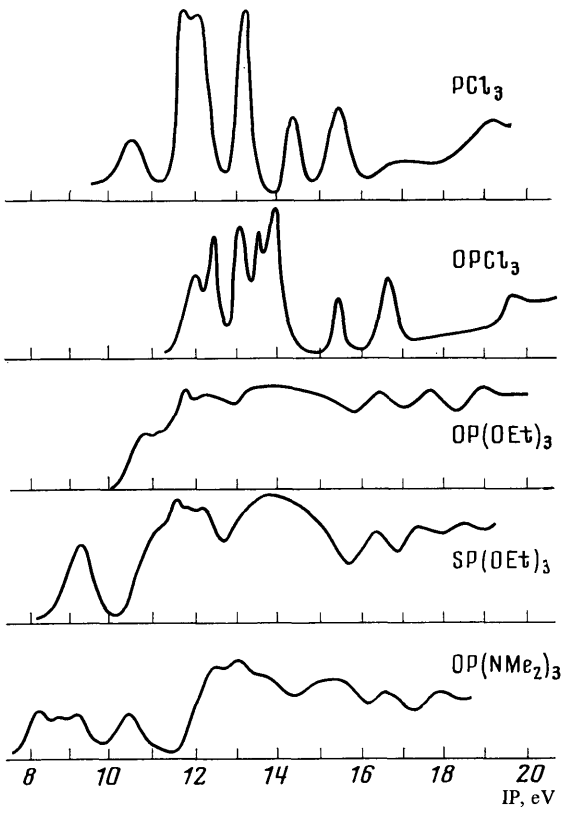



**Figure 12.** Photoelectron spectra of certain compounds of the type WPXYZ[58,90,91].

In contrast to the $WPX_3$ molecules under consideration, a number of data for the compound $OP(NMe_2)_3$ indicate the mixing of the $p_\pi,O$ orbital with the nitrogen $n$ orbitals. This mixing of the orbitals greatly reduces the ionisation potentials of the $n$ orbitals and increases the ionisation energy of the $p_\pi,O$ orbital. The dependence of the ionisation potentials corresponding to ionisation from the $p_\pi,W$ orbital on the constants $\sigma^*$ and $\sigma^{ph}$ has been examined[58]. The nitrogen-containing molecules of the phosphoryl series constitute a special group; owing to mixing with the nitrogen $n$ orbitals, the ionisation potentials corresponding to ionisation from the $p_\pi,O$ orbital in such compounds are larger than in the case where account is taken of the inductive influence alone.

**Table 6.** The vertical ionisation potentials of the compounds SPXYZ and OPXYZ referring to the $p_\pi$ orbital of the W=P bond[37,58,68,89-91].

| XYZ | $IP_1^V$ | XYZ | $IP_m^V$ |
|---|---|---|---|
| SPXYZ * | | OPXYZ * | |
| $Cl_3$ | 10.15 | $Cl_3$ | 11.91 |
| $Cl_2(OEt)$ | 9.81 | $Cl_2OEt$ | 11.46 |
| $Cl(OEt)_2$ | 9.41 | $Cl(OEt)_2$ | 10.96 |
| $(OEt)_3$ | 8.96 | $(OEt)_3$ | 10.54 |
| $Cl_2Ph$ | 9.47 | $(OMe)_3$ | 10.81 |
| $Cl_2NMe_2$ | 9.35 | $Cl(OPr)_2$ | 10.89 |
| $Cl(NMe_2)_2$ | 8.75 | $Cl_2OPh$ | 11.40 |
| $(NMe_2)_3$ | 8.05 | $Cl(CH_2Cl)_2$ | 10.75 |
| $Br_3$ | 9.89 | $(OEt)(CH_2Cl)_2$ | 10.19 |
| $Cl(CH_2Cl)_2$ | 9.54 | $Cl_2Me$ | 11.49 |
| $(OBu)_3$ | 8.28 | $Br_3$ | 11.07 |
| $Et_2OPr$ | 8.55 | $Cl_2(NMe_2)$ | 11.28 |
| $Me_3$ | 8.53 | $Cl(NMe_2)_2$ | 10.90 |
| | | $(NMe_2)_3$ | 10.44 |
| | | $(OEt)_2NHNH_2$ | 10.90 |
| | | $(Me)_3$ | 9.76 |
| | | $F_3$ | 13.52 |

*The values of $IP_1^V$ are quoted for SPXYZ.
**$IP_3^V$ for XYZ = $Cl_2OPh$, $Cl(NMe_2)_2$, or $(OEt)_2NHNH_2$, $IP_2^V$ for XYZ = $Cl_2NMe_2$, $IP_4^V$ for XYZ = $(NMe_2)_3$, and $IP_1^V$ in the remaining cases.

**Table 7.** Energies of ionisation from $a$- and $e$-type orbitals and the differences between them (eV).

| Orbital | $SP(OEt)_3$ | $OP(OEt)_3$ | $SPCl_3$ | $OPCl_3$ | Orbital | $PCl_3$ |
|---|---|---|---|---|---|---|
| $1e$ | 8.96 | 10.54 | 10.15 | 11.91 | $1a_1$ | 10.53 |
| $1a_2$ | 10.73 | 10.96 | 12.03 | 12.37 | $1a_2$ | 11.73 |
| $2e$ | 11.43 | 11.56 | 12.62 | 13.00 | $1e$ | 12.03 |
| $2e-1a_2$ | 0.70 | 0.60 | 0.59 | 0.63 | $1e-1a_2$ | 0.30 |
| $2e-1e$ | 2.47 | 1.02 | 2.49 | 1.15 | | |

Direct experimental evidence for the delocalisation of the $p_\pi,O$ orbital in the direction of the atoms of the substituents is provided by the photoelectron spectrum of $OPBr_3$.[37] In this compound, spin–orbital splitting of the highest occupied $e$ orbital by the atoms of the substituents is observed, which indicates its delocalisation over the $Br_3$ atoms.

Comparison of the values of $-\Delta G^\circ$ for the formation of the complexes XYZPO...$I_2$ [97] with the ionisation potentials of the compounds XYZPO confirms the interpretation of the $OP(NMe_2)_3$ spectrum and the scheme describing the mixing of the $p_\pi,O$ and $n_N$ orbitals (Fig. 13). $-\Delta G^\circ$ for the compound $OP(NMe_2)_3$ is correlated with a potential intermediate between $IP_4^V$ and $IP_3^V$. $IP_4^V$ refers to the $p_\pi,O$ orbital, but is increased owing to the $p_\pi - n_N$ interaction. A similar effect is manifested also for $OPCl(NMe_2)_2$. In contrast to a series of compounds of the type XYZPO, in

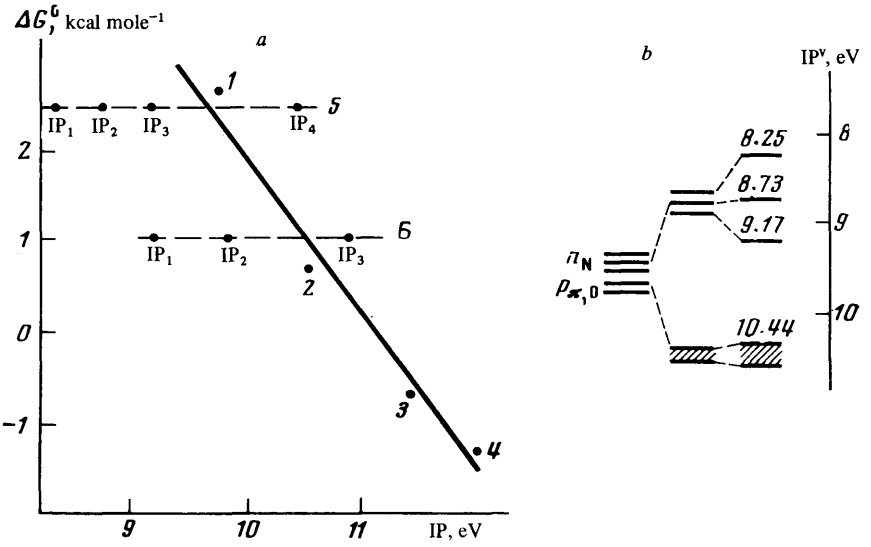



**Figure 13.** Dependence of $-\Delta G^\circ$ for the formation of complexes of the compounds XYZPO with $I_2$ (Paetzold and Niendorf[97]) on $IP_I^V$ for different compounds (*a*) [1) $Me_3PO$; 2) $(EtO)_3PO$; 3) $(EtO)Cl_2PO$; 4) $Cl_3PO$; 5) $(Me_2N)_3PO$; 6) $(Me_2N)_2ClPO$ (the values of several $IP_m^V$ are indicated for compounds *5* and *6*)] and schematic illustration of the interaction between the orbitals of compound *5* (*b*).

the compounds SPXYZ investigated, the energy of the $p\pi$,S orbitals is characterised in all cases by the potential $IP_I^V$. Hence the following relation has been found to hold[92]:

$$-\Delta G^0 = -2.7\ IP_I^V + 25.7.$$

We may note that in the series of dihexylphenylphosphines[69] a linear relation has been observed, as in the compounds WPXYZ, between $pK_a$ characterising the basicity in solution and IP(LEP) of phosphorus:

$$pK_a = -4.8\ IP_n^V + 42.2.$$

**Table 8.** The ionisation potentials of the LEP of the XYZ ligands in the compounds OPXYZ and SPXYZ and their assignments.

| XYZ | IP(LEP), eV | | Assignment |
|---|---|---|---|
| OPXYZ | | SPXYZ | |
| $Cl(OEt)_2$ | 12.28 | 12.00 | LEP, Cl |
| $Cl(CH_2Cl)_2$ | 12.69 | 12.33 | LEP, Cl |
| $Cl_m(OEt)_{3-m}$ | 12.13 | 11.83 | $LEP_{av}$, XYZ |
| $Br_3$ | 11.70 | 11.18 | $LEP_{av}$, $Br_3$ |
| $Cl_2(OEt)$ | 11.89 | 11.59 | LEP, O |
| $Cl_2(NMe_2)$ | 9.87 | 9.92 | LEP, N |

Comparison of the ionisation potentials for the LEP of the substituents X, Y, and Z (both the individual values of $IP_m^V$ and the values averaged with respect to the *n* orbitals) makes it possible to consider the problem of the effective electronegativity of the WP groups. The ionisation potentials $IP_{n_X}$ of the LEP (X = Cl, Br, or OEt) form the sequence $IP_{n_X}(OP) > IP_{n_X}(SP) > IP_{n_X}(P)$, i.e. the effective electronegativity increases in the sequence OP > SP > P. The OP group thus exhibits the greatest electron-accepting influence (Table 8).

**Table 9.** Certain ionisation potentials and NQR frequencies[99] of the compounds OPXYZ and SPXYZ.

| XYZ | OPXYZ | SPXYZ | Assignment of potential |
|---|---|---|---|
| | $IP^V$, eV | | |
| $Cl_2OEt$ | 11.89 | 11.59 | LEP, O |
| $Cl(OEt)_2$ | 11.65 | 11.37 | LEP, O |
| $(OEt)_3$ | 11.36 | 11.20 | $LEP_{av}$, O |
| $Cl_2N(Me)_2$ | 9.87 | 9.92 | LEP, N |
| $Cl(NMe_2)_2$ | 9.31 | 9.62 | LEP, N |
| $(NMe_2)_3$ | 8.72 | 9.13 | $LEP_{av}$, N |
| | $\nu_{P-Cl}$, MHz | | |
| $Cl_3$ | 28.950 | 29.735 | |
| $Cl_2Ph$ | 26.635 | 27.840 | |

The above sequence is infringed by the ionisation potentials of the orbitals localised preferentially at the LEP of nitrogen, which form the sequence SP > OP > P (Tables 8 and 9). For example, in the compounds $WP(NMe_2)_3$ the average ionisation potentials of the nitrogen LEP form the sequence 9.13 (SP) > 8.72 (OP) > 8.12 (P). The additional decrease (compared with the inductive influence of the OP group) of the potentials of the nitrogen LEP is due to the resonance interaction of the $p\pi$,O orbitals and the nitrogen *n* orbitals. It is of interest that comparison of both $^{35}Cl$ and $^{14}N$ NQR frequencies yields the same sequence of the effective electronegativities of the groups: SP > OP > P.[98]

Comparison of the ionisation potentials of the LEP of the substituents also makes it possible to examine the role of the W atom in the transmission of the electronic effect of substituents via the WP group (Tables 8 and 9). In the

compounds OPXYZ, the range of variation of the ionisation potentials of the LEP of the OEt or $NMe_2$ group is greater after substitution by chlorine atoms than in the SPXYZ series. In view of its more pronounced electron-accepting properties and greater amount of double bond character, the OP group is apparently a better transmitter of the influence of the X atom in the X–PO–$Y_2$ molecule on the ionisation potentials of the LEP of the $Y_2$ group. The corresponding effects are also shown when the NQR frequencies are compared (Table 9) and in kinetic measurements[100].

We shall next consider the photoelectron spectra and the structures of individual compounds. The compound $SPCl_2Ph$ gives rise to a well resolved spectrum, which makes it possible to determine 14 ionisation potentials[89]. The first ionisation potential (9.47 eV) is due to the $3p_\pi$ electrons of sulphur and the next (9.93 eV) was assigned to the unsplit ($a_2 + b_1$) $\pi$ orbitals of the phenyl group. Thus the addition of the phenyl group to a four-coordinated phosphorus atom, like the addition to a three-coordinated phosphorus atom, does not split the upper $\pi$ level of benzene. According to Vovna et al.,[89] the absence of splitting shows that the $SPCl_2$ substituent exhibits only an inductive influence. Vilkov's electron diffraction data[101] showed that the benzene ring in the compound $OPCl_2Ph$ lies in the plane of the OPC atoms. The mutual orthogonality of the two $\pi$-electron systems (Ph and SP) is apparently the cause of the absence of splitting.

The $OP(OMe)_3$ and $OP(OEt)_3$ spectra obtained by Vovna et al.[91] were interpreted on the assumption that the molecules have $C_{3v}$ symmetry. The three equivalent LEP of the oxygen atom give rise to two semilocalised orbitals of the $a_2$ and $e$ types. Although the photoelectron spectra of these compounds, like that of $SP(OEt)_3$,[90] are poorly resolved, it is possible to establish that the $e$-type orbital lies below the $a_2$ orbital. In terms of the $n$ approximation, this implies $\sigma$-type overlapping of the oxygen LEP (Fig. 9).

However, according to electron diffraction data[102], the compound $OP(OMe)_3$ exists as a mixture of two conformers with $C_3$ symmetry. The calculated energies of the upper levels in the compounds $WP(OR)_3$, like those in $P(OMe)_3$ (Fig. 11), change little when the steric orientation of the methyl groups is varied. Furthermore, the inversion of the relative positions of the $a_2$- and $e$-type levels formed by the oxygen LEP in the compounds $P(OMe)_3$ and $OP(OMe)_3$ is striking: the $e$-type orbital in $P(OMe)_3$ lie above the $a$ orbital[53], while the opposite situation obtains in $OP(OMe)_3$. It is difficult to say whether this is due to experimental error or is a consequence of molecular structure. There is no inversion in the compounds $PHal_3$ and $WPHal_3$.

The spectra of $P(NMe_2)_3$ and $OP(NMe_2)_3$ in the region of the ionisation of the nitrogen LEP contain three peaks of approximately equal intensities (Fig. 12). If the molecules had a threefold symmetry axis, one would expect the presence in the spectrum of two peaks and not three, with an intensity ratio of 1 : 2. The cause of the absence of the spectroscopic manifestation of the $e$ level was not discussed by Vovna and coworkers[89,91], but Betteridge et al., who also obtained the photoelectron spectrum of $OP(NMe_2)_3$, put forward three hypotheses[53]. Firstly, the observed photoelectron spectrum may be a result of a superposition of several spectra, secondly the P–N $\sigma$ orbitals may also have low ionisation potentials, and finally, the molecule does not have the $C_{3v}$ symmetry. The authors themselves are inclined to accept the last hypothesis.

The compound $OP(NH_2)_3$ was investigated by X-ray diffraction[103] and it was shown that the positions of the nitrogen atoms deviate appreciably from the $C_{3v}$ symmetry. The O–P–N valence angles differ by 10°. Such appreciable infringement of the $C_{3v}$ symmetry may, however, be a consequence of the formation of intermolecular hydrogen bonds in the crystalline state, while in the gas phase the molecule may have a different structure. Fig. 14 presents a diagram of the $OP(NH_2)_3$ levels, calculated by the CNDO/2 method taking into account $d$ orbitals. In all the versions, the positions of the nitrogen atoms are the same and correspond to the $C_{3v}$ symmetry. Fig. 14 shows that even a change in the positions of two hydrogen atoms causes a significant alteration in the relative positions of the levels. The $e$-type orbital, localised preferentially at the nitrogen atoms should be split on reduction of symmetry to $C_s$ into widely separated $a'$ and $a''$ orbitals, in agreement with experiment. Such a marked dependence of the energies of the orbitals on the configuration of the atoms (in contrast to the data in Fig. 11) is apparently a consequence of the greater delocalisation of the nitrogen LEP compared with the oxygen LEP.

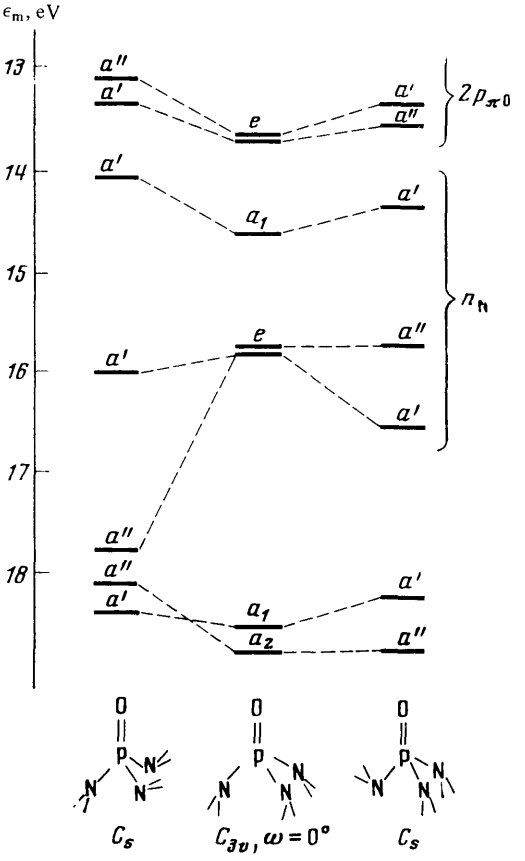



**Figure 14.** Theoretical dependence of the energy of the $OP(NH_2)_3$ orbitals on structure (calculation by the CNDO/2 method).

Like other phosphorus ylids, the compound $Me_3P{=}CH_2$ has a low ionisation potential, which indicates the accumulation of a large negative charge on the carbon atom of the $CH_2$ group, which has been confirmed by CNDO/2 calculations. The only band in the region of low ionisation energies, determining the first ionisation potential, arises in

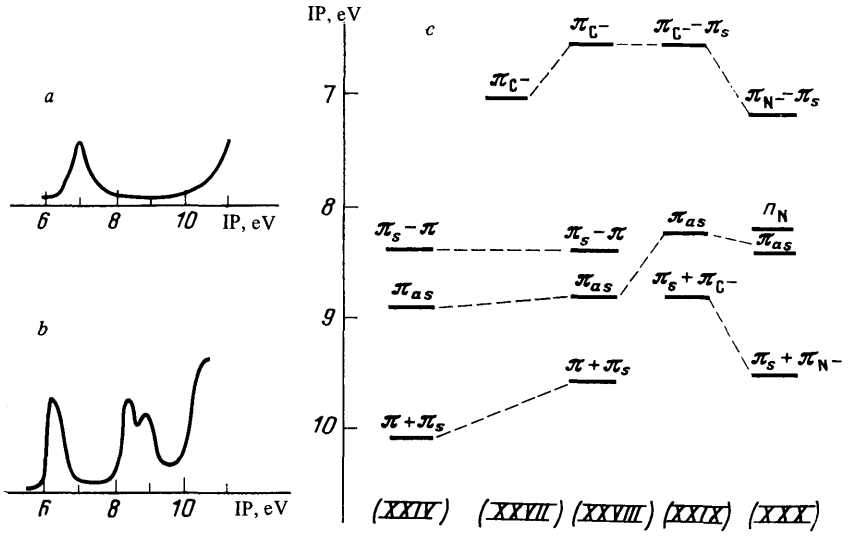



**Figure 15.** Photoelectron spectra: *a*) compound (XXVII); *b*) compound (XXIX); *c*) $IP_m^v$ correlation diagram for compounds (XXVI)–(XXX).[94]

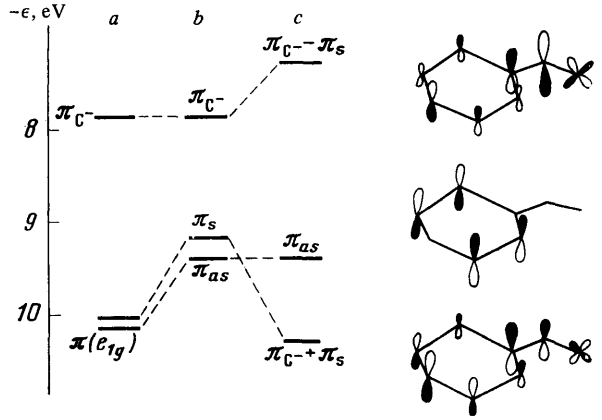
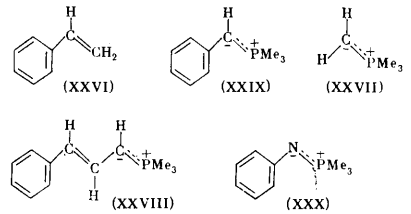



**Figure 16.** Analysis by the CNDO/2 method of the electronic structure of compound (XXIX); orbital energies of compounds (XXVII) and benzene (*a*) and compound (XXIX) allowing for Coulombic interaction but not for the conjugation of the ylid and phenyl fragments (*b*) and taking into account both forms of interaction (*c*).[94,104]

the $Me_3P{=}CH_2$ spectrum following ionisation from the "carbanionic" $\pi_{C^-}$ orbital, which is localised preferentially at the carbon atom of the $CH_2$ group[94] (Fig. 15).




Two additional bands, due to ionisation from orbitals localised preferentially in the phenyl substituent, appear in the $Me_3P{=}CHPh$ spectrum. The first is the $\pi_{as}(a_2)$ benzene orbital, which does not interact with the "carbanionic" $\pi_{C^-}$ orbital by virtue of symmetry, and the second characterises the energy of the mixed $\pi_S + \pi_{C^-}$ orbital, where $\pi_S$ is the symmetrical $\pi(b_1)$ orbital. The first ionisation potential is determined by the energy of the $\pi_{C^-} - \pi_S$ orbital (Fig. 15). The experimentally observed splitting of the energies of the $\pi_{as}$ and $\pi_S + \pi_{C^-}$ orbitals, which is particularly pronounced in $Me_3P{=}NPh$, indicates the conjugation of the "carbanionic" centre with the phenyl substituent.

It is remarkable that the energy of ionisation from the $\pi_{as}$ orbital as well as from the $\pi_S + \pi_{C^-}$ orbital is smaller than the ionisation potential of benzene, which shows that not only $IP_1$ but also the ionisation energies corresponding to the removal of electrons from orbitals localised preferentially in the phenyl substituent decrease under the influence of the field of the negative charge of the "carbanionic" centre. CNDO/2 calculations (Fig. 16), carried out by Ostoja Starzewski et al.,[104] reveal clearly the successive influence of the field and conjugation on the energies of the upper occupied orbitals.

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The photoelectron spectra of compounds of two-, three-, and four-coordinated phosphorus were examined above. The information obtained about the electronic structures of these molecules in the gas phase is extensive and has been interpreted fairly unambiguously; it demonstrates the fruitfulness of the application of the PES method to the chemistry of organophosphorus compounds, the centenary of the birthday of one of the founders of which, Academician A. E. Arbuzov, has been celebrated by the scientific community of the USSR.

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# The Kerr Effect and the Structure of Organophosphorus Compounds

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The results of research on the steric and electronic structures of organophosphorus compounds with the aid of the Kerr effect and the combined employment of the Kerr effect and other physical methods (dipole moments, depolarisation of Rayleigh light scattering, spectroscopic methods) are surveyed. The additive refractions, polarities and polarisabilities of phosphorus bonds are analysed and data are presented on the conformational analysis of acyclic phosphorus-containing molecules and four-, five-, and six-membered phosphorus-containing heterocycles.
The bibliography includes 130 references.

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## I. INTRODUCTION

The distribution of electron density in the molecule (polarity) and the ability of the electron clouds to shift under the influence of an electric field (polarisability) are fundamental properties of matter, which in many respects determine its structure and reactivity. There are only a few experimental methods for the direct investigation of the electrical and electro-optical characteristics of molecules. Among these, the dipole moment method (DM), which yields information about the polarity of molecules, occupies an important place. The less widely used methods of double refraction in an electric field (the Kerr effect) and of the depolarisation of Rayleigh light scattering are the only ones available for the study of polarisability.

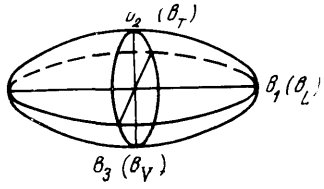
The polarisability $\alpha$ is defined as the dipole moment $\mu_{ind}$ induced by a unit electric field: $\alpha = \mu_{ind}/E$. For an isotropic species, the resultant vector of the induced moment is parallel to the applied field vector **E**. The polarisabilities of anisotropic species parallel and at right angles to the vector **E** are not equal ($\alpha_{\parallel} \neq \alpha_{\perp}$) and the induced dipole forms an angle with the vector **E**.

The anisotropic nature of a substance leads to the phenomenon of double refraction following the application of an electric field, i.e. at a given wavelength $\lambda$ the refractive index $n$ assumes different values in the directions parallel and at right angles to the applied field and we have $\Delta n = n_{\parallel} - n_{\perp} = B\lambda E^2$, where $B$ is the Kerr constant, determined by the properties of the substance itself. The molar Kerr constant ${}_mK$, which is defined as the difference between the molecular refractions $R$ for light polarised parallel and at right angles to **E**, is used in chemistry: ${}_mK = (R_{\parallel} - R_{\perp})/E^2$. For mixtures, ${}_mK$ is additive, so that the Kerr constant for a mixture of $n$ isomers is

$$ {}_mK_{exp} = \sum_{i=1}^{n} {}_mK_i N_i $$

where $N_i$ are the mole fractions of the isomers in the mixture and $\sum N_i = 1$.

In a theoretical treatment, the polarisabilities in different directions are described with the aid of the ellipsoid of polarisability




with three principal axes $b_1$, $b_2$, and $b_3$ for a molecule or $b_L$, $b_T$ and $b_V$ for an individual bond, where $b_L$ is the longitudinal polarisability and $b_T$ and $b_V$ are the transverse and vertical polarisabilities respectively (the letter $b$ denotes optical polarisability, i.e. the electron shift in the electromagnetic field of the light wave). It is assumed that $b_L$ has the same direction as the bond. For axially symmetrical bonds, $b_L \neq b_T = b_V$.

In the general case, polarisability must be regarded as a function of the orientation of the species relative to the direction of the polarising field **E**. In a cartesian coordinate system, each component of the induced moment ($m_x$, $m_y$, and $m_z$) is a function of three components of **E** ($E_x$, $E_y$, and $E_z$). In terms of matrix notation, one can write $\mu_{ind} = \Phi E$, where $\Phi$ is the polarisability tensor:

$$ (\Phi) = \begin{vmatrix} b_{xx} & b_{xy} & b_{xz} \\ b_{yx} & b_{yy} & b_{yz} \\ b_{zx} & b_{zy} & b_{zz} \end{vmatrix} . $$

The components of this tensor are the induced moments arising in the direction of the $i$ axis when the field acts along the $j$ axis. The polarisability tensor is a symmetrical tensor of the second rank. The invariants of the tensor are its trace and anisotropy, equal to the difference between the principal axes of the polarisability ellipsoid: $\gamma = b_L - b_T$. The trace of the tensor $b$ determines the molecular refraction of the substance. The components of the molecular polarisability tensor are closely related to the following three experimentally determined characteristics of the molecule:

1) The refraction $R_\infty$ extrapolated to the infinite wavelength:

$$P_E = R_\infty = \frac{4\pi N}{9}(b_{xx} + b_{yy} + b_{zz}), \quad (2)$$

where $P_E$ is the electronic polarisation. The polarisability determined from molecular refraction is the average optical polarisability:

$$\bar{b} = (b_1 + b_2 + b_3)/3 . \quad (3)$$

2) The coefficient of the depolarisation of the scattered light ${}_2\delta^2_\infty$:

$${}_2\delta^2_\infty = \frac{(b_{xx} - b_{yy})^2 + (b_{xx} - b_{zz})^2 + (b_{yy} - b_{zz})^2 + 6(b^2_{xy} + b^2_{xz} + b^2_{yz})}{(b_{xx} + b_{yy} + b_{zz})^2} . \quad (4)$$

3) The molar Kerr constant of the substance containing anisotropic ($K_1$) and dipole ($K_2$) components:

$${}_mK = K_1 + K_2 , \quad (5)$$

$$K_1 = \frac{2\pi N}{9kT} \cdot \frac{P_D}{45P_E}[(b_{xx} - b_{yy})^2 + (b_{xx} - b_{zz})^2 + (b_{yy} - b_{zz})^2 + 6(b^2_{xy} + b^2_{xz} + b^2_{yz})] , \quad (6)$$

$$K_2 = \frac{2\pi N}{9kT} \cdot \frac{1}{45kT}[m^2_x(2b_{xx} - b_{yy} - b_{zz}) + m^2_y(2b_{yy} - b_{xx} - b_{zz}) + m^2_z(2b_{zz} - b_{xx} - b_{yy}) + 6(m_x m_y b_{xy} + m_x m_z b_{xz} + m_y m_z b_{yz})] , \quad (7)$$

where $P_D$ is the deformation polarisation.

Eqn. (7) includes the components of the dipole moment along the coordinate axes, so that the magnitude and direction of the molecular dipole moment must be known in order to find ${}_mK$.

The majority of studies carried out previously involved the measurement of the Kerr effect and the refraction [1,2]. Investigation of the depolarisation of Rayleigh light scattering gives rise to new possibilities both for applied structural research and in the study of detailed intramolecular interactions and electron redistributions [3].

This review is devoted to the principal results and possibilities which are available to investigators of organophosphorus compounds using the Kerr effect method in conjunction with Rayleigh light scattering data in many instances. Much attention has also been devoted to the methodological aspect of the application of the dipole moment method, since dipole moments in many respects determine the validity of the calculation of ${}_mK$.

## II. THE KERR CONSTANTS OF PHOSPHORUS COMPOUNDS. THE ADDITIVE POLARITIES AND POLARISABILITIES OF PHOSPHORUS BONDS

### 1. The Kerr Constants of Phosphorus Compounds

The major advances achieved in the application of electro-optical methods to the study of the steric and electronic structures of organic compounds belonging to a wide variety of glasses (see the relevant reviews [1-3]) gave rise to the hope that these methods will be useful in the investigation of organophosphorus componnds, which are characterised by a wide variety of intramolecular electronic interactions: involving the lone electron pair (LEP), the multiple bond of phosphorus, etc.

Table 1 lists the phosphorus compounds investigated with the aid of the Kerr effect up to 1977 [4-32] (the numbering of the compounds in Table 1 is used henceforth in the text and in the other Tables). The first studies in this field, starting from 1961, were carried out by Le Fevre and coworkers [4,7,11,17,20,23,32] for twenty identically substituted compounds of three- and four-coordinated phosphorus. Certain difficulties, which will be noted below, limited further structural research.

Research involving the determination of the Kerr constants and of the degrees of depolarisation of Rayleigh light scattering in organophosphorus compounds was begun in Kazan in 1970 under the general supervision of Academician B. A. Arbuzov.

**Table 1.** The experimental Kerr constants for phosphorus compounds.

| No. of compound | Compound | Solvent* | μ, D | $10^{12}{}_mK$** | Refs. |
|---|---|---|---|---|---|
| | Acyclic compounds | | | | |
| I | $PCl_3$ | b | 0.89 | −10.9 | 4 |
| II | $OPCl_3$ | b | 2.42 | −73.8 | 4 |
| | ditto | c.t. | 2.47 | −46 | 5 |
| III | $SPCl_3$ | c.t | 1.37 | 65 | 5 |
| IV | $ClH_2OPCl_2$ *** | c | 1.97 | 30 | 6 |
| V | $(CH_3O)_3P$ | b | 1.81 | 38 | 7 |
| VI | $(C_2H_5O)_3P$ | b | 1.80 | −4.4 | 7 |
| VII | $(iso\text{-}C_3H_7O)_3P$ | b | 1.82 | −47 | 7 |
| VIII | $(n\text{-}C_{10}H_{21}O)_3P$ | b | 1.75 | −153 | 7 |
| IX | $(C_6H_5O)_3P$ | b | 1.51 | −52 | 7 |
| | ditto | c | 1.63 | 32.5 | 8 |
| X | $(CH_3O)_3PO$ | b | 3.18 | −88 | 7 |
| XI | $(C_2H_5O)_3PO$ | b | 3.12 | −135 | 7 |
| XII | $(n\text{-}C_3H_7O)_3PO$ | b | 3.18 | −184 | 7 |
| XIII | $(iso\text{-}C_3H_7O)_3PO$ | b | 2.84 | −128 | 7 |
| XIV | $(C_5H_{10}O)_3PO$ | b | 3.14 | −207 | 7 |
| XV | $(t\text{-}C_4H_9O)_3PO$ | c.t. | 2.33 | 63 | 9 |
| XVI | $(C_6H_5O)_3PO$ | b | 2.89 | −133 | 7 |
| XVII | $(CH_3O)_3P$ | c.t. | 2.71 | 138 | 10 |
| XVIII | $(CH_3)_3P$ | d | 1.19 | −10.1 | 11 |
| XIX | $(CH_3)_3PO$ | d | 4.39 | −39.5 | 11 |
| | ditto | b | 4.29 | 387 | 11 |
| XX | $(CH_3)_3PS$ | d | 4.87 | 634 | 11 |
| | ditto | b | 4.73 | 1.1 | 11 |
| XXI | $(ClCH_2)_3PO$ | c.t. | 2.34 | −55 | 12 |
| XXII | $(ClCH_2)_2(CH_3)PO$ | c.t. | 2.96 | 44 | 13 |
| XXIII | $(ClCH_2)_2(CH_3)PO$ | c.t. | 2.57 | 33.6 | 14 |
| XXIV | $(BrCH_2)_2(CH_3)PO$ | c.t. | 3.70 | 74 | 15 |
| XXV | $(BrCH_2)_3PO$ | c.t. | 3.61 | −128 | 15 |
| XXVI | $CH_3P(O)Cl_2$ | c.t. | 3.35 | −102 | 5 |
| XXVII | $CH_3ClCHP(O)Cl_2$ | c.t. | 2.97 | −68 | 16 |
| XXVIII | $CH_3P(S)Cl_2$ | c.t. | 2.92 | −13 | 5 |
| XXIX | $CCl_3P(S)Cl_2$ | c.t. | 1.83 | −66 | 5 |
| XXX | $(C_6H_5)_3P$ | b | 1.50 | −100 | 17 |
| XXXI | $(C_6H_5)P(CH_3)_2$ | c | 1.20 | 1** | 18 |
| XXXII | $(p\text{-}CH_3C_6H_4)P(CH_3)_2$ | c | 1.40 | 5±2** | 19 |
| XXXIII | $(p\text{-}CNC_6H_4)P(CH_3)_2$ | d | 4.40 | 132** | 18 |
| XXXIV | $(C_6H_5)P(t\text{-}C_4H_9)_2$ | c | 1.50 | 2** | 18 |
| XXXV | $(p\text{-}CH_3C_6H_4)P(t\text{-}C_4H_9)_2$ | c | 2.12 | 10±3** | 19 |
| XXXVI | $(C_6H_5)_3PO$ | b | 4.49 | −828 | 20 |
| | ditto | c.t. | 4.44 | −590 | 21 |
| XXXVII | $(p\text{-}ClC_6H_4)_3PO$ | c.t. | 3.14 | −579 | 21 |
| XXXVIII | $(m\text{-}ClC_6H_4)_3PO$ | c.t. | 4.78 | −453 | 21 |
| XXXIX | $(p\text{-}CH_3C_6H_4)_3PO$ | c.t. | 5.02 | −1159 | 21 |
| XL | $(m\text{-}CH_3C_6H_4)_3PO$ | c.t. | 4.57 | −556 | 21 |
| XLI | $(C_6H_5)_2P(O)CCl_3$ | c.t. | 3.81 | 240 | 22 |
| XLII | $(p\text{-}CH_3C_6H_4)_2P(O)CCl_3$ | c.t | 4.75 | −1 | 22 |
| XLIII | $(p\text{-}ClC_6H_4)_2P(O)CCl_3$ | c.t | 2.82 | 100 | 22 |
| XLIV | $(p\text{-}CH_3C_6H_4)P(O)(CH_3)_2$ | c.t | 4.30 | 30** | 18 |
| XLV | $(p\text{-}ClC_6H_4)P(O)(CH_3)_2$ | d | 4.60 | 24.9** | 18 |
| XLVI | $(p\text{-}CH_3C_6H_4)P(O)(t\text{-}C_4H_9)_2$ | c.t | 4.85 | 44.4** | 18 |
| XLVII | $(C_6H_5)_3PS$ | b | 4.79 | −446 | 20 |
| XLVIII | phosphonitrile chloride trimer | b | 0.14 | 2.1 | 23 |
| | 1,3-Thiaphosphetans | | | | |
| XLIX | 3-chloro-3-thiono- | c.t | 2.18 | 205 | 24 |
| L | 3-methoxy-3-oxo- | c.t | 2.76 | −44 | 25 |
| LI | 3-methoxy-3-thiono | c.t | 2.68 | 6.8 | 25 |
| | 1,3,2-Dioxaphospholanes | | | | |
| LII | 2-chloro-*** | c | 3.12 | 85.5 | 26 |
| LIII | 2-chloro-4-methyl- | c | 3.47 | 102.8 | 26 |
| LIV | DL-2-chloro-4,5-dimethyl- | c | 3.84 | 84.9 | 26 |
| LV | *meso*-2-chloro-4,5-dimethyl- | c | 3.63 | −61.1 | 26 |
| LVI | 2-chloro-4,4,5,6-tetramethyl- | c | 3.38 | −53.8 | 26 |
| LVII | 2-chloro-2-oxo- | c.t | 4.72 | 313 | 126 |
| LVIII | 2-chloro-4-methyl-2-oxo- | c.t | 5.30 | 437 | 126 |
| LIX | DL-2-chloro-4,5-dimethyl-2-oxo- | c.t | 5.50 | 405 | 126 |
| LX | *meso*-2-chloro-4,5-dimethyl-2-oxo- | c.t | 5.49 | 334 | 126 |
| LXI | 2-chloro-4,4,5,5-tetramethyl-2-oxo- | c.t | 5.89 | 602 | 126 |
| LXII | 2-chloro-2-thiono- | c.t | 4.57 | 479 | 126 |
| LXIII | 2-chloro-4-methyl-2-thiono- | c.t | 4.83 | 968 | 126 |
| LXIV | DL-2-chloro-4,5-dimethyl-2-thiono- | c.t | 5.45 | 675 | 126 |
| LXV | *meso*-2-chloro-4,5-dimethyl-2-thiono- | c.t | 5.38 | 676 | 126 |
| LXVI | 2-chloro-4,4,5,5-tetramethyl-2-thiono- | c.t | 5.56 | 886 | 126 |
| LXVII | *o*-phenylene phenyl phosphite | c | 2.05 | −35.5 | 8 |
| LXVIII | *oop*-tri-t-butylphenyl *o*-phenylene phosphite | c | 2.00 | 157 | 8 |

Table 1. (cont'd.)

| No. of compound | Compound | Solvent* | μ, D | $10^{12}{}_mK$** | Refs. |
|---|---|---|---|---|---|
| | 1,3,2-Dioxaphosphorinanes | | | | |
| LXIX | 2-chloro- | c | 3.47 | 164 | 6,27 |
| LXX | 2-chloro-5,5-dimethyl*** | c | 3.66 | 215 | 6,27 |
| | ditto | d | 3.21 | 198 | 6,27 |
| LXXI | 2-chloro-4-methyl- | c | 3.60 | 121 | 27 |
| LXXII | 3,9-dichloro-2,4,8,10-tetraoxa-3,9-spiro[5,5]undecane | d | 2.36 | —69 | 6 |
| LXXIII | 2-chloro-5,5-dichloromethyl | c | 2.76 | 21.4 | 127 |
| LXXIV | 2-chloro-5,5-dibromomethyl | c | 2.31 | —23.2 | 127 |
| LXXV | 2-chloro-2-oxo- | c.t | 5.89 | 556 | 29 |
| LXXVI | 2-chloro-2-thiono- | c.t | 5.50 | 1355 | 30 |
| LXXVII | 2-chloro-4-methyl-2-thiono- | c.t | 5.54 | 1195 | 30 |
| LXXVIII | 2-methyl-2-oxo- | c.t | 4.24 | 63 | 29 |
| LXXIX | 2-oxo-2-triphenylmethyl | c.t | 4.38 | 534 | 29 |
| LXXX | *cis*-2,4-dimethyl-2-oxo- | c.t | 6.36 | 346 | 128 |
| LXXXI | 2-methyl-2-thiono- | c.t | 3.90 | 4.36 | 30 |
| LXXXII | 2,4-dimethyl-2-thiono- | c.t | 5.37 | 1175 | 30 |
| LXXXIII | *cis*-2-methoxy-4-methyl- | c | 2.87 | 12.5 | 31 |
| LXXXIV | *trans*-2-methoxy-4-methyl- | c | 3.40 | 39.3 | 34 |
| LXXXV | *cis*-2-methoxy-4-methyl-2-oxo- | c.t | 6.07 | 344 | 31 |
| LXXXVI | *trans*-2-methoxy-4-methyl-2-oxo- | c.t | 4.46 | 165 | 31 |
| LXXXVII | *cis*-2-methoxy-4-methyl-2-thiono- | c.t | 5.51 | 929 | 31 |
| LXXXVIII | *trans*-2-methoxy-4-methyl-2-thiono- | c.t | 3.93 | 298 | 31 |
| LXXXIX | 2-phenoxy- | c | 2.75 | —83 | 129 |
| XC | 2-(*p*-bromophenoxy)- | c | 3.82 | 470 | 129 |
| XCI | 2-(*p*-nitrophenoxy)- | c | 6.32 | 3257 | 129 |
| XCII *** | 2-(*oop*-tri-t-butylphenoxy)- | c | 2.82 | —88 | 129 |
| XCIII | 2-(*o*-nitrophenoxy)- | c | 5.44 | 63 | 129 |
| XCIV | *cis*-2-hydro-4-methyl-2-oxo- | c.t | 5.77 | 541 | 130 |
| XCV | *trans*-2-hydro-4-methyl-2-oxo- | c.t | 4.19 | 160 | 130 |
| XCVI | 2-hydro-5,5-dimethyl-2-oxo | c.t | 4.72 | 274 | 130 |
| XCVII | 2-hydro-5,5-bis(chloromethyl)-2-oxo- | c.t | 4.55 | 142 | 127 |
| XCVIII | 2-hydro-5,5-bis(bromomethyl)-2-oxo | c.t | 4.51 | 28 | 127 |
| XCIX | 5,5-dimethyl-2-phenyl- | c | 3.31 | —298 | — |
| C | $CH_3C(CH_2O)_3P$ | d | 4.15 | 368 | 32 |
| CI | $CH_3C(CH_2O)_3PO$ | d | 7.10 | 1519 | 32 |
| CII | $CH_3C(CH_2O)_3PS$ | d | 6.77 | 2637 | 32 |
| | 1,3,2-Dithiophosphorinanes | | | | |
| CIII | 2-chloro- | c | 3.18 | 78 | — |
| CIV | 2-phenyl- | c | 3.42 | —344 | — |
| CV | 2-methyl-2-thiono- | c.t | 4.22 | 639 | — |
| CVI | 2-methoxy-2-oxo-1,2-oxaphosphorinane | c.t | 4.46 | 314 | 128 |

*Solvents: d = dioxan; b = benzene; c.t. = carbon tetrachloride; c = cyclohexane.

**Here and henceforth in the text the constants ${}_mK$ are understood to be multiplied by $10^{-12}$. The exceptions are compounds (XXXI)–(XXXV) and (XLIV)–(XLVI) for which the values of ${}_mK$ were determined to within $10^{-11}$.

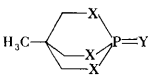
***The degrees of depolarisation of Rayleigh light scattering $2\delta^2_\infty \times 10^3$ were determined for these compounds and the following values were obtained: 8.3 for (IV); 11.4 for (LII); 17.4 for (LXX); 3.4 for (XCII); 4.6 for (CIII).

## 2. The Additive Computational Scheme for Phosphorus Compounds

The theoretical treatment of the electrical and electro-optical properties of molecules is based on the hypothesis that they are additive. A characteristic dipole moment vector and polarisability tensor can be ascribed to each chemical bond or group of atoms. This is usually done on the basis of experimental data for a limited number of molecules, called the model compounds. The bond parameters obtained in this way make it possible to calculate the physical constants of a large set of molecules. The additive values of the bond parameters are effective and express not only the properties of the bonds themselves but also the influence on the latter of neighbouring substituents in the model compounds. The mutual influence may change on passing to systems with another environment; in this case, the deviations from additivity serve as a measure of the intramolecular interaction.

The validity of the valence-optical additive scheme can be regarded as firmly established to a zeroth approximation [33]. This scheme can be extended not only to the dipole moments and the anisotropic bond polarisabilities but also to the derivatives of these quantities with respect to changes in bond length, serving thus as the basis of the modern theory of intensities in infrared and Raman spectra, which is in good agreement with experiment [33].

The simplest identically substituted molecules, known *a priori* not to exhibit conformational isomerism, are chosen for phosphorus derivatives as model compounds. These substances are of the type $PX_3$ and $Y{=}PX_3$, in which the threefold symmetry axis coincides with the direction of the resultant dipole moment of the P–X and P=Y bonds and with the direction of the longitudinal $b_1$ axis of the molecular polarisability ellipsoid. For non-regular groups P–X–R, where X = O, S, NR, etc., the model compounds used [32,34] are rigidly fixed bicyclic systems of the type



Y = LEP, O, S,

where internal rotation is impossible. The corresponding additive parameters of the phosphorus bonds may be calculated from the experimental dipole moments and Kerr constants ${}_mK$ by a vector or tensor expansion with the subtraction of certain parameters of the carbon bonds. As mentioned above, refraction data are also necessary in order to find the axes of the polarisability ellipsoids.

The numerical values of the phosphorus bond refractions have been analysed most fully by Tolkmith [35]. On the basis of extensive experimental data (for 500 phosphorus compounds), he concluded that the refraction of the given bond depends both on the environment of the phosphorus atom itself and on the nature of the substituent in the P–X–R chain. The phosphorus bond refractions most frequently employed are listed in Table 2.

Table 2. The refractions of the phosphorus bonds for the D line of Na. [35]

| Bond | $R_D$ | Bond | $R_D$ | Bond | $R_D$ |
|---|---|---|---|---|---|
| $P^{III}$ LEP | 5.4 | P—$NC_2$ | 1.3 | P—Cl | 6.95 |
| P—OH, P—OP | 1.45 | P—N=C | 1.9 | P—Br | 10.2 |
| P—OC, P—OSi | 1.35 | P—$C_{sp^3}$ | 1.85 | P—Si | 3.4 |
| P—SH | 6.25 | P—$C_{arom}$ | 2.75 | P—P | 3.5 |
| P—SC, P—SSi | 5.65 | P—C≡N | 2.55 | P=O | 4.15 |
| P—SP | 5.3 | P—$CCl_3$ | 2.7 | P=S | 11.9 |
| P—SeP | 7.3 | P—C=O | 2.05 | P=Se | 15.6 |
| P—$NH_2$ | 1.7 | P—H | 2.2 | P=N | 5.8 |
| P—NHC, P—NP | 1.5 | P—F | 1.5 | | |

It follows from the above that the creation of an additive computational scheme is based on a comparison of data for compounds of three- and four-coordinated phosphorus. The former ($PX_3$) serve as a basis for the determination of the P–X bond parameters. The P=Y bond parameters are determined as the vector or tensor differences between the corresponding experimental values for $PX_3$ and $YPX_3$. A weak aspect of such calculation is the hypothesis that the parameters of the $P^{III}$–X and $P^{IV}$–X bonds remain unchanged. Evidently, in most cases the inaccuracy of the result should be compensated implicitly by a distortion

of the values for P=Y. However, the difference is caused not only by the different states of hybridisation of the central atom, but also by the uncertainty of the contribution of the phosphorus(III) LEP to the required parameters in the initial $PX_3$ molecules.

### 3. The Influence of the Dipole Moment of the Lone Electron Pair on the Results of Calculations

The problem of the degree of displacement of the centre of gravity of the LEP electron cloud relative to the positively charged atomic nucleus ($\bar{x}$), which determines the LEP dipole moment ($m_{LEP} = 2e\bar{x}$) is widely discussed in the literature. However, the direct experimental determination of $\bar{x}$ is extremely difficult. The proposed methods [36,37] are laborious and not very reliable, since the experimental error is close to the postulated displacement of the charge. For a phosphorus atom with a valence angle of 93.4°, analysis of the intensities of the absorption bands in infrared spectra [36] yielded 0.2 D. Comparison of the experimental dipole moments of triarylphosphines and the valence angles led the authors [38] to the conclusion that the maximum phosphorus(III) LEP dipole moment is 2.93 D. Smaller values follow from quantum-mechanical calculations: 1.35 D [27] (valence angle 100°) and 1.15 D in phosphine. [39]

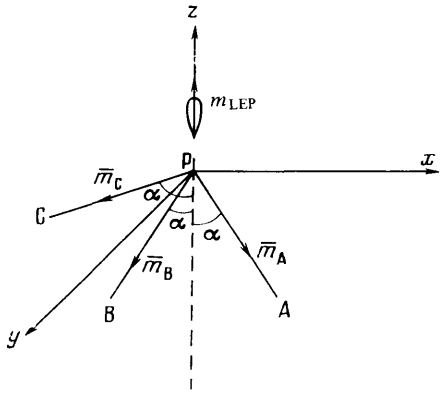



**Figure 1.** The configuration of the P(ABC) molecule in the cartesian coordinate system.

According to Mauret and Fayet [40], the dipole moment of trialkylphosphines (1.6 D) is equal to $m_{LEP}$ as a consequence of the similarity of the electronegativities of the carbon and phosphorus atoms. The unknown parameter may be determined on the basis of the vector additive scheme for the dipole moments of several compounds, specifying $m_{LEP}$ as an independent vector together with the bond dipole moments, as has been done in a number of studies [41-43]; $m_{LEP} = 0.92$ D [41] and $m_{LEP} = 1.49$ D [43] was obtained. Calculations of this kind are sensitive to the chosen angular parameters. When the latter are equal, the relation between the molecular and the required dipole moments is in most cases linear, deviations from linearity being caused not only by the contribution of the LEP moment but also by non-additivity factors, appearing as a result of the mutual influence of the atoms and the differences between the valence angles. In such cases, a small (in absolute magnitude) change in the non-additivity factor can ultimately lead to a wide variation in the parameters being determined. This in fact explains the fairly large difference (approximately 0.6 D) between the values found by Matrosov et al. [41] and Chernokal'skii et al. [43]

Thus the problems of the absolute value of the LEP moment of the phosphorus atom can be regarded as still open. However, in the light of the problems solved with the aid of the dipole moments and Kerr effect methods, it is important to determine the influence of the dipole moment of the lone electron pair $m_{LEP}$ on the magnitude and direction of the resultant dipole moment. We shall consider this problem for non-identically substituted molecules of the type P(ABC), since in the case of molecules with symmetrical substitution $m_{LEP}$ enters implicitly into the bond moments of the given atom obtained by the vector resolution of the experimental dipole moments of model compounds. Three symetrically substituted compounds $PA_3$, $PB_3$, and $PC_3$ with the molecular dipole moments $\mu A$, $\mu B$, and $\mu C$ serve as the model compounds for the determination of the P–A, P–B, and P–C bond moments designated by $m_A$, $m_B$, and $m_C$. Each bond moment $m_i$, where $i$ = A, B, or C, is calculated as follows:

$$m_i = \frac{\mu_i - m_{LEP}}{3\cos\alpha}, \qquad (8)$$

where $\alpha$ is the angle formed by the bond with the three-fold symmetry axis (Fig. 1).

The dipole moment $\mu$ of the compound P(ABC) is then expressed by the following sum:

$$\mu^2 = [m_{LEP} + \cos\alpha\,(m_A + m_B + m_C)]_z^2 + \left[m_A \sin\alpha - \right.$$
$$\left. - \frac{1}{2}(m_B + m_C)\sin\alpha\right]_x^2 + [2(m_B - m_C)\sin\alpha]_y^2 . \qquad (9)$$

The substitution in this expression of the bond moments determined for symmetrical compounds by Eqn. (8) (for identical angles) leads to the final expression

$$\mu^2 = \left[\frac{(\mu_A + \mu_B + \mu_C)}{3}\right]_z^2 + \left[\frac{(2\mu_A + \mu_B + \mu_C)}{6}\tan\alpha\right]_x^2 +$$
$$+ \left[\frac{2(\mu_B - \mu_C)}{3}\tan\alpha\right]_y^2, \qquad (10)$$

in which $m_{LEP}$ cancels out fully.

Eqn. (10) shows that, for the determination of the magnitude and direction of the resultant molecular moments of asymmetrically substituted compounds, in most cases [with the exception of substances of the type $PH_n(CH_3)_{3-n}$ with $n$ = 1–3, where the valence angles at the phosphorus atom are appreciably less than 100°C] there is no need for the introduction of the vector of the LEP moment as an independent parameter. Since the compounds considered [$PA_3$, $PB_3$, $PC_3$, and P(ABC)] can differ by their intramolecular interactions, the contributions of the interaction moment, called above the non-additivity factor, must be introduced into Eqns. (9) and (10).

### 4. The Dipole Moments of Phosphorus Bonds

The disposition of the bonds at the phosphorus atoms may be regarded as nearly tetrahedral, if the fourth bond is represented by the lone electron pair.

Mathematically this is analogous to the tetrahedral orientation of bonds at a carbon atom; consequently the

vector of the LEP moment is analogous to the vector of the C–H bond dipole moment, which serves as a basis for the determination of the dipole moments of all the remaining bonds of organic compounds. It follows from Eqn. (10) that the absolute value of $m_{LEP}$ has no influence on the results of calculations, but is closely related to the intermediate values of $m_i$, i.e. to the bond moments. This fact can explain the existence of several sets of bond moments differing by the initial data. The principal requirement for a correct calculation of dipole moments is therefore a unique set of initial parameters. For phosphorus compounds, the number of such systems of parameters is increased owing to the different absolute values of $m_{LEP}$ adopted by different investigators.

Table 3. The dipole moments of phosphorus bonds.

| Bond | Bond dipole moments, D |
|---|---|
| P — O | — 0.48[48]; — 0.6[10]; — 0.75[49]; 0[6,50]*; 0.54 (1.35)[22]; 1.1 (0.91)[42] |
| P — S | — 0.85[1] [$S_2$P (S) C]**; —0.25[52] [$S_2$P (S) C]**; — 0.58[52] [$S_2$P (S) Cl]**; — 0.8; 0 (0.92)[42] |
| P — F | 0.72[24]; 1.4 (0.91)[42]; —0.56[50]; 1.02[53] |
| P — Cl | 0.66[54]; 0.56[27]; 0.81[53]; 1.53 (1.35)[27]; 1.2 (0.9)[42]; —0.42[49] |
| P — Br | 0.36[53]; 1.1 (0.9)[42] |
| P — I | 0.0[53]; 0.7 (0.9)[42] |
| P — H | —0.36[29]; 0.1 (0.9)[42]; 0.371 (0.2)[55]; 1.0 [$O_2$P (O) H][56]; —0.36 [$O_2$P (O) H]; — 0.13—0.67[38] |
| P — Se | 1.24[57] |
| P — N | 0.31[58]; —1.4 and — 2.10 (P—Cl)[58]***; ~ 0 (P—$NMe_2$)[58]; —0.8 (P=S)[58]***; 0.03[59]; 0.4 (1.35)[60]; 0.8 (P)$^{IV}$[60]; —0.8; —1.8; — 1.4 (PNCO)[61] |
| P—$C_{sp^3}$ | —0.58[24]; —0.39 ($Et_3$P)[54]; —0.6[62]; — 0.1 (0.9)[42]; — 0.94[50]; 0.690 (0.2)[55]; — 1.11[49] |
| P—$C^{***}_{sp^2}$ (olefin) | —0.7 (0.9)[42]; — 0.75[50]; — 0.9[62] and — 0.82[63] [(C=C) $O_2$PO] |
| P — $C_{sp^2}$ (phenyl) | —0.39[65]; 0.4 (0.9)[42]; — 0.16 ($Me_3PC_6H_5$Me-p)[19]; —0.57 [(t-$C_4H_9$)$_2$$PC_6H_4$Me-p][19] |
| P — $C_{sp}$ | 1.3 (0.9)[42]; ~ 0.5 [(C ≡ C) $O_2$PO][62] |
| P= N | 0.6[50]; 2.27[66] |
| P = O**** | 4.1[42] и 3.13[5] [$Cl_3$PO]; 3.0 [$R_2N_3$PO][5]; 4.1 and 3.40[5] [$Me_3$PO]; 2.95 [$Ph_3$PO][5,20]; 2.95[20,34]; 2.90[67]; 3.9 (0.9)[42] [$O_3$PO]; 3.40 [$C_2$P (O) Cl][24] |
| P= S***** | 2.62[34]; 3.97 (1.35)[30]; 3.25[53]; 3.6 (0.9)[42] [$O_3$PS]; 2.03[5]; 3.2 (0.9)[42]; 3.88[5]; 4.6 (0.9)[42] [$C_3$PS]; 3.3[20,34] [$Ph_3$PS]; 3.26 [$C_2$ (O) PS][24]; 3.15[24] and 2.63[5] [$C_2$ClPS]; 2.91 [$C_2$FPS] |

*Despite the identical values of $m_{P-O}$, the calculations in Refs. 6 and 50 were based on different initial data: $m_{C-O}$ = 1.12 D, found from the dipole moments of tetrahydropyran and 1,3-dioxan ($m_{H-C}$ = 0.28 D and $m_{LEP}$ = 0) was used in Ref. 6, while $m_{P-O}$ was calculated from the dipole moment of the bicyclic phosphite (C); in Ref. 50, the moment $m_{Alk-O}$ = 0.87 D was determined from the measured dipole moments of dialkyl esters after eliminating the contribution of the rotational vibrations of the molecule to the polarisation, while $m_{P-O}$ was calculated on the basis of a compound whose bonds are fixed in space—triethyl phosphite, for which the *cis*, *cis*, *cis*-conformation was adopted, but was not subsequently confirmed by an electron diffraction study of trimethyl phosphite[70].

**In the calculation of $m_{P-S}$ and $m_{P-N}$ in Refs. 52 and 58, the P=S bond moment was treated as a constant value equal to 2.62 D.

***The interaction moments in different conjugated systems were calculated in Refs. 48 and 63–65.

****The high sensitivity of $m_{P=O}$ to the electronegativities of the substituents was demonstrated in Refs. 50, 60, and 68: $m_{P-O} = 4.80 - 0.353\,\Sigma X$, where $X$ is the Thomas–Chattenden "shift constant".

*****According to Refs. 60 and 69, $m_{P=S} = 9.75 - 0.924\,\Sigma X$.

One of the first studies on the analysis of the dipole moments of organophosphorus compounds was performed in Kazan by Arbuzov and Rakov[44]. The bond dipole moments were examined most fully and systematically for the first time by Arbuzov and Shavsha[45–47]. It is nowadays postulated that the bond moments depend to a large extent on the environment at the phosphorus atom. Table 3 presents some of the bond dipole moments most widely used in calculations. If $m_{LEP} \neq 0$ and if the bond moments have been determined from the dipole moments of compounds asymmetrically substituted relative to the phosphorus atom, then Table 3 indicates in brackets, after the dipole moment, the value of $m_{LEP}$ adopted by the authors and the intermediate environment at the phosphorus atom. The dipole moments calculated taking into account $m_{LEP}$ appear to be more reliable in the light of the existing theoretical ideas. However, as shown above, in the additive calculation of dipole moments this is not important and identical results are obtained.

It follows from the data in Table 3 that the phosphorus bond dipole moments are extremely sensitive to the environment and in the analysis of the dipole moments of phosphorus compounds it is therefore desirable to examine the entire set of bonds. The method of isoelectric maps[6], whereby it is possible to find simultaneously bond and structural parameters, is extremely promising in this respect. It is described in detail in Section IV for 1,3,2-dioxaphosphorinane derivatives as an example.

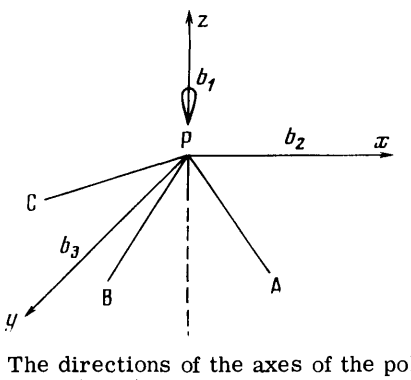



Figure 2. The directions of the axes of the polarisability ellipsoid of the P(ABC) molecule.

## 5. The Anisotropy of the Polarisability of Phosphorus Bonds

In the calculation of the additive parameters of the polarisability ellipsoids of phosphorus bonds, the problem of the allowance for the LEP contribution remains obscure, as for dipole moments. We shall place a symmetrically substituted molecule $PA_3$, $PB_3$, or $PC_3$ in a cartesian coordinate system, as shown in Fig. 2 for the P(ABC) molecule. Denoting the molecular anisotropy of polarisability by $\Gamma_i = b_1 - b_2$, it is possible to calculate the anisotropy of the polarisability of the $i$th bond:

$$\gamma_i = \frac{\Gamma_i - \gamma_{LEP}}{4.5\cos^2\alpha - 1}. \qquad (11)$$

The differences between the diagonal elements and the non-diagonal components of the molecular polarisability

tensor matrix of the P(ABC) molecule, which are necessary for the calculation of ${}_{m}K$, can be calculated in conformity with Eqns. (6) and (7):

$$
\begin{aligned}
b_{xx} - b_{yy} &= -\gamma_A(1-\cos^2\alpha) - \sum_{i=B,C} 0.5\gamma_i(1-\cos^2\alpha);\\
b_{xx} - b_{zz} &= \gamma_A(1-2\cos^2\alpha) + \sum_{i=B,C} \gamma_i(0.25-1.25\cos^2\alpha) - \text{LEP};\\
b_{yy} - b_{zz} &= -\gamma_A\cos^2\alpha + \sum_{i=B,C} \gamma_i(0.75-1.75\cos^2\alpha) - \text{LEP};\\
b_{xy} &= \sum_{i=B,C} (\mp\gamma_i \sin^2\alpha\cdot\cos 60^\circ\cdot\sin 60^\circ);\\
b_{xz} &= -\gamma_A\cos\alpha\cdot\sin\alpha + \sum_{i=B,C} (\gamma_i\cos\alpha\cdot\sin\alpha\cdot\cos 60^\circ);\\
b_{yz} &= \sum_{i=B,C} (\mp\gamma_i\cos\alpha\cdot\sin\alpha\cdot\cos 60^\circ).
\end{aligned}
\qquad (12)
$$

**Table 4.** The parameters of the polarisability ellipsoids of bonds and groups of atoms in phosphorus compounds.

| Group of atoms or bond | $b_1$ or $b_L$ | $b_2$ or $b_T = b_V$ | Compound | Refs. |
|---|---|---|---|---|
| $O_3P$ | 4.13 | 3.50 | C | 32 |
| $P^{III}-O$ | 0.86 | 1.45 | C | 1 |
| $P^{III}-O$ | 1.09 | 1.34 | LXXIV | 129 |
| $P^{III}-O$ | 2.28 | 0.74 | IV | 6 |
| $P^{III}-O$ | 2.52 | 0.62 | XCIX | ** |
| $P^{III}-O$ | 2.54 | 0.61 | LII | 6 |
| $P^{III}-O$ | 3.05 | 0.35 | LXX | 6 |
| $P^{III}-O$ | 3.32 | 0.21 | XCII | 129 |
| $P^{III}-O$ (Ph) | 2.82 | 0.47 | XCII | 129 |
| $O_3PO$ | 4.19 | 2.75 | CI | 32 |
| $O_3PS$ | 8.69 | 4.92 | CII | 32 |
| $P^{IV}-O$ | 0.15 | 0.74 | CI | 32 |
| $P^{III}-C_{sp^3}$ | 2.28 | 0.79 | XVIII | 11 |
| $P^{IV}-C_{sp^3}$ | 1.57 | 0.08 | XIX | 11 |
| $P^{III}-C_{sp^2}$ (aryl) | 1.20 | 1.50* | — | 1 |
| $P^{III}-C_{sp^2}$ (aryl) | 3.28 | 0.79 | — | ** |
| $P^{IV}-H$ | 0.1 | 1.2 | XCIV, XCV | 130 |
| $P^{III}-S$ | 3.24 | 2.59 | CIII | ** |
| $P^{III}-Cl$ | 5.12 | 2.46 | I | 4 |
| $P^{III}-Cl$ | 4.55 | 2.75 | IV | 6 |
| $P^{III}-Cl$ | 3.60 | 3.23 | LII | 6 |
| $P^{III}-Cl$ | 2.46 | 3.79 | CIII | ** |
| $P^{III}-Cl$ | 2.21 | 3.91 | LXX | 6 |
| $P^{IV}-Cl$ | 4.75 | 1.63 | XXVIII | 5 |
| $P^{IV}-Cl$ | 4.14 | 1.75 | II | 4 |
| $P^{IV}-Cl$ | 1.76 | 3.07 | LXXVI | 30 |
| P = O | 2.0 | 1.50 | XIX | 11 |
| P = O | 2.08 | 1.43 | LXXV | 5 |
| P = O | 2.19 | 1.38 | CI, XCIV | 32 |
| P = O | 2.54 | 1.02 | II | 5 |
| P = S | 6.72 | 3.46 | CII | 32 |
| P = S | 7.0 | 3.90 | XX | 11 |
| P = S | 7.47 | 3.08 | XXVIII, XXIX | 5 |
| P = S | 7.88 | 2.72 | III | 5 |

*Calculated from the molecular refraction and the empirical equation relating $b_L$ and the bond length[1].
**Calculated by the author of the review.
***See Section III.

Substitution of $\gamma_i$ from Eqn. (11) in Eqn. (12) leads to expressions where the contribution of the LEP vanishes after appropriate mathematical operations, and only the experimental quantities $\Gamma_A$, $\Gamma_B$, and $\Gamma_C$ remain, i.e. there is no need to take into account in an explicit form the LEP polarisability ellipsoid. Taking into account the absolute value of the LEP polarisability $b = 6.3$ Å$^3$ found by Tolkmith[35], it is possible to calculate the required parameters of the four-coordinated phosphorus bonds: they are equated to the differences between the axes of the polarisability ellipsoids of the bonds and the isotropic lone pair of the tervalent atom. Table 4 presents the parameters of the polarisability ellipsoid of bonds and groups of atoms obtained in this way.

We may note the wide variation of the bond polarisability parameters, particularly on passing from symmetrically substituted to asymmetrically substituted compounds. This invalidates the usually employed method of calculation for such systems (see above) and requires a non-trivial approach. For this reason, compounds of three- and four-coordinated phosphorus will be henceforth considered separately.

### 6. The Solvent Effect

In the practical application of the values quoted in Table 1, particular attention must be paid to the possible interaction of the given compounds with the solvent. Thus Le Fevre's attempt to use the parameters found for the polarisability ellipsoids of the phosphite and phosphate groups in the analysis of the structures of the trialkyl phosphites (V)–(VIII) and the trialkyl phosphates (X) to (XVI) was unsuccessful[7]. It was subsequently observed that the experimental values of ${}_{m}K$ in benzene differ considerably from those determined in other solvents [see the data for compounds (IX), (XIX), (XX), and (XXVI) in Table 1]. This can be explained by the formation of complexes by phosphorus compounds with benzene[11], so that the conclusions reached by Le Fevre and coworkers[7,17,20] are incorrect. The use of the bond polarisability ellipsoids found for compounds (I), (II), (XXX), (XXVI), and (XLVII), whose ${}_{m}K$ values were determined in benzene, also requires particular caution.

## III. THE STERIC AND ELECTRONIC EFFECTS IN PHOSPHORUS(III) COMPOUNDS

The use of the Kerr effect in conformational analysis and in the study of intramolecular electronic effects requires the knowledge of the polarisability ellipsoids of bonds or groups of atoms. Comparison of the experimental constants ${}_{m}K$ and the values calculated for various rotational isomers permits conclusions about the steric structure, while comparison of the true values and those obtained on the basis of the additive resolution of the polarisability ellipsoids gives rise to the possibility of analysing the electron redistribution in the molecules being compared. The dipole moments and the constants ${}_{m}K$ are calculated from the bond lengths and valence angles (see the relevant reviews for phosphorus compounds[74-76]) by the method of Corey and Sneen[77].

The data in Table 1 show that the values of ${}_{m}K$ for 2-X-1,3,2-dioxaphosphorinane molecules have been most fully investigated. These compounds have been used traditionally in the Kazan School of Chemistry. As early as the beginning of the 1950s, A. E. Arbuzov and coworkers developed methods for the synthesis of various saturated phosphorus-containing heterocycles[71-73] and began the first studies of their physical and chemical properties.

It is noteworthy that phosphorus(III) compounds are characterised by a wide variety of effects due to the mutual influence of atoms; this is shown particularly by the wide scale of changes in the chemical shifts due to the phosphorus atomic nucleus in $^{31}P^{III}$ NMR (from −230 to +450 p.p.m.) compared with four- (from −130 to +115 p.p.m.) and five-coordinated phosphorus (from −30 to +100 p.p.m.)

The problem therefore arises of the validity of employing the usual additive parameters for the calculation, since incorrect results may be obtained when no account is taken of the high sensitivity of the electrical and electro-optical bond characteristics to electronic interactions.

This hypothesis was confirmed in a study of the structure of one of the simplest 1,3,2-dioxaphosphorinanes – 2-chloro-1,3,2-dioxaphosphorinane (LXIX), which exists solely as the chair conformer. The calculation of dipole moment and the constant $_mK$ for compound (LXIX) from the parameters found from the corresponding values for symmetrically substituted derivatives leads to the conclusion that the P–Cl bond is equatorial[27]:



$\mu_A = 2.94$ D; $_mK = -101$ $\mu_e = 3.37$ D; $_mK = 144$

$\mu_{exp.} = 3.47$ D; $_mK_{exp.} = 164$

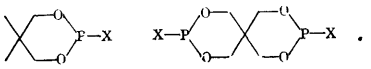
This conclusion conflicted with electron diffraction data[78] and the analysis of $^1$H NMR spectra[79–82] and chemical reactions[82], but agreed with the calculation of the band contours in vibrational spectra[83]. It may be that the inaccuracies of the additive phosphorus bond parameters led to erroneous results in the application of the dipole moment and Kerr effect methods.

The ideal solution to the problem of the selection of the additive parameters for solving conformational problems was one in which both bond and structural parameters are determined simultaneously. Bearing in mind that the exact calculation of $_mK$ is impossible without knowledge of the exact values of the dipole moments, we shall consider initially how correct are the bond dipole moments employed.

## 1. The Nature of the Electron Density Distribution in 2-X-1,3,2-Dioxaphosphorinanes

The simultaneous determination of the phosphorus bond dipole moments ($m_{P-O}$ and $m_{P-X}$) and of the orientation (axial or equatorial) of the exocyclic substituent X, i.e. three unknown parameters, is possible by extending the range of compounds investigated which are known *a priori* to have identical structures (the so called isoconformational compounds) but different directions of the molecular dipole moment.

It is useful to compare 2-X-1,3,2-dioxaphosphorinanes with their 5-spiro-analogues, which have been indeed shown to have identical structures by the study of steric interactions[84] and by the analysis of $^1$H NMR spectra[85]:



The symmetry of spiro-compounds is such that the dipole moments of the ring P–O bonds have little effect on the final results as a consequence of the mutual cancellation of the $m_{P-O}$ values. The dipole moment of compound (LXIX), calculated with the usual parameters for the equatorial conformation (3.37 D), is closer to the experimental value (3.47 D) than the moment for the axial conformation (2.94 D), whereas there is no doubt that the P–Cl bond in the spiro-analogue (LXXII) has the axial orientation [$\mu_{aa} = 2.01$; $\mu_{ee} = 3.53$; $\mu_{exp} = 2.10$ D (Arbuzov et al.[6])].

A method for the simultaneous determination of the structure and phosphorus bond dipole moments has been proposed[6] on the basis of data for the two types of compounds considered. The bond polarities $m_{P-O}$ and $m_{P-X}$ were treated as the unknown quantities. Vector summation of the bond dipole moments makes it possible to express the experimental dipole moments of the compounds as functions of the unknown quantities $m_{P-O}$ and $m_{P-X}$ for the axial and equatorial conformations. Each of the three equations described a three-dimensional surface in the space defined by the coordinates $m_{P-O}$, $m_{P-X}$, and the resultant moment $\mu$. Their intersection by the $\mu^2_{exp}$ plane yields constant-property lines whose projections on to the $m_{P-O}$ and $m_{P-X}$ planes are illustrated graphically in Fig. 3 (for X = Cl). The method may be referred to as the method of isoelectric maps. An analytical solution of the systems of equations is also possible, but the graphical procedure is simpler and clearer. The solution, consisting of a compatible set of bond moments for both types of compounds, are given by the points of intersection of the straight lines representing $\mu^2_{exp}$ for compound (LXXII) with the curves corresponding to $\mu^2_{exp}$ for compound (LXIX). The requirement that the values obtained are physically significant, i.e. that the parameters thus found do not differ greatly from the values obtained for the dipole moments of symmetrically substituted compounds, serves as a criterion of the validity of the particular solution. Fig. 3 shows that, for the equatorial conformation of the P–Cl bond, the phosphorus bond moments satisfying simultaneously the experimental dipole moments have improbable values; for the axial orientation of the chlorine atom, the unique solution $m_{P-O} = -0.72$ D and $m_{P-Cl} = 0.92$ D [6] is acceptable. The higher polarity of P–Cl bond in 2-chloro-1,3,2-dioxaphosphorinane compared with $PCl_3$ is consistent with the lower $^{35}$Cl NQR frequency and the greater length of the P–Cl bond[86].

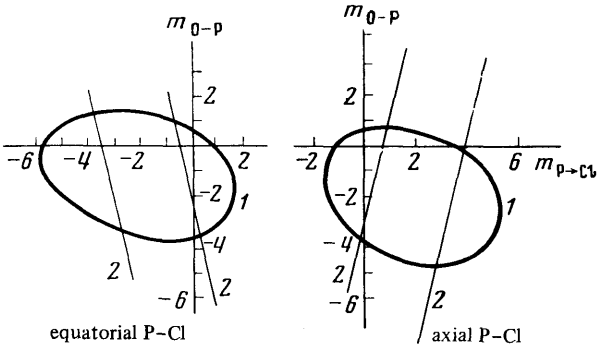



**Figure 3.** Dependence of the squares of the dipole moments of compounds (LXX) (curve *1*) and (LXXII) (curve *2*) on the dipole moments of the P–O ($m_{O \to P}$) and P–Cl ($m_{P \to Cl}$) bonds.

Of the eight possible solutions for X = $NEt_2$ (Fig. 4), only one is realistic—with $m_{P-O} = 0.65$ and $m_{P-N} = 1.37$ D; it corresponds to the equatorial position of the P–N bond[87]. In 2-phenyl-1,3,2-dioxaphosphorinanes (Fig. 5), two solutions are most probable: $m_{Ph-P} = -0.95$ and $m_{O-P} = 0.06$ D for the axially oriented phenyl group and

$m_{Ph-P}$ = 0.96 and $m_{O-P}$ = 0.43 D for its equatorial position. By resorting to the dipole moment of a third isoconformational compound, namely 5-methyl-5-nitro-2-phenyl-1,3,2-dioxaphosphorinane ($\mu_{exp}$ = 6.23 D),[88] a choice between these two possible solutions still cannot be made. Since comparison of the experimental dipole moments of triphenylphosphine and its tri-*p*-substituted derivatives shows that the moment of the Ph–P group is directed towards the benzene ring, we give preference to the first solution.

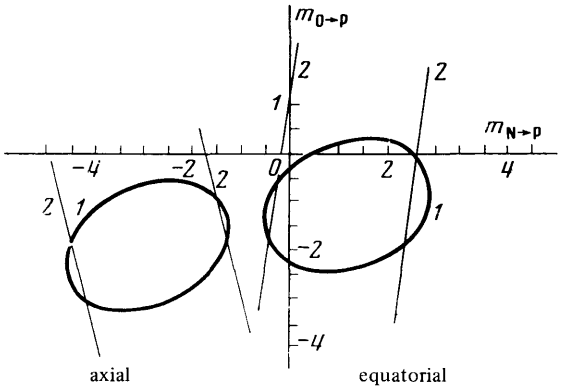



**Figure 4.** Dependence of the squares of the dipole moments of 2-diethylamino-1,3,2-dioxaphosphorinane (curve *1*) and its 5-spiro-analogue (curve *2*) on the dipole moments of the P–O ($m_{O\to P}$) and P–N ($m_{N\to P}$) bonds.

The symmetry of the substitution of phosphorus atoms in 2-alkoxy-1,3,2-dioxaphosphorinanes (X = O-Alk) eliminates the necessity for the determination of the P–O bond dipole moment and one can therefore assume that the calculation of the dipole moments of these compounds using $m_{P-O}$ = 0,[6] found from the dipole moment of the bicyclic phosphite (C), is valid. Determination of the structure of compounds of this type is a more difficult problem, since, apart from the position of the exocyclic bond, it is necessary to determine the orientation of the P–O–Alk fragment relative to the phosphorus LEP (*cis*-, *trans*-, or *gauche*-, Fig. 6). Graphical comparison of the values of $\mu^2$ for two isoconformational compounds—2-ethoxy-1,3,2-dioxaphosphorinane and the 5-spiro-analogue (Fig. 7*a*)—makes it possible to determine two unknown structural parameters: the axial position of the exocyclic P–O bond and the *gauche*-orientation of the ethoxy-group[84]. The application of an analogous method to 2-phenoxy-1,3,2-dioxaphosphorinanes (Fig. 7*b*)[84,129] on the assumption that the values of $m_{P-O}$ for the ring and exocyclic bonds are equal leads to the conclusion that the phenoxy-group has the *cis*-orientation. However, in the compounds examined the environment at the phosphorus atom is not rigorously symmetrical, since the exocyclic P–O bond adjoins the benzene ring and not the alkyl group.

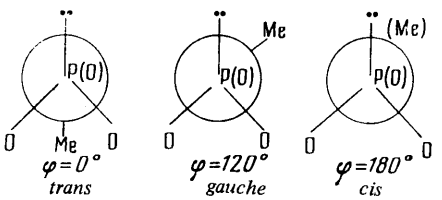



**Figure 6.** Internal rotation relative to the exocyclic P–O bond determined by the dihedral angle $\varphi$.

A change in the dipole moments of the P–O bonds should not lead to a sharp alteration of the principal structural conclusions—they can change only to give the *gauche*-conformation. If one disregards structural parameters, then there are only two unknown quantities—the dipole moments of the exocyclic and ring P–O bonds; it is therefore quite sufficient to examine two isoconformational compounds whose dipole moments are not linearly related: compound (LXXXIX) and its 5-spiro-analogue ($\mu_{exp}$ = 2.89 D). In setting up systems of equations for $m_{Ph-O(PIII)}$ corresponding to the *cis*- and *gauche*-forms, 1.10 D was used[8]. Simultaneous solution of each system of equations yielded the following parameters:

$m_{O-P(acyclic)}$ = 0.22 and $m_{O-P(cyclic)}$ = +0.8 D for the *cis*-form;

$m_{O-P(acyclic)}$ = −0.8 and $m_{O-P(cyclic)}$ = +0.42 D for the *gauche*-form.

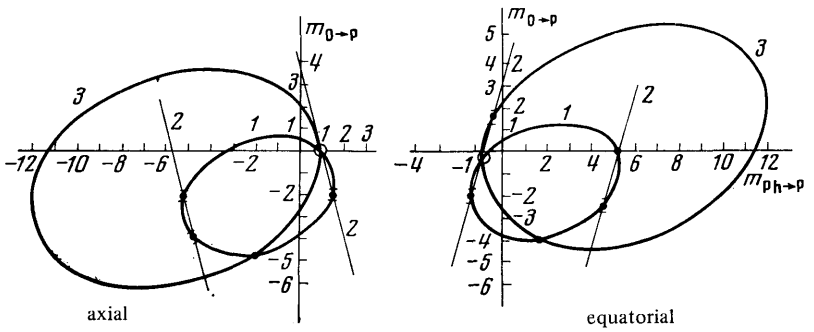



**Figure 5.** Dependence of the squares of the dipole moments of 2-phenyl-1,3,2-dioxaphosphorinane (curve *1*), its 5-spiro-analogue (curve *2*), and the 5-methyl-5-nitro-derivative (curve *3*) on the dipole moments of the P–O ($m_{O\to P}$) and Ph–P ($m_{Ph\to P}$) bonds.

A choice can be made between these two sets, i.e. the third structural parameter can be found, only when additional dipole moment data for other isoconformational compounds are resorted to: the *p*-bromo derivative of compound (XC) and the *p*-nitro-derivative of compound (XCI). The results of the calculations show that the agreement with experiment is reached only for the *cis*-form. The bond polarity data obtained made it possible to estimate the angle of rotation of the benzene ring in the *o*-substituted (*o*-bromo- and *o*-nitro-) derivatives. The experimental data ageee with the calculated results for the structure where the benzene ring is perpendicular to the plane of the P–O–$C_{aryl}$ bonds.

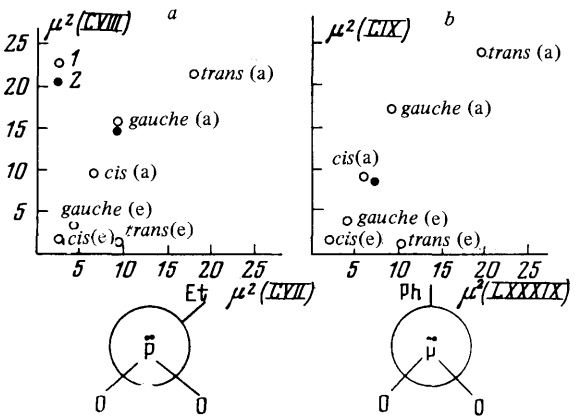



**Figure 7.** Graphical relations between the squares of the dipole moments of 2-ethoxy-1,3,2-dioxaphosphorinane (CVII) and its 5-spiro-analogue (CVIII) (*a*) and between the squares of the dipole moments of 2-phenoxy-1,3,2-dioxaphosphorinane (LXXXIX) and its 5-spiro-analogue (CIX) (*b*): 1) calculated values; 2) experimental values.

Table 5. The dipole moments of phosphorus bonds in 2-X-1,3,2-dioxaphosphorinanes $O_2PX$ according to data obtained by the isoelectric map method.

| Environment at P | Dipole moment | Substituent X | | | | |
|---|---|---|---|---|---|---|
| | | O(Ph) | Cl | O(Et) | Ph | $N(Et_2)$ |
| $O_2PX$: | $m_{P-O}$ | −0.8 | −0.72 | −0.32 | 0.06 | 0.65 |
| | $m_{P-X}$ | 0.22 | 0.92 | 0.14 | 0.95 | 0.37 |
| $PX_3^*$: | $m_{P-X}$ | 0 | 0.56 | 0 | 1.18 | 0.31 |

*See corresponding footnotes to Table 3.

The phosphorus bond dipole moments presented in Table 5 demonstrate the extreme electronic lability of phosphorus(III) compounds as a function of the environment at the phosphorus atom.

We emphasise yet again that the bond dipole moments obtained are effective values and thus reflect the nature of the redistribution of electron density. When a comparison is made with the bond polarities of symmetrically substituted phosphorus compounds, a deviation from these values is observed for exocyclic bonds. The greatest deviation $\Delta m_{P-Cl} = 0.36$ D is directed towards the chlorine atom and indicates its electron-accepting properties. The P–O ring bonds undergo much greater changes: whereas in the compound with $X = NEt_2$ there is a redistribution of electron density to the extent of approximately $0.4e$ from the phosphorus atom to the neighbouring oxygen atoms with an almost unchanged $m_{P-N}$, in the compound with X = Cl or OPh virtually the same electron density ($0.44e$) is transmitted from the ring oxygen atoms to the phosphorus atom. The nature of the electron redistribution for X = OEt and Ph is approximately the same. Consequently a strong geminal interaction, which depends on the nature of the atom X and is strongly reflected in the properties of the O–P bonds, is observed in the $O_2P$–X series. A possible mechanism for this interaction is examined below.

2. The Intramolecular Interactions and the Anisotropy of the Polarisability of the $P^{III}$– Cl Bond

The problem of the simultaneous determination of the bond polarisability ellipsoids and molecular conformations is mathematically more complex than the determination of dipole moments. We shall consider this problem for the $O_2PCl$ group in compound (LXX), since there are no grounds for doubting the validity of the electro-optical parameters of the carbon bonds. The group has a plane of symmetry and one must therefore determine four independent parameters: three polarisability axes and their orientations defined by the angle $\varphi$ (Fig. 8). A necessary condition for the solution of this problem is an increase in the number of experimental parameters either by extending the range of isoconformational compounds or by increasing the number of methods used. As in the previous section, compound (LXX) and its spiro-analogue (LXXII) were examined and their $_mK$ constants were determined. Determinations of the depolarisation of scattered light for compound (LXX) served as an additional method.

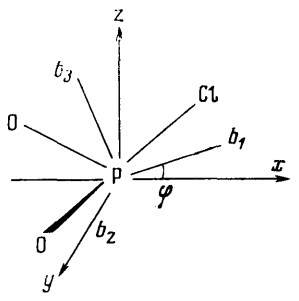



**Figure 8.** The directions of the axes of the polarisability ellipsoid of the $O_2PCl$ group.

The experimental values of $_mK$ for compounds (LXX) and (LXXII) and of $_2\delta^2_\infty$ for compound (LXX) were expressed as functions of the unknown quantities $\gamma_{P-O}$ and $\gamma_{P-Cl}$ for the axial and equatorial conformations. The equations obtained are presented in Fig. 9 in a graphical form. The limits of the rectangle denote the region outside which the bond polarisabilities have no physical significance.

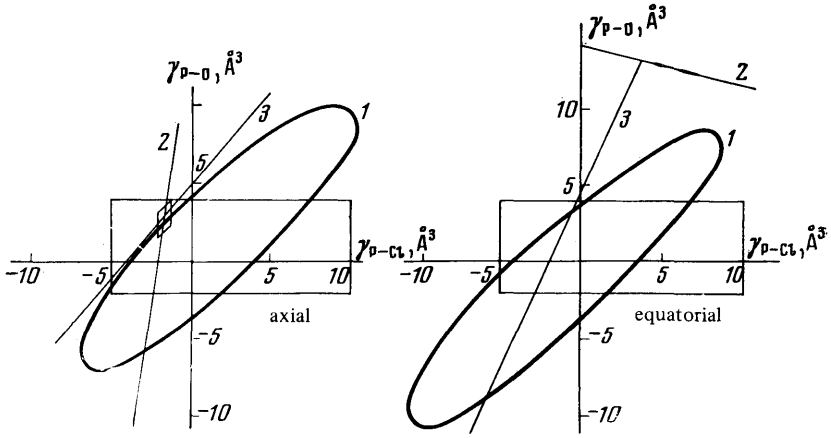



**Figure 9.** Dependence of $\gamma^2$ (curve *1*) and $K_2$ (curve *2*) for compound (LXX) and of ${}_mK$ (curve *3*) for compound (LXXII) on the anisotropy of the P–O and P–Cl bond polarisabilities; $|\gamma^2| = {}_2\delta^2_\infty (b_{xx} + b_{yy} + b_{zz})^2$.

Analysis of the graphical relation shows that a full set of values of $\gamma_{P-O}$ and $\gamma_{P-Cl}$ (the points of intersection of the straight lines and the ellipse) is possible only for the axial disposition of the P–Cl bond, since in this case three lines converge in one region. The tensor summation of the values $\gamma_{P-O} = 2.7$ and $\gamma_{P-Cl} = -1.7$ obtained yields the polarisability ellipsoid for the $PO_2Cl$ group with $b_1 = 6.8$, $b_2 = 7.8$, and $b_3 = 3.0$ Å$^3$ and the angle $\varphi = -7$ between $b_1$ and the plane of the $PO_2$ fragment (Fig. 8). The principal axes of the polarisability ellipsoid for the $PO_2Cl$ group may be determined more accurately without considering each bond separately and hence without introducing the hypothesis of their axial symmetry ($b_T \neq b_V$). The solution of three equations with three experimental values using the total group polarisability (17.56 Å$^3$) for the four unknown parameters yields two sets of polarisability ellipsoids: $b_1 = 6.437$, $b_2 = 3.369$, $b_3 = 7.537$, and $\varphi = -13°$; $b_1 = 6.783$, $b_2 = 7.871$, $b_3 = 3.135$, and $\varphi = -10°$. The second set almost coincides with the values obtained in terms of the approximation of axial symmetry, which proves the validity of the approach employed. The values obtained describe satisfactorily the structure of the 4-methyl derivative (LXIX) and of compound (LXXI).[6]

The axes of the bond polarisability ellipsoids may be determined by the joint examination of data derived by two related methods—double refraction and the depolarisation of Rayleigh light scattering—for the same compound. Thus the graphical representation of experimental values of ${}_mK$ and $10^{-3}\ {}_2\delta^2_\infty$ for 2-chloro-1,3,2-dioxaphospholane as a function of the unknown $\gamma_{P-O}$ and $\gamma_{P-Cl}$ showed[6] that the only possible solution, where the ellipse and the straight line intersect, corresponds to the axial position of the chlorine atom with $\gamma_{P-O} = 1.93$ and $\gamma_{P-Cl} = 0.37$ Å$^3$.[6]

The successive application of the methods considered above for the determination of the anisotropy of bond polarisabilities can also lead to satisfactory results. For example, the analytical solution of the system of two equations for the axial and equatorial conformations of 2-chloro-1,3,2-dithiaphosphorinane (CIII), the experimental values ${}_mK = 78$ and ${}_2\delta^2_\infty = 4.6 \times 10^{-3}$ for which were expressed as functions of the unknown $\gamma_{P-S}$ and $\gamma_{P-Cl}$, led to four possible versions: (1) 0.65 and −1.33 and (2) −3.04 and −0.76 Å$^3$ for the axial conformation and (3) 2.97 and 2.18 and (4) −3.97 and −1.84 Å$^3$ respectively for the equatorial conformation. The latter solution is unlikely owing to the high negative values of $\gamma$. The choice from the three remaining solutions (i.e. the determination of the third structural parameter) was made by examining the values of ${}_mK$ for 2-phenyl-1,3,2-dithiaphosphorinane (CIV): the high negative value ${}_mK = -344$ may be obtained in only one case—when the P–Ph bond is axial, $\gamma_{P-S} = 0.65$ Å$^3$, and the plane of the benzene ring is perpendicular to the plane of symmetry of the molecule. Using the average bond polarisabilities (Table 2), it is possible to calculate the components of the polarisability tensor of the P–S bond: $b_L = 3.24$ and $b_T = b_V = 2.59$ Å$^3$; the corresponding values for the P–Cl bond are $b_L = 2.46$ and $b_T = b_V = 3.79$ Å$^3$.

The anisotropies of phosphorus bond polarisabilities in methyl phosphorodichloridite (IV) were calculated for the observed electron-diffraction structure[89] (angle of deviation of the methoxy-group from the *cis*-position $\varphi = 17°$): $\gamma_{P-O} = 1.54$ and $\gamma_{P-Cl} = 1.78$ Å$^3$.[36] The latter value is intermediate between the corresponding parameters for phosphorus trichloride and cyclic phosphoromonochloridites. The P–Cl bond length also varies in parallel with $\gamma_{P-Cl}$.[6] The observed parallel variation may be useful in the determination of the values of $\gamma_{P-Cl}$ for the substituted phosphites $PCl_n(OR)_{3-n}$.[6]

All the facts presented above show that the environment of the phosphorus(III) atom has a marked influence on the system of mobile electrons. This precludes the use of homogeneous electro-optical characteristics even for compounds of the same class but conformationally inhomogeneous. A change in the anisotropy of the phosphorus bond polarisabilities has been observed[6] in 2-chloro-1,3,2-dioxaphospholane and its 4,4,5,5-tetramethyl analogue (LXI). The cause of this is associated with the difference between the conformations: the first compound has the form of an envelope with an axial P–Cl bond and the second has the form of a half-chair; as a result of this, the P–Cl bond length[90,91] and the shielding of the phosphorus nucleus[6] are altered. Thus, phosphorus(III) compounds require a special non-trivial approach, where all the unknown structural and bond parameters are found simultaneously for a series of isoconformational compounds.

The cause of such unusual mobility of the electron cloud of phosphorus(III) has not so far been elucidated, but it is apparently associated with intramolecular interactions. Analogous deviations from the additivity of polarisability for an asymmetric environment have been observed in $\alpha$-chloromethyl ether[92] and methanesulphonyl chloride[3]. The anomalous behaviour of $\alpha$-chloroethers[93] and compounds of Group IV elements with $\alpha$-carbofunctional groups[94] is manifested also in other properties and can be explained by intramolecular coordination of the type of a three-centre bond formed by $\sigma$ electrons (the so called $\alpha$-effect[93]). The involvement of the oxygen LEP creates an excess of $\pi$ electrons at the chlorine atom and the $^{35}Cl$ NQR frequency falls compared with alkyl chlorides. An analogous decrease of frequencies has been observed[86] also for the asymmetric phosphorochloridites $ROPCl_2$ and $(RO)_2PCl$ compared with phosphorus trichloride. The variation of the frequencies and of the P–Cl bond length cannot be explained by the involvement of the vacant *d* orbitals of the phosphorus atom, since this should have led to a deficiency of electrons at the chlorine atom[86].

Other, alternative mechanisms of the observed effect have also been proposed: direct interaction of the geminal atoms in the direction of the field[95] and hyperconjugation of the LEP of the oxygen atom with the C–Cl bond[96]. The possibility of the $\sigma$, $\pi$ conjugation for the phosphorus atom has been discussed recently[97]; it was noted that hyperconjugation with $\sigma$-bonds formed by the elements in the Third Period should be observed. By analogy with pyranoid derivatives, for the axial position of the P–Cl bond the oxygen *p* orbital is disposed in a manner "convenient" for overlapping with the antibonding $\sigma^*$ orbital of the P–Cl bond. This type of delocalisation strengthens the P–O bond and weakens the P–Cl bond. In fact, the P–Cl bond length in 2-chloro-1,3,2-dioxaphosphorinane (2.128 Å) is much greater than in phosphorus trichloride (2.043 Å).[86] The formation of many-centre bonds is also stereospecific and is possible only for the axial conformation. Whatever the mechanism of the observed interaction, it should lead to an increase of the perpendicular component of the polarisability ($b_T = b_V$) of the bond with the chlorine atom: this was observed in phosphorochlorodites, 2-chloro-1,3,2-dithiaphosphorinanes, chloro- and bromoarsenites[99,100], and $\alpha$-chloroethers[92]. The concept of the delocalisation of the LEP of the oxygen atom to the antibonding orbital of the exocyclic bond explains, within the framework of the general theory of molecular orbitals, the anomeric effect[98,101] and the *gauche*-effect[101,102], i.e. the stabilisation of the conformations which were established above for phosphorus(III)-containing heterocycles; the present author therefore believes that this concept is preferable, although it does leave many problems unsolved.

### 3. The Anisotropy of the Polarisability of $P^{III}$–O Bonds.

The above analysis of the bond dipole moments in 2-X-1,3,2-dioxaphosphorinanes showed that the P–O bonds within the ring undergo the greatest changes. The redistribution of electron density should lead to an alteration of the anisotropy of the polarisability. The value $\gamma_{P-O} = -0.59$ Å$^3$, most widely used in the literature, was obtained by Le Fevre[1] on the basis of $_mK$ for the bicyclic phosphite (C), determined in dioxan, but it is inconsistent with the values of $_mK$ for compounds of the 1,3,2-dioxaphosphorinane series. Thus the value of $\gamma_{P-O}$ for 2-chloro-1,3,2-dioxaphosphorinane (2.7 Å$^3$), 2-chloro-1,3,2-dioxaphospholane (1.93 Å$^3$), and methyl phosphorodichloridite (1.54 Å$^3$) were presented in the previous section. The determination of the steric structures (see Section I) of the 2-alkoxy-[84] and 2-phenoxy-derivatives[129] of compound (LXXXIX) and of 2-phenyl-1,3,2-dioxaphosphorinanes (XCIX) makes it possible to calculate the phosphorus bond polarisability eliipsoids. For the axial *gauche*-conformation of the methoxy-group[84], $\gamma_{P-O} = -0.25$ Å$^3$ in compound (LXXXV).[129] The phenoxy-group in compound (XCII) has the axial *cis*-orientation and its benzene ring is arranged at right angles to the plane of symmetry of the molecule[129]; the anisotropies of the exocyclic and ring P–O bond polarisabilities, calculated for this structure, are respectively 2.35 and 3.11 Å$^3$.[129]

The axial orientation of the phenyl group in 5,5-dimethyl-2-phenyl-1,3,2-dioxaphosphorinane (XCIX) was demonstrated in Section III. Such a bulky substituent can occupy the axial position only when the plane of the benzene ring is perpendicular to the plane of symmetry of the molecule (as was found for 2-phenyl-1,3,2-dithiaphosphorinane in Section III, by Martin and Robert[103], and from the analysis of $^1H$ NMR spectra[104] and X-ray diffraction data[105]). When $_mK_{exp} = -298$ is expressed as a function of two unknown parameters, the following relation is obtained:

$$13.43\gamma_{P-O} + 0.78\gamma_{P-C(Ph)} = 26.43,$$

the analysis of which shows that reasonable solutions are possible only for positive values of $\gamma$, $\gamma_{P-O}$ being capable of variation over the very narrow range 1.8–2.0 Å$^3$, whereas the range of the corresponding solutions for $\gamma_{P-C(Ph)}$ is somewhat wider—from 0.6 to 2.9 Å$^3$. A positive value of $\gamma_{P-C_{sp^2}(Ph)}$ is also obtained on the hypothesis that the anisotropies of the $P-C_{sp^3}$ and $P-C_{sp^2}$ bond polarisabilities are close, differing by the exaltation of the total polarisability. The latter is expressed in terms of the difference between the refractions (Table 2). Then $b_L = 3.28$ and $b_T = 0.79$ Å$^3$. The value $\gamma = 2.49$ Å$^3$ obtained appears more reliable than the value calculated by Le Fevre[1] on the basis of the empirical relation between $b_L$ and the bond length ($\gamma = -0.3$ Å$^3$, Table 4).

The data presented show that $\gamma_{P-O}$ is positive in most cases. We may note the similarity of $\gamma_{P-O}$ and $m_{P-O}$ for phenoxy-derivatives and 2-chloro-1,3,2-dioxaphosphorinane, which shows that the electronic interactions are related.

The determination of the anisotropy of the P–O bond polarisability permits the solution of complex conformational problems associated with the determination of several structural parameters, one or two of which vary continuously. In such cases, the combined and successive application of related methods to a series of isoconformational compounds is most effective. This procedure has been partly demonstrated above in the analysis of molecular and bond dipole moments and of the anisotropies of the P–O bond polarisabilities in 2-phenoxy-1,3,2-dioxaphosphorinanes. The last stage in the structural study of such molecules involves the determination of the angle of rotation of the benzene ring, which may be found from the $_mK$ data for compounds (LXXXIX)–(XCI). The calculations were made for the *cis*-axial orientation of the phenoxy-group found above, with the parallel and perpendicular arrangements of the plane of the benzene ring relative to the plane of the $P-O-C_{aryl}$ bonds. The following values were used for the $O-C_6H_4-Br-p$ and $O-C_6H_4-NO_2-p$ fragments: $b_1 = 18.23$, $b_2 = 13.47$, and $b_3 = 9.38$ Å$^3$, calculated from Le Fevre's data[1], and $b_1 = 18.99$, $b_2 = 12.62$, and $b_3 = 7.62$ Å$^3$.[106] The smallest calculated values were obtained for the perpendicular conformation and agree best with experiment.

In phenyl *o*-phenylene phosphites, the structural problem reduces to the determination of the following unknowns: the angle of the non-planarity of the five-membered ring $\Psi$, the position of the exocyclic bond, the angle of rotation relative to the P–O bond $\varphi$, and the angle of rotation of the benzene ring of the phenoxy-group $\theta$, the first and last parameters varying continuously (Fig. 10).

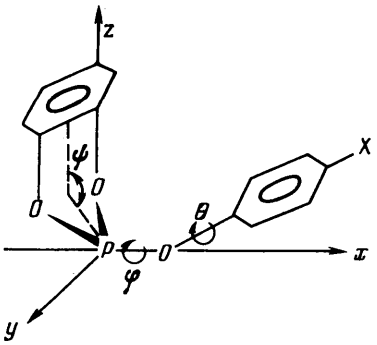



**Figure 10.** Determination of the steric structure of *o*-phenylene phenyl phosphites.

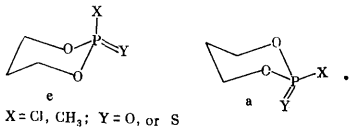
The joint examination of the dipole moment of phenyl *o*-phenylene phosphite (LXVII) itself and of its *p*-bromo- and *p*-methoxy-derivatives permits the determination of the dihedral angle of the bending of the five-membered ring (155°) corresponding to the axial position of the exocyclic bond, and the *gauche*-orientation of the phenoxy-group may be demonstrated[8]. The angle of rotation of the benzene ring was calculated from the Kerr effect data for the observed conformation[8]. The angle was varied from 0° (when the plane of the benzene ring and the plane formed by the P–O–C bonds coincide) to 180° in 30° steps. The positive direction of rotation was assumed to be that in which the position of the aryl group closest to the phosphorus moves away from the oxygen atom. A 35° angle corresponds to the experimental value of ${}_{m}K$. The strong steric interactions in the *oop*-tri-t-butyl derivative (LXVIII) induce a reorientation of the benzene ring: the experimental value of ${}_{m}K$ changes sign [157 for compound (LXVII) and −35.5 for compound (LXVIII)], which corresponds to an additional displacement of the benzene ring from the initial plane: the angle increases to 90°.[8]

## IV. THE STRUCTURES OF FOUR-COORDINATED PHOSPHORUS COMPOUNDS

Since four-coordinated phosphorus forms highly polar and anisotropic bonds (Tables 3 and 4), the dipole moments and the values of ${}_{m}K$ are very sensitive to conformational changes. In view of the necessity to test the validity of and to refine the additive values for phosphorus(IV) bonds, studies were begun on systems which are simple as regards conformation and where the probable number of rotational isomers does not exceed two. 1,3,2-Dioxaphosphorinanes, investigated by a wide variety of physical methods, may be included among them. Comparison of the results of several investigations may serve as a criterion of the validity of the methods of calculation employed. Conformational analysis of heterocyclic molecules is a problem of independent interest—the study of the influence of the nature of the substitutent at the phosphorus atom on the structure of the molecule as a whole.

### 1. Conformational Analysis of Heterocyclic Molecules

Owing to the absence† of rotational isomerism in the exocyclic part of the molecule, the set of the probable conformations of the acid chlorides and methyl derivatives of 1,3,2-dioxaphosphorinanes is reduced to a minimum: there are two chair forms with the axial (a) or equatorial (e) orientations of the P=Y bond:




The existence of conformations other than the chair conformations has not been confirmed by NMR data[107,108]

Table 6 presents the experimental and calculated values (the standard parameters found from the constants ${}_{m}K$ for symmetrically substituted compounds were used for the phosphorus bonds: $\gamma_{P-O} = -0.59$; $\gamma_{P-C} = 1.49$; $\gamma_{P-Cl} = 2.66$ Å$^3$, subject to the conditions that $\gamma_{C-C} = 0.71$ and $\gamma_{C-O} = 0.43$ Å$^3$.[1] We shall compare initially data for the thiono-derivatives (LXXVI) and (LXXVII), on the one hand, and (LXXXI) and (LXXXII), on the other. While the polarities of the acid chlorides (LXXVI) and (LXXVII) are similar, the dipole moments of compounds (LXXXI) and (LXXXII) differ markedly, which indicates a difference between their conformations. The dipole moments and the constants ${}_{m}K$ found for compounds (LXXXII) and (LXXVII) are closest to the values calculated for the chair form with an equatorial thiophosphoryl group (Table 6). The stabilisation of one conformer is possible for the *cis*-configuration of the 4-methyl group and the P=Y bond. The constant ${}_{m}K$ for this structure agrees with the experimental value for compound (LXXXII). The satisfactory agreement confirms the applicability of the additive P–O, P=S, and P–C bond polarisabilities and makes it possible to determine the structure of compound (LXXXI), which exists in the form of an equilibrium mixture of two chair forms, where the conformation with the thiophosphoryl group in the axial position predominates (mole fraction 0.8).

The phosphorochlorothioate (LXXVI) is conformationally homogeneous[111] and, according to dipole moment measurements, has the chair form with an equatorial thiophosphoryl group[30]. However, all the calculated values of ${}_{m}K$ proved to be much lower than the experimental results[30]; for this reason, the effective anisotropy of the P–Cl bond polarisability, determined from the experimental ${}_{m}K$ for this compound ($\gamma_{P-Cl} = -1.31$ Å$^3$), was considered. The value obtained led to the identification of the equatorial conformation (for the P=Y bond) of the 4-methyl analogue (LXXVII) [30] and the phosphorochloridate (LXXV).[29]

In connection with the study of the problem of internal rotation about the O–P bond, it was of greatest interest to investigate compounds symmetrically substituted relative to the phosphorus atom—2-alkoxy-derivatives of

†The rotation of the methyl group does not affect the calculated dipole moment and the constant ${}_{m}K$.

Table 6. The calculated and experimental parameters for 1,3,2-dioxaphosphorinanes with phosphorus(IV).

| Substituents | | Compound | Parameter | Experimental value | Calculated* | |
|---|---|---|---|---|---|---|
| at P atom | at $C_{(4)}$ atom | | | | P = Y (e) | P = Y (a) |
| $CH_3$, S | H | LXXXI | μ, *D* | 3.90 | 5.89 | 3.92 |
| | | | $_mK$ | 436 | 1287 | 204 |
| $CH_3$, S | $CH_3$ | LXXXII | μ, *D* | 5.37 | 5.89 | 3.92 |
| | | | $_mK$ | 1175 | 1273 (a); 1168 (e) | 243 (a); 202 (e) |
| Cl, S | H | LXXVI | μ, *D* | 5.30 | 5.46 | 4.22 |
| | | | $_mK$ | 1356 | 714 | —110 |
| Cl, S | $CH_3$ | LXXVII | μ, *D* | 5.54 | 5.46 | 4.22 |
| | | | $_mK$ | 1195 | 1341 (a); 1294 (e) | 111 (a); 74 (e) |
| Cl, O | H | LXXV | μ, *D* | 5.89 | 5.77 | 3.81 |
| | | | $_mK$ | 556 | 753 | 123 |
| H, O | $CH_3$** | LXCIV | μ, *D* | 5.77 | 5.85 | 3.78 |
| | | | $_mK$ | 541 | — | — |
| H, O | $CH_3$** | LXCV | μ, *D* | 4.19 | 5.85 | 3.78 |
| | | | $_mK$ | 160 | — | — |
| $CH_3$, O | $CH_3$** | LXXX | μ, *D* | 6.36 | 6.06 | 3.97 |
| | | | $_mK$ | 346 | — | — |
| $CH_3O$, O | $CH_3$** | LXXXV | μ, *D* | 6.07 | 5.41 (*c*); 7.6 (*t*); 5.91 (*g*) | 3.14 (*c*); 5.22 (*t*); 3.75 (*g*) |
| | | | $_mK$ | 344 | 390 (*c*); 978 (*t*); 354 (*g*) | 60 (*c*); 182 (*t*); 1 (*g*) |
| $CH_3O$, O | $CH_3$** | LXXXVI | μ, *D* | 4.46 | 5.41 (*c*); 7.6 (*t*); 5.91 (*g*) | 3.14 (*c*); 5.22 (*t*); 3.75 (*g*) |
| | | | $_mK$ | 165 | 390 (*c*); 978 (*t*); 354 (*g*) | 60 (*c*); 182 (*t*); 1 (*g*) |
| $CH_3O$, S | $CH_3$** | LXXXVII | μ, *D* | 5.51 | 509 (*c*); 6.89 (*t*); 5.58 (*g*) | 2.85 (*c*); 4.94 (*t*); 3.50 (*g*) |
| | | | $_mK$ | 929 | 1016 (*c*); 2173 (*t*); 848 (*t*) | 177 (*c*); 531 (*t*); 170 (*g*) |
| $CH_3O$, S | $CH_3$** | LXXXVIII | μ, *D* | 3.93 | 5.09 (*c*); 6.89 (*t*); 5.58 (*g*) | 2.85 (*c*); 4.94 (*t*); 3.50 (*g*) |
| | | | $_mK$ | 298 | 1016 (*c*); 2173 (*t*); 848 (*t*) | 177 (*c*); 531 (*t*); 170 (*g*) |

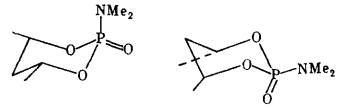
*(a) represents the axial position of the methyl group at $C_{(4)}$ and (e) represents the corresponding equatorial position.
**In conformity with the analysis of $^1$H NMR spectra [31,109,110], only the equatorial orientation of the methyl group at $C_{(4)}$ was considered for these compounds; (*c*), (*t*), and (*g*) represent calculations for the *cis*-, *trans*-, and *gauche*-conformations of the $OCH_3$ group.

1,3,2-dioxaphosphorinanes. The probability of conformational equilibrium between two chair forms (which would greatly complicate the solution of the conformational problem) was ruled out by the introduction of the 4-methyl group into the ring. Oxidation and addition of sulphur to the *cis*- and *trans*-isomers of 2-methoxy-4-methyl-1,3,2-dioxaphosphorinane yielded two pairs of geometrical isomers of the corresponding phosphates and phosphorothioates, for which the dipole moments and the constants $_mK$ were determined and calculated (Table 6). Joint analysis of the results obtained by spectroscopic methods ($^1$H NMR, infrared, and Raman spectroscopy) and of the dipole moments and the constants $_mK$ made it possible tp identify the structures produced [the multiple bond is in the equatorial and axial positions respectively in the *cis*- and *trans*-isomers of compounds (LXXXV) and (LXXXVII)] and to reach a conclusion about the stereospecificity of the chemical reactions investigated [31].

Earlier studies [29,30] of the Kerr effect in 1,3,2-dioxaphosphorinanes containing phosphorus(IV) were based on a preliminary analysis of the initial bond parameters and, where necessary, effective quantities were considered. The determination of the fundamental characteristics of the steric structures of compounds of this class (the greater tendency towards equilibrium between two chair forms compared with tervalent phosphorus analogues, the dependence of the conformation of the heterocycle on the nature of the exocyclic substituent, and the general nature of the conformational behaviour of compounds with phosphoryl and thiophosphoryl groups) makes it possible to analyse in greater detail the electrical and the electro-optical parameters of the phosphorus bonds. It was noted above that it is necessary to compare for this purpose the corresponding compounds with three- and four-coordinated phosphorus.

Section III presented the necessary data for 2-X-1,3,2-dioxaphosphorinanes with X = Cl, OAlk, $NR_2$, etc.

On the basis of the polarities of the *cis*- and *trans*-isomers of *cis*-4,6-dimethyl-2-dimethylamino-1,3,2-dioxaphosphorinane and their known steric structures [112], it is possible to determine the polarity of the phosphoryl group: 3.33 and 3.60 D were obtained for its equatorial and axial positions respectively [113].




μ = 5.80 D μ = 4.05 D

The difference between the dipole moments indicates the stereospecificity of the intramolecular interactions: the lower dipole moment of the equatorial phosphoryl group is apparently associated with the more pronounced conjugation between this group and the lone electron pairs of the ring oxygen atoms. Indeed, according to quantum-mechanical calculations, the multiplicity of the equatorial P=Y bond is greater than that of the axial bond [113]. The non-equivalence of the bond dipole moments in the two chair conformations was also noted for 2-methyl-2-thiono-1,3,2-dioxaphosphorinane. [30]

The identification of the conformations of two stereoisomeric 2-hydro-4-methyl-2-oxo-1,3,2-dioxaphosphorinanes (XCIV) and (XCV) [109,110] made it possible to revise the parameters of the polarity and polarisability of the phosphorus bonds [130] and to calculate the previously unknown anisotropy of the P–H bond polarisability, namely $\gamma_{P-H} = -1.1$ Å$^3$. [130]

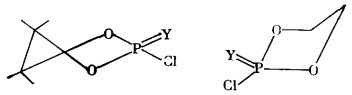


(XCIV): μ = 5.77 D; $_mK$ = 541; $m_{P=O}$ = 2.95 D, $\gamma_{P=O}$ = 0.81 Å$^3$;
(XCV): μ = 4.19 D; $_mK$ = 160; $m_{P=O}$ = 3.48 D, $\gamma_{P=O}$ = 0.3 Å$^3$.

The values obtained proved useful for the investigation of the steric structures of compounds (XCVI)–(XCVIII), which are involved in a complex conformational equilibrium[127].

Spectroscopic study of the phosphorochloridate (LXXV)[114] and the phosphorochlorothioate (LXXVI) [111], demonstrated their conformational homogeneity; the dipole moments and analysis of the $^1$H NMR spectra indicate a chair conformation with the equatorial position of the double bond. The parameters determined for this structure have the following values: $m_{P=O}$ = 2.40 D, $\gamma_{P=O}$ = 1.34 Å$^3$, $m_{P=S}$ = 2.10 D, and $\gamma_{P=S}$ = 3.06 Å$^3$ (Arshinova et al.[126]) (they differ somewhat from the values quoted by Arbuzov and Arshinova[5], who carried out the calculation on the basis of $\gamma_{P=O}$ and $\gamma_{P-Cl}$ calculated for $_mK$ in dioxan solutions).

The dipole moments and the constants $_mK$ for 2-chloro-2-oxo- and 2-chloro-2-thiono-1,3,2-dioxaphospholanes (LVII)–(LXVI) [126] were analysed on the basis of the results. According to Arshinova et al.[126], the 4,4,5,5-tetramethyl derivatives have the half-chair conformation; for the remaining compounds investigated, the envelope ring conformation, with the carbon atom displaced from the plane of the ring, is believed to be the most probable. The multiple bond is oriented preferentially pseudoaxially:



(LXI), (LXVI) (LVII), (LXII)

Four-membered rings constitute a more complex case for the conformational analysis of heterocycles, since one of the structural parameters (the angle of ring nonplanarity) varies continuously. The dipole moment and the constant $_mK$ for 3-chloro-3-thiono-1,3-thiaphosphetan (XLIX) were calculated as functions of the dihedral ring bending angle $\theta$, which was varied from 120°, when the P=Y bond is arranged pseudoequatorially, to 180°, when the ring is planar, and further to 240°, when the P=Y bond becomes pseudoaxial[24]. Electron diffraction data for the geometry of 3-chloro-3-oxo-1,3-thiaphosphetan were used in the calculation[115] and the parameters found for thietan were used for the C–S bond: 0.86 D; $b_L$ = 2.05; $b_T$ = 1.61 Å$^3$.[116] The experimental dipole moment of compound (XLIX), which is 2.18 D, agrees with the calculated minimum value (2.17–2.20 D) for $\theta$ = 130 to 150°. Joint examination of the dipole moment and the constant $_mK$ shows that the angle is 135°.[24] In the 3-oxo-derivative, the oxygen atom, whose bulk is smaller, may also occupy the pseudoaxial position, which leads to the coexistence of a whole set of conformers. Calculation of the energies of the conformations by Hoffmann's method confirmed this hypothesis[24].

In the corresponding 3-methoxy-1,3-thiaphosphetans (L) and (LI), the conformational problem is complicated owing to the rotational isomerism of the methyl group relative to the P–O bond. The number of possible conformations increases by a factor of three and simple comparison of the calculated and experimental parameters does not allow an unambiguous choice[25]. The procedure involving the joint application of two related methods, proposed by Vereshchagin et al.[116], in which one plots the calculated $_mK$ against the square of the dipole moment, is particularly useful in such situations. The point corresponding to the experimental values defines the required parameters. Fig. 11 illustrates the graphical relations obtained. The positions of the experimental points identify unambiguously the conformations of compound (L) and (LI). Both substances have the same dihedral ring bending angle (135–140°) as the value found for the acid chloride (XLIX) and the pseudoaxial methoxy-groups have the *gauche*-orientation. An analogous structure was found also for the phenoxy-derivatives[25].

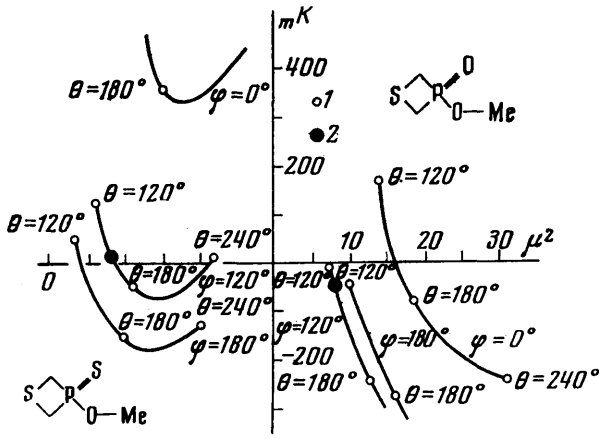



**Figure 11.** Graphical relation between the Kerr constants and the squares of the dipole moments of 3-methoxy-1,3-thiaphosphetans; $\theta$ is the dihedral angle of the nonplanarity of the four-membered ring and $\varphi$ the angle determining the rotation relative to the P–O bond: 1) calculated values; 2) experimental values.

The examples examined show how effective is the joint graphical interpretation of data derived by two related methods. Problems which are insoluble by each method separately can be solved unambiguously by means of a graphical comparison. Other examples If the combined application of physical methods, which lead to new possibilities in the conformational analysis of complex systems, are given below.

## 2. Internal Rotation in Acyclic Compounds

The main difficulty in the employment of the Kerr effect in structural studies on acyclic molecules is due to the uncertainty of the bond parameters. The problem of their selection for compounds which are asymmetrically substituted relative to the phosphorus atom has been analysed[6] in relation to dichloromethylphosphine oxide (XXVI) and sulphide (XXVIII) as examples. In the former case, the dipole moment and the constant $_mK$ can be expressed in terms of the parameters determined for phosphoryl chloride. In the latter case [compound (XXVIII)], there is no additivity and the determination of the bond characteristics requires the use of an additional compound having the same environment at the phosphorus atom but a different direction of the dipole moment. Dichloro-(trichloromethyl)phosphinesulphide (XXIX) has such properties. Joint examination of the constants $_mK$ for both compounds leads to the following values: $\gamma_{P-Cl}$ = 3.12 and $\gamma_{P=S}$ = 4.39 Å$^3$; these differ appreciably from the

values found for symmetrically substituted compounds. We shall therefore consider henceforth substances where the four-coordinated phosphorus atom has the same immediate environment.

The infrared spectra, dipole moments, and the constants $_mK$ of chloromethyldiphenylphosphine (XXII) indicate the existence of two conformers in proportions of 0.9 : 1.[13] Comparison of the dipole moments and the constants $_mK$ with the calculated values makes it possible to identify these structures: *trans*-, *gauche*- ($_mK$ = 55 for the *trans*-disposition relative to the P=O bond and −58 for the *gauche*-disposition, the experimental value being 44). The agreement between the conclusions obtained by the three methods confirms the validity of the chosen model and makes it possible to investigate more complex systems, where one considers the rotation of two irregular groups of the type $CH_3P(O)(CH_2X)_2$ in compounds (XXIII) and (XXIV). These substances are interesting from the standpoint of the observation of the mutual influence of the rotating groups. They have a large number of possible conformations, of which there are six for the *gauche*- and *trans*-dispositions of the bonds. Analysis of the infrared bands in the spectra of crystalline compounds (XXIII) and (XXIV) and their solutions with different dielectric constants of the medium led to the conclusion that two conformers are in thermodynamic equilibrium. On the plot of the square of the dipole moment against $_mK$, the experimental point for compound (XXIII) ($_mK$ = 33.6) corresponds best to equilibrium between the *trans*,*trans*- ($_mK$ = 7.9) and *trans*,*gauche*-forms (the calculated value for the latter is 101 and 122 respectively for the clockwise or anticlockwise 60° rotation of the C–C bond relative to the eclipsed position) (Fig. 12)[14]. The replacement of chlorine atoms by bromine in the halogenomethyl groups led to an appreciable alteration of the preferred conformations: the conformer with the *trans*-orientation of the C–Br bond was displaced from the equilibrium. The *trans*,*gauche*-form ($_mK$ = 1.67), which exists in equilibrium with the *gauche*,*gauche*-form ($_mK$ = −240) is the most stable; the experimental values is 74.[15]

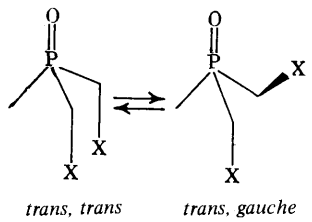



**Figure 12.** The preferred conformations of acyclic molecules.

The much more complex case of the rotation of three irregular halogenomethyl groups was investigated in relation to the trihalogenomethylphosphine oxides (XXI) and (XXV). When the eclipsed forms are excluded, the number of conformers is seven. The combined application of the data obtained by several physical methods (infrared spectroscopy, dipole moment measurements, and the Kerr effect) for dihalogenomethyl derivatives showed[12,15] that the replacement of the halogen also alters the composition of the conformational equilibrium mixture. Whereas the proportions of the *trans*, *trans*, *trans*- and *gauche*, *gauche*, *gauche*-forms are 0.8 : 0.2 for X = Cl,[12] in the case of the bromo-derivative the first of these forms is displaced from equilibrium and the *trans*, *trans*, *gauche*-conformer predominates[15].

The problem of the internal rotation about the P-heteroatom bonds is of interest as regards conformations. The greatest number of studies have been concerned with the P–O bond, despite the fact that the nature of the potential energy curve for this bond has still not been finally established. As mentioned above, the study of the structures of the methyl phosphinate esters (L) and (LI) and of their structural analogues with the phenyl group led to the conclusion that only the *gauche*-conformer in relation to the phosphoryl or thiophosphoryl linkage exists. The *gauche*-orientation of the methoxy-group has been established for the *cis*-isomers of 1,3-butylene phosphates (LXXXIII) and phosphorothioates (LXXXV)[31] (Table 6). In all the cases quoted, the alkoxy-group occupies the axial position, where the steric interaction with hydrogen atoms may constitute a significant obstacle to the realisation of the conformation which is more stable from the standpoint of the electronic properties. Indeed, for the equatorial orientation of the P–OR group in the corresponding *trans*-isomers of compounds (LXXXIV) and (LXXXVI), conformational equilibrium between the *trans*- and *gauche*-forms was observed (Table 6). The equilibrium was confirmed by infrared and Raman spectra[31]. In five-membered rings, the steric interactions of the exocyclic P–OR bond with the remainder of the molecule may be greatly reduced owing to the planar structure of the 1,3,2-dioxaphospholen[117,118] or phospholen[49] ring or, in the case of the envelope conformation, of the 1,3,2-dioxaphospholan ring with the carbon atom at the apex[119]. This also leads to the *trans*-orientation being greatly preferred.

Among acyclic molecules, the trialkyl phosphates (X), (XV), and (XVII), whose dipole moment spectra and, for the last two compounds, also the constants $_mK$ have been investigated[9,10], are closest to the systems investigated. Graphical comparison of the squares of the dipole moments and the constants $_mK$ for compound (XVII), taking into account the populations of the conformations known from the infrared spectra, showed that the *gauche*, *gauche*, *cis*-form predominates in the conformational equilibrium[9]. This conclusion is disputed by Egorov et al.[50], whose analysis of the dipole moments led to the detection of the equilibrium between the *trans*, *trans*, *gauche*- and *trans*, *trans*, *trans*-conformers, the dipole moments being calculated from the bond dipole moments, which have been criticised[10]. The conclusion reached by Raevskii et al.[9] also appears unlikely. It is didficult to imagine an equilibrium mixture of *cis*, and *gauche*-forms, between which there is no energy barrier according to quantum-mechanical calculations[120–122]. It is more correct to consider intermediate forms with a torsional angle ranging from 120° (*gauche*) to 180° (*cis*) and further to 240° (*gauche*) in the "cisoid" conformations. Instead of the formal sixteen structures, one can then postulate six. After revising the structure of trialkyl phosphorothioates from these standpoints, the authors[10] concluded that the conformer with the cisoid or *gauche*-disposition of all the OR groups predominates in the thermodynamic equilibrium between the conformers of compound (XVII). The *gauche*,*gauche*, *gauche*-conformer of compound (XV) is fully stabilised.

3. The Conjugation Effects

Measurements of Kerr constants and light scattering constitute a unique procedure for the investigation of the rotation of the plane of the benzene ring relative to the element–phenyl bond. On the basis of data derived by these two methods, it is possible to determine reliably the conformations of aromatic compounds in solutions, since the anisotropy of the polarisability of the phenyl group is very large [1–3]. At the phosphorus atom, the conjugations with the lone electron pair, the multiple bond, or the vacant *d* orbitals have different stereospecificities so that the solution of this type of conformational problem yields directly information about the strength and nature of the possible conjugation effects, which are determined by the orientation of the aryl groups.

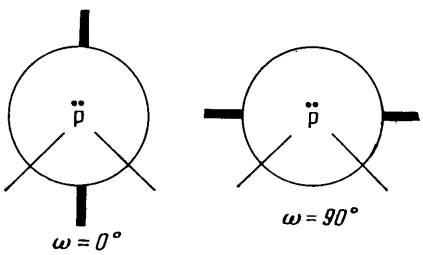



**Figure 13.** The rotation of the benzene ring relative to the Ph–P bond.

In this sense, monoaryl derivatives are of greatest interest, since additional aromatic groups at the phosphorus atom can lead to the steric repulsion of the substituents in the *o*-positions of the aryl groups. It was shown above for 2-phenyl-1,3,2-dioxaphosphorinane (XCIX) and 2-phenyl-1,3,2-dithiaphosphorinane (CIV) that the most preferred conformation is one where the plane of the benzene ring is perpendicular to the plane of symmetry of the molecule ($\omega = 90°$ in Fig. 13), but the *syn*-axial interactions [the 2-phenyl groups in compounds (XCIX) and (CIV) are arranged axially] prevents the realisation of the alternative conformation, so that it is desirable to examine less sterically overloaded molecules of the type $PX_2Ph$ and their oxides. Such phosphines [compounds (XXXI)–(XXXV) and (XLIV)–(XLVI)] have been investigated [18,19]. In the calculation for the $C_{sp^2}$–P bond, the value $\gamma = -0.3$ Å$^3$, obtained by a semiempirical method, was used. For the two conformations with $\omega = 0$ and 90°, the authors [18,19] obtained the following values of the Kerr constant (the values of $10^{11}{}_mK_{0°}$, $10^{11}{}_mK_{90°}$, $10^{11}{}_mK_{exp}$ are quoted): 3, −4, and 1 for (XXI); 4, −3, and 5 ± 2 for (XXXII); 96, 90, and 132 for (XXXIII); 6, −8, and 2 for (XXXIV); 7, −17, and 10 ± 3 for (XXXV); 33.4, −73.8, and 30 for the oxide (XLIV); 24.2, −85.9, and 24.9 for the oxide (XLV); 35.3, −46.7, and 44.4 for the oxide (XLVI). In all cases the plane of the benzene ring coincides, according to these data, with bisector of the RPR angle ($\omega = 0°$) and the LEP of phosphorus(III) or the phosphoryl group in the case of phosphine oxides is thus coplanar with the benzene ring, which rules out the possibility of the $p-\pi$ interaction with the LEP. We may note that the conformation with $\omega = 0°$ differs in principal from the conformation of dimethylaniline [123] and its derivatives, where the molecule is a flattened pyramid and $\omega = 90°$. *p*-Aminobenzoic acid has a similar structure [124]. The change in the conjugation of the aromatic system with the LEP of phosphorus(III) and nitrogen(III) may play a definite role in the alteration of the conformations of the phenyl derivatives of these elements. According to Raevskii et al.[18], the energy of the $p-\pi$ conjugation in phosphorus(III) compounds is insignificant owing to the considerable amount of *s* character of the phosphorus(III) LEP orbital and cannot compete with the energy of the steric interactions between the hydrogen atoms of the phenyl group and the substituents at the phosphorus atom.

When two aryl groups are present, the *o*-hydrogen atoms in the observed bisector conformation, located within the pyramid, approach one another and suffer steric repulsion, so that there is a possibility of the displacement of the two aromatic rings from the plane. Having adopted an initial situation in which the plane of each aryl group is perpendicular to the $C_{sp^2}$–P–$C_{sp^2}$ plane and having analysed the graphical relation between ${}_mK$ and the angles of rotation of the phenyl groups, the authors [22] concluded that the conformation of the molecules of compounds (XLI)–(XLIII) is close to that where each aromatic ring is perpendicular to the $C_{sp^2}$–P–$C_{sp^2}$ plane, with a possible deivation up to 15° in the direction leading to the eclipsing of the phosphoryl group. The occurrence of the bisector conformation ($\omega = 32°$) is hindered by the strong steric interaction between the inner *o*-hydrogen atoms.

The steric repulsion of the *o*-hydrogen atoms within the pyramid increases by a factor of three on passing to the triaryl derivatives, so that one may expect an even greater twisting of the molecules. The symmetrically substituted triphenylphosphine (XXX), its oxide (XXXVI), and its sulphide (XLII) were investigated for the first time by Le Fevre [17,20], but the constants ${}_mK$ were determined in benzene. Since the subsequent measurement of ${}_mK$ for compound (XXXVI) in carbon tetrachloride [21] led to significantly different results, we shall consider only the latter study. Comparison of the experimental ${}_mK$ and the values calculated assuming $C_3$ symmetry for compounds (XXXVI)–(XL) yielded the following angles of rotation of the benzene ring: 55°, 65°, 49°, 60°, and 52° respectively. According to the authors [21], the introduction of substituents such as the chlorine atom of the methyl group causes flattening, which may be accounted for by the conjugation of the aromatic rings with the phosphorus *d* orbitals; the influence of the direct polar conjugation with the phosphoryl group is significant in *p*-chloro-derivatives.

The Kerr effect method may be useful in the study of the steric and electronic structures of organophosphorus compounds. The joint application of the Kerr effect and other physical methods is particularly promising, gives rise to wide possibilities, and makes it possible to investigate complex conformational problems associated with the determination of several unknown parameters. The combined use of several methods permitted systematic and specific investigations of the influence of the nature of substituents at the phosphorus atom on the conformation of the molecule and of the nature of the hindered rotation relative to the P–O, P–C, P–Ph, etc. bonds in compounds of three- and four-coordinated phosphorus.

Organophosphorus compounds, which are distinguished by a wide variety of intramolecular interactions, are excellent objects for the investigation of such interactions by electro-optical methods. The graphical isoelectric and isoanisotropic map methods make it possible to

estimate quantitatively the electron redistributions occurring in the molecules being compared and hence provide a justification for conclusions concerning the nature, magnitude, and direction of the electronic effects. The conclusion concerning the extreme electronic lability of phosphorus(III) compounds, which makes it virtually impossible to employ the usual additive scheme in calculations on asymmetrically substituted compounds, is of interest in this sense.

The determination of the additive bond characteristics and the development of methods for their determination permit the study of systems where the phosphorus atom has a different coordination. Compounds of five-coordinated phosphorus and heteroaromatic systems are of special interest for the investigation of steric and electronic structures. The different coordination causes a radical alteration of the nature of the intramolecular interactions [with the phosphorus(III) lone electron pair, with the multiple bonds involving phosphorus(II) and phosphorus(IV), and with the *d* orbitals of phosphurus(V)], so that comparison of the conformations and internal rotations for identical phosphorus bonds in the $P^{III}$–$P^{IV}$–$P^{V}$ series (and in certain cases also for $P^{II}$ and $P^{VI}$) leads to the prospect of the direct investigation of the influence of intramolecular interactions on molecular conformation.

Simultaneous examination of the electrical and electro-optical properties of conjugated and heteroaromatic phosphorus compounds permits the determination of the nature of the distribution of electron density and of the direction of the exaltation of polarisability induced by the introduction of the phosphorus atom. Such studies have been carried out for pyridine and its derivatives[125]. Comparison with phosphorus-containing analogues will make it possible to investigate the conjugation problem in detail.

Further development of research on the application of the Kerr effect to organophosphorus compounds will involve the formulation in greater detail and extension of the additive system of bond and group polarities and polarisabilities. The lack of rigorously tested parameters for many phosphorus bonds is a serious obstacle. The creation of new methods and the development of earlier non-trivial methods for the simultaneous determination of bond and structural characteristics should be of great assistance.


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# Kinetics of the Hydrolysis of Phosphate Esters

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The available information about the kinetics of the hydrolysis of phosphate esters in neutral, alkaline, and acidic media is considered and the mechanisms of the hydrolysis of various reactive forms of mono-, di-, and tri-esters are discussed. A systematic account is given of the rate constants, taking into account the type of ester and its reactive form.
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## I. INTRODUCTION

Quantitative data on the reactivities of the labile P-O-C ester linkages, which are frequently encountered in various organophosphorus compounds, are of intersst for a number of scientific disciplines. The hydrolytic reactions of phosphate esters have been the subject of vigorous kinetic studies in view of their extensive practical applications in engineering, agriculture, and medicine, and the growing interest of investigators in the mechanisms of biochemical processes in which individual phosphate esters play an important role.

The reactivity of ester linkages involving the phosphorus atom can vary within very wide limits (by a factor greater than $10^{10}$) and it is therefore often necessary to estimate it *a priori*. Theoretical methods for the estimation of the reaction rate constants have not has yet been adequately developed and one therefore usually employs empirical correlations based on the principle of linear relations between the free energies of various chemical processes. It is important to arrange systematically the results accumulated and to express them in a form convenient for analytical research.

## II. FUNDAMENTAL DATA ON THE MECHANISMS OF THE HYDROLYSIS OF P-O-C ESTER LINKAGES

The mechanisms of reactions involving nucleophilic substitution at the phosphorus atom, including the hydrolysis of ester linkages, have been frequently discussed[1-8]. Under certain conditions, there is a possibility of monomolecular heterolytic cleavage of the bond between phosphorus and the group to be eliminated ($S_N1P$ mechanism) and of bimolecular substitution with attack by the nucleophile on phosphorus in the rate-determining stage of the reaction ($S_N2P$ mechanism). Nucleophilic substitution reactions involving phosphorus acid esters can also take place at the carbon atom of the ester linkage.

The anionic forms of phosphate monoesters[9-11] and monoacyl phosphates[12,13] are hydrolysed via the $S_N1P$ mechanism. The metaphosphate ion, formed in the hydrolysis of such compounds, is unstable owing to its coordination unsaturation and is rapidly hydrated. The $S_N2P$ mechanism is more common. Studies of the hydrolysis of certain cyclic esters of phosphorus acids have shown that it proceeds as described by Westheimer[6]. The formation of a bond between phosphorus and the attacking nucleophile leads to five-coordinated phosphorus in the transition state, the structure of which may be represented by a trigonal bipyramid with the axial disposition of the eliminated and introduced groups. This geometry is supported by data for the molecular structures of five-coordinated phosphorus compounds, in which the axial bonds are longer and weaker than the equatorial bonds[14,15].

Westheimer[6,16] discussed the possibility of the existence of a relatively unstable intermediate compound with five-coordinated phosphorus in the hydrolysis of cyclic phosphates. Rapid exchange of ligands between the axial and equatorial positions in the intermediate via the pseudorotation of the bipyramid could ensure the simultaneous cleavage of the endo- and exo-cyclic ester linkages, which has been observed experimentally.

Bimolecular substitution of the $S_N2P$ type is also characteristic of the alkaline hydrolysis of many phosphorus acid esters. In neutral and acidic media, the POAlk linkages are frequently hydrolysed with the cleavage of the C-O bond (via the $S_N2$ or $S_N1$ mechanism) at the carbon atom of the alkoxy-group[7,8,17-19].

The hydrolysis of partly esterified phosphoric acid may be complicated by the involvement in the mechanism of various ionic forms of the substrate. At different pH, the monoesters exist in the form of the dianions $ROPO_3^{2-}$, the monoanions $ROPO_3H^-$, the neutral molecules $ROP(O).(OH)_2$, and the protonated form $ROP(OH)_3^+$. The considerable differences between the successive dissociation constants of these species are responsible for the preferential existence of only one or two of them at a fixed pH of the medium. Because of this, only some of the many possible reaction pathways actually occur under specific conditions. The displacement of the ionisation equilibria as the pH is altered changes the reactive species and frequently the reaction mechanism.

## III. KINETICS OF THE HYDROLYSIS OF PHOSPHATE ESTERS

The kinetics and mechanisms of the hydrolysis of phosphate esters, higher polyphosphates, and mixed anhydrides, such as acetyl phosphate, have been examined in a review[7] devoted mainly to the hydrolysis of polyphosphates; earlier results are described in other communications[5,8]. The existence of three series of phosphate esters—the monoesters $ROPO_3H_2$, the diesters $(RO)_2PO_2H$, and triesters $(RO)_3PO$—as well as their

different ionic species differing in the degree of protonation necessitated a systematic arrangement in groups of the available kinetic data in terms of the type of ester and its reactive form. Each group may include data for esters reccting via different mechanisms. In some cases, the observed rate constant may be a compound quantity reflecting the overall rate of reaction proceeding via two or more parallel mechanisms.

## 1. Hydrolysis of Phosphate Monoesters

Phosphate monoesters are dibasic acids with $pK_{a1} = 1$ to 2 and $pK_{a2} = 6-7$.[3,9] As mentioned above, the monoesters can exist in four forms differing in the charge and degree of protonation. For each of them, it is possible to postulate hydrolytic mechanisms involving nucleophilic attack by a water molecule on the phosphorus atom or the carbon of the ester linkage and monomolecular heterolysis with the cleavage of the bond at the phosphorus or carbon atom. The site of cleavage of the bond during the reaction can be reliably determined by an isotope method and a conclusion may be reached concerning the mechanism on the basis of kinetic data. The variation of the observed rate constant with the acidity of the medium is due to the influence of the latter on the relative contents of the different monoester species; for this reason, the involvement of the individual species in the reaction mechanisms is elucidated by analysing the dependence of the effective rate constant on pH. According to the data in Ingold's book[20], studies on the influence of the pH of the medium on the rate of hydrolysis of monoalkyl phosphates began at the end of the past century.

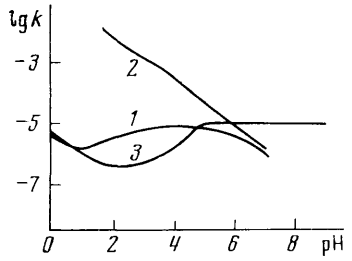



Figure 1. Dependence of lg $k$ on the pH of the medium in the hydrolysis of monoesters: 1) $C_2H_5OP(O)(OH)_2$ at 100°C [21]; 2) t-$C_4H_9OP(O)(OH)_2$ at 74°C [29]; 3) 2,4-$(NO_2)_2$. .$C_6H_3OP(O)(OH)_2$ at 25°C.[10]

The type of dependence of the rate constant for the hydrolysis of monoesters on pH encountered most frequently is described by curve *1* in Fig. 1. The rate of reaction $dc/dt$ depends only on the concentration of the monoanions over a wide range of pH:

$$\frac{dc}{dt} = k[ROPO_3H^-] = kc\frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2},$$

where $c$ is the overall concentration of the monoester in solution:

$$c = [ROPO_3^{2-}] + [ROPO_3H^-] + [ROP(O)(OH)_2];$$

$K_1$ and $K_2$ are the first and second ionisation constants of the monoester. The rate constant passes through a maximum at $pH = (pK_1 + pK_2)/2$, where the relative content of the monoanion is a maximum, which indicates a much higher reactivity of the monoanion compared with the dianion and the neutral molecule. Plots of the rate of hydrolysis against pH have been investigated for a series of monoalkyl and monoaryl phosphates[9,10,21-27,31-36]. The rate maximum in the pH range 3–5 has been observed for many monoesters, but such behaviour is not general. On the other hand, when the neutral molecule is more reactive than the monoanion, the rate constant increases monotonically with decrease of pH (curve *2*). Relations of this kind are characteristic of the monoesters which hydrolyse with the cleavage of the C–O bond via the $S_N1$ mechanism with formation of a carbonium ion[28-30], and also of certain monoacyl phosphates[12,13]. The dependence of the rate of hydrolysis of highly reactive monoaryl and acyl phosphates on pH is described by curve *3* in Fig. 1. A higher reactivity of the dianion compared with that of the monoanion corresponds to this type of dependence. For all three types of relation, the rate constants increase on passing to highly acidic media as a result of acid hydrolysis. The protonated form of the monoester is involved in the latter.

Detailed information is now available about the site of the dissociation of the bond in the hydrolysis of phosphate monoesters with participation of different reactive species. The cleavage of the bonds at the phosphorus atom has been demonstrated on many examples for monoaryl phosphates reacting as the monoanions[25], the dianions[11,39,40], the neutral molecules[25], and the protonated forms[25]. The bond at the phosphorus atom is also dissociated in the monoanions of alkyl phosphates[23,29,32,34,41], except for the t-butyl ester in which the C–O bond is partly cleaved[28].

The hydrolysis of neutral monoalkyl phosphate molecules proceeds with the rupture of the C–O bond, as shown for methyl phosphate[23] and t-butyl phosphate[28]. In the acid hydrolysis of monomethyl and monoethyl phosphates, simultaneous cleavage of the bonds at the phosphorus and carbon atoms takes place[23,32], while in the hydrolysis of the isopropyl and t-butyl esters, the C–O bonds are ruptured exclusively[28,32].

The rate of hydrolysis of many phosphate monoesters is very low at the usual temperatures and in many studies the kinetics have been investigated at 100°C. We adjusted some of the constants in Table 1 to these conditions on the basis of the temperature relations. The rate constants for the monoanions of many monoalkyl phosphates increase after the introduction of electron-accepting substituents in the alkyl group. A similar effect has been observed also for the monoanions of monoaryl phosphates. An exception is provided by the data quoted in the paper of Mhala et al.[38] The rate constants for the hydrolysis of the monoanions of aryl and acyl phosphates are higher by 1.5–2 orders of magnitude than the corresponding values for the monoanions of alkyl phosphates. This is probably due to the favourable role of the resonance interaction of the ester oxygen with the benzene ring or the carbonyl group, which may compete with the effect of the $p\pi - d\pi$ conjugation between oxygen and phosphorus, which weakens the P–O bond ruptured in the reaction.

The inductive effect of the electron-accepting groups and the resonance delocalisation of the lone electron pairs of the ester oxygen atom must have an unfavourable influence on the proton transfer to the group being eliminated, which is believed[5,9,11] to facilitate the rupture of the P–O bond in the monoanions. Since the rate constants actually increase as the basic properties of the ester oxygen are reduced, the variation of another factor, which more than compensates for the decrease of the basicity of the oxygen,

is probably responsible for the increase of the reactivity. This factor may be the decrease of the energy of the ruptured bond. Owing to the opposed effects of these factors, whose influences on the reactivity are not comparable in magnitude, the dependence of the rate constants on the nature of the groups eliminated is weakened, which is confirmed when the slopes of the lg $k$–p$K_a$ relations are compared for the monoanions and dianions[9,11]. In the dianions, there is no proton transfer to the eliminated group and the reactivity is determined solely by the bond energy. For the monoanions of aryl and alkyl phosphates, the dependence of lg $k$ on the p$K_a$ of the eliminated group is characterised by a slope several times smaller than the slopes of the corresponding relation for the dianions of aryl and acyl phosphates[11].

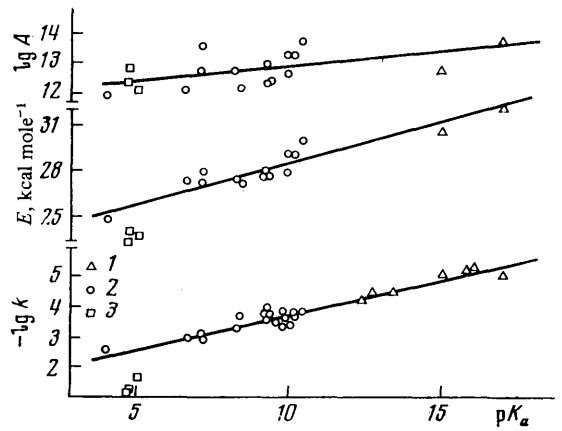



Figure 2. Dependence of the parameters lg $k$, $E$, and lg $A$ for the hydrolysis of the monoester monoanions at 100°C on the p$K_a$ of the eliminated group. The p$K_a$ values were taken from Refs. 9 and 11, the sources indicated therein, and from Refs. 46–49: 1) alkyl phosphates; 2) aryl phosphates; 3) acyl phosphates.

Fig. 2 illustrates the variation of lg $k$ with p$K_a$ for monoanions, expressed by the equation†

$$\lg k = -0.23pK_a - 1.38 \quad (n = 25;\ r = 0.97;\ s = 0.2),$$

which differs only slightly from that quoted by Kirby and Varvoglis[11]. With decrease of the p$K_a$ of the eliminated group, the rate constant for the hydrolysis of monoanions increases and the activation energy $E$ and the pre-exponential factor diminish (Fig. 2). Hence it follows that the reactivity increases owing to the decrease of $E$. The very low values of $E$ and lg $A$ quoted by Mhala et al.[38] for the monoanions of 4-bromophenyl and 2-methoxyphenyl phosphates do not fit on the plots of $E$ and lg $A$ against p$K_a$ in Fig. 2, in contrast to the remaining data. The markedly higher reactivity of the monoanions of acyl phosphates is due to the additional decrease of $E$ compared with the value expected from the plot of $E$ against p$K_a$.

†Here and henceforth $n$ is the number of compounds, $r$ the correlation coefficient, and $s$ the standard deviation.

The higher reactivity of the monoanions of acyl phosphates is probably associated with the unusual mechanism of their hydrolysis. A proton may be transferred to the oxygen of the carbonyl group and not to the anhydride oxygen[12]. The mechanism established for the monoanions of certain carbamoyl phosphates, which are hydrolysed with the cleavage of the C–O bonds, is more significantly different[50].

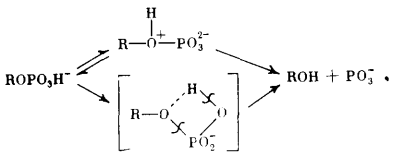
Table 1. The rate constants for the hydrolysis of phosphate monoester monoanions $ROPO_3H^-$ at 100°C and the parameters of the equation $k = A\exp(-E/RT)$.

| R | $10^6k$, $s^{-1}$ | $E$, kcal mole$^{-1}$ | lg$A$ ($s^{-1}$) | References |
|---|---|---|---|---|
| $CH_3$ | 8.23 | 30.6 | 12.81 | 23 |
| $C_2H_5$ | 6.0 | — | — | 22 |
| $C_3H_7$ | 5.1[a] | — | — | 31 |
| iso-$C_3H_7$ | 9.7 | 32.1 | 13.80[a] | 32 |
| n-$C_4H_9$ | 6.0 | 31 | 12.94 | 24 |
| n-$C_5H_{11}$ | 4.8[a] | — | — | 31 |
| iso-$C_5H_{11}$ | 5.9 | 29.6 | 12.12[a] | 30 |
| $(CH_3)_3CCH_2$ | 1.06 | — | — | 33 |
| n-$C_6H_{13}$ | 4.2[a] | — | — | 31 |
| $(CH_3)_3CCH_2CH_2$ | 0.92 | — | — | 43 |
| $CH_2{=}C(CH_3)CH_2CH_2$ | 7.1 | 35.7 | 15.75[a] | 30 |
| $(CH_3)_2C(OH)CH_2CH_2$ | 6.4 | — | — | 30 |
| $HOCH_2CH(OH)CH_2$ | 13.5 | 29.9 | 12.63 | 34 |
| $(HOCH_2)_2CH$ | 27.7 | 30.3 | 13.18 | 34 |
| $H_3N^+CH_2CH_2$ | 31 | 29.6 | 12.83 | 34 |
| $(C_2H_5)N^+H_2CH_2CH_2$ | 28[a] | — | — | 35 |
| $(C_2H_5)_2N^+HCH_2CH_2$ | 28[a] | — | — | 35 |
| $(CH_3)_3N^+CH_2CH_2$ | 18 | 24.3 | 9.49 | 44 |
| $H_3N^+CH_2CH_2CH_2$ | 12[a] | — | — | 31 |
| $H_3N^+(CH_2)_4$ | 6.2[a] | — | — | 31 |
| $H_3N^+(CH_2)_5$ | 7.7[a] | — | — | 31 |
| $H_3N^+(CH_2)_6$ | 4.2[a] | — | — | 31 |
| 3-$(C_5H_4N^+H)CH_2$ | 27[a] | 29.3 | 12.61 | 36 |
| 2-$(C_5H_4N^+H)CH_2$ | 69[a] | 28.2 | 12.35 | 36 |
| $CH_3C(O)NHCH_2CH_2$ | 15[a] | — | — | 31 |
| $HOC(O)CH_2CH_2$ | 11[a] | — | — | 31 |
| $HOC(O)CH_2$ | 39[a] | — | — | 31 |
| $NCCH_2CH_2$ | 11[a] | — | — | 31 |
| $NCCH_2$ | 39[a] | — | — | 31 |
| $HC{\equiv}CCH_2$ | 26 | — | — | 27 |
| $F_3CCH_2$ | 57 | — | — | 11 |
| $FCH_2CH_2$ | 13[a] | — | — | 45 |
| $(FCH_2)_2CH_2$ | 28[a] | — | — | 45 |
| $F_2CHF_2CCH_2$ | 39[a] | — | — | 45 |
| Glucose-1- | 11 | 30 | 12.70 | 29 |
| Glucose-6- | 20 | 30.5 | 13.20[a] | 37 |
| $C_6H_5$ | 289 | 29.0 | 13.32 | 25 |
| 4-$CH_3C_6H_4$ | 230 | 29.0 | 13.26 | 25 |
| 2-(t-$C_4H_9$)$C_6H_4$ | 40 | — | — | 9 |
| 4-(t-$C_4H_9$)$C_6H_4$ | 178 | — | — | 9 |
| 2,6-$(CH_3)_2C_6H_3$ | 161 | 30 | 13.77[a] | 9 |
| 2,6-(t-$C_4H_9$)$_2$4-$CH_3C_6H_2$ | 33.5 | — | — | 9 |
| 2-$ClC_6H_4$ | 230 | 27 | 12.17[a] | 9 |
| 4-$ClC_6H_4$ | 180[a,b] | 27.5 | 12.36 | 38 |
| 4-Cl-3-$CH_3C_6H_3$ | 186[a] | 27.5 | 12.38 | 38 |
| 4-$BrC_6H_4$ | 110[a] | 21.7 | 8.75 | 38 |
| 2-$CH_3OC_6H_4$ | 470[a] | 21.4 | 9.21 | 38 |
| 4-$CH_3OC_6H_4$ | 420[a] | 22.9 | 10.04 | 38 |
| 4-$C_2H_5OC_6H_4$ | 120[a] | 19.4 | 7.45 | 38 |
| 3-$(CO_2^-)C_6H_4$ | 270[a] | 27.7[a] | 12.66[a] | 26 |
| 4-$(CO_2^-)C_6H_4$ | 350[a] | 28.0[a] | 12.94[a] | 26 |
| 3-$(COOH)C_6H_4$ | 380[a] | 27.9[a] | 12.92[a] | 26 |
| 4-$(COOH)C_6H_4$ | 720[a] | 28.3[a] | 13.44[a] | 26 |
| α-Naphthyl | 150[a] | 30.6[a] | 14.10[a] | 26 |
| β-Naphthyl | 360[a] | 29.8[a] | 14.02[a] | 26 |
| 3-$NO_2C_6H_4$ | 573 | 27.3[a] | 12.76[a] | 9 |
| 4-$NO_2C_6H_4$ | 1050[a] | 27.2 | 12.82[a] | 9 |
| 2-$NO_2C_6H_4$ | 1450[a] | 28 | 13.56[a] | 9 |
| 3,5-$(NO_2)_2C_6H_3$ | 1 310 | 27.3[a] | 12.11[a] | 11 |
| 2,4-$(NO_2)_2C_6H_3$ | 3 080 | 24.8 | 12.02[a] | 11 |
| $CH_3C(O)$ | 65 000 | 23.1 | 12.33 | 12 |
| $(CH_3)_2CHCH_2C(O)$ | 60 000 | 24.0 | 12.84 | 13 |
| $(CH_3)_3CC(O)$ | 24 000 | 23.5 | 12.17 | 13 |

[a]These values were calculated by the author of the review from data in the studies quoted.
[b]According to Bunton et al.[9], $k = 302 \times 10^6$ $s^{-1}$ at 100°C.

High activation energies are characteristic of almost all the monoanions investigated. Estimates of the activation entropies from the pre-exponential factors listed in Table 1 yield in most cases $\Delta S^{\neq} \simeq 0 \pm 5$ cal mole$^{-1}$ k$^{-1}$,

in agreement with the monomolecular $S_N1P$ mechanism of the rate-limiting stage of the hydrolytic reaction. A proton may be transferred to the eliminated group either in the rapid pre-equilibrium process or synchronously with the dissociation of the bond at the phosphorus atom[11]:



Nor can one exclude the possibility of the involvement of a water molecule in the proton transfer[41]. The six-membered ring formed in the reaction with participation of water may be less strained than the four-membered ring without water.

The small kinetic isotope effect in the hydrolysis of the monoanion of methyl phosphate ($k_{H_2O}/k_{D_2O} = 0.87$)[23] shows that in alkyl esters the proton transfer occurs in the pre-equilibrium stage and not in the rate-limiting stage. However, for highly reactive monoanions, the situation may change in favour of the mechanism with the synchronous proton transfer. In particular, this is indicated by the much greater isotope effect in the hydrolysis of the monoanion of 2,4-dinitrophenyl phosphate ($k_{H_2O}/k_{D_2O} = 1.45$).[11]

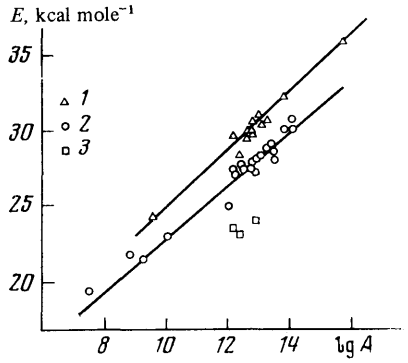
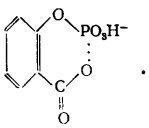



Figure 3. Relation between $E$ and $\lg A$ for the hydrolysis of monoester monoanions: 1) alkyl phosphates; 2) aryl phosphates; 3) acyl phosphates.

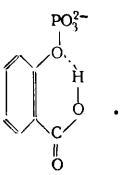
The parameters of the Arrhenius equation $E$ and $\lg A$ for the monoanions of alkyl phosphates tend to cancel out, which has also been noted for aryl phosphates (Fig. 3). There is no general relation between $E$ and $\lg A$ for alkyl and aryl phosphates, although they fit on a single straight line in the plot of $\lg k$ against $pK_a$. Possibly a unique line is obtained only approximately owing to the similarity of the influence of the conjugation effect on the ionisation of phenols and the reaction under consideration.

The metaphosphate ion formed on cleavage of the bond in the monoanions is rapidly hydrated, which hinders the demonstration of its formation. At low water concentrations in the reaction medium, the hydration is accompanied by the polymerisation of the metaphosphate ions; the formation of trimetaphosphate has been demonstrated in the hydrolysis of a concentrated solution of potassium monophenyl phosphate[51]. Attempts have been made at an indirect confirmation of the formation of the metaphosphate ion by studying the composition of the solvolysis products of monoesters in aqueous alcoholic media[5,8]. It was assumed that the metaphosphate ion reacts non-selectively with water and alcohol, giving a product ratio corresponding to the composition of the aqueous alcoholic medium. However, the metaphosphate ion formed on hydrolysis in many cases reacted preferentially with alcohol, which may be due to the selective solvation by one of the components of the solvent of the substrate and of the metaphosphate ions formed[5,11].

In the hydrolysis of certain monoanions, intramolecular catalysis was observed in some cases. The monoanions of *o*-carboxyphenyl and *o*-carboxynaphthyl phosphates are particularly reactive[26,52]. For example, $E = 24.1$ and $\lg A = 12.97$ for the monoanion of salicyl phosphate[52], so that the rate constant at 100°C is $7.1 \times 10^{-2}$ s$^{-1}$. This value is approximately 200 times greater than the *m*- and *p*-carboxyphenyl phosphates and higher than all the constants quoted in Table 1. To explain the exceptionally high rate of hydrolysis of the monoanions of salicyl phosphate and similar esters, the authors suggested[26,52] intramolecular nucleophilic catalysis by the carboxylate group with the possible formation of an acyl phosphate as an intermediate:



Bender and Lawlor later showed[53] that the acyl phosphate cannot be an intermediate owing to the relatively low rate of hydrolysis and pointed out the possibility of intramolecular acid catalysis in the hydrolysis of salicyl phosphate and similar esters:



The intramolecular catalysis by the hydroxy-group, demonstrated for the monoanions of 8-hydroxy-1-naphthyl phosphate[53] and 3-hydroxy-2-pyridylmethyl phosphate[54], involves a similar mechanism. Catalysis by the $N^+$–H group has been demonstrated for 2-pyridylmethyl and 2-pyridylethyl phosphates[55].

At high pH values, phosphate monoesters exist as doubly charged anions. The reactivity of the dianions of monoalkyl phosphates is extremely low and for this reason there are virtually no kinetic data for such species. The dianions of aryl phosphates are more reactive than their alkyl analogues. As for the monoanions, the rate of reaction increases in the presence of electron-accepting substituents in the eliminated group. Comparison of the data in Tables 1 and 2 shows that the activation energy as well as the pre-exponential factor for the hydrolysis of the dianions are as a rule higher than for the monoanions.

The estimation of the values of $\Delta S^{\neq}$ from the data presented in Table 2 shows that they are positive in all cases. In this connection, a monomolecular mechanism has been proposed[10-12] for the rate-limiting stage of the hydrolysis of the dianions:

$$ROPO_3^{2-} \rightarrow PO_3^- + RO^- .$$

The alternative hypothesis, according to which the mechanism can be regarded as involving a bimolecular reaction between the hydroxide ion and the monoanion of the monoester, was disproved[10,11], because it would necessitate the assumption of an unrealistically high rate constant for the latter process. The rate-limiting stage does not include proton transfer from the solvent, as shown by the absence of a kinetic isotope effect in the hydrolysis of the dianion of 2,4-dinitrophenyl phosphate[11]. The high slope of the relation between lg $k$ and the p$K_a$ for the eliminated group is consistent with an $S_N1P$ reaction mechanism[9,11]. According to the data in Table 2, this relation (at 100°C) is described by the following equation for the dianions of aryl phosphates:

$$\lg k = -1{,}01\ pK_a + 3.15 \quad (n = 10,\ r = 0{,}991,\ s = 0{,}3)$$

Table 2. Kinetic parameters of the hydrolysis of phosphate monoester dianions $ROPO_3^{2-}$ in aqueous solutions.

| R | $10^4k$, $s^{-1}$ (100°C) | $E$, kcal mole$^{-1}$ | lg$A$ ($s^{-1}$) | References |
|---|---|---|---|---|
| $C_2H_5$ | <0.0001b | — | — | 27 |
| t-$C_4H_9$ | <0.002b | — | — | 42 |
| $H_2N(CH_2)_4$ | 0.0006b | — | — | 31 |
| $(CO_2^-)CH_2CH_2$ | 0.48a,b | — | — | 31 |
| $HC{\equiv}CCH_2$ | 0.069b | — | — | 27 |
| Glucose-6- | 1.02 | 33 | 15.3 | 37 |
| 3-$NCC_6H_4$ | 0.064a,b | — | — | 35 |
| 4-$NCC_6H_4$ | 0.096a,b | — | — | 35 |
| 3-$(CO_2^-)C_6H_4$ | 0.0024a,b | — | — | 35 |
| 4-$(CO_2^-)C_6H_4$ | 0.0039a,b | — | — | 35 |
| 2-$(CO_2^-)C_6H_4$ | 1.5a,b | — | — | 35 |
| 3-$NO_2C_6H_4$ | 0.023 | — | — | 9 |
| 4-$NO_2C_6H_4$ | 0.65 | 31.2 | 14.09 | 40 |
| 2-$NO_2C_6H_4$ | 1.16 | — | — | 9 |
| 2,5-$(NO_2)_2C_6H_3$ | 63a | 28 | 14.20a | 10 |
| 2,4-$(NO_2)_2C_6H_3$ | 1500a | 26 | 14.41a | 10 |
| 2,6-$(NO_2)_2C_6H_3$ | 3300a | 26 | 14.74a | 10 |
| $CH_3C(O)$ | 650a | 26.0 | 14.04a | 13 |
| $(CH_3)_3CC(O)$ | 49a | 28.3 | 14.27a | 13 |

aSee footnote to Table 1.
bThe rate constants in 1 $N$ NaOH solution are quoted.

A similar slope (−1.23) has been found (at 39°C) for the dianions of aryl and acyl phosphates[11]. Comparison with the analogous relation for the monoanions shows that, for p$K_a$ < 5.8, the dianions are more reactive than the monoanions, as mentioned previously[11].

The dianion of salicyl phosphate 2-$(CO_2^-)C_6H_4OPO_3^{2-}$ hydrolyses approximately 500 times faster than the dianions of $m$- and $p$-carboxyphenyl phosphates[35]. This is probably due to the intramolecular nucleophilic catalysis by the carboxylate anion, postulated initially for the hydrolysis of the monoanion of salicyl phosphate[26,52]. Intramolecular catalysis by the hydroxyl has been observed in the hydrolysis of the dianion of 3-hydroxy-2-pyridylmethyl phosphate[54]. The hydrolysis of the dianion of glucose-6-phosphate[37] can apparently also be accelerated as a result of the intramolecular catalysis by the OH group.

At pH < 1, the ionisation of the acid groups of the monoesters is suppressed and they exist predominantly in the neutral form $ROP(O)(OH)_2$, which is usually unreactive. For monoalkyl phosphates, which are incapable of undergoing the cleavage of the C–O bond via the formation of a carbonium or a hydroxycarbonium ion, the dependence of the reaction rate constant on pH has a minimum in the pH range 0–1.[22-24] Owing to the low reactivity of the neutral form compared with the monoanion and the protonated form, the hydrolysis in this region is frequently represented by the sum of the reactions involving the monoanions and the neutral and protonated forms, which complicates the estimation of the reactivity of the neutral monoester molecules. The simplest example is provided by the hydrolysis of phenyl and $p$-cresyl phosphates, for which the absence of acid catalysts has been suggested because of the insignificant change in the reaction rate constant in $HClO_4$ solutions. The rate constant was attributed (after subtracting the contribution due to the monoanion) to the reaction proceeding via the neutral form[25]. For many substituted aryl phosphates, acid catalysts begins to be manifested in the region where the monoanion makes a large contribution to the overall reaction and a reliable estimate of the reactivity of the neutral molecules becomes impossible[9,10].

Table 3. Kinetic parameters of the hydrolysis of the neutral forms of phosphate monoesters $ROP(O)(OH)_2$.

| R | $10^6k$, $s^{-1}$ (100°C) | $E$, kcal mole$^{-1}$ | lg$A$ ($s^{-1}$) | References |
|---|---|---|---|---|
| $CH_3$ | 0.5 | — | — | 23 |
| $C_2H_5$ | 0.7 | — | — | 32 |
| n-$C_3H_9$ | 0.89 | 16 | 3.32a | 24 |
| iso-$C_3H_7$ | 0.3 | — | — | 32 |
| $(CH_3)_2C{=}CHCH_2$ | 240 000 | 22.6 | 12.62a | 30 |
| Glucose-1- | 29 000a | 31.0 | 16.63 | 29 |
| t-$C_4H_9$ | 150 000a | 33.3 | 18.58a | 28 |
| $C_6H_5$ | 30.5 | — | — | 25 |
| 4-$CH_3C_6H_4$ | 24 | — | — | 25 |
| 4-$ClC_6H_4$ | 72a | 28.5 | 12.55 | 38 |
| 2-$CH_3OC_6H_4$ | 160a | 19.4 | 7.56 | 38 |
| 4-$C_2H_5OC_6H_4$ | 23a | 20.2 | 7.20 | 38 |

aSee footnote to Table 1.

Table 3 lists the rate constants for the hydrolysis of the neutral molecules of certain monoesters. It is noteworthy that the neutral molecules of monoalkyl and monoaryl phosphates react via different mechanisms. Alkyl phosphates are involved in reactions of the $S_N2$ and $S_N1$ type at the carbon atom[5,23,28-30,32], while in aryl phosphates substitution at the phosphorus atom takes place[25].

By considering jointly data for the hydrolysis of the dianions, monoanions, and neutral molecules of monoesters, one may note a definite similarity of the mechanisms of the reactions involving the dianions and monoanions and the clear difficulty of a similar mechanism for the neutral molecule. The $S_N1P$ mechanism is manifested in the purest form in the hydrolysis of the dianions. The latter shows that the capacity for the elimination of the metaphosphate ions depends strongly on the p$K_a$ of the eliminated group and diminishes as the p$K_a$ increases. In the series of monoanions, the elimination of the metaphosphate ion is complicated by the proton transfer to the eliminated group. The role of the proton transfer should probably be small in the case of aryl phosphates with readily removed groups and the sequence of rate constants observed for such compounds (dianion > monoanion) reflects the reactivity in the processes proceeding via an $S_N1P$ mechanism. The significant role of the additional factor (proton transfer) in the hydrolysis of monoanions in which the p$K_a$ values of the eliminated groups are high leads to an alteration of this sequence (the monoanion

becomes more reactive). The reactivity via an $S_N1P$ mechanism decreases further on passing to the neutral molecule. The absence of the cleavage of the C–O bond in the hydrolysis of the neutral molecules of monoalkyl phosphates is consistent with this observation. The hydrolysis of the neutral molecules of monoaryl phosphates probably proceeds via an $S_N2P$ mechanism[9].

The acid catalysed hydrolysis of phosphate monoesters has been studied in a number of investigations[9,10,25,28,29,32,33,38,56]. The acid hydrolysis of the phenyl and alkyl esters proceeds via different mechanisms. Two parallel reactions, leading to the dissociation of the P–O and C–O bonds at comparable rates, have been demonstrated for the alkyl esters[23,32], but in the esters eliminating a carbonium ion there is exclusive dissociation of the C–O bond[28,29,32]. The dependence of the rate constant on the stoichiometric acid concentration over a wide range of compositions and at a constant ionic strength has been found for the acid hydrolysis of methyl and ethyl phosphates[23,32]. On this basis, a bimolecular mechanism was proposed for each of the parallel processes. It is suggested that the rate-limiting stage involves nucleophilic attack by an $H_2O$ molecule on the phosphorus or carbon atom in the ester linkage of the protonated form of the ester[23]. In the acid hydrolysis of the t-butyl and isopropyl esters, only the C–O bond is cleaved. The linear dependence (with a slope of unity) of lg $k$ on the acidity function $H_0$ indicates the unimolecular cleavage of the protonated form. The assessment of the reaction mechanism with the aid of Bunnett's criterion also confirms the unimolecularity of the rate-limiting stage[32]. Fig. 4 shows that the hydrolysis of isopropyl phosphate, which proceeds via unimolecular heterolysis (curve *2*), is most sensitive to changes in the acidity of the medium. The behaviour of acyl phosphates in acid hydrolysis shows a definite analogy with that of methyl and ethyl phosphates, although the dissociation of the C–O bond is preferred for acyl phosphates[56]. An increase of the hydrolysis rate constant in proportion to the stoichiometric acidity of the solution at a constant ionic strength has been established for certain acyl phosphates (Table 4) and a bimolecular reaction mechanism is therefore proposed[56].

phenyl phosphates with electron-donating groups in the benzene ring has been postulated[9,10,25] in view of the insignificant change in the rate constant in concentrated solutions of strong acids. In this connection, one should note that the involvement of the protonated form of the ester is probable in acid hydrolysis. If the rate constant for the reaction proceeding via the protonated form ($k_{SH^+}$) is greater than the rate constant for the reaction involving the neutral molecule ($k_S$), then the observed rate constant $k = k_S + k_{SH^+}$ should increase on conversion of the ester into the protonated form. On the other hand, when $k_S > k_{SH^+}$, the observed rate constant should decrease with increase of the acid concentration. One may assume, with some approximation, that the invariance of the rate constant as the acid concentration is altered over a fairly wide range indicates the similarity of the rate constants $k_S$ and $k_{SH^+}$.

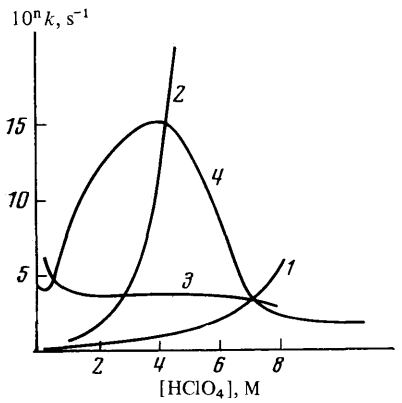



Figure 4. Dependence of the rate constants for the hydrolysis of monoesters on the acid concentration: 1) $C_2H_5OP(O)(OH)_2$, $n = 6$, 100°C [32]; 2) iso-$C_3H_7OP(O)(OH)_2$, $n = 5$, 100°C [32]; 3) $C_6H_5OP(O)(OH)_2$, $n = 5$, 100°C [25]; 4) 4-$NO_2C_6H_4OP(O)(OH)_2$, $n = 5$, 73°C.

Table 4. Kinetic parameters of the hydrolysis of the protonated forms of phosphate monoesters $ROP(OH)_3^+$ in aqueous acid media.

| R | Composition of medium | $10^4k$, $s^{-1}$ (100°C) | $E$, kcal mole$^{-1}$ | lg$A$ ($s^{-1}$) | References |
|---|---|---|---|---|---|
| $CH_3$ | 4$M$ $HClO_4$ | 0.15 | 25 2 | 9.94[a] | 32 |
| $C_2H_5$ | 4$M$ $HClO_4$ | 0.099 | 29.3 | 12.16[a] | 32 |
| iso-$C_3H_7$ | 4$M$ $HClO_4$ | 10.5 | 31.0 | 15.18[a] | 32 |
| Glucose-6- | 4,6$M$ $HClO_4$ | 0.58 | 24 | 9.8 | 37 |
| $C_6H_5$ | 3,8$M$ $HClO_4$ | 0.366 | — | — | 25 |
| 3-$NO_2C_6H_5$ | 4$M$ $HClO_4$ | 3.0[a] | 20 | 8.22[a] | 10 |
| 4-$CH_3C(O)C_6H_4$ | 4$M$ $HClO_4$ | 4.1[a] | 22.7[a] | 9.91[a] | 25 |
| 4-$NO_2C_6H_4$ | 4$M$ $H_2SO_4$ | 15.0[a] | 18.7 | 8.06 | 25 |
| 2-$NO_2C_6H_4$ | 4$M$ $HClO_4$ | 20[a] | 20 | 9.03 | 10 |
| 2,4-$(NO_2)_2C_6H_3$ | 6$M$ $HClO_4$ | 290[a] | 18 | 9.0 | 10 |
| $CH_3C(O)$ | 2.87$M$ HCl | 50 000[a] | 21.8 | 13.47[a] | 56 |
| $(CH_3)_3CC(O)$ | 2.87$M$ HCl | 7 200[a] | 21.8 | 12.63[a] | 56 |
| $(CH_3)_3CCH_2C(O)$ | 2.87$M$ HCl | 155 000[a] | 23.8 | 15.13[a] | 56 |

[a]See footnote to Table 1.

Acid hydrolysis of monoaryl phosphates includes a reaction at the phosphorus atom[25]. The absence of an acid-catalysed reaction of phenyl phosphate and substituted

The slope of the plot of lg $k$ against p$K_a$ for acid hydrolysis, amounting to −0.5,[9,10] is smaller than for the reactions of dianions, but larger than for monoanions. Judging from the data in Table 4, the activation entropies for the acid hydrolysis of aryl phosphates are significantly lower than for reactions of mono- and di-anions, which suggests a bimolecular mechanism of the acid hydrolysis of monoaryl phosphates.

In a rigorous consideration of acid hydrolysis, account must be taken of the effects due to changes in the ionic strength and the activity of water with increase of the concentration of acid. It has been shown[10,25] that the rate of the acid-catalysed hydrolysis of aryl phosphates passes through a maximum in concentrated solutions of acids. However, the maximum disappears if the rate of reaction is measured in solutions at a constant ionic strength. Since the influence of salts and acids on the activity of water is similar, the maintenance of a constant ionic strength in solution smooths out the changes in the activity of water. Hence it follows that the maximum on the curves relating the rate constant to the concentration of acid may be attributed to a change in the activity of water. The rate

of hydrolysis of 2-methoxy-, 4-methoxy-, and 4-ethoxyphenyl phosphates in perchloric acid solutions at a constant ionic strength was independent of the acidity of the medium[38]. It was noted above that such behaviour probably indicates similar values of the rate constants for the reactions involving the neutral and protonated forms.

## 2. Hydrolysis of Phosphate Diesters

Phosphate diesters contain a single acid group at the phosphorus atom with $pK_a = 1-2$ (Kirby and Warren[3]) and can participate in reactions as anionic, neutral, and protonated species. The reactivity of the diester anions is very low, the anions of five-membered cyclic esters being an exception. The difficulty of the unimolecular heterolysis of the P=O bond in the diester anions also shows that the relatively high reactivity of the monoester monoanions is due to the special role of the P–O–H fragment in the reaction mechanism. Proton transfer to the eliminated group in the hydrolysis of monoester monoanions constitutes in essence a variety of the intramolecular catalysis by the acidic hydroxyl. In bimolecular nucleophilic substitution reactons, conditions for nucleophilic attack on the diester anion are unfavourable for two reasons. The first is the displacement of electron density from the oxygen atom to phosphorus, which makes the latter less electrophilic. The second factor, which is important in reactions with negatively charged nucleophiles, is the electrostatic repulsion of the two anionic species involved in the reaction.

The reactivity of neutral diester molecules is much higher than that of the anions. Analysis of the dependence of the rate constants for the hydrolysis of diesters on pH [25,57-64] reveals an increase of reactivity in the sequence

$$(RO)_2PO_2^- < (RO)_2P(O)OH < (RO)_2P(O)(OH)_2^+.$$

Typical relations between the rate constants and pH are illustrated in Fig. 5.

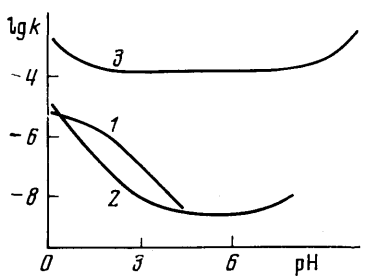



Figure 5. Dependence of lg $k$ on pH for the hydrolysis of diesters at 100°C: 1) $(CH_3O)_2P(O)OH$ [57]; 2) $(C_6H_5O)_2$. $.P(O)OH$ [25]; 3) $[2,4-(NO_2)_2C_6H_3O]_2P(O)OH$.[58]

The kinetics and mechanism of the hydrolysis of dimethyl phosphate have been investigated in detail[57]; a similar behaviour should probably be expected also for many other dialkyl phosphates which do not show a tendency towards the elimination of alkyl groups in the form of carbonium ions. In the pH range 0–5, the dependence of the rate constant for the hydrolysis of dimethyl phosphate on pH differs sharply from the corresponding dependence for monomethyl phosphate, the hydrolysis rate constant of which has a maximum at pH 4.[23] Dimethyl phosphate hydrolyses extremely slowly at pH > 4 even at high temperatures, which precludes the determination of the rate constant for the reaction of its anion with water; when the pH is reduced, there is a monotonic increase of the reaction rate, which continues also in strongly acidic media. In the pH range 1–4, the increase of the rate constant is proportional to the relative content of neutral dimethyl phosphate molecules in equilibrium with the anions[57].

Experiments with $H_2^{18}O$ have shown that hydrolysis of the neutral dimethyl phosphate molecule proceeds via two parallel mechanisms with the cleavage of the P–O and C–O bonds. In the acid and alkaline hydrolysis, the dissociation of these bonds also takes place at comparable rates[57,65]. A bimolecular nucleophilic substitution mechanism has been adopted for reactions involving the neutral molecule and dimethyl phosphate species protonated at both reaction centres[57], in agreement with the mechanisms of the analogous processes for monomethyl and trimethyl phosphates. Data for the reactivity of various forms of dimethyl phosphate are presented in Table 5. Near pH ~ 1, mainly the neutral forms of dialkyl phosphates are present and the contribution of acid hydrolysis to the overall rate is insignificant judging from the data for dimethyl phosphate. Comparison of the rate constants at pH 1.25 [57,61] therefore yields the correct idea about the variation of the reactivities of neutral dialkyl phosphate molecules in the following sequence [the values of $10^6k$ ($s^{-1}$) at 100°C and pH 1.24 are quoted]:

$$\underset{4,56}{(\text{iso-}C_3H_7O)_2P(O)OH} > \underset{3,13}{(CH_3O)_2P(O)OH} > \underset{0,8}{(p\text{-}C_3H_7O)_2P(O)OH}.$$

Table 5. The rate constants for the hydrolysis of various reactive forms of dimethyl phosphate[57] at 100°C in aqueous solutions.

| Ruptured bond | $10k$, $s^{-1}$ | | $10^6k$, litre $mole^{-1}$ $s^{-1}$ |
|---|---|---|---|
| | $(CH_3O)_2PO_2^-$ | $(CH_3O)_2P(O)OH$ | $(CH_3O)_2P(OH)_2^+$ |
| P–O | $<10^{-3}$ | 0.9 | 0.11 |
| C–O | $<10^{-3}$ | 3.3 | 0.91 |

The high reactivity of the di-isopropyl ester can be due to the $S_N1$ mechanism of the reaction with elimination of a carbonium ion, as in the case of tri-isopropyl phosphate[66].

The dimethyl phosphate anion is extremely stable and the kinetics of its alkaline hydrolysis have been investigated at 115° and 125°C.[67] Extrapolation of these data to 25°C yields the approximate rate constant listed in Table 6. Under the conditions of alkaline hydrolysis, dimethyl phosphate reacts mainly via the carbon atom, which results in the cleavage of the C–O bond to the extent of 90%.[65]

In neutral, acidic, and alkaline media, aromatic diesters hydrolyse with the dissociation of the P–O bond[25,58,59]. Some contribution by the dissociation of the C–O bond was noted only for bis-(2,4-dinitrophenyl) phosphate[62], the benzene ring of which is activated (in relation to aromatic nucleophilic substitution) by two strong electron-accepting groups. Diaryl phosphates have low $pK_a$ values, the determination of which is difficult. Probably owing to the lack of $pK_a$ values, the dependence of the rates of hydrolysis of diaryl phosphates on pH in

order to estimate the rate constants for the hydrolysis of the neutral molecules was not analysed[58] and only the rate constants for the hydrolysis of the anions were obtained. The anions of diaryl phosphates are much more reactive than those of dialkyl phosphates and certain kinetic data for their interaction with water (spontaneous hydrolysis) and hydroxide ions are available (Tables 6 and 7). The low activation entropy for the spontaneous hydrolysis of the anion of bis-(2,4-dinitrophenyl) phosphate ($\Delta S^{\neq}$ = −26 cal mole$^{-1}$ K$^{-1}$) indicates a bimolecular mechanism of their reaction with water[58,59]. The kinetic isotope effect $k_{H_2O}/k_{D_2O}$ = 1.5 observed for this reaction suggests the occurrence of general base catalysis by a second water molecule[58]. The bimolecular $S_N2P$ mechanism was also adopted for the alkaline hydrolysis of the diester anions[59]. The negative charge on the oxygen atom, capable of being delocalised to the reaction centre via a $p_\pi$–$d_\pi$ interaction, inhibits significantly the nucleophilic attack by the hydroxide ion. This increases the activation energy, which is higher by several kcal mole$^{-1}$ for the diester anions than for the full esters of phosphoric acid.

Table 6. The rate constants for the spontaneous hydrolysis of diaryl phosphate anions $(RO)_2PO_2^-$ in water.

| R | $10^7k$, s$^{-1}$ (100°C) | References |
|---|---|---|
| $C_6H_5$ | 0.03 | 25 |
| 3-$NO_2C_6H_4$ | 0.0503 | 58 |
| 2-$NO_2C_6H_4$ | 0.562 | 58 |
| 4-$NO_2C_6H_4$ | 0.630 | 58 |
| 4-Cl-2-$NO_2C_6H_3$ | 4.08 | 58 |
| 4-$CH_3C(O)$-2-$NO_2C_6H_3$ | 122 | 58 |
| 2,4-$(NO)_2C_6H_3$* | 1550 | 58 |

*According to Kirby and Younas[58], $E$ = 19.6 kcal mole$^{-1}$ and lg $A$ = 7.77. The value of lg $A$ (s$^{-1}$) was estimated by the present author.

The influence of the structure of diaryl phosphate anions on the rate of their reaction with water has been investigated[58]. The dependence of lg $k$ on the p$K_a$ for the phenols formed in the reaction at 100°C is expressed by the equation[58]

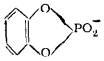
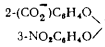
$$\lg k = -0.97pK_a - 0.20.$$

The authors[58] noted that the sensitivity of the reaction to the nature of the eliminated group in diarl phosphate anions is much greater than in the monoester monoanions. However, one must bear in mind that, in the reaction series under consideration, the coefficient of p$K_a$ reflects not only the influence of the eliminated group but also of the remaining group and the latter is not constant either. If it is assumed that both groups have the same effect on the rate of reaction, the slope of the relation between lg $k$ and p$K_a$ calculated per eliminated group is lower by a factor of 2 (0.5). An analogous relation between lg $k$ and the p$K_a$ of the eliminated group (or the remaining group, since both are varied) exists in the alkaline hydrolysis of phosphate diester anions (Fig. 6). For the hydrolysis at 25°C, it corresponds to the equation

$$\lg k = -0.80\,pK_a + 0.76 \quad (n = 4,\ r = 0.996,\ s = 0.27).$$

The rate constant for the alkaline hydrolysis of dimethyl phosphate as well as the rate constants for the hydrolysis of diaryl phosphates are described by this equation when account is taken of the reaction of dissociated P–O bonds in the reaction (10%).

Table 7. Kinetic parameters of the alkaline hydrolysis of phosphate diester anions in aqueous solutions.

| Anion | $10^5k$, litre mole$^{-1}$ s$^{-1}$ (25°C) | $E$, kcal mole$^{-1}$ | lg $A$[e] | References |
|---|---|---|---|---|
| $(CH_3O)_2PO_2^-$[b] | $3\cdot10^{-6}$ | 28.2 | 10.20[a] | 67 |
| $(C_6H_5O)_2PO_2^-$ | 0.015[a] | 15.9[a] | 4.83[a] | 69 |
| $(4\text{-}NO_2C_6H_4O)_2PO_2^-$[c] | 0.58 | 18.3 | 8.23 | 71 |
| $[2,4\text{-}(NO_2)_2C_6H_3O]_2PO_2^-$ | 301 | 16.6 | 9.65[a] | 59 |
|  | 36.5 | — | — | 67 |
|  | 630[a] | 15.8 | 9.38[a] | 75 |
|  | 440 | 17.1 | 10.18 | 70 |
|  | 40 500 | — | — | 69 |
|  | 15 600 | 10.5 | 6.89 | 74 |
|  | 550 | 14.2 | 8.15 | 74 |
|  | 210 | 13.7 | 7.36 | 74 |
|  | 0.19; 0.003[d] | 16.2; 22.2[d] | 6.15; 8.76[d] | 74 |
|  | 1 860 | 17.5 | 11.10[a] | 63 |

[a]See footnote to Table 1.
[b]The P–O bond is cleaved to an extent of approximately 10% during the reaction.
[c]The reaction was investigated in 20% aqueous ethanol solution.
[d]Parameters for the elimination of epoxypropane.
[e]$A$ in litre mole$^{-1}$ s$^{-1}$.

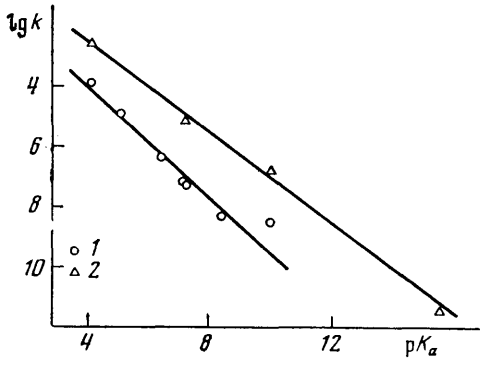


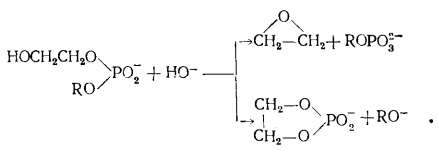

Figure 6. Dependence of lg $k$ on the p$K_a$ of the eliminated group for the spontaneous [$k$ (s$^{-1}$) at 100°C (line *1*)] and alkaline [$k$ (litre mole$^{-1}$ s$^{-1}$) at 25°C (line *2*)] hydrolysis of phosphate diester anions.

Five-membered cyclic phosphate esters exhibit an unusually high reactivity, the rate of their hydrolysis being higher by a factor of $10^7$–$10^8$ than that of acyclic diesters[57,68-70]. According to Westheimer[6], the much

higher reactivity of five-membered cyclic phosphates is partly due to the steric strain in the five-membered rings. Neutral and alkaline hydrolysis of the ethylene phosphate anion includes the cleavage of the P–O bond[65]. In the acid-catalysed hydrolysis, there is oxygen exchange between the phosphoryl group of ethylene phosphate and $H_2^{18}O$, the rate of which is comparable to the rate of cleavage of the ester bond. Since the oxygen exchange does not require the opening of the ring, it was assumed that the ring strain is reduced on formation of the intermediate containing the five-coordinated phosphorus atom[65]. The enthalpy of hydrolysis of the ethylene phosphate anion quoted by Westheimer and coworkers[68] is higher by 4.5 kcal mole$^{-1}$ than for the diethyl phosphate anion, which confirms the strain in the cyclic ester.

Penta-alkoxyphosphoranes with five-membered rings are known to be formed more readily than the acyclic analogues[72] and this confirms indirectly the possibility of the involvement of such structures in the mechanism of the hydrolysis. The favourable effect of the stereochemistry of the transition state on the reaction is indicated by the activation entropy $\Delta S^{\neq} = -15$ cal mole$^{-1}$ K$^{-1}$ found for the alkaline hydrolysis of the dimethylvinylene phosphate anion[70]. The mechanism of the hydrolysis of cyclic phosphates has been discussed in detail in a review[6].

The acceleration of the hydrolysis of certain phosphate diesters owing to intramolecular catalysis has been observed. Intramolecular catalysis in the hydrolysis of β-hydroxyalkyl phosphate anions is important for the understanding of the mechanisms of certain biochemical reactions[73,74]. It has been established that the alkaline hydrolysis of anions containing the β-hydroxyalkyl group proceeds via two competing mechanisms, one of which involves the formation of an oxiran ring on elimination of the β-hydroxyalkyl group and the other is associated with the intermediate formation of a five-membered cyclic phosphate:



The oxiran ring and the five-membered cyclic phosphate are then rapidly converted into a glycol and a glycol phosphate. The ratio of these products depends on the second alcoholic moiety of the ester if the latter is an alkoxyalkyl group. However, the exclusive elimination of phenoxides in the reaction was observed for aryl β-hydroxyalkyl phosphates. The rate of reaction depended on the p$K_a$ of the eliminated phenols or alcohols if the fraction of the observed rate constant referring to hydrolysis via a five-membered cyclic phosphate was considered for the latter[73].

Another example of intramolecular catalysis in the hydrolysis of phosphate diesters is the nucleophilic catalysis by the carboxylate group in the *o*-position relative to the ester linkage in aryl 2-carboxyphenyl phosphates[63]. The alkaline hydrolysis of the anions of these esters is $10^7$–$10^8$ faster than that of the analogous compounds without a $CO_2^-$ group in the *o*-position. The intermediate formation of a cyclic acyl phosphate during this reaction was demonstrated[63].

### 3. Hydrolysis of Phosphate Triesters

The hydrolysis of triesters is a potentially multistage process whose final product is phosphoric acid. The first stage, involving a change in the structure of the substrate, is considered in this section. Owing to the tribasic nature of phosphoric acid, there is a considerable scope for the alteration of the structures of triesters by the synthesis of mixed compounds with different alcoholic groups. The study of the kinetics of the hydrolysis of trialkyl phosphates began in the past century[76,77]; nevertheless, the number of triesters investigated hitherto is small (Table 8–10).

Table 8. Kinetic parameters of the spontaneous hydrolysis of phosphate triesters in water.

| Compound | $10^6k$, s$^{-1}$ (100°C) | $E$, kcal mole$^{-1}$ | lg$A$ (s$^{-1}$) | References |
|---|---|---|---|---|
| $(CH_3O)_3PO$ | 36.5 | 22.7 | 8.86[a] | 79 |
| $(CH_3O)_2P(O)OC_2H_5$ | 39.5[b] | — | — | 84 |
| $CH_3OP(O)(OC_2H_5)_2$ | 18.6[b] | — | — | 84 |
| $CH_3OP(O)(OCH_2CH{-}CH_3)_2$ (O) | 29[a] | 19.2 | 6.71 | 91 |
| $(CH_3O)_2P(O)OCH{=}CCl_2$ | 660[a] | 23.3[a] | 10.47[a] | 85 |
| $(C_2H_4O)_3PO$ | 9.1[a] | 24.4 | 9.25 | 90 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_2H_5)_2$ | 98[a] | 22.5[a] | 9.17[a] | 85 |
| $4\text{-}CH_3SO_2C_6H_4OP(O)(OC_2H_5)_2$ | 98[a] | 22.5[a] | 9.17[a] | 85 |
| $(C_6H_5O)_3PO$ | 0.06[c] | — | — | 79 |
| $(iso\text{-}C_3H_7O)_3PO$ | 4.5 (at 90°C) | — | — | 66 |
| $(t\text{-}C_4H_9O)_3PO$ | 30[d] (at 60°C) | — | — | 66 |

[a]See footnote to Table 1.
[b]The values at 101–102°C and pH 4.7–4.9 are quoted.
[c]In water–dioxan (66 vol.%).
[d]In water–ethanol (50 vol.%).

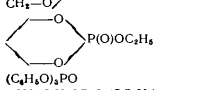
Table 9. Kinetic parameters of the spontaneous hydrolysis of cyclic phosphate esters at 25°C.

| Compound | $10^5k$, s$^{-1}$ (25°C) | $E$, kcal mole$^{-1}$ | lg$A$ (s$^{-1}$) | References |
|---|---|---|---|---|
| $CH_3{-}O\diagdown P(O)OCH_3$ (CH$_3$–O) | 2.3 | — | — | 86 |
| $CH_3C(O)O\diagdown P(O)OC_2H_5$ ($CH_3C(O)O$) | 830 | 8.4 | 4.12 | 92 |
| $CH_3C(O)O\diagdown P(O)OC_3H_7\text{-}n$ ($CH_3C(O)O$) | 940 | 10.8 | 5.89 | 92 |
| $CH_3C(O)O\diagdown P(O)OC_4H_9\text{-}n$ ($CH_3C(O)O$) | 660 | 9.8 | 4.97 | 92 |
| $CH_3C(O)O\diagdown P(O)OC_4H_9\text{-}iso$ ($CH_3C(O)O$) | 470 | 8.3 | 3.79 | 92 |
| $2,4\text{-}(NO_2)_2C_6H_4OPO(CH_2)_3O$ (O) | 0.26 | 15.5[a] | 5.77[a] | 80 |

[a]See footnote to Table 1.

In reactions involving neutral triester molecules, the attack by the nucleophile may be directed to the phosphorus or carbon atom of the ester linkage. Water and the hydroxide ion react with trialkyl phosphates in conformity with Pearson's concept of the interaction of hard and soft acids and bases. In alkaline hydrolysis, the reaction centre is the phosphorus atom, while in the reaction with water or in spontaneous hydrolysis the reaction centre is the α-carbon atom of the alkoxy group of the ester. Using $H_2^{18}O$, it was possible to establish that the dissociation of the P–O bond occurs in the alkaline hydrolysis of alkyl[78,79] and aromatic[79,80] esters, but in the reaction with water these two types of ester linkages, POAr and POAlk, are cleaved via different mechanisms. Aromatic nucleophilic substitution is known to proceed readily only when the benzene ring contains strongly electron-accepting groups[20],

**Table 10.** Kinetic parameters of the alkaline hydrolysis of phosphate triesters in aqueous solutions.

| Compound | $10^3k$, litre mole$^{-1}$ s$^{-1}$(25°C) | $E$, kcal mole$^{-1}$ | lg$A$ (litre mole$^{-1}$ s$^{-1}$) | Refs. |
|---|---|---|---|---|
| $(CH_3O)_3PO$ | 0.146 | 15.9 | 7.82 | 79 |
| $(C_2H_5O)_3PO$ | 0.0132 | 15 3[a] | 6.32[a] | 71 |
| $CH_3OP(O)(OCH_2CH{-}CH_2)_2$ (O) | 2.2 | 15.1 | 8.41 | 91 |
| $(C_2H_5O)_2P(O)OCH{=}CH_2$ | 2.0 | — | — | 94 |
| $(C_2H_5O)_2P(O)OCH_2CH_2N^+(CH_3)_3$ | 30 | — | — | 93 |
| $(C_2H_5O)_2P(O)OP(O)(OC_2H_5)_2$ | 2630 | — | — | 93 |
| $(CH_3O)_2P(O)OCH(CH_3)C(O)CH_3$ | 387 000 | — | — | 95 |
| | 9000[b] | — | — | 95 |
| $(C_2H_5O)_2P(O)OCH(CH_3)C(O)CH_3$ | 64 000 | — | — | 95 |
| $(iso\text{-}C_3H_7O)_2P(O)OCH(CH_3)C(O)CH_3$ | 2200 | — | — | 95 |
| $(C_6H_5O)_2P(O)OCH(CH_3)C(O)CH_3$ | 820 000 | — | — | 95 |
| $CH_2{-}O$ \| $CH_2{-}O$ $P(O)OCH_3$ | 64 000 | — | — | 86 |
|  $P(O)OC_2H_5$ | 0.57[a] | 13.8 | 6.87 | 97 |
| $(C_6H_5O)_3PO$ | 14.0 | 9.2 | 4.91 | 96 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_6H_5)_2$ | 490 | — | — | 100 |
| $4\text{-}NO_2C_6H_4OP(O)(OCH_3)_2$ | 39 | 12.2 | 7.55[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_2H_5)_2$ | 11 | 13.5 | 7.95[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_3H_7)_2$ | 7.45 | 13.0 | 7.43[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_3H_7\text{-}iso)_2$ | 1.00 | 14.5 | 7.64[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_4H_9\text{-}n)_2$ | 7.2 | 13.2 | 7.55[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_4H_9\text{-}iso)_2$ | 6.2 | 13.2 | 7.52[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_4H_9\text{-}s)_2$ | 0.48 | 14.3 | 7.20[a] | 98 |
| $4\text{-}NO_2C_6H_4OP(O)(OC_6H_{13}\text{-}n)_2$ | 7.5 | — | — | 100 |
| $4\text{-}H_2NC_6H_4OP(O)(OC_2H_5)_2$ | 0.243 | — | — | 49 |
| $4\text{-}(CH_3)_2NC_6H_4OP(O)(OC_2H_5)_2$ | 0.278 | — | — | 49 |
| $4\text{-}CH_3OC_6H_4OP(O)(OC_2H_5)_2$ | 0.280 | — | — | 49 |
| $4\text{-}C_2H_5C_6H_4OP(O)(OC_2H_5)_2$ | 0.325 | — | — | 49 |
| $4\text{-}(iso\text{-}C_3H_7)C_6H_4OP(O)(OC_2H_5)_2$ | 0.337 | — | — | 49 |
| $4\text{-}CH_3C_6H_4OP(O)(OC_2H_5)_2$ | 0.353 | — | — | 49 |
| $C_6H_5OP(O)(OC_2H_5)_2$ | 0.463 | — | — | 49 |
| $3\text{-}CH_3OC_6H_4OP(O)(OC_2H_5)_2$ | 0.622 | — | — | 49 |
| $4\text{-}CH_3SC_6H_4OP(O)(OC_2H_5)_2$ | 0.742 | — | — | 49 |
| $4\text{-}(CO_2^-)C_6H_4OP(O)(OC_2H_5)_2$ | 0.920 | — | — | 49 |
| $4\text{-}ClC_6H_4OP(O)(OC_2H_5)_2$ | 1.15 | — | — | 49 |
| $4\text{-}BrC_6H_4OP(O)(OC_2H_5)_2$ | 1.26 | — | — | 49 |
| $4\text{-}IC_6H_4OP(O)(OC_2H_5)_2$ | 1.29 | — | — | 49 |
| $3\text{-}ClC_6H_4OP(O)(OC_2H_5)_2$ | 1.56 | — | — | 49 |
| $3\text{-}BrC_6H_4OP(O)(OC_2H_5)_2$ | 1.65 | — | — | 49 |
| $4\text{-}CH_3C(O)C_6H_4OP(O)(OC_2H_5)_2$ | 3.23 | — | — | 49 |
| $4\text{-}NCC_6H_4OP(O)(OC_2H_5)_2$ | 6.37 | — | — | 49 |
| $3\text{-}NO_2C_6H_4OP(O)(OC_2H_5)_2$ | 6.38 | — | — | 49 |
| $2\text{-}(CH_3)_2NC_6H_4OP(O)(OC_2H_5)_2$ | 0.148 | — | — | 49 |
| $2\text{-}(iso\text{-}C_3H_7)C_6H_4OP(O)(OC_2H_5)_2$ | 0.172 | — | — | 49 |
| $2\text{-}C_2H_5C_6H_4OP(O)(OC_2H_5)_2$ | 0.192 | — | — | 49 |
| $2\text{-}CH_3OC_6H_4OP(O)(OC_2H_5)_2$ | 0.367 | — | — | 49 |
| $2\text{-}IC_6H_4OP(O)(OC_2H_5)_2$ | 1.92 | — | — | 49 |
| $2\text{-}BrC_6H_4OP(O)(OC_2H_5)_2$ | 2.38 | — | — | 49 |
| $2\text{-}ClC_6H_4OP(O)(OC_2H_5)_2$ | 2.60 | — | — | 49 |
| $2\text{-}NO_2C_6H_4OP(O)(OC_2H_5)_2$ | 22.2 | — | — | 49 |

[a]See footnote to Table 1.
[b]The rate constant for the cleavage of the P–$OCH_3$ bond.

so that the spontaneous hydrolysis of aromatic esters, like the alkaline hydrolysis, usually takes place at the phosphorus atom [79,80]; the same type of cleavage of P–OAr bonds is characteristic of the acid hydrolysis [80]. The spontaneous and acid hydrolysis of alkyl esters takes place with rupture of the C–O bond [66,79,81,82]. As a rule the POAr ester linkages are less resistant to hydrolysis than the POAlk linkages and in the alkaline hydrolysis of mixed compounds the P–OAr bonds are cleaved preferentially. It has been shown for dibenzyl *p*-nitrobenzoyl phosphate that the anhydride linkage is the most reactive [83], being hydrolysed at the carbonyl carbon atom. Fig. 7 shows that plots of the hydrolysis rate constants for certain triesters against pH have a plateau in the region of weakly acid pH values. The extent of the plateau on the side of high pH values is determined by the ratio of the rate constants for the alkaline and spontaneous hydrolysis and on the side of low pH values by the ratio of the rate constants for the acid and spontaneous hydrolysis and the p$K_a$ for the protonated form of the ester. In the region of the plateau, the reaction between the neutral trialkyl phosphate molecule and water may proceed via an $S_N2$ or $S_N1$ mechanism at the carbon atom of the ester linkage. A mechanism of the $S_N1$ type, involving the cleavage of a carbonium ion, has been demonstrated for esters of secondary and tertiary alcohols [66].

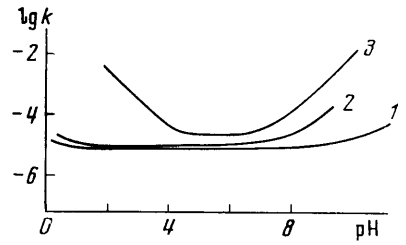



**Figure 7.** Dependence of the rate constants for the hydrolysis of triesters on the pH of the medium: 1) $(C_2H_5O)_3PO$ at 101°C [84]; 2) $4\text{-}NO_2C_6H_4OP(O)(OC_2H_5)_2$ at 70°C [85]; 3) ethylene methyl phosphate at 25°C. [86]

The kinetic isotope effect for trimethyl and triethyl phosphates ($k_{H_2O}/k_{D_2O}$ = 1.25) agrees with the hypothesis of an $S_N2$ mechanism of the spontaneous hydrolysis of these esters [81,87]. The low values of $\Delta S^{\neq}$ for the esters (−18 and −20 cal mole$^{-1}$ K$^{-1}$ respectively) are consistent with a bimolecular rate-limiting stage. A significantly greater isotope effect for the solvent ($k_{H_2O}/k_{D_2O} \simeq 2$) was noted in the cleavage of the P–OAr bond in the spontaneous hydrolysis of 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinanes, which enabled the authors [80] to postulate the occurrence of general base catalysis by a second water molecule in the reaction via an $S_N2P$ mechanism involving the phosphorus atom.

Unsubstituted trialkyl phosphates are insensitive to acid catalysis. In the hydrolysis of trimethyl phosphate, the replacement of water by a 3 M $HClO_4$ solution increases the rate of reaction by [only] 20%. [79] Appreciable catalysis by 0.5 M $H_2SO_4$ of the hydrolysis of triethyl phosphate was not observed either [81]. The appearance of an acid-catalytic effect is promoted by carrying out the reaction in aqueous organic media, where the rate of spontaneous hydrolysis is sharply reduced owing to the decrease of the activity of water [81,87]. The low sensitivity of trialkyl phosphates to acid catalysis may be attributed to the long distance between the site of addition of the proton (the phosphoryl group) and the reaction centre. The high negative activation entropy for the acid hydrolysis of triethyl phosphate and the low isotope effect ($k_{H_2O}/k_{D_2O}$ = 0.6 in 0.56 M $HClO_4$) served as a basis for the adoption of a bimolecular reaction mechanism, including proton transfer in the equilibrium stage [81].

An isokinetic relation of the compensation type and covering the $\Delta S^{\neq}$ range from 0 to −50 kcal mole$^{-1}$ K$^{-1}$ has been established between the activation parameters in the acid hydrolysis of triesters [88]. It probably due to the gradual transition from an $S_N2$ to an $S_N1$ mechanism as the structure of the trialkyl phosphate is altered.

In contrast to trimethyl and triethyl phosphates, the rate constants for the hydrolysis of which increase monotonically with increase of the concentration of acid in aqueous organic media (Fig. 8), the rate constants for the acid hydrolysis of aromatic esters passes through a

maximum, whose position depends on the nature of the ester and the acid employed, as for mono- and di-aryl phosphates[25,80].

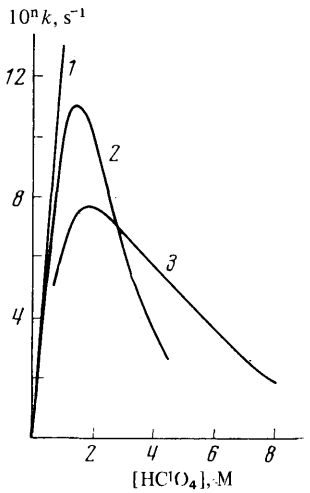


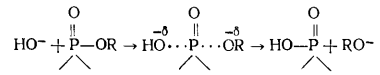

**Figure 8.** Dependence of the rate constants for the hydrolysis of triesters on the $HClO_4$ concentrations: 1) $(C_2H_5O)_3PO$, $n = 6$, in water–dioxan (35%) at 101°C [81]; 2) $(C_6H_5O)_3PO$, $n = 5$, in water–dioxan (60%) at 100°C [25]; 3) $4\text{-}NO_2C_6H_4OP(O)(OC_6H_5)_2$, $n = 4$, in water–dioxan (5%) at 100°C. [89]

The acid hydrolysis of *p*-nitrophenyl diphenyl has been studied in detail[89]. In this case, the maximum is due to the strong negative salt effect in concentrated solutions of inorganic acids. At a constant ionic strength, the hydrolysis rate cojstant therefore increases in proportion to the stoichiometric acidity and has no maximum. The use of Bunnett's improved method makes it possible to characterise the reaction mechanism in terms of the slope of the relation

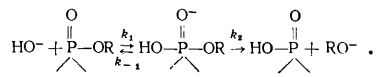
$$\lg k + H_0 = f(\lg c_{H^+} + H_0),$$

where $H_0$ is the acidity function and $c_{H^+}$ the stoichiometric concentration of $H_3O^+$. In $H_2OS_4$, HCl, and $HClO_4$ solutions, these relations had slopes of 1.5, 1.1, and 1.25 respectively, which is characteristic of reactions with a slow proton transfer in the rate-limiting stage. Similar slopes (1–1.4) were obtained for the corresponding relations in the acid hydrolysis of monoaryl phosphates[89]. In HCl solution, the maximum corresponds to an acid concentration of 6 M; the parameters of the Arrhenius equation under these conditions are $E = 14.8$ kcal mole$^{-1}$ and $\lg A = 5.4$, whence $\Delta S^{\neq} = -39$ cal mole$^{-1}$ K$^{-1}$.[89] The value $\Delta S^{\neq}$ obtained indicates the vigorous solvation of the transition state, in the formation of which the activity of water plays an important role. In conformity with these findings, the rate of acid hydrolysis is reduced by a factor of approximately 2 when the reaction is carried out in a 60% aqueous solution of dioxan. According to Bunton[5], the attack by a water molecule on the phosphorus atoms in the acid hydrolysis of the P–O–Ar linkages may proceed in unison with proton transfer to the ester molecule, complete proton transfer not being obligatory for the attainment of the transition state.

The alkaline hydrolysis of phosphate triesters, which is as a rule described by a kinetic equation for second-order reactions and has an $S_N2P$ mechanism, has been investigated in greatert detail[1–8]. Two types of $S_N2P$ mechanisms are possible for the alkaline hydrolysis. In one of them, the synchronous formation and cleavage of bonds in the transition state is postulated:



In the other version, the successive addition of the nucleophile and removal of the eliminated group with participation of a metastable intermediate compound in the reaction is postulated:



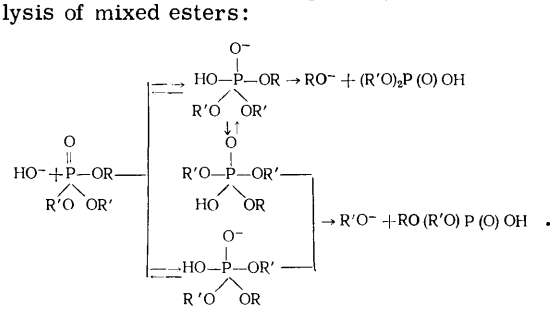
According to the method of steady-state concentrations, the observed rate constant is a compound quantity. The rate of this reaction $dc/dt$ is expressed by the equation

$$\frac{dc}{dt} = k_1 k_2 c\,[HO^-]/(k_{-1} + k_2),$$

where $c$ and $[HO^-]$ are the concentrations of the ester and the hydroxide ions respectively. It follows from the last equation that, for comparable values of $k_{-1}$ and $k_2$, oxygen should be exchanged during the reaction between the phosphoryl group of the ester and water. It has been shown for triphenyl phosphate that in reality there is no exchange between $H_2^{18}O$ and phosphate triesters during alkaline hydrolysis[79]. This is probably due to the low stability of the negatively charged phosphorans[97]. In the absence of oxygen exchange, one may assume that $k_2 \gg k_{-1}$ and the expression for the reaction rate simplifies to

$$dc/dt = k_1 c\,[HO^-].$$

In the alkaline hydrolysis of diethyl *p*-nitrophenyl phosphate and *p*-nitrophenyl diphenyl phosphate, $k_{H_2O}/k_{D_2O} \simeq 1$ (more precisely 0.87 and 1.10 respectively), which agrees with the hypothesis of the nucleophilic attack by the hydroxide ion on the phosphorus atom in the rate-limiting stage[100]. The activation entropies $\Delta S^{\neq} < -20$ cal mole$^{-1}$ K$^{-1}$, which can be found from the data in Table 10, are also consistent with this hypothesis. The increase in the complexity of the $S_N2P$ mechanism may be due to the rapid ligand exchange between non-equivalent positions in the intermediate compound[99], for which a bipyramidal structure is postulated. According to Westheimer[6], as a result of the pseudorotation of the bipyramid the hydrolysis of cyclic phosphates may involve the formation of various reaction products. The hypothesis of pseudorotation in the intermediate is difficult to prove, as can be seen from the general scheme for the possible pathways in the alkaline hydrolysis of mixed esters:



When the influence of the structure on the rate of spontaneous, acid, and alkaline hydrolysis of triesters is considered, one may note a definite analogy in the influence of the nature of the alcoholic ester moieties on the rate of hydrolysis of phosphate mono-, di-, and tri-esters. Electron-accepting substituents in alkyl and aryl groups usually favour the dissociation of ester linkages, which is confirmed for triesters by the data in Tables 8–10.

The esters of secondary and tertiary alcohols exhibit a higher reactivity during spontaneous hydrolysis than those of primary alcohols owing to the ease of the cleavage of the C–O bonds via an $S_N1$ mechanism[66], which is analogous to the behaviour of the corresponding phosphate mono- and di-esters. An unusually high reactivity has been observed for five-membered cyclic esters, which hydrolyse in neutral, acid, and alkaline media $10^6$–$10^8$ faster than their six- or seven-membered cyclic analogues and cyclic esters[86,97]. Among five-membered cyclic phosphates, derivatives of vinylene phosphate are particularly unstable[92].

The influence of the structure of triesters on the rate of spontaneous and acid hydrolysis cannot be considered in greater detail owing to the scarcity of the available data. It has been shown for the alkaline hydrolysis[101] that the dependence of lg $k$ on the p$K_a$ of the eliminated group is close to linearity when the nature of the eliminated group is altered in the sequence OAlk, OAr, OP(O)$R_2$, F. However, using detailed data for the kinetics of the alkaline hydrolysis of substituted aryl diethyl phosphates[98], one may note that a more rigorous linear relation between lg $K$ and the p$K_a$ of the eliminated groups is observed when the nature of such groups is altered only slightly. For example, Fig. 9 shows that the relation between lg $k$ and the p$K_a$ of the eliminated group of aryl diethyl phosphates is described (at 25°C) by the equation

$$\lg k = -0.57\mathrm{p}K_a + 2.48 \quad (n = 27,\ r = 0.976,\ s = 0.1),$$

which differs from the general relation

$$\lg k = -0.42\mathrm{p}K_a + 0.86 \quad (n = 29,\ r = 0.974,\ s = 0.2),$$

where the rate constants for the hydrolysis of triethyl phosphate and tetraethyl pyrophosphate are included. One should note, however, that the relation (at 39°C)

$$\lg k = -0.41\mathrm{p}K_a + 2.79,$$

whose slope is close to that of the general relation, has been obtained for the alkaline hydrolysis of 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinanes[80], whose structures are very similar to those of aryl diethyl phosphates.

The intramolecular catalysis of the hydrolysis of phosphate triesters has been investigated in a number of studies[95,102–106]. In the hydrolysis of aryl 2-carboxyphenyl phosphates intramolecular nucleophilic catalysis by the ionised carboxy-group led to the preferential cleavage of the P–OAr bond[63], which was explained by the inhibition of pseudorotation in the five-coordinated intermediate compounds containing two negatively charged oxygen atoms in the equatorial positions of the bipyramidal structure. In triesters of similar structure [but without a carboxylate group], there is only one negatively charged ligand in the equatorial position and pseudorotation is not hindered. The ready transfer of the salicylate oxygen to the axial position of the bipyramid ensures the possibility of the formation of two reaction products. Salicylic acid is the main product (96%) of the hydrolysis of 2-carboxyphenyl diphenyl phosphate in alkaline media, but in the region of acid pH the elimination of phenol predominates (90%).[104] The intermediate formation of an acyl phosphate in an alkaline medium has been established for the reaction with hydroxylamine; it was shown that the rate of formation of the acyl phosphate is close to the rate of hydrolysis of the substrate. The ratio of the two reaction products (salicylic acid and phenol) depended on the p$K_a$ of the phenol when the latter contained substituents, a decrease of p$K_a$ favouring the elimination of the phenol[104].

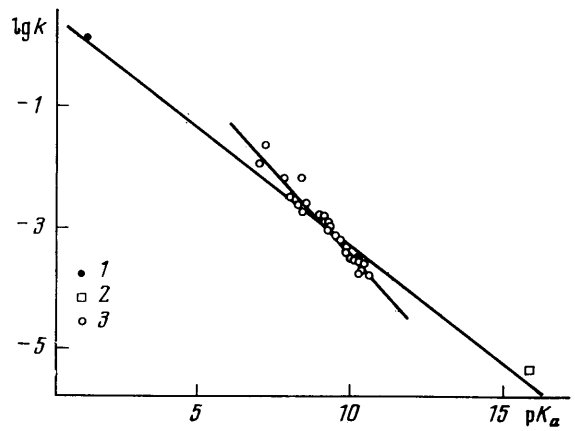



Figure 9. Dependence of lg $k$ on the p$K_a$ of the eliminated group in the alkaline hydrolysis of triesters at 25°C: 1) tetraethyl pyrophosphate (lg $k$ – lg 2); 2) triethyl phosphate (lg $k$ – lg 3); 3) aryl diethyl phosphates.

In the hydrolysis of dialkyl 2-carboxyphenyl phosphates, intramolecular catalysis, accelerating the hydrolysis of such esters by a factor of approximately $10^7$ relative to the corresponding compounds without a carboxy-group, was also observed[103]. Other examples of intramolecular catalysis in the hydrolysis of phosphate triesters have been described[102,105,106].

In conclusion, we may note that the data presented in this review characterise the kinetics of the hydrolysis of an extremely small proportion (approximately 140 compounds) of the many thousands of phosphate mono-, di-, and tri-esters available at the present time. The need for further studies of the kinetics of the hydrolysis of phosphate esters is therefore evident. The author believes that the data, a systematic account of which has been given in this review, will be useful in the consideration of various problems concerning the determination of the relation between the structure and reactivity of phosphates.

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# Phosphorus Nitrides

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The literature data on the methods of preparation, structures, and properties of phosphorus nitrides PN, poly(phosphorus nitrides) (PN), ($P_3N_5$), etc., poly(phosphorus oxynitride) (NPO), and its thio-analogue (NPS) are surveyed and their practical applications, in particular as unique starting materials, formed as a result of the direct binding of molecular nitrogen, in the manufacture of phosphorus-nitrogen fertilisers are examined.
The bibliography includes 169 references.

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## I. INTRODUCTION

More than 100 years have elapsed since the first synthesis of phosphorus nitrides[1], but fairly complete and reliable data on their structures and properties have been obtained only recently. This can be explained by the specific features of the high-temperature synthesis of such systems, the wide variety of their polymeric forms, and the difficulty of studying them. Nevertheless the possibility of extensive practical applications of phosphorus nitrides continues to attract the attention of specialists in various branches of chemistry, physics, engineering, and agriculture. Systematic research in this field was carried out at the beginning of the century in Germany, in the 1930's in France, and after the war in the USA.[1] Studies on poly(phosphorus nitrides) have developed recently to a considerable degree in the Soviet Union.

Unfortunately the review literature on phosphorus nitrides[1-4] does not describe adequately the advances in the study of their structures, properties, and reactivities. In Allcock's book[5], wholly devoted to phosphorus–nitrogen systems, there are no data whatever on these compounds. All these factors make it useful to publish the present review, which covers the classical research and the entire modern literature published up to January 1976 known to the authors.

## II. THE SYNTHESIS, PROPERTIES, AND ELECTRONIC STRUCTURE OF THE PN MOLECULE

### 1. Synthesis

Monomolecular phosphorus nitride, detected spectroscopically for the first time by Curry and Herzberg[6], is stable in the vapour state at temperatures between approximately 450° and approximately 800°C. At lower temperatures, PN is deposited on the walls of the vessels in the form of an amorphous polymer, while at higher temperatures it decomposes into the elements[7-10].

The free energies of the gas-phase formation of PN molecules via the reactions

$$P_2 + N_2 = 2PN\ , \quad (1)$$
$$2P + N_2 = 2PN\ , \quad (2)$$
$$P_4 + 2N_2 = 4PN \quad (3)$$

are respectively 12, −97, and 68 kcal mole$^{-1}$ at 298 K and 3, −53, and −3 kcal mole$^{-1}$ at 2000 K according to calculations[11]. Thus phosphorus nitride is formed comparatively readily only when nitrogen interacts with atomic phosphorus [reaction (2)]. Low temperatures are optimum for the occurrence of this reaction, but $P_2$ molecules dissociate above 2500–3000 K†. The synthesis of PN from $P_2$ and $N_2$ requires a large expenditure of energy. The formation of phosphorus nitride via reaction (3) is even less likely, particularly since $P_4$ dissociates into diatomic phosphorus about 1500°C.[12,13]

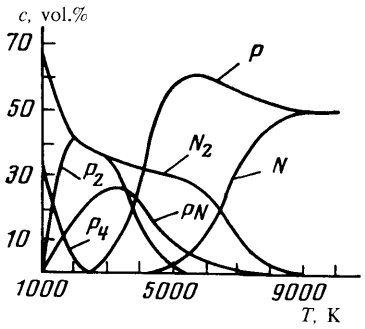
The equilibrium composition of the homogeneous phase incorporating P, $P_2$, $P_4$, N, $N_2$, and PN (see Figure) was calculated by Krasnokutskii and coworkers[13,14] (see also Vil'k et al.[12]). It was shown that, in the temperature range 1000–10 000 K and pressures in the range 0.1–1000 atm and for $N_2 : P_2$ ratios of 1–4, there is a possibility of direct synthesis of PN from $P_2$ and $N_2$. The concentration of PN at 1000 atm and 5000 K reaches 33.8%. The optimum conditions for the synthesis are as follows: temperature 2500–3000 K, pressure 1–10 atm, and a nitrogen : phosphorus ratio of 2. Under these conditions, the PN concentration is 20.5% and the energy consumed is 0.177 kW h mole$^{-1}$.[13,14] A further increase of temperature leads to the decomposition of phosphorus nitride. According to calculations, the temperature of the greatest thermal stability of phosphorus nitride is related to pressure in the system by the expression

$$T_{stab} = 3{,}236p^{0{,}06295} \cdot 10^3 \pm 20\ \text{K}\ . \quad (4)$$

†The temperature range 3200–3250 K corresponds to the maximum proportion of phosphorus nitride formed by reaction (2).[12]

An increase of pressure in the system to 1000 atm leads to an increase of the PN concentration in the gas only by a factor of 1.4, so that it is pointless to employ such a pressure in the synthesis of phosphorus nitrides[13,14].

Ginderich[15] carried out a careful experimental study on the thermodynamics of the formation of PN molecules. He investigated the equilibrium in the vapour phase over the UP–BN system. The enthalpies of reactions (1) and (2) were determined mass-spectrometrically. The values of $\Delta H^{\circ}_{298}$ obtained are respectively 47.6 and −65.3 kcal mole$^{-1}$.




The calculated equilibrium composition of the P–N system at a pressure of 1 atm and for nitrogen : phosphorus = 1.

The kinetics and equilibria in the reactions involving the synthesis and decomposition of PN molecules below 905°C were investigated by Huffman et al.[9] The equilibrium constant in the synthesis of PN from diatomic molecules [reaction (1)] was found to be 0.01 at 900°C and 0.2 at 2000°C. The heat of formation of PN via reaction (1) is −14 kcal mole$^{-1}$. The activation energy for reaction (1) was calculated as approximately 31 kcal mole$^{-1}$ from the above value and from the observed activation energy for the decomposition of the PN molecule into $P_2$ and $N_2$. Having compared this value with the dissociation energies of $N_2$ and $P_2$, the authors[9] concluded that N and P atoms are not involved in the formation of the activated complex in the synthesis of phosphorus nitride. However, the activation energy, corrected using Ginderich's data[15] (approximately 47 kcal mole$^{-1}$), shows that this conclusion is not adequately justified. The hypothesis that the rate of formation of PN is not the factor responsible for the low yield of phosphorus nitride also appears to be premature.

Fedorov and coworkers[13,16] investigated the kinetics of the synthesis of PN in the temperature range 3000–7000 K. By numerical integration on a computer of the system of differential equations corresponding to chain, molecular, atomic, and overall mechanisms, they showed that a satisfactory agreement between calculated and experimental parameters is obtained only for the interaction between atoms:

$$P + N + M \rightarrow PN + M \qquad (5)$$

where M is a third body—an atom or molecule (or the reactor wall). The reaction

$$P_2 + M \rightarrow P + P + M \qquad (6)$$

does not affect the yield of PN, which can be explained by the high rate of decomposition of the molecules of the initial phosphorus. Thus the nitrogen content in the product and the rate of formation of the latter are determined solely by reaction (5), whose rate constant is $1.25 \times 10^9$ litre$^2$ mole$^{-2}$ s$^{-1}$ under these conditions.

The efficiency of the synthesis of PN molecules from the elements may be increased by using an electric discharge or catalysts to initiate the dissociation of the parent molecule. The interaction of the nitrogen atoms, obtained by exposing the $N_2$ molecule to a microwave discharge, with $P_4$ molecules in the temperature range 100–400° has been investigated by Khanna et al.[17] According to these authors, the upper limit to the rate constant for the second-order reaction

$$P_4 + N \xrightarrow{k} [P_4N] \begin{cases} \rightarrow (P_xN_y) + P \\ \xrightarrow{[N]} P_4 + N_2 \end{cases} \qquad (7)$$

is approximately $5 \times 10^{12}$ cm$^3$ mole$^{-1}$ s$^{-1}$.

The mechanism of the formation of phosphorus nitride molecules in a low-temperature plasma has been analysed by Mel'nik et al.,[18] who showed that the synthesis of PN should proceed via a complex mechanism involving a series of competing stages. This chain process is initiated by the formation of phosphorus atoms from $P_4$ and $P_2$ molecules and also by the formation of $P_3$ radicals.

The dependence of the rate of synthesis of PN molecules from the elements in a glow discharge on the potential $u$, the discharge current $i$, and the pressure $p$ in a closed reactor was studied by Millers and coworkers[19]. Mathematical treatment of experimental data showed that there are maxima in the rate of absorption of nitrogen as a function of pressure, the optimum values of which are 0.08–0.1 and 0.03–0.06 mmHg. There is a linear relation between the rate of reaction and the discharge current. The change in the mass of nitrogen in the reactor, characterising the reaction dynamics, is described by the equation

$$dm = -miK(p, i, u)dt, \qquad (8)$$

where $K(p) = ce^{\alpha/p}$ and $c$ and $\alpha$ are constants for the given $i$ and $u$. The same workers investigated the interaction of phosphorus and nitrogen in a glow discharge for different methods of supplying nitrogen to the reactor[19] (see also the Addendum to this review).

## 2. Physical Constants, Electronic Structures, and Properties

The upper limit to the dissociation energy of the PN molecule (7.8 eV) has been determined by the Birge–Sponer linear extrapolation of the observed energies of the vibrational levels in the ground state[6,7]. A detailed study of the electronic spectra of this molecule led to $D^0_0$ = 6.3 eV (obtained by extrapolation of the energy of the vibrational levels of the lowest excited state $A^1\Pi$). It has been noted[7] that the relatively small number of the identified vibrational levels (10 out of the 95 possible levels in the ground state and 9 out of the 76 possible levels in the excited state) may be the cause of the possible error in the determination of the dissociation energy from spectroscopic data. The study of the equilibrium in an equiatomic mixture of nitrogen and phosphorus at temperatures in the range 895–905°C led to $D^0_0$ = 7.1 eV.[9] A somewhat higher value (7.57 eV) was obtained by Vu and Karlson[20]

in a study of the evaporation of $P_3N_5$, but their investigation has been criticised[15,21]. The value of $D_0^0$ obtained from the analysis of the thermodynamics of the evaporation of phosphorus nitride is 7.0 eV.[21] However, the most reliable dissociation energy has been found by Ginderich[15]. The dissociation energies of the $P_2$ and PN molecules which he calculated are listed in Table 1.

Table 1. Comparative characteristics of the $N_2$, PN, and $P_2$ molecules.

| Parameter | $N_2$ | PN | $P_2$ | References |
|---|---|---|---|---|
| $E_{dis}$ (exp.), eV | 9.90 | 6.43 | 5.08 | 15, 31 |
| Interatomic distance, Å | 1.094 | 1.49085 | 1.894 | 7, 22, 48 |
| Vibration frequency, $cm^{-1}$ | 2359.61 | 1337.24 | 780.43 | 7, 48 |
| Ionisation potential, eV | 15.8 | 11.85 | 10.2* | 20, 31, 40 |
| Energy of corresponding single bond, kcal | 38 | 70 | 50 | 51 |
| Population of 3*d* orbital, el.units | 0.06 | 0.12 | 0.17 | 32, 35, 37 |
| $\Delta E$**, eV | 2.58 | — | 2.53 | 32, 35, 37 |
| $E^b$***, eV | 5.27 | 1.80 | 0.06 | |
| Additional molecular correlation energy, eV | 4.63 | 4.63 | 5.02 | |

*Value obtained by the LCAO-MO SCF method[37].
**The decrease of the total energy following the inclusion of 3*d* orbitals in the calculation.
***$E^b$ are the dissociation energies of the molecules obtained by quantum-chemical calculations.

The rotational spectrum of the PN molecule in the microwave range was studied recently[22]. Measurements were made of the frequencies of five lines of the quadrupolar hyperfine structure corresponding to the rotational transitions in the ground and first excited states; using literature data, the effective rotational, centrifugal distortion, and vibrational-rotational interaction constants were calculated from them. The calculated interatomic distance agrees well with the value found earlier from the analysis of the vibrational spectrum (Table 1). The millimeter and submillimeter regions of the rotational spectrum of phosphorus nitride have been studied[23].

The potential curves for the ground and first excited states of phosphorus nitrides were calculated using Lippincot's three-parameter function[24]. The dissociation energies obtained for the above two states are 6.3 and 4.0 eV (the dissociation energies of the $P_2$ molecule in the corresponding $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$ states are 5.1 and 2.2 eV). Witchel[25] calculated the internuclear distance in the $A^1\Pi$ state of the PN molecule (1.5466 Å). Szoke[26] used a semiempirical method for the derivation of the potential energy function for the PN molecule as well as $P_2$ and $N_2$. It was shown that the Rydberg–Klein–Rees potential, obtained from the known spectroscopic constants and extrapolated with the aid of the Rydberg and Lippincot potentials, agrees with the experimental data over a wide range of internuclear distances.

Sankaraharayanan[27,28] calculated the Frank–Condon factors for certain bands of the $A^1\Pi - X^1\Sigma^+$ system, the electron transition moment for interatomic distances in the range 1.426–1.630 Å, and the relative probabilities of the transitions, which made it possible to explain the characteristic features of the vibronic spectrum of the PN molecule. Silver and Moller[29] showed that the values of the Frank–Condon factors obtained from the relative band intensities in the resonance fluorescence spectrum agree well with the theoretical values. The same workers used the Hanle effect to determine the lifetime of the $A^1\Pi$ state of the PN molecule as 230 ± 70 ms.[29]

The thermodynamic functions of the PN molecule in the temperature range 273–15 000 K have been calibrated by Potter and Di Stefano[30] (see also Ref. 31). The results of two non-empirical calculations for the ground ($^1\Sigma^+$) state of the PN molecule by the LCAO-MO SCF method have been published[32,34]. A calculation similar to the calculation by the Hartree–Fock method has been carried out by McLean and Yoshimine[32]. The basis set included 25 σ and 13 π Slater-type functions proportional to $e^{-\zeta r}$, where ζ is a parameter usually referred to as the exponent in quantum-chemical literature. Boyd and Lipscomb[34] used the minimum basis set of Slater-type functions and, in the case of the phosphorus atom, took into account the 3*d* functions, whose exponents were varied. The electronic configuration of the PN molecule obtained by *ab initio* calculations, namely ... $5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4$, is analogous to that calculated for the $^1\Sigma_g^+$ states of the $N_2$ and $P_2$ molecules[35–37]‡. The contribution of the atomic orbitals of phosphorus to the upper occupied molecular orbitals of PN is fairly large, which is the reason for the smaller ionisation potential of the PN molecule compared with that of $N_2$ (Table 1).[32,39]§

Table 1 presents the dissociation energies of the $N_2$, PN, and $P_2$ molecules obtained from the most accurate of the published non-empirical calculations. These values differ from the experimental energies by the additional molecular correlation energy, equal to the difference between the correlation energies for the above molecules and for their constituent atoms[41]. The additional molecular correlation energies found in this way are virtually identical for the $N_2$ and PN molecules and differ slightly from the value for the $P_2$ molecule, which is probably too high. This may be caused, on the one hand, by the similarity of the correlation energies of the electrons in the inner shells of the molecules and their constituent atoms and, on the other, by the similarity of the bonds in these diatomic molecules.

A clear idea about the characteristics of the distribution of electron density in PN, $P_2$, and $N_2$ is provided by the full and difference maps of charge density. The formation of the above diatomic orbitals leads to an increase of electron density in the region between the nuclei along the molecular axis and to a decrease in density at the nuclei and in the direction away from the molecular axis[34,42,43]. The concentration of electronic charge in the internuclear region together with the overlapping of the atomic orbitals is known to play an important role in bond formation. The relative decrease in the density of the electron cloud in the internuclear region is responsible for the decreased stability of the above diatomic orbitals in the sequence $N_2 > PN > P_2$. This is caused by the presence in the phosphorus atoms of additional inner filled shells and by the lower capacity of the phosphorus valence orbitals for *sp* hybridisation compared with the corresponding valence orbitals of the nitrogen atom[37,39]. Analysis of the difference maps characterising the distribution of the π and σ

‡The agreement between the calculated and experimental molecular orbital energies for the $N_2$ and PN molecules has been analysed[38,39].

§According to Wu and Fehlner's data[40], the photoelectron spectrum of PN has two distinct maxima at 11.85 and 12.52 eV, which may be attributed to the σ and π levels.

electron densities, shows that the contribution of $\pi$ electrons towards bonding diminishes in the sequence $N_2 > PN > P_2$. Analysis of the overlap populations leads to an analogous conclusion[36,39,42,44].

The inclusion in the calculation of 3*d* orbitals, which play the role of polarising terms in the above three molecules, leads to an increase of electron density in the bonding region[42,45]. The population of the 3*d* orbitals increases when nitrogen atoms are replaced by phosphorus atoms. The changes in the total energies, occurring when the 3*d* orbitals are included in the calculations for the $P_2$ and $N_2$ molecules, are in their turn virtually identical (Table 1). According to Boyd's data[42], the change in the exponent of the 3*d* atomic orbitals from 1.0 to 1.5 (the optimum values for non-empirical calculations with an unbalanced basis set) leads to an increase of the overall overlap population, which diminishes somewhat on further contraction of the 3*d* orbitals. The optimum value of the $\sigma$-bonding component of the overlap population also corresponds to the optimum value of the exponent, since the $\pi$-bonding component diminishes monotonically with decrease in the size of the 3*d* orbitals. The overlap population of the $d^{\sigma}$ phosphorus orbitals with the corresponding nitrogen orbitals increases monotonically under these conditions, the overlap population of the phosphorus $d^{\pi}$ orbitals diminishes, and the kinetic energy of the electrons and the sum of the molecular orbital energies increase[42].

The heteroatomic PN molecule has a dipole moment, which has been measured (2.75 D) by Raymonda and Klemperer[46] from the electrical resonance spectrum in a molecular beam. They also described the dependence of the dipole moment and the quadrupole interaction constant on the vibrational state of the molecule. The dipole moment is due to a redistribution of electron density in the PN molecule compared with the "non-interacting" atoms. Using his method for subdividing space into regions corresponding to atoms and the results of a non-empirical calculation[32], Politzer[47] calculated the effective charges $\Delta q$ of the P and N atoms (0.25 and −0.25 a.u. respectively) and the distances from the centres of the positive and negative charges to the centre of the interatomic distance (0.715 and 0.768 Å). The centre of the negative atomic charge is beyond the nuclei, owing to the presence of the lone electron pair at the nitrogen atom. Politzer's calculated effective atomic charges are somewhat smaller than the values obtained by the LCAO-MO SCF method in terms of the CNDO/2 valence approximation[49] with and without allowance for the 3*d* functions of the phosphorus atom¶ ($|\Delta q| = 0.35$ and 0.45 a.u. respectively[39,45]).

As already mentioned, the phosphorus nitride molecule is stable over a narrow temperature range. The simplest derivatives of PN, the great structural variety of which has frequently led to some confusion in the interpretation of experimental data[1], are also extremely labile. In this situation, it is necessary to employ, together with physicochemical data, the results of quantum-chemical calculations of various characteristics of such systems, and also to calculate the potential surfaces for the chemical reactions. A logical investigation of the relation between the electronic structure and properties of phosphorus nitride and its derivatives is being carried out by one of the authors of the review[39,45,52,53].

¶The exponents of the 3*d* orbitals were assumed to be 1.6, in agreement with the value optimised by Boyd[42].

A fragment of the potential surface for the protonation of the PN molecule has been calculated[45] by the CNDO/2 method. It was found that the minimum total energy corresponds to a nearly linear geometry of the cation with the proton attached to the nitrogen atom. In the $(HNP)^+$ cation, the polarity of the H–N bond is low as a result of the acceptance by the proton of electrons from the *s* orbital of the nitrogen atom and the $p^{\pi}$ orbital of the phosphorus atom. The overall population of the 3*d* orbitals in the cation, calculated by the CNDO/2 method, hardly changes relative to the PN molecule and there is only a redistribution of electron density between the $d^{\pi}$ and $d^{\sigma}$ orbitals.

The characteristic features of the electronic structures of the $H_2NP$ and $H_4NP$ isomers have been analysed[52] and the relation between the electronic structure and properties of aminophosphine $H_2NPH_2$ has been examined theoretically in detail[53–56].

## III. METHODS OF PREPARATION AND PROPERTIES OF POLY(PHOSPHORUS NITRIDES) (PN), $(P_3N_5)$, ETC.

A common feature of the PN and $P_2$ molecules is the formation of polymers with different structures, which is not characteristic of nitrogen. Aggregation leads to the formation of new $\sigma$ bonds (two additional bonds per diatomic molecule), the sums of the energies of which for PN and $P_2$ are greater than the dissociation energies of the diatomic molecules by approximately 62 and 33 kcal respectively, while in the case of $N_2$ the sum is smaller by 114 kcal (Table 1). Thus the ability of phosphorus nitride to form stable polymeric systems should be more pronounced than that of phosphorus.

Polymeric compounds of nitrogen and phosphorus, whose composition corresponds to the formulae $(P_3N_5)$, $(P_4N_6)$, and (PN), have been described. Variable-composition compounds with nitrogen : phosphorus ratios in the range 0.9–1.7 are also possible[1].

### 1. The Synthesis and Properties of (PN)

Poly(phosphorus nitride) (PN) was obtained for the first time[57] by exposing a mixture of nitrogen and white phosphorus vapours under a pressure of 200 mmHg to a silent electric discharge at a potential of 4000–15 000 V. It was noted that at pressures less than 200 mmHg, red phosphorus, which limits the reaction, is formed simultaneously with (PN). The action of a silent electric discharge on a mixture of nitrogen and phosphorus vapour has also been investigated in other studies[58,59]. Mourey and Wetroff[10] obtained (PN) by passing nitrogen and phosphorus vapours (at an overall pressure of 1 atm) through an electric arc maintained between tungsten electrodes by a potential of several thousands of volts. Poly(phosphorus nitride) is also formed when nitrogen atoms interact with phosphine,

$$N + PH_3 = PH_2 + HN,$$
$$PH_2 + N = PN + H_2,$$

in the temperature range 80–290°C,[60] when a high-frequency discharge is passed through a mixture of nitrogen and phosphorus trichloride[29], when phosphorus trichloride interacts with ammonia at −78°C,[61] in the reaction of triphosphonitrile chloride with sodium[62,63], etc.

At room temperature, (PN) is a stable yellow (possibly owing to contamination with phosphorus) amorphous powder, which is insoluble in water, liquid ammonia, and the

usual organic solvents[64,65]. The polymer sublimes without leaving a residue[9,62] and condenses below 500°C. It dissolves readily, but more slowly than $(P_3N_5)$ in hot sulphuric acid with formation of phosphoric acid, ammonium sulphate, and sulphur dioxide[65]. It is readily oxidised by peroxides and sodium nitrate[62]. Above 500°C, it reacts with chlorine to form the trimeric phosphonitrile chloride contaminated with phosphorus pentachloride[66-68] and it also reacts with atomic nitrogen[69] and ammonia[9] to form $(P_3N_5)$.

## 2. The Synthesis of $(P_3N_5)$

A solid substance with a composition $(P_3N_5)$ was obtained for the first time by Briegleb and Genther[70] in 1862 by the reaction of magnesium nitride with phosphorus pentachloride:

$$5Mg_3N_2 + 6PCl_5 = 2P_3N_5 + 15MgCl_2 .$$

Both Briegleb and Genther[70] and later investigators (Schneider[71] and Stock and Grunberg[72]) were unable to isolate in a pure form the phosphorus nitride obtained in this way; the product was also contaminated with a small amount of magnesium and chlorine. Nor could a pure product be obtained by the reaction of $NH_3$ with $(NPCl_2)_3$.[73] A fairly effective method for the preparation of pure $(P_3N_5)$, based on the reaction of phosphorus pentasulphide with ammonia, was developed at the beginning of the present century by Stock and Hoffman[74]:

$$40NH_3 + 3P_2S_5 = 2P_3N_5 + 15(NH_4)_2S .$$

The phosphorus nitride produced in this reaction consists of an extremely porous mass[59].

The method of synthesising phosphorus nitrides by heating phospham ($PN_2H$) at 400–700°C has become very common. This reaction was discovered by Besson[75] in 1892. Phospham is usually obtained by the prolonged heating of the products of the reaction of ammonia with phosphorus pentachloride and by heating to 800°C tri- and tetra-phosphonitrile chlorides[4], diamidotetrachlorophosphorus nitride[76], and hexa-aminophosphonitrile chloride[4].

Thermodynamic calculation of the equilibrium composition of the P–N system in the temperature range 1000–10 000 K, in the pressure range 0.1–1000 atm, and for N : P ratios of 1–4, 12, and 24 showed[13,14] that the synthesis of the poly(phosphorus nitride) $(P_3N_5)$ via the reaction

$$3PN(gas) + N_2 = (P_3N_5) \qquad (9)$$

at high temperatures can be extremely effective. At atmospheric pressure below 1100 K, virtually the entire PN is converted into $(P_3N_5)$. An increase of pressure makes it possible to condense the nitride at higher temperatures. It has been noted that the highest yield is obtained when nitrogen interacts with phosphorus in the high-temperature homogeneous region with subsequent quenching of the reaction products at a temperature below 1100 K. On quenching to room temperature, the maximum yield of $(P_3N_5)$ corresponds to the maximum concentration of PN obtained in the homogeneous region (2500–3500 K). The minimum energy expenditure (3.26 kW h $kg^{-1}$ at 2500 K, 1 atm, and N : P = 2) corresponds to the same conditions. By increasing the pressure, it is possible to increase the content of the nitride in the product to 48 wt.% (for N : P = 1), but this entails an increase of the energy expenditure to 4–5 kW h $kg^{-1}$. On raising the N : P ratio, one can obtain a $(P_3N_5)$ concentration in the product up to 61 wt.%, but the energy expenditure then increases to 4.3 kW h $kg^{-1}$.[13,14]

A study of the synthesis of $(P_3N_5)$ in a flow-type arc reactor showed that the maximum yield of the product is reached at temperatures greatly exceeding that of the maximum thermal stability of PN, whence it was concluded that the process proceeds under non-equilibrium conditions[14].

The synthesis of $(P_3N_5)$ in the presence of an incandescent tungsten wire is also a non-equilibrium process. The rate-limiting stage in the formation of solid phosphorus nitride from $P_2$ and $N_2$ molecules at temperatures in the range 1720–2127 K is the catalytic dissociation of $P_2$ into atoms[9]. This follows from the similarity of the activation energy for this reaction (approximately 59 kcal at approximately 1800 K) to the dissociation energy of $P_2$ and also from the observed relation between the rate constant for the formation of phosphorus nitride $k$ and the concentration of $P_2$:

$$d c_{P_2}/d t = k c_{P_2}^{1/2} .$$

The process probably includes a stage in which $P_2$ is adsorbed on the surface of the tungsten wire, phosphorus atoms are removed from the surface, and then react with nitrogen in the gas phase†. It is apparently possible to explain in this way the deviation of the composition of the solid product formed under experimental conditions (N : P = 1.03–1.19) from the equimolecular composition of the initial gaseous mixture.

According to the authors[9], the reaction of a phosphorus atom with an $N_2$ molecule leads to the formation of the complex PNN, which may react with another phosphorus atom. The resulting groups probably combine to form the polymer (PN) or continue to grow, colliding alternately with nitrogen and phosphorus molecules until the molecular N : P ratio reaches the highest possible value (as in $P_3N_5$).

## 3. The Structure and Properties of Poly(phosphorus nitrides)

The synthesis usually yields the amorphous phosphorus nitride $(P_3N_5)$, which may be converted into a crystalline form by heating in a stream of nitrogen or ammonia above 800°C.[69] The study of the crystal structures of phosphorus nitrides is of considerable interest because of their potential wide variety and structural similarity to the corresponding modifications of phosphorus, from which the structures of phosphorus nitrides may be formally derived by a regular (or stochastic) replacement of phosphorus atom by nitrogen atoms[2]. However, bearing in mind the high thermal stability of phosphorus nitrides with a regular structure and also the sequence of the energies of the single and multiple NN, NP, and PP bonds (Table 1), one may assume *a priori* that such compounds cannot contain fragments with single and multiple NN bonds as well as the –P=P– and –P=N– linkages. Thus the principal structural element in phosphorus nitrides must be the single P–N bond and the multiple $\rangle$P=N– bond. We may note that the average bond energy (68.3 kcal) calculated from the energy of formation of the amorphous (PN)[77] is virtually identical with the energy of the P–N bond in $(Me_2N)_3P$[50] (Table 1). Crystalline phosphorus nitrides

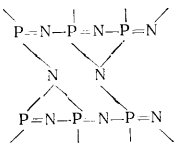
† Tungsten nitrides and phosphides are not formed at these temperatures[1].

are obtained in the form of powders, which are stable up to 700°C; on subsequent heating to the melting point or sintering, the powders may decompose or their structure may change[78-80].

X-Ray diffraction analysis showed[81] that ($P_3N_5$) crystallises in the hexagonal system with formation of spherulites 2–5 μm in size. A tetragonal modification, formed when phosphorus oxynitride is acted upon by ammonia, has also been detected[82,83]. The crystals of this modification have dimensions of approximately 30 μm. By treating the tetragonal modification with ammonia, it is possible to obtain the hexagonal modification. The converse transition cannot be achieved[84]:

$$(P_3N_5)\ \text{(tetragon.)} \xrightarrow[850^\circ C]{NH_3} (P_3N_5)\ \text{(hexagon.)} \xrightleftharpoons{NH_3+O_2}$$
$$\rightleftarrows (NPO) \xrightleftharpoons[O_2+NH_3]{NH_3\ \text{slow}} (P_3N_5)\ \text{(tetragon.)}$$

On the basis of the analysis of the infrared spectra, Steger[85] suggested that amorphous ($P_3N_5$) has a three-dimensional structure:



Judging from infrared spectroscopic data, the hexagonal modification of ($P_3N_5$) has an analogous but more ordered structure in which the phosphorus atom forms four σ bonds and one π ($pd$) bond with the neighbouring nitrogen atoms[84]. The infrared spectrum of the tetragonal modification has no band with $\nu_{max} = 1260\ cm^{-1}$, which may be attributed to the antisymmetric vibrations of the $\geq P=N-$ linkages[5]; this is regarded[84] as evidence for the presence in such systems of five P–N bonds. This band is also absent from the infrared spectrum of the crystalline modification of ($P_3N_5$) obtained from the hexagonal modification on treatment with ammonia at 500°C and approximately 40 atm.[86] The X-ray diffraction pattern of this modification differs from that of the tetragonal modification identified by Millers and coworkers[82].

Under the usual conditions, the phosphorus nitrides ($P_3N_5$) are white or yellowish highly stable substances, which are insoluble in water and organic solvents and are resistant to the action of dilute nitric and hydrochloric acids and alkalis[59,65]. ($P_3N_5$) can be dried in air at 120°C without risk of decomposition, which begins above 700°C at the normal pressure.

The evaporation of ($P_3N_5$) at 690–950°C has been investigated[20]. A combination of mass-spectrometric measurements with a study of the overall rate of diffusion of the preparation was employed. Under the conditions of congruent evaporation and for equal ionisation cross-sections of the PN and $P_2$ molecules, the partial pressures of $N_2$, PN, and $P_2$, corresponding to the overall reaction (8) at 970–1270 K, were determined. Owing to a number of methodological inadequacies and the lack of identification of the test substance, the thermodynamic characteristics for the evaporation process obtained in the above study involve large systematic errors. Thus the calculated dissociation energy of PN is appreciably higher than the value in Table 1. In order to determine the ratios of the partial pressures of PN, $P_2$, and $N_2$, Gordienko et al.[21] used a thermodynamic method of calculation. They analysed the temperature variation of the equilibrium constants for the reactions expressed in terms of the mass-spectrometric currents corresponding to the vapour components. Analysis of the mass spectra obtained at 950–1100 K and for an ionisation energy of approximately 30 eV showed that the evaporation of the hexagonal and tetragonal modifications of ($P_3N_5$) corresponds to the consecutive occurrence of reaction (9) and the reverse reaction (1). The mechanism of the evaporation of the two modifications is the same. However, the strength of the chemical bonds in the tetragonal modification is greater than in the hexagonal modification, which is confirmed by the higher heats of evaporation (111.0 and 105.1 kcal $mole^{-1}$ respectively) and the higher heats of formation (352.4 and 339.5 kcal $mole^{-1}$ respectively).

On heating in a stream of nitrogen, phosphorus nitride ($P_3N_5$) decomposes into elemental nitrogen and phosphorus; in a stream of hydrogen, phosphorus and ammonia are formed[59,64,65] and in a stream of air one obtains a residue consisting of $P_2O_5$.[59] Like (PN), phosphorus nitrides of the type ($P_3N_5$) can be chlorinated at 700°C with formation of triphosphonitrile chlorides[68]; on interaction with fluorine or nitrogen trifluoride, they give rise to the trimers and tetramers of phosphonitrile fluorides[87]. On heating in a sealed tube, nitric acid decomposes ($P_3N_5$) quantitatively. The ease of decomposition of phosphorus nitride by hot concentrated sulphuric acid has been used by Postnikov and Kuz'min[59] in chemical analyses. Phosphorus nitrides are also decomposed on fusion with alkalis and alkali metal salts. Heating of phosphorus nitride with lead, arsenic, antimony, etc. oxides leads to the liberation of the corresponding elements in a free state[59]. When ($P_3N_5$) interacts with fused magnesium, the phosphonitrile amide $PN(NMg)_2$ is formed; the analogous reaction with calcium begins at 200°C.[88]

The action of water on phosphorus nitrides has been studied in detail[1,59,89,90]. When ($P_3N_5$) is heated with water it does not dissolve at all and does not decompose. On treatment with steam at 150°C, the period during which amorphous phosphorus nitrides are 50% hydrolysed is about 55 h. Subsequent heating increases the rate of decomposition. Above 250°C under pressure, quantitative hydrolysis takes place in 2–3 h in accordance with the equations

$$PN + 3H_2O = (NH_4)H_2PO_4,$$
$$P_3N_5 + 12H_2O = 2(NH_4)_2HPO_4 + (NH_4)H_2PO_4,$$

amorphous phosphorus nitride (PN) hydrolysing more slowly at the same temperatures than ($P_3N_5$). The activation energy for the hydrolysis of ($P_3N_5$) is about 30 kcal $mole^{-1}$.[1]

The poly(phosphorus nitride) ($P_4N_6$) is an intermediate in the reaction of phosphorus trichloride with ammonia:

$$PCl_3 \xrightarrow{+NH_3} P(NH_2)_3 \xrightarrow[500-600^\circ]{-NH_3,H_2} (P_4N_6) \xrightarrow[750^\circ]{-N_2} (PN).$$

It is a yellowish substance which ignites spontaneously in air and is hydrolysed by water more readily than (PN).[89,91] Analysis of the hydrolysis products showed that the ratio of phosphorus(V) and phosphorus(III) in this compound is three and that ($P_4N_6$) is not a simple mixture of the phosphorus nitrides ($P_3N_5$) and (PN).[3] By allowing phosphorus trichloride to react with sodium azide, Grudmann and Ratz[92] obtained a coloured substance, which is hexa-azidophosphonitrile $[PN(N_3)_2]_3$. Phosphorus azides $P(N_3)_3$ as well as $OP(N_3)_3$ are exceptionally unstable and explosive[4].

## IV. METHODS OF PREPARATION AND PROPERTIES OF POLY(PHOSPHORUS OXYNITRIDE) (NPO) AND ITS THIO-ANALOGUE (NPS)

The NPO and NPS molecules have not been identified, but, bearing in mind the somewhat greater affinity of phosphorus for oxygen and sulphur[50], the results of the studies of the infrared spectra of the corresponding monomeric forms, as well as data on the structure and properties of poly(phosphonitrile halides) ($Hal_2PN$) (Allcock[5]) and nitrous oxide, these molecules presumably have a linear geometry with a two-coordinated phosphorus atom. These structures are preferred owing to the greater capacity for involvement in bonding of the 3*d* orbitals of the atoms of elements in the Third Period compared to the corresponding elements in the Second Period[93].

Poly(phosphorus oxynitride) (NPO), obtained for the first time by Gerhardt in 1846[1], exists in amorphous and crystalline forms, like the phosphorus nitride ($P_3N_5$). Amorphous (NPO) is obtained by heating phosphoric acid triamide $OP(NH_2)_3$ *in vacuo*[94] or by the reaction of phosphonitrile chlorides with metal oxides[95].‡ A detailed study of the first reaction has been carried out recently[96, 97]. Analysis of the infrared spectra of the condensation products showed that the P=N–P group is apparently formed as a result of the elimination of an $NH_3$ molecule with formation of the P–NH–P group and its subsequent rearrangement to P=N–P. Thus the formation of (NPO) from $OP(NH_2)_3$ can be represented by the following scheme:

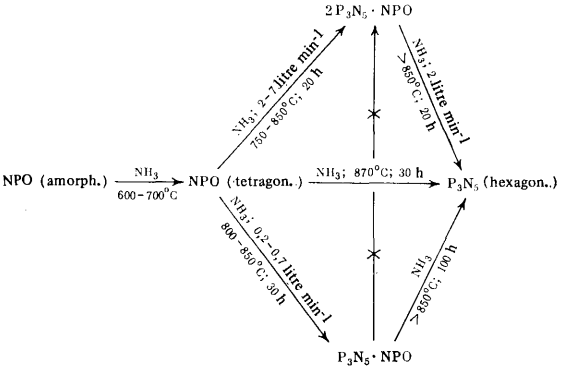
$$OP(NH_2)_3 \xrightarrow[\sim 100^\circ]{-NH_3} (NH_2)_2P(O)—NH—P(O)(NH_2)_2 \xrightarrow[\sim 300^\circ]{-NH_3}$$
$$\rightarrow H_2N—[NP(O)—NH]_n—N \xrightarrow{450-500^\circ} (NPO)\,.$$

The white poly(phosphorus oxynitride) formed has a coarsely porous structure and a relatively small specific surface[98]. This white substance melts above 1000° with formation of black vitreous bodies, which exist in three and more forms. Under normal conditions, (NPO) is insoluble in water and the usual solvents[98]. On heating, atmospheric water causes the dissociation of the PN bond with subsequent substitution of the $NH_2$ groups by OH via a tautomeric rearrangement[96,97]. The final product of the hydrolysis of (NPO) at 175°C is $(NH_4)H_2PO_4$. Poly(phosphorus oxynitride) is resistant to the action of dilute acids and alkalis, but readily decomposes on fusion with alkalis, forming ammonia and alkali metal phosphates. It reacts with concentrated sulphuric acid to form ammonium phosphate[98]: at 800°C, it reacts with chlorine and gives rise to $POCl_3$ and traces of phosphonitrile chlorides[68]. Above 550°C, it is appreciably volatile, losing approximately 55% of its weight in 4 h.[96]

When it is pressed under a pressure of 140 atm at 800°C, (NPO) is converted into a ceramic, which is not very resistant to hydrolysis[99]. The preparation of crystalline (NPO) has been described[100]. Poly(phosphorus oxynitride) crystallises in the tetragonal system[83].

The results of mass-spectrometric studies on the composition of the vapour of crystalline (NPO), formed on evaporation *in vacuo* (0.2 mmHg) at 905–1225 K, have been published[101]. A method analogous to that employed in the study[21] of the evaporation of ($P_3N_5$) was used and it was found that (NPO) vaporises without change in the composition of the solid phase. The $N^+$, $N_2^+$, $PN^+$, $P_2^+$, $P_4^+$, and $P_4O_{6-10}^+$ ions were detected in the spectra, the principal vapour components being $N_2$, PN, $P_2$, and $P_4O_{10}$.

The conversion of poly(phosphorus oxynitride) into ($P_3N_5$) on treatment with ammonia has been investigated in detail[102,103]. When X-ray-amorphous (NPO) interacts with ammonia, different products are obtained depending on the temperature, the ammonia flow rate, and the duration of heating: crystalline (NPO); a crystalline phase with the empirical formula ($P_3N_5$.NPO); the crystalline phase ($2P_3N_5$.NPO), which was not described previously. The overall interaction of amorphous (NPO) can be represented by the following scheme:




Phosphorus thionitride (NPS) is obtained by the ammonolysis of phosphorus pentasulphide[74,104,105]:

$$P_4S_{10} + 4NH_4Cl \rightarrow 4(NPS) + 6H_2S + 4HCl\,.$$

The yield of product after heating for 2 h at approximately 300°C reaches 85%. (NPS) is a grey insoluble diamagnetic substance, which decomposes at approximately 600°C. It reacts with hydrogen at 450°C to form ammonia, hydrogen sulphide, and phosphine. The reaction with chlorine proceeds in accordance with the equation

$$2(NPS) + 3Cl_2 \rightarrow 2(Cl_2PN) + S_2Cl_2\,,$$

the product being phosphonitrile chlorides having different molecular weights[105]. The reaction with dry hydrogen chloride at 350°C involves the mechanism

$$(NPS) + 4HCl \rightarrow NH_4Cl + SPCl_3\,.$$

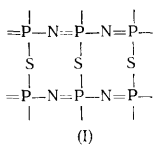
The adduct ($AlCl_3$.NPS), which is stable up to approximately 700°C, is formed when phosphorus thionitride reacts with aluminium chloride at 350°C.[105]

The sulphur in (NPS) may be substituted by oxygen under comparatively mild conditions, for example on boiling with water for a short time.[1]

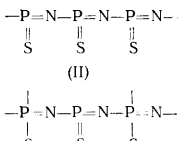
On the basis of infrared spectroscopic data, Steger[85] suggested that the most probable structure of phosphorus oxynitride is one containing phosphonitrile and phosphate chains. This type of structure is preferred also in view of the considerable difference (approximately 80 kcal) between the sum of the energies of two P–O bonds and the energy of the P=O bond. On the other hand, the difference between the energies of two P–S bonds and the P=S bond is only 12 kcal.[50] Thus, together with structure (I) analogous to that proposed for (NPO), non-cross-linked or

‡ There is also an indication that (NPO) may be formed during the simultaneous oxidation of nitrogen and phosphorus in a low-temperature plasma[18].

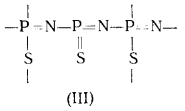
partly cross-linked structures (II) and (III) are possible for phosphorus thionitride:



(I)



(II) NPS



(III)

## V. ELECTROPHYSICAL PROPERTIES OF PHOSPHORUS NITRIDES

As already mentioned, it is quite appropriate to attempt to draw analogies when one considers the characteristic features of the structures and properties of various modifications of phosphorus, phosphorus nitrides, and their derivatives.

Orthorhombic black phosphorus is known to be a semiconductor[106]; the electrical conductivity of polycrystalline black phosphorus is a maximum at 40 K.[107] At very high pressures and low temperatures, phosphorus acquires the properties of a superconductor[108,109].

The presence of a large number of electrons capable of being delocalised in phosphorus nitrides is apparently the reason why the specific conductances of phosphorus oxynitride and nitride show an exponential temperature dependence, which is characteristic of semiconducting materials[79]§. In the temperature range 286–800 K, the specific conductances of the substances investigated decrease in the sequence

$$(P_3N_5)^{cr} > (NPO)^{cr} > (NPO)^{am} .$$

The electrical d.c. resistances of phosphorus thionitride have been investigated[111] in the range 20–120°C. At 20°C, the specific conductance of (NPS) is $1.5 \times 10^{-9}$ $\Omega^{-1}$ $cm^{-1}$, exceeding by several orders of magnitude the specific conductances of the cyclic phosphazenes $(X_2PN)_3$, which are $10^{-11}$–$10^{-13}$ $\Omega^{-1}$ $cm^{-1}$. According to the authors[111], the greater number of conjugated bonds and $\pi$ electrons in phosphorus thionitrides [see Structures (I)–(III)] compared with phosphazenes should be responsible for the mainly electronic nature of the conduction, which is ohmic at an electric field strength of 500–1000 V $cm^{-1}$. It was noted, that in the temperature range employed, the energy gap $E\sigma$ is virtually constant at 0.82 eV. The conductivity of (NPS) and $E\sigma$ are appreciably influenced by the applied pressure. For pressures of 100, 300, 500, and 1000 atm at 20°C, the resistivities are $9.3 \times 10^9$, $1.4 \times 10^9$, $6.9 \times 10^8$, and $4.7 \times 10^8$ $\Omega$ cm respectively and the values of $E\sigma$ vary in the range 0.04–1.80 eV.[111]

The extension of the temperature range in the measurement of the conductivities of phosphorus nitrides towards lower values is of considerable interest. We may recall here the metallic conduction in the (NS) polymer at liquid helium temperatures and its superconducting properties at 0.3 K.[112–115]

Poly(phosphorus selenonitride) (NPSe), which has not so far been synthesised, may possess interesting electrophysical properties.

§ Powders pressed into discs, clamped in an evacuated cell, were investigated. The excess of $p$ electrons is apparently responsible also for the weak photoluminescence of (NPO).[110]

## VI. PRACTICAL APPLICATIONS AND INDUSTRIAL SYNTHESIS OF PHOSPHORUS NITRIDES

### 1. Applications of Phosphorus Nitrides

Phosphorus nitrides are already used in engineering. It has been shown that $(P_3N_5)$ is an active diffusant when a silicon surface is saturated with phosphorus[116]. The possibility of employing $(P_3N_5)$ in the manufacture of semiconductors is also indicated in a patent[117]. Like (NPO), poly(phosphorus nitride) is a more convenient gas absorber than red phosphorus in the manufacture of incandescent lamps and similar apparatus[118,119]. Cellulose articles containing 10% $(P_3N_5)$ or 12% (NPO) are resistant to spontaneous inflammation and combustion and the addition of phosphorus nitride does not impair the mechanical properties of articles[120].

Further study of the binding (by reaction with phosphorus) of molecular nitrogen in the poly(phosphorus nitrides) $(P_3N_5)$ and (PN), which constitute an extremely attractive ballast-free starting material for the preparation of phosphorus–nitrogen fertilisers[59]¶, is of undoubted interest. The need for such research has become particularly urgent recently owing to a number of economic and technological causes. Among these, mention should be made of the increasing requirement for fertilisers† due to the growing world population, the reduced yield of grain crops per unit weight of fertilisers[127,129], the increasing price of fertilisers, and also the increasing cost of agricultural production (per unit weight of fertilisers)[130–134], the disproportion in the manufacture and consumption of individual components of fertilisers in developed and under-developed countries[127], etc.

The hydrolysis of phosphorus nitrides results in the formation of ammonium phosphates, which are widely used in the manufacture of fertilisers (including complex, solid, and liquid fertilisers), animal feed‡, and for technical purposes[126,134–136]. Ammonium phosphates are obtained by the reaction of ammonia with phosphoric acids or phosphorus pentoxide, formed when elemental phosphorus is combusted[126,137–139]. The desirability of employing phosphorus itself in the manufacture of phosphorus-containing compounds increases from year to year in view of the increasing development of the electrothermal manufacture of phosphorus. This is due to the gradual exhaustion of phosphate ores with a high $(P_2O_5)$ content, the increasingly stringent requirements for the purity of

¶ The direct employment of $(P_3N_5)$ as a fertiliser in a pure form is hardly possible in view of its resistance to different reagents under the usual conditions. Allison[121] introduced $(P_3N_5)$ into soil under the required conditions in order to convert nitrogen into a nitrate form. Since this conversion was not observed, he concluded that $(P_3N_5)$ as such cannot serve as a satisfactory fertiliser. Other workers[122,123], who investigated the decomposition of $(P_3N_5)$ in heated soil, later arrived at a similar conclusion. A systematic study of the possible employment of different compounds with PN bonds as fertilisers has been carried out[124,125] (see also Mattinghley and Taligudden[126]).

† During the last 15 years, the world requirement for combined nitrogen increased by 400% and for phosphorus by 150%[127] (see also Kodama[130]).

‡ The production of chemical additives to animal feed in the USSR will reach 5 million tonnes in 1980.[128]

the products§, and the possibility, in principle, of a fairly complete extraction of secondary components from slags in electrothermal manufacturing processes: fluorine, lanthanides[140,141], etc. The preparation of ammonium phosphates by the hydrolysis of phosphorus nitrides, which are formed directly from nitrogen and phosphorus, will reduce the cost of phosphoric¶, sulphuric, and nitric acids, which are used in the manufacture of phosphorus-containing fertilisers[138,142], and also of ammonia†.

An undoubted advantage of this method of synthesis is the absence of waste, which is important for the protection of the environment, the transportability of phosphorus nitrides, and also the possibility of preparing from them various compositions with nutrient substances.

The use of phosphorus nitrides as the starting materials for the preparation of phosphonitrile halides[66-68] and their derivatives, which have recently found extensive practical applications[5,145-147] in catalysis, etc., is no less promising.

## 2. Industrial Synthesis

The methods of obtaining phosphorus nitrides on an industrial scale were already outlined before the war. Miner[148] patented a method for the large-scale synthesis of (PN) based on the reaction of phosphorus halides with metal nitrides. However, the direct synthesis from the elements is more promising. It is recommended that ($P_3N_5$) be obtained by the direct reaction of nitrogen and phosphorus at a pressure of 1000 atm at 850 K.[149,150] An approximately analogous method has been proposed in a patent[151]. Quite recently Krasnokutskii and coworkers[13,152] investigated the interaction of nitrogen with gaseous phosphorus in a flow-type electric arc reactor. Nitrogen was passed to the electric arc chamber of the reactor where it was heated to a temperature of approximately 6500–7000 K, emerging from the anode-nozzle in the form of a jet, into which phosphorus vapour heated to 600°C was introduced. It was found that the content of bound nitrogen increases with the space velocity of the gases and the enthalpy of nitrogen, reaching approximately 25% by weight for the optimum volume of the reaction chamber, contact time (approximately $10^{-3}$ s), and temperature (3000–4500 K). The experimentally obtainable maximum contents of bound nitrogen are close to the amount in the P–N system found by thermodynamic calculation for the experimental conditions[14,152]. Kinetic studies are essential for a more complete description of the specific features of the given process.

The efficiency of the high-temperature method of manufacture of phosphorus nitrides follows from a comparison of the energy expenditures characterising various thermal processes in which molecular nitrogen is combined (Table 2).[152]

Table 2. Energy expenditure in manufacturing processes[138].

| Method of binding atmospheric nitrogen | Maximum product concentration, vol.% | Minimum energy expenditure per tonne of bound nitrogen, $10^3$ kW h |
|---|---|---|
| Formation of nitrogen oxides | 8 | 27.9 |
| Formation of dicyanogen | 59 | 17.2 |
| Simultaneous formation of hydrogen cyanide and acetylene | 11 | 10.6 |
| Formation of phosphorus nitride | 50* | 7.6 |

*Weight percentages.

Methods involving the combined initiation of this reaction (high temperature, discharge, irradiation) as well as catalytic processes are no less promising. Urbain[153,154] suggested that nitrogen and phosphorus vapours be compressed over a catalyst consisting of aluminium, titanium, magnesium, and bauxite in the presence of traces of cobalt, aluminium, and potassium oxides above 900°C. A scheme for an industrial apparatus, in which phosphorus nitride is manufactured on a scale consistent with the synthesis of fertilisers, has been proposed in a patent[155]. The recommended process includes the thermal generation of phosphorus vapour, the reaction of which with molecular nitrogen is initiated by an electric discharge.

The importance of plasmas has recently greatly increased in chemical engineering[156,157]. In the synthesis of phosphorus nitrides, plasmas may be used not only to initiate the reaction between nitrogen and phosphorus molecules but also to obtain elemental phosphorus from phosphorus-containing ores[157,158].

A decrease of the intrinsic cost of the manufacture of phosphorus nitride would be possible if the gases from phosphorus furnaces containing 14% of phosphorus and 86% of carbon monoxide were used instead of pure phosphorus[158]. This would permit the elimination of the stages involving the condensation of phosphorus and its consequent evaporation. The corresponding thermodynamic analysis showed that the quasi-equilibrium composition of the $N_2$–P–CO system hardly differs from the composition of the $N_2$–P system presented in Fig. 1. In the temperature range 1000–4000 K, only P, $P_2$, $N_2$, CO, and PN are present in the system in large amounts. The maximum concentration of PN in the mixture reaches approximately 7 vol.%. It was noted that the concentrations of polyatomic phosphorus and nitrogen oxides may be neglected in the above temperature range[158].

Vinokurov et al.[159] made a thermodynamic analysis[158] of the possibility of obtaining phosphorus nitrides (as well as phosphorus and iron) from ferrophosphorus, which is a waste product in high-temperature electrothermal manufacture. The highest yield of phosphorus nitride (22 wt.%) in the nitrogen plasma is ensured at a temperature of 3300 K and for the ratio nitrogen : ferrophosphorus = 1 : 1. The highest concentration of PN in the gas phase (26%) should be reached for the ratio ferrophosphorus : nitrogen = 8 : 1 at 3300 K.

§In the course of the current 5-year plan in the USSR, it is planned to obtain mineral fertilisers containing not less than 40% of nutrient substances[128].

¶According to Greek's data[143], 80% of the phosphoric acid obtained in industry is used to synthesise phosphorus fertilisers.

†Synthetic ammonia serves at the present time as the starting material for the synthesis of the majority of products containing bound nitrogen. The manufacture of ammonia has reached a high degree of technical sophistication. However, its manufacture may require a large capital expenditure and expensive materials, and, furthermore is based on a hydrocarbon starting material[144], the availability of which is limited.

Presumably further experimental and theoretical research will lead to the development of an effective industrial method for the synthesis of phosphorus nitrides and will give rise to further prospects for their employment in various branches of science and engineering. On the other hand, the study of phosphorus nitrides and their derivatives will permit a deeper understanding of their general properties and will make it possible to discover differences between the structures, properties, and reactivities of compounds with single and multiple NN, NP, and PP bonds.

## ADDENDUM

Mention should be made of the following data published during the preparation of the review for printing. One of the principal disadvantages of the high-temperature methods of synthesis of phosphorus nitrides is the use of the readily inflammable and toxic white phosphorus, some of which remains in the reaction product. The application of ion bombardment for the evaporation of phosphorus makes it possible to avoid the heating of the apparatus under laboratory conditions[160]. The resulting amorphous nitride contains no white phosphorus, which makes it possible to open the reactor and carry out experiments with the product in air.

Table 3. The effective charge on the phosphorus atoms in poly(phosphorus nitride) $(P_3N_5)$*.

| $\Delta q^P$, e.u. | | | |
|---|---|---|---|
| *A* | *B* | *C* | *D* |
| 1.65 | 0.63 | 1.08 | 1.1 |

*Method of calculation: *A*) from the estimate of the total number of electrons removed from the orbitals of the phosphorus atom[166]; *B*) from the change in the effective charge in a sphere with a radius equal to the covalent radius of phosphorus[167]; *C*) from the empirical relation[168]

$$\Delta q = 0.813\sqrt[4]{E_b^{2p} - 130.1};$$

*D*) by a method based on the combination of the Boron–Haber cycle with Kapustinskii's lattice equation[168].

A simple method was proposed recently for the preparation of (NPO).[161,162] The one-stage synthesis includes the interaction of concentrated phosphoric acid, pyrophosphoric acid, $P_4O_{10}$, and ammonium phosphates or urea with melamine, guanamines, and trialkyl($C_{1-3}$)-1,3,5-triazines at 500–750°C.

A convenient method for the synthesis of $P(N_3)_3$, $PO(N_3)_3$, and $P(N_3)_5$ as well as a detailed study of the structures of these compounds by vibrational and NMR spectroscopy were published by Volgnandt and Schmidt[163]. According to Pelavin et al.,[164] the interaction of phosphorus pentafluoride with an excess of sodium azide in acetonitrile at −20°C can be represented schematically as follows:

$$PCl_5 + 10NaN_3 \begin{cases} \nearrow P(N_3)_5 + 5NaCl + 5NaN_3 \\ \searrow NaP(N_3)_6 + 5NaCl + 4NaN_3 \end{cases}.$$

The hexa-azidophosphate anion hydrolyses in accordance with the equation

$$P(N_3)_6^- + 2H_2O \rightarrow PO_2(N_3)_2^- + 4HN_3 .$$

A number of attempts have been made to determine the effective charge of phosphorus $\Delta q$ in $(P_3N_5)$ from the binding energies, obtained from X-ray photo electron spectra, of the 2*p* electrons of phosphorus ($E_b^{2p}$) in $(P_3N_5)$ and red phosphorus (133.2 and 130.1 eV respectively—Table 3). Naturally the employment of different models in calculations gives rise to a different significance and different values of the calculated effective charges.

Veprek and Koos[169] showed that a dielectric constant of $(P_3N_5)$ varies linearly with temperature in the range 77–525 K. Phase transformations were not observed in the temperature range 300–765 K, but the structure of $(P_3N_5)$ synthesised from the elements in an ultrahigh frequency discharge depends on the precipitation temperature. At a precipitation temperature of 265°C, it is amorphous, while at higher temperatures a crystalline product is obtained. The dielectric strength of $(P_3N_5)$ is $0.9 \times 10^7$ W $cm^{-1}$.

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# Chemistry of Dihydrophenophosphazines

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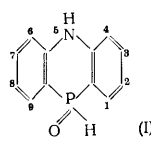
Work during recent years on the synthesis and investigation of 5,10-dihydrophenophosphazines is summarised. It is suggested that these compounds containing tervalent phosphorus may be of interest as pharmacological preparations. A complete list of 5,10-dihydrophenophosphazines synthesised by 1976 is given, together with 40 references.

CONTENTS

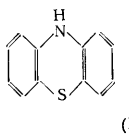
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## I. INTRODUCTION

Almost all our knowledge of 5,10-dihydrophenophosphazines has been obtained during the past 16 years, for only 5 papers had been published on them before 1960.[1] In 1890 Michaelis and Schenk reported[2,3] that diphenylamine reacts with phosphorus trichloride at 250°C; elementary analysis of the substance obtained by hydrolysing the reaction mass suggested three possible structures. In 1938 Sergeev and Kudryashov[4] improved the method of preparation, and proved by chemical methods that it had a dihydrophenophosphazine structure. In 1960 the structure of the product obtained by Michaelis et al.[2-5] was finally established: Häring[6] identified it as 5,10-dihydro-10-oxophenophosphazine (I).



(I)

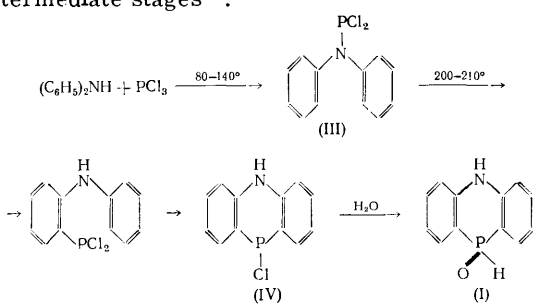


(II)

5,10-Dihydrophenophosphazines are phosphorus analogues of phenothiazines. Derivatives of phenothiazine (II) are used as antioxidants and therapeutic preparations[7,8]. A few patents have claimed that dihydrophenophosphazines may also find application in analogous fields of technology and medicine[9-11].

## II. METHODS OF SYNTHESIS

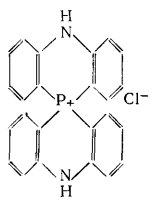
The preparation of dihydrophenophosphazines by the action of phosphorus trichloride on diphenylamine or its homologues has been described in the greatest detail[6,12]. The process is conducted at normal pressure in the absence of a catalyst, by gradually raising the temperature to 200–210°C. The reaction passes through a series of intermediate stages[12]:



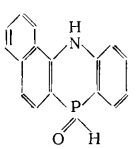
(1)

In agreement with the suggested mechanism, the dihydrophenophosphazine (I) has been synthesised[12] by the thermolysis of the previously prepared chloro-amide (III). Intermediate formation of (III) is supported also by the fact that *N*-methyldiphenylamine[13] and *N*-methylditolylamine[12] do not react with phosphorus trichloride under the above conditions. The suggestion that reaction terminates at the formation of 10-chloro-5,10-dihydrophenophosphazine (IV) is less strongly based, since the reaction mass is treated with water in the procedure adopted[4,6,12], and the acid chloride (IV) has not once been isolated. It is possible that the main component of the reaction mixture before hydrolysis is a polymer containing phosphorus–nitrogen bonds, not the acid chloride (IV).

Reaction between diphenylamine and phosphorus trichloride yields a mixture of substances. The chief side-product is 5,5′-dihydro-10,10′-spirobiphenophosphazinium chloride (V).[12,14]



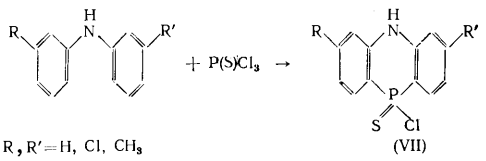
(V)



(VI)

The limits of applicability of reaction (1) have not yet been determined, but naphthylphenylamine is known to react with phosphorus trichloride similarly to diphenylamine, the products being 7,12-dihydro-7-oxobenzo[*c*]-phenophosphazine (VI) and the corresponding spiro-compound[12].

The use of thiophosphoryl chloride has also been suggested for converting diarylamines into 5,10-dihydrophenophosphazines[9]:



(2)

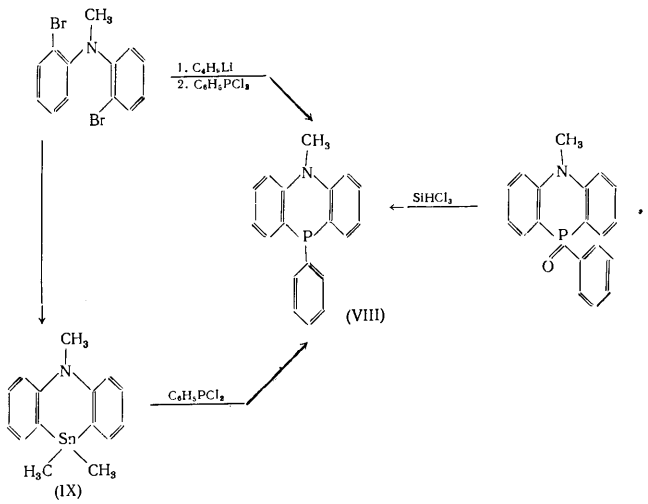
R, R′ = H, Cl, $CH_3$ (VII)

In contrast to the reaction with phosphorus trichloride, the acid chlorides, 10-chloro-5,10-dihydro-10-thionophenophosphazines (VII), have been isolated and identified. The patent description[9] does not indicate the yields of these compounds (VII), but from other information[1] it appears that, of the two procedures—in the absence of a

solvent under pressure at 200°C or in boiling *o*-dichlorobenzene at normal pressure—the former gives the higher yields.

Derivatives of phenothiazine (II) have found widespread therapeutic use, e.g. as antihistamines [8,15]. Synthetic work on 5,10-dihydrophenophosphazines [6,9,16-18] has been stimulated by the efforts to find new medicinals like phenothiazines. Hitherto these attempts have not achieved real success, which can be explained formally by the fact that only phenothiazines containing bivalent sulphur possess biological activity, whereas the 10-oxo- and 10-thiono-5,10-dihydrophenophosphazines tested [6,9,16-18] are analogues of phenothiazine *S*-oxides. It is more likely that medicinals will be found among phenophosphazines containing a tervalent phosphorus atom.

These latter compounds may be synthesised by analogy with 5,10-dihydro-5-methyl-10-phenylphenophosphazine (VIII): [19-21]

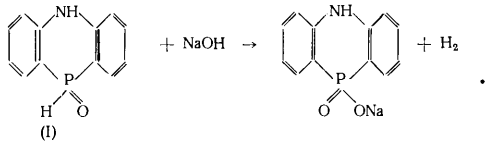



*N*-Alkyl-*oo'*-dibromodiphenylamines are difficultly accessible, which restricts the possibilities of their use for the synthesis of 5,10-dihydrophenophosphazines [13,19]. The latter can be obtained by replacing the tin atom in heterocycles of the type (IX), [20] which demonstrates the greater thermodynamic stability of phosphorus–carbon than of tin–carbon bonds, but this method is of no synthetic value, since the initial 5,10-dihydrophenazastannines are obtained from the same *oo'*-dibromodiphenylamines. In many cases the most rational method for obtaining dihydrophenophosphazines containing tervalent phosphorus atoms may be reduction [21] of the corresponding *P*-oxides or *P*-sulphides.

## III. REACTIONS OF DIHYDROPHENOPHOSPHAZINES

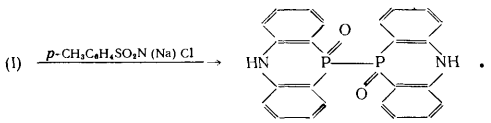
### 1. Reactions of the Heteroatoms

Derivatives of 5,10-dihydrophenophosphazine are usually obtained from the 10-oxo-compound (I) as starting material. The latter undergoes the reactions characteristic of oxides of secondary phosphines [22]: it adds at an activated multiple bond, and can be alkylated and oxidised at the phosphorus atom. Several methods have been prepared for oxidising (I) to phenophosphazinic acid—with air in boiling tetralin [4,6], or with hydrogen peroxide in acetic acid [6] or in aqueous alkali [12]—but in the last case the use of hydrogen peroxide is not necessary, since boiling aqueous alkali converts the phenophosphazine (I) smoothly into a salt of phenophosphazinic acid [23]:

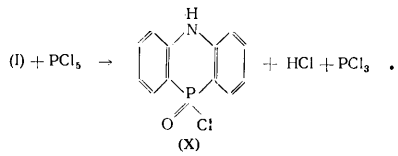



(The mechanism of the oxidation of oxides of secondary phosphines in alkaline media has been discussed in Ref. 24.)

Elementary iodine and chloramine T effect a different course of oxidation, converting (I) into 5,5'-dihydro-10,10'-dioxo-10,10'-diphenophosphazinyl [6]:

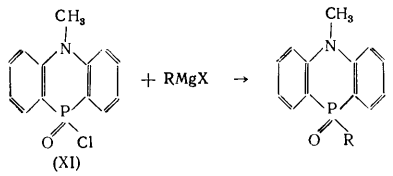



If the final aim is to prepare derivatives of phenophosphazinic acid, it is most rational to use phosphorus pentachloride as oxidant [25]:



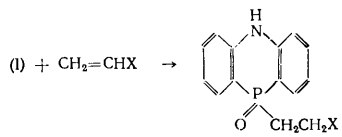

Phenophosphazinic esters and amides can be obtained by replacing the chlorine atom in the acid chloride (X). [6,11,17,25,26] The thio-acid chlorides (VII) undergo analogous reactions with alcohols and amines [1,6,11,17,18], but in this case the products of esterification must be further investigated to differentiate between thionic and thiolic isomers $\diagdown$PS.OR and $\diagdown$PO.SR. [6,18]

The acid chloride (XI) reacts with organomagnesium compounds with the formation of phosphorus–carbon bonds [21]:




R=CH$_3$, C$_6$H$_5$; X=I, Br .

However, most of the phenophosphazines containing exocyclic phosphorus–carbon bonds have been obtained directly from the phenophosphazine (I) by addition to alkenes and azomethines [16,27]. The reaction conditions depend on the structure of the alkene. With acrylic acid and its derivatives, for example, the process is conducted without a solvent and without a catalyst at 140–170°C: [27]



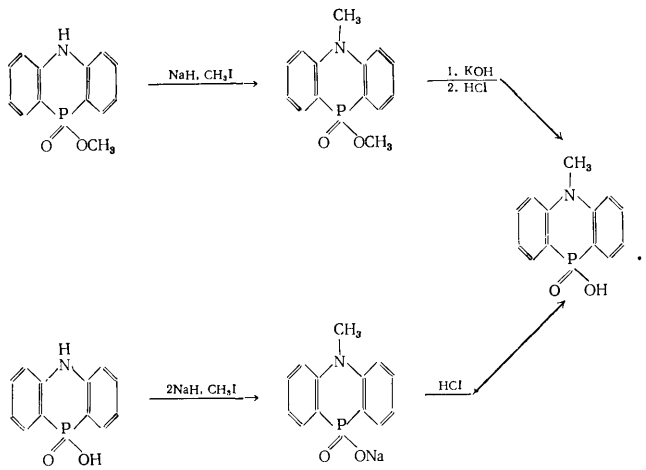

X=COOH, COOCH$_3$, CN .

1-Phenylprop-2-en-1-one adds to (I) in the presence of sodium ethoxide in alcoholic solution at 20°C. [16] At the

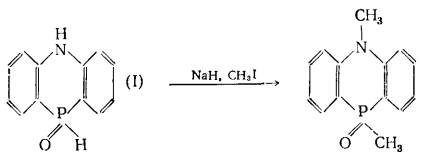
present time no kinetic data are available for a correlation to be sought between the reactivity and the structure of the reactants; moreover, not all the facts can be explained even qualitatively. Thus it has been established[16] that the phenophosphazine (I) does not add to azodicarboxylic ester, but it reacts with the dimorpholide of the acid in boiling ethanol in the absence of catalysts.

Examination of published results[16,27] leads to the preliminary conclusion that the reactivity of multiple bonds towards (I) increases in the sequence N:N < C:C < C:N. Addition takes place at the phosphorus atom independently of the nature of the multiple bond[16,27]. In view of these facts, Häring's conclusion[6] that phenyl isocyanate adds at the nitrogen atom in the phenophosphazine (I) cannot be accepted without proof.

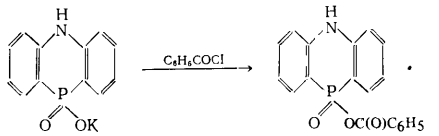
The nitrogen atom can be alkylated[21,23] when its nucleophilic character has been enhanced by ionisation of the imino-group $\rangle NH \rightarrow \rangle N^-$:




Under the corresponding conditions the phenophosphazine (I) yields a dimethylated product[21]:




When protolysis of the nitrogen–hydrogen bond is excluded, the nucleophilicity of the imino-group is extremely low. Thus a phenophosphazinate salt undergoes benzoylation at the oxygen atom, not at the nitrogen atom[6]:

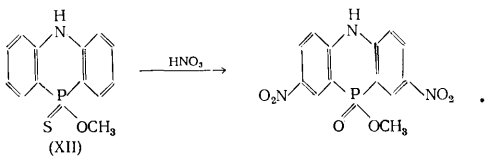



Thus the activity of the nucleophilic centres in dihydrophenophosphazines diminishes in the sequence $\rangle N^- > \rangle PO.O^- > \rangle NH$.

2. Electrophilic Aromatic Substitution

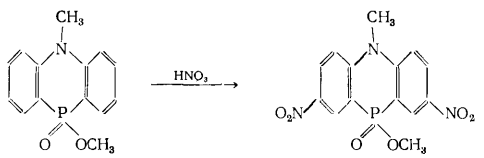
At 5°C molecular bromine in formic acid oxidises 5,10-dihydro-10-oxophenophosphazine (I) and simultaneously brominates its benzene rings[6], forming a mixture of products of different degrees of bromination, among which a dibromo-5,10-dihydro-10-hydroxy-10-oxophenophosphazine (dibromophenophosphazinic acid) predominates in which the positions of the bromine atoms have not been established. It is not known whether phenophosphazinic acid is brominated under the same conditions, and therefore the sequence of oxidation and substitution is obscure.

According to McHattie[1] the 10-thionophenophosphazine (XII) does not react with the *p*-nitrobenzenediazonium ion, whereas in boiling nitric acid it undergoes simultaneous nitration and oxidation:




(XII)

Nitration of 5,10-dihydro-10-methoxy-5-methyl-10-oxophenophosphazine in acetic acid yields the dinitro-product (XIII), whose structure has been proved unambiguously by proton magnetic resonance[23]:




(XIII)

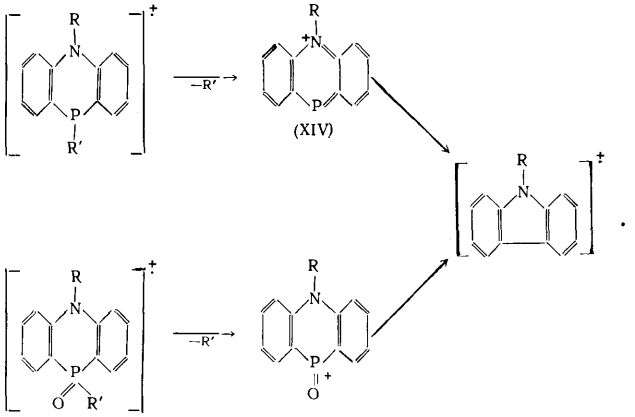
## IV. PHYSICOCHEMICAL PROPERTIES

Since 1960 the infrared spectra have been used to identify dihydrophenophosphazines. In no case have the vibrations been calculated, and the frequencies representing vibrations of the heterocycle have not been identified. Investigators working with 5,10-dihydro-10-oxophenophosphazines usually mention the frequency of the P=O bond[6,12,18,21,23]. The frequency of stretching vibrations of this bond is lower in dihydrophenophosphazines containing imino-groups, perhaps owing to formation of intermolecular hydrogen bonds, and appears in the range 1150 to 1195 $cm^{-1}$.[12,18] Alkylation of the nitrogen raises the frequency to 1180–1240 $cm^{-1}$.[21,23] Thus the original assignment[6] of bands at 1340–1350 $cm^{-1}$ to vibrations of the P:O bond is incorrect.

Among nuclear magnetic resonance methods only proton resonance has been used to investigate 5,10-dihydrophenophosphazines, mainly to identify alkyl groups attached to the nitrogen and phosphorus atoms[12,20,21]. In the $^1H$ n.m.r. spectrum of the dinitro-compound (XIII), however, the chemical shifts of non-equivalent aromatic protons differ so considerably that the spectrum in this region could be completely deciphered[23]. The spin–spin interaction constants in the (XIII) molecule, $^3J(PH) = 14.0$ and especially $^4J(PH) = 7.2$ Hz, are considerably larger than those in triphenylphosphine oxide and its substituted derivatives, where the corresponding values are 11.2–12.4 and 1.8–2.7 Hz.[28,29]

Data have been published on the mass spectra of individual dihydrophenophosphazines[12,21,23,30]. The main

routes by which these compounds break down can be represented by the scheme

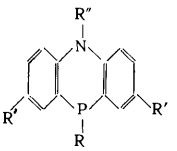


The ion (XIV) is the chief product in the mass spectra of the tervalent phosphorus derivatives, even with ionising radiation of energy 30 eV.[21] Oxidation of the phosphorus atom enhances the stability of the molecular ion, which is usually the main product in the spectra of 5,10-dihydro-10-oxophenophosphazines.

Table 1. Electronic spectra of 10-substituted (R) 5,10-dihydro-5-methyl-10-oxophenophosphazines[21].

| R | Solvent | $\lambda_{max}$, nm (lg ε) | | | |
|---|---|---|---|---|---|
| $CH_3$ | alcohol | 220 (4.50) | 273 (4.25) | 301 (3.92) | 327 (3.76) |
| $C_6H_5$ | alcohol | 226 (4.50) | 275 (4.15) | 306 (3.81) | 336 (3.80) |
| $OCH_3$ | alcohol | 223 (4.21) | 272 (4.31) | 299 (4.00) | 337 (3.80) |
| Cl | dioxan | 231 (4.44) | 273 (4.23) | 305 (3.95) | 346 (3.81) |

Table 2. 5,10-Dihydrophenophosphazines



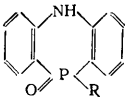
| R | R′ | R″ | M.p., °C | Identification | Ref. |
|---|---|---|---|---|---|
| $OC_2H_5$ | H | H | 151.5—152 | — | 4 |
| $CH_3$ | H | $CH_3$ | 102—103 | methiodide, infrared, $^1H$ nmr, ultraviolet spectra | 21 |
| $C_6H_5$ | H | $CH_3$ | 159—160 | methiodide, infrared, $^1H$ nmr, ultraviolet spectra | 10, 19—2 |
| $C_6H_5$ | Br | $CH_3$ | 227—229 | infrared, $^1H$ nmr, ultraviolet spectra | 20, 21 |
| $C_6H_5$ | H | $C_2H_5$ | 96.5—98 | — | 10, 19 |
| $C_6H_5$ | $CH_3$ | $CH_3$ | 144—146 | infrared, $^1H$ nmr, ultraviolet spectra | 20 |

In the opinion of Freedman and Styles[31] the ultraviolet spectra of phenophosphazinic acids indicate conjugation of a quinquevalent phosphorus atom with the π-electron system of aromatic rings. Table 1 shows that the character of the spectrum, and hence of conjugation in phenophosphazines, is little affected by the nature of substituents attached to the phosphorus atom.

The adiabatic ionisation potentials of four dihydrophenophosphazines have been determined[32] by photoionisation mass spectroscopy. The values of 6.90 ± 0.05 eV obtained for 5,10-dihydro-5-methyl-10-phenylphenophosphazine (VIII) lies within the range given for *N*-methylphenothiazine (6.60—6.96 eV [33,34]). Since the pharmacological activity of phenothiazines is attributed to their low ionisation potentials[34,35], it is very likely that pharmacological products can be based also on 5,10-dihydrophenophosphazines.

Tables 2—5 contain a complete list of all the 5,10-dihydrophenophosphazines reported in periodicals, patents,

Table 3. 5,10-Dihydro-10-oxophenophosphazines

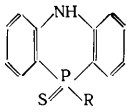


| R | M.p., °C | Identification | Ref. |
|---|---|---|---|
| H | 215—216 | Ti, U salts | 4,5 |
| H | 219—222 | ultraviolet spectrum | 11 |
| H | 214—216 | hydro-bromide, -chloride, ultraviolet, infrared spectra | 6,12 |
| OH | above 250 | Ag salt | 4 |
| OH | 270—274 | ultraviolet spectrum | 12,31 |
| OH | 274—275 | K salt, infrared spectrum | 6,23 |
| OH | 284—286 | — | 1 |
| Cl | 290 (decomp.) | infrared spectrum | 6,25 |
| $OCH_3$ | 112—114 | — | 4 |
| $OCH_3$ | 224—225 | infrared spectrum | 6,23 |
| $SCH_3$ | 265—267 | infrared spectrum | 6,18 |
| $SCH_3$ | 275—276 | ultraviolet spectrum | 11 |
| $C_4H_5$ | — | mass spectrum | 30 |
| $NHCH_2CH_2OH$ | 232 | — | 17 |
| $OC_2H_5$ | 99 | — | 4 |
| $OCH_2CH_2Cl$ | — | — | 36 |
| $SC_2H_5$ | 221—222 | infrared spectrum | 18 |
| $CH_2CH_2COOH$ | 245—246 | — | 27 |
| $CH_2CH_2CN$ | 226—227 | — | 27 |
| $NHCH_2CH{=}CH_2$ | 254 | — | 17 |
| $NHC_3H_7$ | 254 | — | 17 |
| $SC_3H_7$-n | 174—176 | infrared spectrum | 18 |
| $CH_2CH_2C(O)CH_3$ | 195—196 | — | 27 |
| $CH_2CH_2COOCH_3$ | 162—163 | — | 27 |
| $CH(CH_3)CH_2COOH$ | 148—149 | — | 27 |
| $-CHC(O)OC(O)CH_2-$ | 247 | — | 27 |
| $NHC_4H_9$ | 238 | — | 17 |
| $N(C_2H_5)_2$ | 244 | — | 17 |
| $-N<^{CH_2CH_2}_{CH_2CH_2}>O$ | 250 | ultraviolet spectrum | 11 |
| $OC_4H_9$ | 139.5—141 | ultraviolet spectrum | 6,11 |
| $SC_4H_9$ | 149—151 | infrared spectrum | 17 |
| $NH(CH_2)_3N(CH_3)_2$ | 185—186 | — | 6 |
| $-N<^{CH_2CH_2}_{CH_2CH_2}>NCH_3$ | 230—235 | — | 26 |
| $-CHCOOCH_3$ <br> $CH_2COOCH_3$ | 208—209 | — | 27 |
| $NHC_6H_5$ | 241 | — | 17 |
| $NHCH_2CH_2N(C_2H_5)_2$ | 191—194 | methiodide | 6 |
| $OCH_2CH_2N(C_2H_5)_2$ | 80—83.5 | methiodide | 6 |
| $OCH_2C_6H_5$ | 179—180 | — | 6 |
| $OC(O)C_6H_5$ | above 340 | infrared spectrum | 6 |
| $O(CH_2)_3N(C_4H_9)_2$ | 42—43.5 | — | 6 |
| $CH(C_6H_5)CH_2C(O)CH_3$ | 181—183 | — | 27 |
| $CH(C_6H_5)CH_2COOCH_3$ | 133—135 | — | 27 |
| $CH(C_6H_5)CH(CN)CONH_2$ | 281—283 | — | 16 |
| $-N-C(O)N<^{CH_2CH_2}_{CH_2CH_2}>O$ <br> $NHC(O)N<^{CH_2CH_2}_{CH_2CH_2}>O$ | 200 (sinters) | — | 16 |
| $O{=}P<^{C_6H_4}_{C_6H_4}>NH$ * | above 300 | infrared spectrum | 6 |
| $-O(O)P<^{C_6H_4}_{C_6H_4}>NH$ ** | above 300 | infrared spectrum | 6 |
| $CH(C_6H_5)NHC_6H_5$ | 182—185 | — | 16 |
| $CH(C_6H_5)NHSO_2C_6H_5$ | 190—191 | — | 16 |
| $CH(C_6H_5)CH_2C(O)C_6H_5$ | 242—244 | — | 16 |
| $CH(COC_6H_5)CH_2C(O)C_6H_5$ | 232—233 | — | 16 |

* 5,5′-Dihydro-10,10′-dioxo-10,10′-biphenophosphazinyl.
** Phenophosphazinic anhydride.

and deposited papers† by the beginning of 1976. They do not include compounds for which the original source gives neither constants nor elementary analyses. Spirobiphenophosphazines are also omitted: all the information on these compounds will be found in papers by Jenkins and Freedman [12,14].

Table 4. 5,10-Dihydro-10-thionophenophosphazines



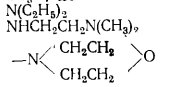
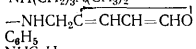
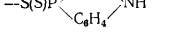
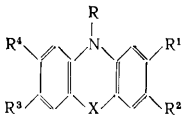
| R | M.p., °C | Identification | Ref. |
|---|---|---|---|
| Cl | 252—254 | — | 9 |
| Cl | 229 5—237.5 | — | 6 |
| OH | 213 | K salt, infrared spectrum | 6,18 |
| OH | 215 | ultraviolet spectrum | 11 |
| OH | 320—322 | triethylamine, piperazine salts | 1 |
| $NH_2$ | 233—235 | — | 1 |
| $NHNH_2$ | 240—241 | — | 1 |
| SH | 322—326 | pyridine, piperazine salts | 1 |
| $OCH_3$ | 184—185.5 | infrared spectrum | 6 |
| $OCH_3$ | 186—187 | — | 18 |
| $OCH_3$ | 194—195 | — | 1 |
| $N(CH_3)_2$ | 276—278 | — | 1 |
| $NHCH_2CH_2OH$ | 185 | — | 17 |
| $OC_2H_5$ | 207—208 | — | 1 |
| $OC_2H_5$ | 211—212 | — | 18 |
| $OC_2H_5$ | 213—214 | ultraviolet spectrum | 11 |
| $OCH_2CBr_3$ | 193—194 | — | 1 |
| $OCH_2CH_2OH$ | 208—209 | — | 1 |
| $NHCH_2CH{=}CH_2$ | 251 | — | 17 |
| $NHC_3H_7$ | 238—239 | — | 17 |
| $OC_3H_7$-n | 178—180 | — | 1,18 |
| $OC_3H_7$-iso | 233—234 | — | 18 |
| $OC_3H_7$-iso | 242—244 | — | 1 |
| $N(C_2H_5)_2$ | 184 | — | 17 |
| $NHCH_2CH_2N(CH_3)_2$ | 142—144 | — | 1 |
|  | 275—276 | ultraviolet spectrum | 11 |
| $NHC_4H_9$-n | 206—207 | — | 1 |
| $OC_4H_9$-n | 130—131 | — | 1 |
| $OCH_2CH_2N(CH_3)_2$ | 167—169 | methiodide | 1 |
| $NH(CH_2)_3N(CH_3)_2$ | 122—124 | — | 1 |
|  | 199—200 | — | 1 |
| $C_6H_5$ | 268—269 | — | 1 |
| $NHC_6H_5$ | 247—248 | — | 1 |
| $NHC_6H_5$ | 238—240 | — | 17 |
| $OC_6H_5$ | 222—224 | — | 1 |
| $OC_6H_4Cl$-p | 204—206 | — | 1 |
| $OC_6H_4NO_2$-p | 250—252 | — | 1 |
| $SC_6H_4NO_2$-p | 259—260 | — | 1 |
| $NHCH_2C_6H_5$ | 184 | — | 1 |
| $OC_6H_4CH_3$-o | 164—166 | — | 1 |
| $NHCH(CH_3)_3N(C_2H_5)_2$ | 135—136 | — | 1 |
| $SC_{12}H_{25}$ | 92—93 | ultraviolet spectrum | 11 |
|  | 320—322 | — | 1 |

Table 2 lists dihydrophenophosphazines containing a tervalent phosphorus atom; Tables 3 and 4 give dihydrophenophosphazines derived from quinquevalent phosphorus, with both the nitrogen atom and the benzene rings unsubstituted; and Table 5 contains the remaining dihydrophenophosphazines with a quinquevalent phosphorus atom. Within each table the compounds are arranged in order of increasing number of carbon atoms in the molecule. The columns headed "identification" list the simple derivatives (salts, hydrochlorides, methiodides) and spectral methods by which the compounds have been characterised.

† McHattie's results are quoted in the book by Mann [1].

Table 5. Substituted 10-oxo- and 10-thiono-5,10-dihydrophenophosphazines



| X | R | $R^1$ | $R^2$ | $R^3$ | $R^4$ | M.p., °C | Identification | Ref. |
|---|---|---|---|---|---|---|---|---|
| P(O)OH | H | H | $NO_2$ | H | H | — | — | 4 |
| P(O)H | H | H | $CH_3$ | H | H | 205—206 | infrared spectrum | 12 |
| P(O)OH | H | H | $CH_3$ | H | H | 270—272 | infrared spectrum | 12 |
| P(O)OH | $CH_3$ | H | H | H | H | 252.5—253 | infrared, ultraviolet spectra | 21,23 |
| P(O)OH | $CH_3$ | H | $NO_2$ | $NO_2$ | H | above 320 | infrared spectrum | 23 |
| P(O)Cl | $CH_3$ | H | H | H | H | 217—220 | infrared, ultraviolet, $^1H$ nmr spectra | 21 |
| P(O)Cl | $CH_3$ | H | $NO_2$ | $NO_2$ | H | 264—267 | — | 23 |
| $P(O)OCH_3$ | H | H | $NO_2$ | $NO_2$ | H | 344—345 | — | 1 |
| P(O)H | H | H | $CH_3$ | $CH_3$ | H | above 400 | infrared spectrum | 12 |
| P(O)OH | H | H | $CH_3$ | $CH_3$ | H | 289 (decomp.) | infrared spectrum | 12 |
| $P(O)OCH_3$ | $CH_3$ | H | H | H | H | 164—165 | $^1H$ nmr, infrared, ultraviolet spectra | 21 |
| $P(O)OCH_3$ | $CH_3$ | H | $NO_2$ | H | H | 147—149 | $^1H$ nmr, infrared, ultraviolet spectra | 23 |
| $P(O)OCH_3$ | $CH_3$ | H | $NO_2$ | $NO_2$ | H | 275—277 | $^1H$ nmr, infrared, ultraviolet spectra | 23 |
| $P(O)CH_3$ | $CH_3$ | H | H | H | H | 205—207 | $^1H$ nmr, infrared, ultraviolet spectra | 21 |
| P(O)OH | $CH_3$ | H | $CH_3$ | $CH_3$ | H | 276—277 | infrared, $^1H$ nmr, ultraviolet spectra | 12,31 |
| P(O)H * | H | H | H | H | $C_4H_4$ | 238—240 | infrared spectrum | 12 |
| P(O)OH | H | H | H | H | $C_4H_4$ | 290—295 | infrared spectrum | 12 |
| P(O)H | $C_6H_5NHCO$ | H | H | H | H | 227 (decomp.) | — | 6 |
| $P(O)C_6H_5$ | $CH_3$ | H | H | H | H | 162—163 | infrared, $^1H$ nmr, ultraviolet spectra | 21 |
| $P(O)C_6H_5$ | $CH_3$ | H | Br | Br | H | 220—222 | $^1H$ nmr, infrared, ultraviolet spectra | 21 |
| P(S)Cl | H | Cl | H | H | H | 270—272 | — | 9 |
| P(S)Cl | H | $CH_3$ | H | H | $CH_3$ | 283—285 | — | 9 |
| $P(S)OCH_3$ | H | H | $CH_3$ | H | H | 250—260 | — | 1 |
| $P(S)OC_2H_5$ | H | Cl | H | H | H | 190—192 | — | 1 |
| $P(S)OC_2H_5$ | H | H | Cl | H | H | 178—180 | — | 1 |
| $P(S)OCH_3$ | $CH_3CO$ | H | H | H | H | 132—134 | — | 1 |
| $P(S)OCH_3$ | H | $CH_3$ | H | H | $CH_3$ | 228—230 | — | 1 |
| $P(S)OC_2H_5$ | $CH_3CO$ | H | H | H | H | 101—103 | — | 1 |
| $P(S)OC_2H_5$ | H | $CH_3$ | H | H | $CH_3$ | 228—230 | — | 1 |

*7,10-Dihydro-7-oxobenzo[*c*]phenophosphazine (VI).

## ADDENDUM

Four more papers on dihydrophenophosphazines appeared [37-40] while the manuscript was being prepared for press. The Reviewers have collaborated with Bychkov [37] in developing a simple and effective method for synthesising phenophosphazinic acid. The proton magnetic resonance spectrum of the dinitro-compound (XIII), described in a deposited paper [23], has now been published in a more accessible source [38]. X-Ray examination of 5,10-dihydro-5-methyl-10-phenylphenophosphazine (VIII) shows that the molecule is not planar, the angle between the planes of the phenylene rings being 145° [39].

Petrov et al. [40] have improved the method of isolating the phenophosphazine (I) from the mixture of products of reaction (1). 5,10-Dihydro-10-oxophenophosphazines containing hydroxymethyl and aminomethyl groups attached to the phosphorus atom have been obtained from this compound (I), and the infrared spectra have been discussed in detail [40].

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# Structure and Reactivity of Esters of Thio-acids of Three-coordinated Phosphorus

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The structure and the chemical behaviour of thio-esters of three-coordinated phosphorus $R_nP(SR')_{3-n}$ ($n = 0-2$) are examined, and their reactions are discussed with electrophilic reagents differing both in the number and in the nature of the electrophilic centres. The peculiar character of such reactions is due primarily to the presence of two competing nucleophilic centres to the ambidenticity of the phosphorus(III)-sulphur(II) group, and to the high reactivity of two-coordinated sulphur (thionic and thiolic) in esters of three- and four-coordinated phosphorus. A list of 170 references is included.

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## I. INTRODUCTION

The chemistry of derivatives of three-coordinated phosphorus is now a well studied field. Structural features and regularities in the chemical behaviour of these compounds have been quite widely discussed in several review papers [1-4] and in monographs published during recent years [5-8].

The structure and the reactivity of compounds of three-coordinated phosphorus containing a phosphorus–sulphur bond have either not been discussed at all in these works [5] or have been only incompletely considered [4,7,8]. However, esters of thio-acids of phosphorus have extremely characteristic properties, distinguishing them strongly from the well studied oxygen analogues. The few papers and their contradictions prevented until recently a comprehensive view of the reactivity of these compounds. Only a series of investigations on the interaction between these esters and several electrophilic reagents, published during recent years, have made it possible to note several general rules controlling these processes.

Esters of thio-acids of three-coordinated phosphorus possess two nucleophilic reaction centres—phosphorus and sulphur—the main feature of the bond between these atoms being that both elements belong to the third period and have electron shells of closely similar structure. Hence considerable competition may be expected between the two atoms in intramolecular donor–acceptor interaction, as well as in reactions with electrophilic and nucleophilic reagents.

The literature shows no abatement of the controversy on the bond structure and intramolecular donor–acceptor interactions in compounds of elements in the third period—silicon, phosphorus, sulphur, and chlorine—especially on the capacity of the lone pairs of electrons on phosphorus(III) and sulphur(II) atoms for $p,\pi$ and $p,d$ interaction. Some workers [6,9-24] have attempted not only to detect but also in several cases to estimate a $+M$ effect in phosphorus(III), whereas others [3,7,25] give results that they regard as evidence of the absence of such an effect. It has been assumed that the $p,\pi$ effect of sulphur(II) is slight [16, 26-28], but larger than that of phosphorus [3].

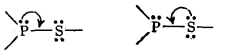
The legitimacy of using ideas on the participation of $d$ orbitals in forming chemical bonds of both $\sigma$ and $\pi$ types has also been discussed. Several workers consider [26,29-35] that even with phosphorus(III) and sulphur(II) the possibility of the participation of $3d$ orbitals in hybridisation cannot be completely excluded. The involvement of $d$ orbitals in $\pi$ bonding explains several peculiarities of compounds of elements in the third period in comparison with the corresponding compounds of elements in the second period [3,36-43]. In the view of other authors [44-46] the role of $d$ orbitals cannot be significant because of their high energy. Attempts have recently been made to explain the peculiarity of compounds of elements in the third period without regard to the main structural feature—the presence of vacant $d$ orbitals in the valency layer—of the electron shells of their atoms [47-51]. The opinion has been expressed [51] that the $d$-orbital concept cannot be correctly used in describing structural features of compounds of elements in the third period.

Within the scope of the method of molecular orbitals the concept of the participation of $d$ orbitals need not in general be introduced into the description of bond formation in molecules containing phosphorus with coordination numbers 3–6. In the valence bond method, which retains the classical structural formula with its two-centre, two-electron bond, $d$ orbitals are enlisted both for describing bonds and in the theory of electron displacements ($p,d$ and $\pi,d$ effects). In the discussion of the acceptor properties of phosphorus an attempt has been made to replace the $d$-orbital concept ($-M$ effect of the phosphorus atom) by that of a negative hyperconjugation effect [51]. At the present time, however, such substitution of one effect by another hardly changes the situation with respect to qualitative ideas on electron displacements in organic molecules.

Data on intramolecular donor–acceptor effects in compounds containing phosphorus–phosphorus and sulphur–sulphur bonds are of especial interest in connection with this problem. The ultraviolet spectra of cyclopolyphosphines have been interpreted [52-57] as supporting a $+M$ effect, which is justified also by quantum-mechanical calculations [54]. Similarly in diphosphines, also on the basis of ultraviolet spectra, the possibility of combined $p,d$ effects has been suggested [58], as a consequence of which both phosphorus atoms are simultaneously donors and acceptors of lone pairs of electrons, which is apparent

in the chemical properties of diphosphines[59]. Similar effects are assumed in natural sulphur, in dihydrogen disulphide, and in dialkyl disulphides[26], and are confirmed also by the abnormally high energy of dissociation of the sulphur–sulphur bond[26,60].

Similarly, the group $>\ddot{P}-\ddot{S}-$ is an ambident system, in which two types of mesomeric displacements



may theoretically occur, the first representing a $+M$ effect and the second a $-M$ effect of the phosphorus atom. In terms of the theory of resonance the ambident system is a resonance hybrid of three structures:

$$>\ddot{P}-\ddot{S}- \leftrightarrow >\overline{P}..=\overset{+}{S} \leftrightarrow >\overset{+}{P}=\overline{S}: .$$

A qualitative estimate has been made of the donor–acceptor interactions in the phosphorus–sulphur bond[61], which are obviously determined primarily by the energies of the highest occupied orbitals and the lowest vacant orbitals of both atoms. Comparison of data[62] on ionisation potentials, electron affinities, and electronegativities of phosphorus and sulphur atoms (Table 1) indicates that sulphur possesses more clearly defined electron-accepting properties ($-I$ and $-M$ effects) than does the phosphorus atom.

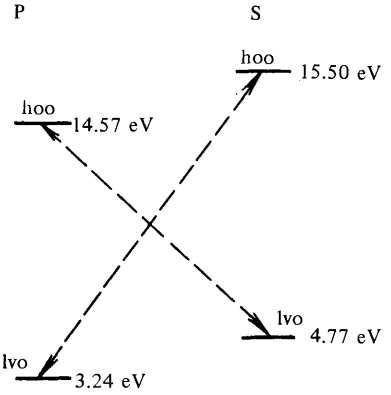



**Figure 1.** Relative arrangement of highest occupied orbitals (hoo) and lowest vacant orbitals (lvo) of phosphorus and sulphur atoms†.

The energy difference between the highest occupied level of phosphorus and the lowest vacant level of sulphur is actually smaller than the corresponding energy difference between sulphur and phosphorus (9.8 and 12.26 eV—Fig. 1)†. Hence electron displacements towards the sulphur atom are energetically more probable. However, the opposite interaction cannot be completely excluded[63]. This is made still more probable by the negative inductive and mesomeric effects of sulphur conferring a considerable positive charge on the phosphorus, which may be partly balanced by reverse $\pi$ bonding. Quite a high degree of delocalisation of electron shells may be expected in such a system from the close proximity of the energy states of phosphorus and sulphur atoms.

† Broken lines are drawn in Fig. 1 to indicate probable electron displacements, not the transfer of an electron from one energy level to another.

Table 1. Ionisation potentials $I$, valency electron affinities $A$, and orbital electronegativities Oel of atoms (for the $sp^3$-hybrid state)[62].

| Element | $I$, eV | $A$, eV | Oel |
|---|---|---|---|
| Phosphorus | 14.57 | 3.24 | 2.79 |
| Sulphur | 15.50 | 4.77 | 3.21 |

## II. ELECTRONIC EFFECTS IN ESTERS OF THIO-ACIDS OF THREE-COORDINATED PHOSPHORUS

The question of electron displacements in compounds $R_nP(SR')_{3-n}$ is probably part of the more general problem, already discussed in a review[3] and in several papers[15,64], of the nature of the interaction of a three-coordinated phosphorus atom with substituents containing a $\pi$-electron system. Among the latter are e.g. the phenyl, vinyl, and ethynyl radicals, the carbonyl group, and obviously groups containing a two-coordinated sulphur atom. It may be supposed that the phosphorus atom in such systems is able to develop both donor and acceptor properties. No generally accepted opinion has yet been reached on which of these effects is inherent in a three-coordinated phosphorus atom in a static (non-reacting) molecule[15,64,65].

Probably no definite conclusions on the direction of electron displacements can at present be drawn from data on dipole moments. The contradictoriness of published values[66–75] is not surprising, since the dipole moment of a molecule is a function of several factors acting simultaneously, whose combined effect is extremely difficult to assess[76,77]. In molecules containing atoms having lone pairs of electrons the dipole moment depends not only on the dimensions, the electronegativities of the atoms, and the bond angles, but mainly on the type of hybridisation of the orbital of the lone pair. Several authors[69,72] made calculations having equated the dipole moment of the lone pair to that of the phosphorus–carbon bond, which can hardly be accepted as correct[77]. The type of hybridisation has been taken into account in calculating dipole moments for several phosphorus(III) compounds[73–75]. However, a method of calculation[78] that had been criticised[31] was used to determine the character of the hybridisation. Nor do the ultraviolet spectra provide an unambiguous indication of the nature of the conjugation in aromatic phosphines[3,6,7,58,79–84].

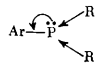
Electronic effects in compounds containing three-coordinated phosphorus have been discussed in terms of proton and phosphorus-31 nuclear magnetic resonance[35,72,85–91]. Attempts were made[87–91] to relate the phosphorus-31 chemical shifts wich such parameters as the electronegativities of substituents, bond angles, degree of $\pi$ bonding, type of hybridisation, character of the lone pair, etc. However, it has not yet proved possible to develop a general theory relating the chemical shift of the phosphorus atom with the structure of the molecules. The most comprehensive investigation[35] also is evidently not free from defects, and has been criticised by several workers[90,92,93].

Nevertheless, certain considerations pertaining to the character of possible interactions of a three-coordinated

phosphorus atom with the $\pi$-electron system of an aromatic ring can be expressed on the basis of published $^{31}P$ n.m.r. data [72,94,95]. Table 2 lists a series of compounds (Nos. 1–9) in which replacement of an alkyl by a phenyl group leads to a down-field shift in the phosphorus-31 resonance signal, e.g.

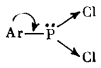
$$\underset{+20.4\ \text{ppm}}{(C_2H_5)_3P} > \underset{+16.0\ \text{ppm}}{(C_2H_5)_2P{-}C_6H_5} > \underset{+8.0\ \text{ppm}}{(C_6H_5)_3P}\ .$$

A low-field displacement of a signal can be attributed to an inductive effect. However, the ethyl and phenyl groups have closely similar electronegativities (2.6 and 2.8), [96,97] differing little from that of the phosphorus atom itself (2.79 for tetrahedral hybridisation [62]). This donor effect may perhaps be regarded as a consequence of $p,\pi$ conjugation of the lone pair of the phosphorus with the aromatic ring, which is favoured by $+I$ effects of the alkyl groups:



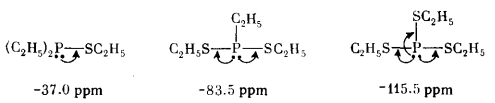
The alkoxycarbonyl group in compounds of the type $R_2PCOOR'$ has a strong electron-accepting action [98], as is indicated by the down-field shift in the resonance signal of the phosphorus nucleus (compounds No. 21–23 compared with No. 1 in Table 2), the infrared absorption by the carbonyl group at 1695–1685 $cm^{-1}$, and certain chemical properties of such compounds. Acetyl phosphides exhibit [100,101] opposite electron displacements, perhaps promoted by the $+I$ effect of the alkyl groups.

On the other hand, the presence of strongly electron-accepting groups (e.g. halogen atoms) attached to the phosphorus atom produces a high-field shift in the resonance signals when ethyl is replaced by phenyl (compounds No. 10–20 in Table 2), which can probably be explained by a $\pi,d$ effect:



Comparison of values of $\delta(^{31}P)$ in several series—(I) Nos. 24 and 25, (II) 26 and 27, and (III) 28 and 29 in Table 2—shows that, relative to propenyl, an alkyl group displaces the resonance signal up-field in the presence of such electron-accepting groups as chloro, alkoxyl, and dialkylamino attached to the phosphorus [99]. Unfortunately, the correlation between $\delta(^{31}P)$ and the structure of substituents bound to the phosphorus atom is satisfactory only for a limited number of compounds of similar structure, and available data are insufficient for final conclusions to be reached.

Comparison of the chemical shifts of phosphorus nuclei in a series of tervalent thio-esters (Table 3) permits an analogous discussion of the electron displacements (in terms of inductive and mesomeric effects) in the ground state of molecules [19,61] in conformity with the above structure of the phosphorus–sulphur bond. Experimental values of $\delta(^{31}P)$ suggest that one or other type of electron displacement will develop (predominate) depending on the nature of the groups R and R', as well as on the number of sulphur atoms combined with the phosphorus (Table 3). In all the series investigated [19,61] the successive replacement of alkyl or phenyl by alkylthio (phenylthio) results in a down-field shift in the resonance signal—Table 3, series (I), compounds No. 1, 5, and 15); (II) Nos. 3, 4, and 15; and (III) Nos. 2, 9, and 13—so that the donor effect of the phosphorus increases with the number of alkylthio-groups because of the strong electron-accepting properties of the sulphur atom, e.g.




Similarly, the replacement of alkylthio by phenylthio produces a low-field shift of the resonance signal in all the cases examined, which is obviously due to the more strongly developed electron-accepting properties of the phenylthio-group—series (I), Nos. 1 and 2, (II) Nos. 4 and 7, (III) Nos. 5 and 9, (IV) Nos. 11 and 12, and (V) Nos. 13 and 15—but in several cases—(I) Nos. 1, 3, and 16; (II) Nos. 4 and 5, and (III) Nos. 7 and 9—a high-field shift of the phosphorus-31 resonance signal is observed.

Strengthened shielding of the phosphorus nucleus can evidently be attributed to displacement of electrons as in the $\pi,d$ effect, e.g. in the sequence

$$\underset{-37\ \text{ppm}}{(C_2H_5)_2PSC_2H_5} < \underset{-32.5\ \text{ppm}}{(C_2H_5)(C_6H_5)PSC_2H_5} < \underset{-26.5\ \text{ppm}}{(C_6H_5)_2PSC_2H_5}$$

Table 2. Phosphorus-31 chemical shifts in compounds PXYZ.

| No. | X | Y | Z | δ, ppm | Ref. | No. | X | Y | Z | δ, ppm | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | +20.4 | 94 | 16 | Cl | Cl | $ClC_6H_4$ | −158.5* | – |
| 2 | $C_2H_5$ | $C_2H_5$ | $C_6H_5$ | +16.0 | 94 | 17 | Cl | $C_6H_5$ | $C_2H_5$ | −119.0* | – |
| 3 | $C_6H_5$ | $C_6H_5$ | $C_6H_5$ | +8.0 | 94 | 18 | Cl | $C_6H_5$ | $C_6H_5$ | −81.5* | – |
| | | | | +5.6 | 72 | 19 | Br | $C_2H_5$ | $C_2H_5$ | −117.0 | 94 |
| 4 | H | $CH_3$ | $C_2H_5$ | +77.5 | 94 | 20 | Br | $C_6H_5$ | $C_6H_5$ | −70.0 | 94 |
| 5 | H | $CH_3$ | $C_6H_5$ | +72.4 | 94 | 21 | $C_2H_5$ | $C_2H_5$ | $COOCH_3$ | +8.0 | 98 |
| 6 | $C_2H_5$ | $C_2H_5$ | $ClC_6H_4$ | +15.9 | 72 | 22 | $C_2H_5$ | $C_2H_5$ | $COOC_2H_5$ | +9.6 | 93 |
| 7 | $C_6H_5$ | $C_6H_5$ | $ClC_6H_4$ | +6.6 | 72 | 23 | $C_2H_5$ | $C_2H_5$ | $COOC_3H_7$ | +9.6 | 98 |
| 8 | $C_2H_5$ | $C_2H_5$ | $CH_3OC_6H_4$ | +17.6 | 72 | 24 | $C_3H_5$ | $N(CH_3)_2$ | $N(CH_3)_2$ | −98.0 | 99 |
| 9 | $C_6H_5$ | $C_6H_5$ | $CH_3OC_6H_4$ | +6.1 | 72 | 25 | $C_3H_7$ | $N(CH_3)_2$ | $N(CH_3)_2$ | −102.0 | 99 |
| 10 | Cl | Cl | $C_6H_5$ | −166* | – | 26 | $C_3H_5$ | $OC_3H_7$ | $OC_3H_7$ | −151.0 | 99 |
| 11 | Cl | Cl | $C_2H_5$ | −196* | – | 27 | $C_3H_7$ | $OC_3H_7$ | $OC_3H_7$ | −157.0 | 99 |
| 12 | Br | Br | $C_6H_5$ | −152 | 94 | 28 | $C_3H_5$ | Cl | Cl | −159.0 | 99 |
| 13 | Br | Br | $C_2H_5$ | −194 | 94 | 29 | $C_3H_7$ | Cl | Cl | −135.0 | 99 |
| 14 | Cl | $CH_3$ | $C_6H_5$ | −83.4 | 94 | | | | | | |
| 15 | Cl | $CH_3$ | $C_2H_5$ | −105.2* | – | | | | | | |

*Values obtained in our laboratory.

Table 3. Phosphorus-31 chemical shifts in compounds PXY(SR).[61]

| No. | X | Y | SR | δ, ppm | No. | X | Y | SR | δ, ppm |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_2H_5$ | $C_2H_5$ | $SC_2H_5$ | −37.0 | 9 | $C_2H_5$ | $SC_6H_5$ | $SC_6H_5$ | −100.0 |
| 2 | $C_2H_5$ | $C_6H_5$ | $SC_6H_5$ | −39.0 | 10 | $C_4H_9$ | $SC_2H_5$ | $SC_2H_5$ | −80.5 |
| 3 | $C_6H_5$ | $C_6H_5$ | $SC_2H_5$ | −26.5 | 11 | $CH_3$ | $SC_2H_5$ | $SC_2H_5$ | −71.0 |
| 4 | $C_6H_5$ | $SC_2H_5$ | $SC_2H_5$ | −75.0 | 12 | $CH_3$ | $SC_6H_5$ | $SC_2H_5$ | −86.5 |
| 5 | $C_2H_5$ | $SC_2H_5$ | $SC_2H_5$ | −83.5 | 13 | $SC_6H_5$ | $SC_6H_5$ | $SC_6H_5$ | −180.0 |
| 6 | $C_6H_5$ | $SC_2H_7$ | $SC_3H_7$ | −78.0 | 14 | $SCH_3$ | $SCH_3$ | $SCH_3$ | −125.0 |
| 7 | $C_6H_5$ | $SC_6H_5$ | $SC_6H_5$ | −90.0 | 15 | $SC_2H_5$ | $SC_2H_5$ | $SC_2H_5$ | −115.5 |
| 8 | $C_3H_7$ | $SC_2H_5$ | $SC_2H_5$ | −81.0 | 16 | $C_2H_5$ | $C_6H_5$ | $SC_2H_5$ | −32.5 |

Thus in this series of compounds phosphorus exhibits acceptor properties towards the phenyl radical.

Hence the $^{31}P$ n.m.r. data listed in Tables 2 and 3 indicate that three-coordinated phosphorus may develop either a donor or an acceptor character depending on the nature of the substituents.

Alkyl groups (ethyl, propyl, butyl) make almost the same contribution to the resonance signal, as is indicated by closely similar values of $\delta(^{31}P)$ for compounds Nos. 5, 8, and 10 in Table 3. An exception is the methyl group, which causes a larger up-field shift of the resonance signal than does phenyl—series (I) Nos. 11 and 4, and (II) Nos. 12 and 7. Similarly strong shielding of the phosphorus nucleus by a methyl group has been explained[71] by hyperconjugation:

$$H_3CP(SR')_2 \leftrightarrow H^+CH_2^-P(SR')_2 .$$

Several workers have shown[102-117] that the phosphorus atom is able to exhibit both a definite acceptor and a donor character even in a dynamic state. This is especially apparent in reactions in which the phosphorus, while not acting as a reaction centre, helps to stabilise the transition state. In some cases[112,113,118] phosphorus exerts an acceptor effect, and the carbanions formed in the reaction are stabilised by *d*-orbital resonance. A similar *d*-orbital effect is observed with silicon and sulphur atoms in the reactions of vinylsilanes[119] and vinyl sulphides[26,120]. In other cases[17,109,110], however, the low energy barrier to pyramidal inversion in certain three-coordinated phosphorus derivatives has been attributed to considerable strengthening in the transition state of the donor effect of phosphorus(III) in the static molecule. According to modern ideas in theoretical chemistry, dynamic electronic effects do not necessarily operate in the same direction as electron displacements in the static molecule[121].

## III. DUAL REACTIVITY (AMBIDENTICITY) OF PHOSPHORUS(III) THIO-ACIDS TOWARDS ALKYL HALIDES

Compounds containing a $\rangle\ddot{P}-\ddot{S}-$ group occupy a special place among ambident derivatives of three-coordinated phosphorus such as esters, amides, and thioesters. Two types of reactions—electrophilic addition $A_E$ at the lone pair and nucleophilic substitution $S_N$—characterise derivatives of three-coordinated phosphorus in conformity with the special structure of its electron shell and depending on the structure of its nearest neighbours and the nature of the reagent[4-6,102]. The same types of reactions occur readily also with compounds containing two-coordinated sulphur[26]. Because of the close similarity in the electron configurations of phosphorus and sulphur atoms, the mechanisms of their reactions should have much in common. This must obviously be borne in mind when considering the interaction of the esters $R_nP(SR')_{3-n}$ with electrophilic reagents.

### 1. Ability of Esters $R_nP(SR')_{3-n}$ to form Onium Derivatives

An element possessing a lone pair of electrons is able to form onium—oxonium, ammonium, phosphonium, sulphonium, etc.—compounds on reaction with electrophilic reagents. Esters of type $R_nP(SR')_{3-n}$ can therefore reasonably be expected to form onium derivatives of two types—quasi-phosphonium and quasi-sulphonium[122-124]:

$$\rangle\ddot{P}-\ddot{S}-R' + R''X \rightarrow \left[\rangle P\langle^{R''}_{\ddot{S}R'}\right]^+X^- ,$$

(I)

$$\rangle\ddot{P}-\ddot{S}-R' + R''X \rightarrow \left[\rangle\ddot{P}-\overset{R''}{\overset{|}{\ddot{S}}}-R'\right]^+X^- .$$

(II)

The quasi-sulphonium structure ascribed[124] to products of the alkylation of trialkyl (triaryl) phosphorotrithioites has since been confirmed[22] by their proton magnetic resonance spectra. Several workers have isolated quasi-phosphonium compounds by treating alkyl dialkylphosphinothioites with alkyl halides[22,123,125] and with other electrophilic reagents[126].

Interesting results have been obtained from the alkylation of dialkyl alkylphosphonodithioites, which form[22,61] mixtures of onium derivatives of both types, the quantitative relations between which vary with the structure of R and R′. To interpret the reactivities of compounds containing P−S, S−P−S, and $S-P\langle^{S}_{S}$ groups use has been made[61,127] of Pearson's concept of hard and soft acids and bases[128,129]. In the ambident system sulphur is a "hard", and phosphorus a "soft", basic centre (sulphur is more electronegative and less polarisable than phosphorus). In esters of type $R_2P.S.R'$, therefore, phosphorus undergoes electrophilic attack by a "soft" electrophilic centre (an $sp^3$-hybrid carbon atom in an alkyl halide), with formation of quasi-phosphonium derivatives of type (I).

The esters $RP(SR')_2$ contain three nucleophilic centres—one "soft" (the phosphorus atom) and two "hard" (the sulphur atoms)—and the displacement of electron density towards the latter weakens the nucleophilic character of the phosphorus atom and increases the probability of attack by an electrophilic species on the "hard" sulphur atom, even if such species is a "soft" acid. As a consequence, a mixture of quasi-phosphonium (I) and quasi-sulphonium

(II) derivatives is formed. In trialkyl phosphorotrithioites four donor centres are competing. The three sulphur atoms greatly deplete the electronic environment of the phosphorus atom, and hence weaken its nucleophilic character. Furthermore, the probability factor favouring attack on the sulphur increases. All this leads to the formation of quasi-sulphonium derivatives (II). The steric factor may play some part, but no information has been published on the role of steric hindrance in these reactions.

Thus the ability to form quasi-sulphonium compounds [61] falls in the sequence

$$(RS)_3P > (RS)_2PR' > RSPR_2'.$$

## 2. Thio-esters of Three-coordinated Phosphorus in the Arbuzov Reaction

The mechanism of the action of alkyl halides on oxygen-containing esters of three-coordinated phosphorus has been studied quite well, although few quantitative data on this reaction are yet available [4-6]. The number of investigations on the behaviour of $R_nP(SR')_{3-n}$ esters ($n = 0-2$) in the Arbuzov reaction is at present quite insignificant.

The peculiar behaviour of diphenylphosphinothious esters with alkyl halides was first investigated by Arbuzov, whose results were reported at the Twelfth Congress of Russian Naturalists and Physicians in 1910. [122] He found that "esters of general type $(C_6H_5)_2P.SR$, as derivatives of tervalent phosphorus and like the corresponding oxygen compounds, isomerise under the influence of alkyl iodides into sulphides containing quinquevalent phosphorus, of general type $(C_6H_5)_2PS.R$. However, the isomerisation of sulphur-containing esters is complicated by secondary reactions, viz. the formation of small quantities of tetra-substituted phosphonium iodides and probably esters of formula $(C_6H_5)_2PSSR$". [123]

Dialkyl- and alkylaryl-phosphinothious esters undergo similar reactions [125,131]. Arbuzov suggested the scheme [122]

$$R_2P(SR') + R''X \rightarrow R_2P(S)R'' + R'X\ , \quad (1)$$

$$2R_2P(SR') \rightarrow R_2PR' + R_2P(S)(SR')\ , \quad (2)$$

$$R_2PR' + R''X \rightarrow [R_2PR'R'']^+X^-\ . \quad (3)$$

Equation (1) represents the main reaction, while (2) and (3) are secondary processes.

Kabachnik et al. [124] showed that trialkyl phosphorotrithioites react unusually with preservation of the coordination number of the phosphorus atom:

$$(RS)_3P + R'X \rightarrow \underset{(II)}{\left[(RS)_2P{-}\overset{R'}{\overset{|}{S}}{-}R\right]^+}X^- \rightarrow (RS)_2PX + R'{-}S{-}R\ .$$

They isolated the acid chlorides $(RS)_2PX$ and the dialkyl sulphides, thus showing for the first time that the reaction may take place at the sulphur atom, not at phosphorus. Decomposition of the quasi-sulphonium salt (II) can evidently be regarded as nucleophilic substitution at three-coordinated phosphorus, the electrophilic character of which is enhanced by the positively charged sulphur.

Mixed *O*- and *S*-esters of phosphorous acid [130] react with alkyl halides to form both the normal Arbuzov products and several secondary products. The appearance of the latter was attributed to the involvement of a second nucleophilic centre—a sulphur atom—as well as the phosphorus.

The reactions of dialkyl alkyl(or aryl)phosphonodithioites are most complicated [132,133]. The researchers [61,127,132,134] suggested a scheme involving several parallel and consecutive processes, each of which could be reproduced in separate experiments:

$$\underset{(III)}{RP(SR')_2} + \underset{(IV)}{R''X} \rightarrow \underset{(V)}{R''R'P(S)SR'} + \underset{(VI)}{R'X} + \underset{(VII)}{RP(SR')X} + \underset{(VIII)}{R'{-}S{-}R''}$$

$$\underset{(IX)}{RP(S)(SR')_2} + \underset{(X)}{RR''P(SR')} \qquad \underset{(XI)}{RR''\ddot{P}(S)X} + \underset{(XII)}{R'{-}S{-}R'}$$

$$(X) + (IV) \rightarrow \underset{(XIII)}{RR''_2P(S)} + (VI)$$

$$(IX) + (VI) \rightarrow \underset{(XIV)}{RP(S)(SR')X} + (XII)\ .$$

Compounds (V) and (VI) are products of an Arbuzov reaction, and are obviously formed by the breakdown of a quasi-phosphonium (I) type of intermediate. The products (VII) and (VIII) result from reaction at a sulphur atom, with intermediate formation of quasi-sulphonium derivatives of type (II). Compounds (IX)–(XIV) are formed by secondary processes occurring in the reaction mixture [61, 134]. The above scheme shows that the complexity is due not only to the dual reactivity (ambidenticity) of these compounds but also to the ease of occurrence of secondary reactions among starting materials and products [61,127,134].

It is by no means always possible to isolate and identify all the products indicated in the above scheme [61,127]. Their reasons for this are the highly reactive character of compounds containing a phosphorus–sulphur bond and the complexity of their isolation consequent on the formation of difficultly separable azeotropic mixtures. In most cases successful separation can be achieved only by means of column, gas–liquid, and thin-layer chromatography [135,136]. Formation of certain products—(XI) (VII), (XIV)—was detected when the course of the process was monitored by $^{31}P$ n.m.r. spectroscopy [61,127,142].

The extremely complicated problem of the relative proportions of the first and second types of reaction (at phosphorus and at sulphur respectively) has been only partly solved [61,127,142]. This work has shown that the structure of the alkyl halide has a significant influence firstly on the extent of reaction at phosphorus and sulphur atoms, and secondly on the reaction velocity. Table 4 gives data on the main reaction products containing phosphorus—(V), (IX), and (X)—obtained from the ratio of the integral intensities of the resonance peaks of the phosphorus nucleus, together with quantitative data, obtained by gas–liquid chromatography, on the contents of the dialkyl sulphides (VIII) and (XII). [127,137] The considerable quantities of the normal Arbuzov reaction product (V) and the low contents (0.5–11.0%) of the dialkyl sulphide (VIII) in the reaction mixture obtained from n-alkyl bromides and the esters (III) indicate that the proportion of reaction at the sulphur is insignificant. The dialkyl sulphide (VIII) was not isolated from the reaction with benzyl bromide, so that in this case reaction at the sulphur probably does not take place at all. In the reactions with secondary and tertiary alkyl bromides the yield of the normal Arbuzov reaction product (V) falls (24–30%), while the yield of the dialkyl sulphide (VIII) increases (9.0–31.4%).

On the basis of the results all the alkyl bromides investigated can be arranged in the sequence

$$t\text{-}C_4H_9 > iso\text{-}C_4H_9 > s\text{-}C_4H_9 \simeq iso\text{-}C_3H_7 > n\text{-}C_4H_9 > n\text{-}C_3H_7 > C_2H_5 > CH_3 > C_3H_5 > C_6H_5CH_2$$

according to their tendency to react with the sulphur [61]. This experimental rule can be stated in terms of the concept of soft and hard acids and bases [61]: the hardness of the $sp^3$ carbon atom in alkyl halides increases in a homologous series and also on passing from primary to secondary and to tertiary compounds [129].

Table 4. Yields (%) of product of the reaction $RP(SR')_2 + R''X$.

| R | R′ | R″ | $\begin{matrix}R\\R''\end{matrix}\!>\!P(=S)\!-\!SR'$ (V) | $R\!-\!P(=S)(SR')_2$ (IX) | $RR''_2P$ (X) | R′—S—R″ (VIII) | R′—S—R′ (XII) |
|---|---|---|---|---|---|---|---|
| $C_6H_5$ | n-$C_4H_9$ | $CH_3$ | 56.5 | 15.8 | 14.8 | 4.3 | 8.6 |
| $C_6H_5$ | n-$C_4H_9$ | $C_2H_5$ | 48.2 | 17.7 | 14.3 | 5.4 | 12.6 |
| $C_6H_5$ | n-$C_4H_9$ | n-$C_3H_7$ | 41.5 | 21.3 | 19.0 | 7.2 | 9.6 |
| $C_6H_5$ | n-$C_4H_9$ | n-$C_4H_9$ | 36.7 | 17.7 | 13.5 | 10.0 | — |
| $C_6H_5$ | n-$C_4H_9$ | s-$C_4H_9$ | 30.3 | 22.5 | 19.8 | 15.4 | 11.8 |
| $C_6H_5$ | n-$C_4H_9$ | t-$C_4H_9$ | 24.0 | 26.1 | — | 31.4 | 18.5 |
| $C_6H_5$ | n-$C_3H_7$ | n-$C_3H_7$ | 48.3 | 19.1 | 18.5 | 4.3 | — |
| $C_6H_5$ | n-$C_3H_7$ | iso-$C_3H_7$ | 28.4 | 31.9 | 25.4 | 9.1 | 2.0 |
| $C_2H_5$ | n-$C_3H_7$ | n-$C_3H_7$ | 41.0 | 27.7 | 21.7 | 5.2 | — |
| $C_2H_5$ | n-$C_3H_7$ | iso-$C_3H_7$ | 26.0 | 23.6 | 21.2 | 21.1 | 8.1 |
| $C_6H_5$ | n-$C_3H_7$ | iso-$C_4H_9$ | 29.0 | 16.0 | 13.7 | 24.7 | 16.0 |
| $C_6H_5$ | n-$C_3H_7$ | n-$C_4H_9$ | 42.9 | 23.5 | 13.5 | 11.6 | 7.7 |
| $C_6H_5$ | n-$C_4H_9$ | $C_6H_5$ | 63.0 | 12.4 | 12.2 | 0.3 | 11.7 |
| $C_6H_5$ | n-$C_4H_9$ | $C_6H_5CH_2$ | 55.3 | 18.9 | 16.3 | — | 9.4 |

The rate curves in Fig. 2 have been plotted from the variation in the concentration of the initial ester $C_6H_5P.(SC_3H_7)_2$ during its reaction with several alkyl bromides determined from the $^{31}P$ n.m.r. spectra [61,127,142]. In order of decreasing rate of reaction with $RP(SR')_2$ the alkyl bromides examined form the sequence

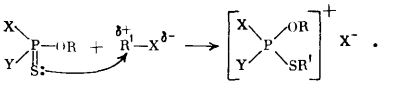
$$CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9 > t\text{-}C_4H_9 \simeq iso\text{-}C_4H_9 > iso\text{-}C_3H_7 > s\text{-}C_4H_9.$$

The principal secondary processes complicating the reaction are [61,127,134] firstly the exchange of sulphur atoms—reductive desulphurisation—and secondly interaction of esters of four-coordinated phosphorus like (V) and (IX) with the alkyl halides [137]. These reactions are due to the ability of both thionic and thiolic sulphur atoms (like phosphorus) to react both with electrophilic and with nucleophilic reagents, because of the presence of lone pairs of electrons and vacant *d* orbitals. Thus a two-coordinated sulphur atom reacts with several nucleophilic reagents, including the three-coordinated phosphorus atom [138–140]. Reactions of several phosphorus(III) compounds with a thiophosphoryl group have been reported [61, 127,134,140,141,143–145]:

$$X_3\ddot{P} + S{=}P\!\lessdot \rightarrow X_3P{=}S + \ddot{P}\!\lessdot \ .$$

The tendency to react with thionic sulphur is not simply related to the nucleophilic character of the reagent, so that the use by certain authors of the terms "thiophilicity" [26,138] or "S-nucleophilicity" [26,139] seems entirely justified.

On the other hand, sulphur(II) is able to react with electrophilic reagents [26]. The high donor power of sulphur in the thiophosphoryl group $>\!P{=}S$ has been investigated by several workers [146–149]. The substituents X and Y favour reaction if they enhance the nucleophilic character of sulphur [148]:



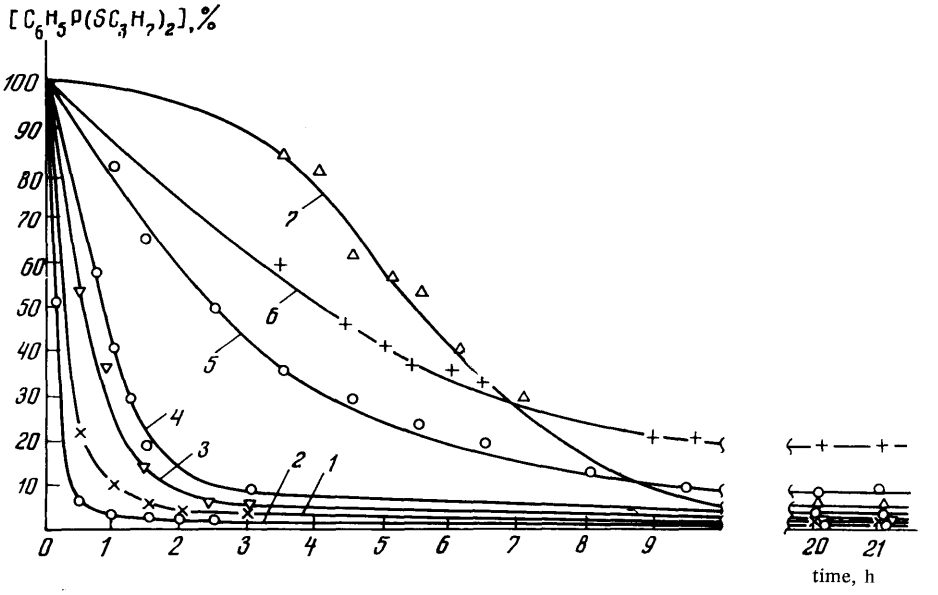



Figure 2. Variation of concentration of $C_6H_5P(SC_3H_7)_2$ with time during reaction with alkyl bromides: 1) $CH_3Br$; 2) $C_2H_5Br$; 3) n-$C_3H_7Br$; 4) n-$C_4H_9Br$; 5) t-$C_4H_9Br$; 6) iso-$C_3H_7Br$; 7) s-$C_4H_9Br$.

Examination of a series of compounds revealed [148] that the infrared absorption frequencies of the thiophosphoryl group can serve as a criterion of reactivity towards electrophilic reagents. Contradictory information has been published on the behaviour of thiolic sulphur towards such reagents: some authors assume [147,148] that thiolic sulphur in the group PO.SR does not react; other publications [137, 150,151] report that reaction does occur. The two sulphur atoms in the group PS.SR may compete, for under mild conditions the thionic sulphur reacts, but on heating the thiolic sulphur may also be involved [137]:

$$RR'P(S)SR'' + R'''Br \begin{cases} \longrightarrow RR'P(S)SR''' + R''Br \\ \xrightarrow[\text{heat}]{} RR'P(S)Br + R''-S-R''' \end{cases}.$$

## IV. REACTIONS WITH HALOGENOCARBONYL REAGENTS

Descriptions have appeared of the reactions of sulphur-containing esters $R_nP(SR')_{3-n}$ with several types of halogenocarbonyl compounds—acetyl chloride [124,152-154], chloral [155-157], chloroacetic and chloroformic esters [61,127, 142,158-162], and chlorinated and brominated acetyl chlorides [61,127,163].

Reactions with chloral are complicated, and the reaction mechanism has not been elucidated. In several cases the multicomponent mixture contains vinyl ethers [157], whose presence suggests that the reaction proceeds partly in conformity with Perkov's scheme.

Acetyl chloride acts on trialkyl phosphorotrithioites, phosphorothious chlorides [124], alkyl(or aryl)phosphonodithious [152] and dialkylphosphinothious [125] esters, and also mixed *O*,*S*-phosphites [153] at a sulphur atom:

$$\rangle P-S-R + CH_3COCl \rightarrow \rangle P-Cl + CH_3COSR$$

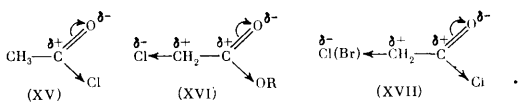
Acyl chlorides act on phospho(i)namidothious esters initially at the nitrogen atom [154]:

$$\begin{matrix} R'S \\ R \end{matrix}\!\!\rangle P-NR''_2 + CH_3COCl \rightarrow \begin{matrix} R'S \\ R \end{matrix}\!\!\rangle P-Cl + CH_3CONR''_2 .$$

The sulphur atom is then attacked:

$$\begin{matrix} R'S \\ R \end{matrix}\!\!\rangle P-Cl + ClCOCH_3 \rightarrow \begin{matrix} Cl \\ Cl \end{matrix}\!\!\rangle P-R + CH_3COSR' .$$

Esters and chlorides of chloro(or bromo)acetic acid differ from acetyl chloride in the nature and number of electrophilic centres:



(XV) (XVI) (XVII)

In chloroacetic esters (XVI) the methylene carbon atom in the $sp^3$-hybrid state is a soft electrophilic centre, whereas the carbonyl carbon atom in the $sp^2$-hybrid state is a hard Lewis acid. It would appear that dual reactivity—reaction of the soft electrophilic centre with phosphorus and of the hard electrophilic centre with sulphur—might be expected in chloroacetic esters. In all the reported cases, however, only one type of reaction—of $R_2PSR'$ and $RP(SR')_2$ esters according to the usual Arbuzov scheme—has been observed [158,159], obviously with intermediate formation of a quasi-phosphonium product:

$$\rangle P-S-R' + (XVI) \rightarrow \left[\rangle P\begin{matrix} SR' \\ CH_2COOR \end{matrix}\right]^+ Cl^- \rightarrow \rangle P(S)CH_2COOR + R'Cl .$$

The reaction is complicated by secondary processes [159], such as nucleophilic attack by phosphorus(III) on thionic sulphur

$$R_2P\begin{matrix} S \\ CH_2COOR'' \end{matrix} + :P\begin{matrix} R \\ SR' \end{matrix} \rightarrow R_2\ddot{P}CH_2COOR'' + R_2P(S)SR'$$

with subsequent formation of a phosphonium salt

$$R_2PCH_2COOR'' + ClCH_2COOR'' \rightarrow [R_2P(CH_2COOR'')_2]^+ Cl^- .$$

In the case of esters of the $RP(SR')_2$ type the quasi-phosphonium salt then breaks down:

$$\left[\begin{matrix} SR' \\ | \\ R-P-CH_2COOR'' \\ | \\ CH_2COOR'' \end{matrix}\right]^+ Cl^- \rightarrow RP(S)(CH_2COOR'')_2 + R'Cl .$$

The probable reason for the complete absence of the second type of reaction—involving sulphur—is that the carbonyl carbon is a considerably less active electrophilic centre in these compounds than is the $sp^3$ carbon atom of the methylene group ($C_{sp^3} > C_{sp^2}$).

Replacement of the alkoxy-group by halogens produces a sharp increase in activity of the $sp^2$-hybrid carbon atom, and chloroacetyl and bromoacetyl chlorides (XVII) react with ethyl(and phenyl)phosphonodithious esters in two ways—at the phosphorus and sulphur atoms—also accompanied by secondary processes [61,127,169]:

$$RP(SR')_2 + Cl(Br)CH_2COCl \rightarrow RP(Cl)SR' + Cl(Br)CH_2COSR' , \quad (4)$$
$$RP(Cl)SR' + Cl(Br)CH_2COCl \rightarrow RPCl_2 + Cl(Br)CH_2COSR' , \quad (5)$$
$$RP(SR')_2 + Cl(Br)CH_2COCl \rightarrow RP(S)(SR')(CH_2COCl) + R'Cl(Br) , \quad (6)$$
$$RP(S)(SR')(CH_2COCl) + RP(Cl)(SR') \rightarrow RP(SR')(CH_2COCl) + RP(S)Cl(SR') , \quad (7)$$
$$RP(S)(SR')(CH_2COCl) + RP(SR')_2 \rightarrow RP(SR')(CH_2COCl) + RP(S)(SR')_2 . \quad (8)$$

Chloroacetyl chloride reacts initially only with the sulphur (Eqns. 4 and 5) by means of the carbonyl electrophilic centre. Under more severe conditions the Arbuzov reaction (6) also takes place. Bromoacetyl chloride reacts with a thioester $RP(SR')_2$ simultaneously at the two nucleophilic centres (4)–(6), with the phosphorus attacking the methylene carbon, and the sulphur attacking the carbonyl carbon. Such behaviour can conveniently be explained in terms of soft and hard acids and bases: phosphorus and methylenic carbon atoms are soft reaction centres, whereas sulphur and carbonyl atoms are hard centres.

Chloroformic esters ClCOOR″ react with phosphonodithious and phosphinothious esters only at the phosphorus atom [160,162]. Reaction with esters of the latter type can be represented by two consecutive processes [162]:

$$R_2PSR' + ClCOOR'' \rightarrow R_2P(S)COOR'' + R'Cl ,$$
$$R_2P(S)COOR'' + R_2PSR' \rightarrow R_2P(S)SR' + R_2PCOOR'' .$$

This appears somewhat unexpected, since there are data [164] indicating that chloroformic ester is a stronger acylating agent than is acetyl chloride, which acts only on the sulphur atom in all types of esters $R_nP(SR')_{3-n}$, as noted above. The electrophilic centre in chloroformic ester is surrounded by three strongly electronegative groups, and therefore carries a high positive charge:

$$Cl-\overset{\overset{O}{\|}}{C}-OR'' .$$

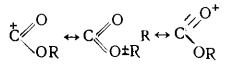
Chloroformic esters should be hard acids. However, the sequence of diminishing hardness [129]

$$CH_3COCl > ClCH_2COCl > ClCOOC_2H_5$$

indicates that chloroformic ester is a less active hard reagent, at least in certain reactions.

Furthermore [164], sodium salts of keto–enols are attacked by chloroformic ester at oxygen (a hard centre), but copper salts at carbon (a soft centre). This can be explained by Nesmeyanov and Kabachnik's concept of dual reactivity [165]. In the case of the copper salt of acetoacetic ester the reaction involves migration of the reaction centre. This is considered [164,165] to occur when the active reagent is strongly electrophilic (i.e. is a hard acid according to Pearson), and the carbon–metal bond is unionised.

With regard to the reactivity of chloroformic ester in the above reaction, the observed features of its chemical behaviour are most consistent with Kornblum's rule [166]. An electrophilic reagent may change its reactivity not only according to the nature of the nucleophile, for even in the same reaction its tendency to react with the softer centre of an ambident system increases on passing from an $S_N1$ to an $S_N2$ mechanism [121,166]. Hence chloroformic ester will interact preferentially with a hard centre (sulphur) only if the reaction conditions favour an $S_N1$ process. If, however, the reaction mechanism is closer to the $S_N2$ type, reaction must be expected at a soft centre, i.e. at phosphorus. This ester is obviously little able to form a stable intermediate carbocation and hence react by an $S_N1$ mechanism: the negative inductive effects of the carbonyl oxygen and of the alkoxy-group, which impair the stability of the carbocation, are stronger than stabilising resonance effects of the type



The slowness of $S_N1$ reaction with $\alpha$-halogenated ketones is explained similarly [167].

On the other hand, steric hindrance to formation of the transition state in $S_N2$ processes is absent from the chloroformic ester molecule owing to the planar structure of the $sp^2$-hybrid carbon atom. Further stabilisation of the transition state may result from overlap of the electron shell of the nucleophilic species with the $\pi$-electron system of the carbonyl group. As a consequence of these factors chloroformic ester shows a greater tendency to react by an $S_N2$ mechanism and therefore to attack the soft centre of the system—the phosphorus atom.

It is clear from the literature also that chloromethyl ether, like chloroformic ester, reacts with the sodium salts of keto–enols at the oxygen atom [168], and with the copper salts at a carbon atom [164]. The tendency of halogenated ethers to react by an $S_N2$ mechanism can probably be explained also by their ability to interact with the soft centre—the phosphorus atom [170]:

$$R_2PSR' + ClCH_2OR' \rightarrow R_2P(S)CH_2OR' + R'Cl, \quad (9)$$

$$R_2P(S)CH_2OR' + R_2PSR' \rightarrow R_2\overset{+}{P}CH_2OR' + R_2P(S)SR', \quad (10)$$

$$R_2\overset{+}{P}CH_2OR' + ClCH_2OR' \rightarrow [R_2P(CH_2OR')_2]^+Cl^-. \quad (11)$$

Thus the results for the reactivities of halogenocarbonyl compounds (and of chloromethyl ethers and esters) towards thio-esters of three-coordinated phosphorus $R_nP(SR')_{3-n}$ ($n = 0-2$) enable them to be arranged in the sequence

$$ClCOOR \approx ClCH_2OR \approx ClCH_2COOR > BrCH_2COCl > ClCH_2COCl > RCOCl$$

of diminishing softness towards the phosphorus atom [61,127]. The tendency of the electrophilic reagent to attack a hard centre in the ambident system—a sulphur atom—increases in the same sequence.

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# Chemistry of α-Nitrohetero-organic Compounds

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Methods of preparation, problems of the establishment of structure and elementotropism, and chemical reactions are surveyed on the basis of 177 references.

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## I. INTRODUCTION

During recent years we have witnessed vigorous development of the chemistry of organoelementary compounds and of nitro-compounds. The results of these investigations have been summarised in a considerable number of monographs and review papers. Hitherto, however, no attempt has been made to examine from a uniform viewpoint the chemistry of compounds in which both a nitro-group and a heteroatom are attached to the same atom of the molecular framework, i.e. the chemistry of α-nitrohetero-organic compounds.

Yet an analysis of the reactions of this class of compounds is of undoubted interest, both theoretical and applied. Indeed, several methods of preparation involve interaction of an ambident nitro-anion with an electrophile in which the positive charge is concentrated mainly on the heteroatom, which may prove interesting in the study of dual reactivity. Furthermore, these compounds are able to develop elementotropism, a phenomenon well known with carbonyl compounds, which can now be considered on new models. On the other hand, the preparation of these α-nitro-compounds and the investigation of their properties will broaden the opportunities for using both hetero-organic compounds and the nitro-derivatives in organic synthesis. There are indications that α-nitrohetero-organic compounds may be used directly in herbicidal and insecticidal compositions, and also as intermediates for the production of surface-active agents, biologically active products, explosives, and finishing agents in the textile industry. The present review summarises results on methods for the preparation of α-nitrohetero-organic compounds, examines the chief principles on which their structure is established, and describes several chemical reactions. It covers the literature to 1974. It does not include data on α-halogeno-α-nitro-compounds, nor certain earlier results, whose reliability is open to doubt.

## II. METHODS OF PREPARATION

### 1. Reaction of Salts of Nitro-compounds with Halogenated Hetero-Organic Compounds

The chief examples of this reaction that have been studied are sulphenylation, silylation, and diethylborylation. Salts of mononitro-compounds react with sulphenyl halides and thiocyanates to form α-nitroalkyl sulphides[1,2]:

$$RSX + [R'R''C(NO_2)]Na \rightarrow RSCR'R''(NO_2) + NaX \quad (1)$$

R = *p*-$MeC_6H_4$, *m*-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$; R' = H, Me, Et, n-Pr; R'' = H, Me; X = Cl, Br, SCN.

Furthermore, corresponding disulphides are also formed†. Anions of polynitro-compounds have been successfully sulphenylated by means of sulphenyl halides and sulphenium salts[4-7]:

$$RC(NO_2)_2^-Z^+ + R'SX \rightarrow RC(NO_2)_2SR' \quad \text{or} \quad RC(NO_2)=N\begin{matrix}\nearrow O\\ \searrow OSR'\end{matrix}$$

R = H, Me, $NO_2$; R' = Me, Ph, *p*-$MeOC_6H_4$, *p*-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$; Z = K, Ag, $(CH_2)_5NH_2$; X = Cl, Br, $SbF_6$, $BF_4$.

The synthesis of nitromethyl trichloromethyl sulphide[8,9]

$$MeNO_2 + CCl_3SCl \xrightarrow[EtOH]{NaOH} (NO_2)CH_2SCCl_3$$

is clearly also a reaction of this type. The preparation of bis-1-nitroalkyl disulphides from the sodium salts of nitroalkanes and sulphur monochloride has been patented[10,11]:

$$RCH(NO_2)^-Na^+ \xrightarrow[ether]{S_2Cl_2} [RCH(NO_2)S]_2$$

R = Alk $C_1$—$C_6$, Ar $C_6$—$C_{15}$.

Nitro-derivatives containing oxidised sulphur are obtained by the action of sulphonyl chlorides on salts of nitro-compounds. In particular, a convenient method has been proposed[12] for synthesising 1-nitroalkyl *p*-tolyl sulphones:

$$RR'C(NO_2)^-K^+ + p\text{-}MeC_6H_4SO_2X \rightarrow p\text{-}MeC_6H_4SO_2CRR'NO_2$$

R = H, Me; R' = H, Me, Et, Ph‡; *p*-$ClC_6H_4$, *p*-$MeOC_6H_4$; RR' = $(CH_2)_5$; X = Br, I.

This reaction takes place by a radical-anion mechanism[12]:

$$Tos\,I + Me_2C(NO_2)^- \rightarrow Tos^- + ICMe_2NO_2$$
$$ICMe_2NO_2 \rightleftarrows I^\cdot + Me_2CNO_2^\cdot$$
$$Tos^- + Me_2CNO_2^\cdot \rightleftarrows Tos\,C(NO_2)Me_2^{\cdot-}$$
$$Tos\,C(NO_2)Me_2^{\cdot-} + ICMe_2NO_2 \rightleftarrows Tos\,C(NO_2)Me_2 + ICMe_2NO_2^{\cdot-}$$
$$ICMe_2NO_2^{\cdot-} \rightarrow I^- + Me_2CNO_2^\cdot \text{ etc.}$$

†Reaction (1) will be discussed in detail in Section IV, 1*a*. The products $CH_3CH(NO_2)SR'''$ (where R''' = $Cl[CH_2]_2$ or *m*-$NO_2C_6H_4$) were oxidised to the corresponding sulphones without being isolated[3].

‡The salt of this nitroalkane was treated also with benzenesulphonyl chloride.

where Tos = $p$-$CH_3C_6H_4SO_2$. $N$-Nitrosulphonamides can be obtained from salts of nitramines and sulphonyl chlorides: e.g.[13]

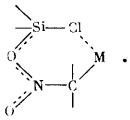
$$Me_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}\underset{\underset{NO_2}{|}}{N}Na + PhSO_2Cl \rightarrow Me_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}\underset{\underset{NO_2}{|}}{N}{-}SO_2Ph \ .$$

Nitro-silyl derivatives are also obtained from salts of nitro-compounds. In contrast to $\alpha$-sulphur-substituted nitro-compounds, however, the only final products are $O$-esters of nitronic acids:

$$M^+[C(NO_2)RR']^- + R''_3SiCl \rightarrow RR'C{=}N{-}O{-}SiR''_3$$

R = R' = $CO_2Me$[14], $NO_2$[15,16]; R = $NO_2$, R' = CN[17]; R'' everywhere Me or Ph.

The potassium salt of trinitromethane and the sodium salt of dimethyl nitromalonate do not react with trimethylchlorosilane§. From this it is concluded[14,16] that the silylation of salts of nitro-compounds by trimethylchlorosilane requires electrophilic assistance in abstracting the leaving group, perhaps in a cyclic transition complex of the type



The silver salts of methylnitramine, $N$-nitrotoluene-$p$-sulphonamide, and ethyl $N$-nitrocarbamate are also silylated by trialkylhalogenosilanes:

$$[RN(NO_2)]Ag + Me_2SiClR' \rightarrow [RN(NO_2)]SiMe_2R'$$

R = Me, R' = H, Me, iso-Pr[20];
R = EtOCO[21], $p$-$MeC_6H_4SO_2$[22], R' = Me.

Diethylboryl derivatives of nitroalkanes have been isolated or detected when diethylboryl chloride acts on salts of the nitroalkanes and functionally substituted nitro-compounds in inert aprotic solvents:

$$[RR'C(NO_2)]M \xrightarrow[-MCl]{Et_2BCl} RR'C{=}N{-}O{-}BEt_2$$

R = Me, R' = Me, CHMeEt, M = Na[23];
R = H, R' = Me, n-Pr, $CO_2Me$, $CONH_2$;
R' = Ph, $CO_2Me$, $CONH_2$; R = R' = $CO_2Me$, M = Na, K[24].

Similarly, diethylboryl derivatives of $N$-nitro-compounds have been obtained by the action of diethylboron chloride on silver salts of several nitramines and $N$-nitroamides[25,26]:

$$[RN(NO_2)]Ag + Et_2BCl \xrightarrow[-AgCl]{} [RN(NO_2)]BEt_2 \ .$$

Reaction between silver salts of nitramines and trialkyltin halides yields organotin derivatives of the nitramines[27]:

$$[R'N(NO_2)]Ag + R_3SnX \xrightarrow[-AgX]{} R'N(NO_2)SnR_3$$

R = Me, Et, Ph; R' = Me, Et, iso-Pr, t-Bu, Ph; X = Cl, Br.

Mercuric chloride reacts with the sodium salt of nitromethane to give the mercury salt of the latter[28-30]:

$$2CH_2NO_2Na + HgCl_2 \rightarrow Hg[CH_2NO_2]_2 \ .$$

§There has been a report[18] (without any experimental data) that $\alpha$-nitroalkyl-trimethylsilyl derivatives are formed by the interaction of sodium salts of primary and secondary nitroalkanes "under specific conditions". Also without experimental support Manzur and Zamudio[19] postulate the intermediate formation of trimethylsilyl methanenitronate in the reaction of trimethylchlorosilane with nitromethane in pyridine.

## 2. Nitration of Hetero-organic Compounds

This method is used only to obtain compounds that are resistant to hydrolysis and do not undergo any great oxidative degradation under the influence of nitrating agents. Mainly the nitration of organosulphur compounds has been reported, with the use of acidic nitrating agents and also alkyl nitrates in the presence of bases.

Many $N$-nitrosulphonamides have been obtained by the nitration of arenesulphonamides with nitric acid or a mixture of sulphuric and nitric acids:

$$ArSO_2NHR \rightarrow ArSO_2NRNO_2$$

Ar = Ph, R = Me, Et[31]; Ar = Ph, $p$-$BrC_6H_4$, $m$-$NO_2C_6H_4$, R = Alk $C_3$—$C_7$,
$(CH_2)_9N(NO_2)SO_2Ph$[32,33]; Ar = Ph, $p$-$MeC_6H_4$, 4-Me-3-$NO_2C_6H_3$, R = H, Me, Et[34-36]; Ar = 4-Me-3-$NO_2C_6H_3$,
R = $CH_2CH_2Br$, $CH_2CHBrMe$, $MeCHCH_2Br$[37] .

Nitrogen pentoxide has been used to nitrate the sodium salts of $N$-alkylsulphonamides[38]:

$$[RSO_2NR']Na + N_2O_5 \rightarrow RSO_2N(NO_2)R' + NaNO_3$$

R = Me, Ph, $p$-$MeC_6H_4$; R' = Me, n-Bu, s-Bu, Allyl .

Trismethylsulphonylmethane on treatment with a mixture of nitric and sulphuric acids gives the nitro-derivative in 68% yield[39]:

$$CH(SO_2Me)_3 \xrightarrow{HNO_3+H_2SO_4} NO_2C(SO_2Me)_3 \ .$$

$\alpha$-Nitro-sulphones are obtained in good yield by nitrating alkyl and aryl sulphones with alkyl nitrates in the presence of bases[40,41]:

$$RCH_2SO_2R' \xrightarrow[Nu]{R''ONO_2} RCH(NO_2)SO_2R'$$

R = H, Et, n-Pr, Ph, $p$-$MeOC_6H_4$, $p$-$ClC_6H_4$;
R' = Alk $C_1$—$C_4$, Ph, $PhCH_2$, $p$-$MeC_6H_4$;
R'' = Et, $C_6H_{11}$; Nu = t-BuOK, $KNH_2/NH_3$.

The nitration of sulphonates with alkyl nitrates in the presence of bases has been studied in detail[42,43]. In the suggested reaction scheme

$$RCH_2SO_3CH_2\overset{|}{C}H \xrightarrow[Nu]{R'ONO_2} \left[H_A{-}\overset{|}{C}RSO_3CH_2\overset{|}{C}H_B\right] \rightleftarrows \underset{\underset{O_2NOR'}{\vdots}}{\phantom{x}} \quad (I)$$

$$\rightleftarrows \left[H_ACR(NO_2)SO_3CH_2\overset{|}{C}H_B + R'O^-\right] \quad (II)$$

$$\left[H_B\overset{|}{C}CH_2OSO_2C(NO_2)R\right]^- \quad (III) \qquad RCH_A(NO_2)SO_3^- \quad (IV) + CH_2{=}C\!\!< \quad (V) \qquad (2)$$

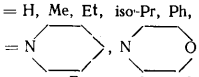
either the normal nitration product (III) or a mixture of compounds (IV) and (V) is formed depending on which proton ($H_A$ or $H_B$) is attacked by the nucleophile $Nu^-$. The composition of the reaction mixture is, of course, determined by the structure of the radical $CH_2CH_B$. In agreement with this, neopentyl sulphonates not containing $H_B$ are smoothly converted into the corresponding nitro-derivatives, whereas the nitration of ethyl and octyl butane-1-sulphonates yields secondary products (potassium 1-nitrobutane-1-sulphonate and oct-1-ene). In full agreement with scheme (2) the nitration of ethyl butane-2-sulphonate does not give the expected ethyl 2-nitrobutane-2-sulphonate but a >50% yield of potassium 2-nitrobutane-2-sulphonate, together with ethyl 3-methylpentane-3-sulphonate[43]:

$$EtCHMeSO_3Et \xrightarrow[2.NH_4Cl]{1.KNH_2/NH_3/EtONO_2} EtC(Me)(NO_2)SO_3K + Et_2CMeSO_3Et \ .$$

Alkyl nitrates can be used also to obtain *NN*-dialkylated α-nitro-sulphonamides¶:

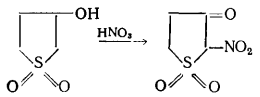
$$RR'CHSO_2NR''_2 + B \xrightarrow[0^\circ]{\text{oxolan}} RR'C^-SO_2NR''_2 \xrightarrow{EtONO_2} \rightarrow RR'C(NO_2)SO_2NR''_2 + EtO^-$$

R = Ph, R′ = H, R″ = Me, B = KH[44];
R = H, Me, Et, iso-Pr, Ph, R′ = H, Me,

$NR''_2$ =  ,

B = t-BuOK, n-BuLi[45].

Nitration is sometimes accompanied by partial oxidation or degradation of the initial organosulphur compound. Thus when acyclic or cyclic 3-hydroxy-sulphones are treated with nitric acid (at 60–90°C), the corresponding 3-keto-2-nitro-sulphones are obtained: e.g. [46]



Several β-keto-sulphides are converted by ethyl nitrate followed by oxidation into the corresponding nitromethyl sulphones [47,48]:

$$RSCH_2COMe + EtONO_2 \xrightarrow{EtONa} RSCH{=}NO_2Na \xrightarrow[AcOH]{H_2O_2} RSO_2CH_2NO_2$$

R = Me, *p*-MeC$_6$H$_4$.

α-Nitroalkylphosphonates have been obtained by nitrating phosphorylated aldehydes, ketones, and β-alkoxy-vinylphosphonates with acetyl nitrate in acetic anhydride[49]:

$$(RO)_2P(O)CH_2COX + AcONO_2 \longrightarrow (RO)_2P(O)CH_2NO_2$$
$$(RO)_2P(O)CH{=}CHOEt + AcONO_2 \longrightarrow \uparrow$$

R = Alk $C_1$—$C_4$; X = H, Me.

### 3. Action of Nitro-compounds on Hetero-organic Derivatives

α-Nitro-derivatives of hetero-organic compounds of many elements—silicon, mercury, thallium, indium, tin, lead, boron, etc.—have been obtained by this method.

Free nitro-compounds and nitramines can be silylated by means of many silylating agents. In particular, functionally substituted mono- and poly-nitro-compounds are silylated in inert aprotic solvents by *NN′*-diphenyl-*N*-trimethylsilylurea:

$$RR'CHNO_2 + PhNHCON(SiMe_3)Ph \rightarrow RR'C{=}N{-}OSiMe_3 + (PhNH)_2CO$$

R=R′=$CO_2Me$[14]; R=$CO_2Me$, R′=H, $NO_2$[50];
R=R′=$NO_2$[16]; R=Me, R′=$NO_2$[17].

This agent was unsuitable for silylating nitroalkanes, for which purpose the stronger donor of a trimethylsilyl group, *NO*-bistrimethylsilylacetamide, was used [17,52]†:

$$RR'CHNO_2 + MeC(OSiMe_3){=}NSiMe_3 \rightarrow RR'C{=}N{-}OSiMe_3 + AcNHSiMe_3$$

R = H, Me, Et, Ph; R′ = H, Me.

Trimethylsilyl derivatives of methylnitramine and *N*-nitro-toluene-*p*-sulphonamide are formed by silylation of the free *N*-nitro-derivatives:

$$RNHNO_2 + Me_3SiX \rightarrow [RN(NO_2)]SiMe_3$$

R = Me[20]; *p*-MeC$_6$H$_4$SO$_2$[22]; X = MeNH, PhNHCONPh, AcNSiMe$_3$.

Lovett [53] patented a method for preparing salts of light metals with trinitromethane, of general formula $MR_n[C(NO_2)_3]_x$ (where M = Li, Be, Mg, B, or Al and R = Alk, $C_6H_5$, aralkyl, or cycloalkyl), to several of which he assigned a covalent structure. These compounds are formed by the action of the metal alkyls on trinitro-methane or halogenotrinitromethanes. However, the absence of experimental data or evidence of the structure of the products casts doubt on the correctness of these results.

Much attention has been paid to the preparation of organomercury nitro-derivatives. Aryl and alkyl derivatives of nitromethylmercury are obviously extremely unstable. Their formation was postulated [54] by the action of nitromethane on phenylmercury hydroxide or bismethyl-mercury oxide, and also by the action of mercury dialkyls on the product of the reaction between mercuric oxide and nitromethane‡. Nevertheless, alkylmercury deriva-tives of polynitroalkanes proved to be comparatively stable compounds [54,55]:

$$R_2Hg + HC(NO_2)_3 \rightarrow RHgC(NO_2)_3$$

R = n-Bu, Ph.

Mercury and silver oxides are convenient starting materials for the preparation of bistrinitromethylmer-cury [56–58], bisfluorodinitromethylmercury [59], and silver derivatives of trinitromethane [60–62]:

$$M_mO + p\text{-}X(NO_2)_2CH \rightarrow M[C(NO_2)_2X]_n$$

M = Hg, X = $NO_2$, F, *m* = 1, *n* = 2;
M = Ag, X = $NO_2$, *m* = 2, *n* = 1.

Intermediate formation of α-nitroalkylplatinates is assumed in the reaction of tetrakistriphenylphosphine-platinum with nitroalkanes [63,64]:

$$Pt(PPh_3)_4 \rightleftarrows Pt(PPh_3)_2 + 2PPh_3$$
$$Pt(PPh_3)_2 \xrightarrow{RR'CHNO_2} \left[ PPh_3,\ C(RR'),\ H{-}Pt,\ O,\ N{=}O,\ PPh_3 \right]$$

R = H, Me; R′ = H, Me.

The preparation has been described of α-mono- and α-poly-nitroalkyl derivatives of thallium [65–67], and also that of α-mononitroalkyl derivatives of indium [68]:

$$R_3M + HC(NO_2)R'_2 \rightarrow R_2MC(NO_2)R'_2 + RH$$

M = Tl, In, R = Me, Et, R′ = H, Me;
M = Tl, R = Et, R′ = $NO_2$, Cl, F.

Good yields of organotin derivatives of nitramines are obtained by the action of a tetra-alkylstannane or bis-trialkylstannyl oxide on primary nitramines [27]:

$$2R'NHNO_2 + (R_3Sn)_2O \rightarrow 2R'N(NO_2)SnR_3 + H_2O$$

R = iso-Pr, R′ = Me, t-Bu;

$$R'NHNO_2 + R_4Sn \rightarrow R'N(NO_2)SnR_3 + RH$$

R = Et, R′ = Me, iso-Pr.

¶ Yet *NN*-dialkyl-α-nitroalkanesulphonamides could not be obtained by nitrating alkanesulphonamides with nitric acid or ethylenesulphonamides with nitrogen sesquioxide [44].

†On silylating nitromethane with *NN′*-diphenyl-*N*-tri-methylsilylurea, Klebe [51] isolated bistrimethylsilyl methazonate. He assumed that trimethylsilyl methane-nitronate was an intermediate in this reaction.

‡ The nitromethyl-phenylmercury described by Petukhov [30] was actually phenylmercury fulminate [54]:

$$PhHgOH + MeNO_2 \rightarrow [PhHgCH_2NO_2] \rightarrow PhHgONC + H_2O.$$

Several hetero-organic derivatives of amines react with nitro-compounds[69-71]§:

$$L_mM(NR_2)_n + nR'R''CHNO_2 \rightarrow L_mM(O{-}N{=}CR'R'')_n + nR_2NH$$
$$\downarrow O$$

R = Me, Et, $SiMe_3$; R′ = H, Me; R″ = H, Me; L = Me, Et; M = Sn, Pb ($n = 1$, $m = 3$), Hg ($n = m = 1$).

Triethylboron reacts with α-nitroalkenes to form diethylboryl alkanenitronates[73]:

$$2R'CH{=}C(NO_2)R + 2BEt_3 \rightarrow \left[R'CH(Et)CR{=}N\begin{matrix}O\\ \diagdown\\ OBEt_2\end{matrix}\right]_2$$

R=R′=Me; R=Me, R′=Et; R= iso-Pr, R′=Me.

## 4. Replacement of Halogen in Halogenated Nitro-compounds

The first synthesis of an α-nitrohetero-organic compound from a halogenonitro-compound was accomplished in 1872, when nitromethanedisulphonic acid $NO_2CH(SO_3H)_2$ was obtained[74] from picryl chloride and potassium sulphite. The formation of this product was probably due to development of the properties of a "positive" halogen by one of the chlorine atoms. Reaction between chloronitro-compounds and sodium or ammonium sulphite has been successfully used also to obtain salts of other sulphonic acids[44,75]:

$$RR'C(NO_2)Cl + M_2SO_3 \rightarrow RR'C(NO_2)SO_3M \xrightarrow{HCl} RR'C(NO_2)SO_3H$$

where M = K or $NH_4$ and R, R′ = H, Alk, cycloalkyl, $C_6H_5$, or a heterocyclic radical.

Studies have been made on the reactions of picryl chloride and bromide with mercapto-derivatives of thiazole and thiadiazole[76,77], aliphatic and aromatic thiols[78], and also alkali-metal sulphides and sodium hydrogen sulphide[79]. It was assumed that derivatives of nitrotrithio-orthoformic esters $(RS)_3CNO_2$ or mercapto-derivatives of the type $(HS)_3CNO_2$ were formed as intermediates. Mono- and di-bromonitro-methane and also -ethane react similarly with arenethiols in alkaline medium[80]. However, intermediate sulphur-containing α-nitro-derivatives were neither isolated nor identified[76-80].

Halogenonitroalkanes have been successfully used to obtain α-nitro-sulphones[1,81-84]:

$$RR'C(NO_2)X + R''SO_2Na \rightarrow R''SO_2CRR'(NO_2) \quad (3)$$

R and R′=H, Alk $C_1$–$C_3$, $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$; R″ = Ph, p-$MeC_6H_4$, p-$BrC_6H_4$, $C_{10}H_7$; X=Cl, Br, I.

It is interesting that one of the nitro-groups in a polynitro-compound may play the part of a halogen[84]:

$$Me_2C(NO_2)_2 + PhSO_2Na \rightarrow Me_2C(NO_2)SO_2Ph \quad . \quad (4)$$

Kornblum et al. have shown[84] that reactions (3) and (4) have a radical-anion mechanism:

$$Me_2CI(NO_2) + PhSO_2^- \rightarrow Me_2CI(NO_2)^{\cdot-} + PhSO_2^{\cdot}$$
$$Me_2CI(NO_2)^{\cdot-} \rightarrow Me_2C(NO_2)^{\cdot} + I^-$$
$$Me_2C(NO_2)^{\cdot} + PhSO_2^- \rightarrow [Me_2C(NO_2)SO_2Ph]^{\cdot-}$$
$$[Me_2C(NO_2)SO_2Ph]^{\cdot-} + Me_2C(NO_2)I \rightarrow Me_2C(NO_2)SO_2Ph + Me_2CI(NO_2)^{\cdot-} \quad .$$

§Products of undetermined structure had earlier been isolated[72] from the reaction of a dialkylaminotrialkyltin with nitromethane.

The one-electron oxidation of diphenylmercury by tetranitromethane or a halogenotrinitromethane in solvents of various polarities—acetonitrile, sulpholan, chloroform—yields phenyltrinitromethylmercury[85]:

$$Ph_2Hg + C(NO_2)_4 \rightarrow [Ph_2Hg^+C(NO_2)_4^{\cdot-}] \rightarrow Ph^{\cdot} + NO_2^{\cdot}$$
$$\downarrow \qquad\qquad\qquad\qquad \downarrow RH \quad \downarrow$$
$$PhHgC(NO_2)_3 \qquad\qquad C_6H_6 \quad N_2O_4 \quad .$$

Reaction of triphenylphosphine with a bromonitroalkane involves intermediate formation of an α-nitroalkylphosphonium bromide, but different workers interpret differently the further changes undergone by these products[80,86-89].

Trialkyl phosphites and dialkyl phosphorohalidites obviously form with halogenonitroalkanes unstable products of the type $>P(:O).O.N(\rightarrow O):CCR'$,[90] but no evidence has been given[80,89,90] for the structure of the unstable nitro-derivatives.

## 5. Other Methods of Preparation

Other reactions are known that result in the formation of α-nitrohetero-organic compounds. Thus nitromethane and nitrocyclohexane are sulphonated by the dichloroethane, pyridine, and dioxan complexes of sulphur trioxide[91] to give insignificant yields of sulphonated products.

α-Nitroalkanesulphonyl chlorides were obtained[92] by the photochemical chlorosulphonation of $C_{1-10}$ aliphatic nitro-compounds:

$$RCH_2NO_2 + SO_2 + Cl_2 \xrightarrow{h\nu} NO_2CHR(SO_2Cl) \quad .$$

However, no physical constants of the products isolated were given, and attempts to repeat this reaction have been unsuccessful[44].

Acyl esters of dinitromethanenitronic acid are converted by treatment with 2,4-dinitrobenzenesulphenyl chloride into 2,4-dinitrophenyl trinitromethyl sulphide[93]:

$$(NO_2)_2C{=}N\begin{matrix}O\\ \diagdown\\ OCOR\end{matrix} + (NO_2)_2C_6H_3SCl \rightarrow (NO_2)_2C_6H_3SC(NO_2)_3 \quad .$$

Reaction of sodium toluene-*p*-sulphinate with the potassium salts of nitroalkanes and iodine in dimethylformamide yields α-nitro-sulphones[12]:

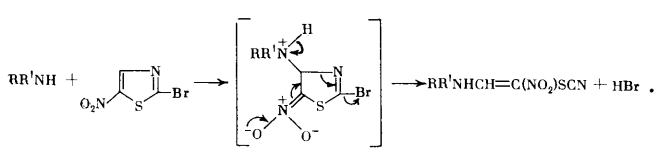
$$p\text{-}MeC_6H_4SO_2Na + RR'C{=}NO_2K + I_2 \rightarrow p\text{-}MeC_6H_4SO_2C(NO_2)RR'$$
R=H, Me, R′=H, Me, Et; RR′=$(CH_2)_5$ .

A simple method for obtaining α-nitroisoalkylphosphonates is to oxidise the α-aminoisoalkylphosphonates[49]:

$$(RO)_2P(O)CRMeNH_2 \xrightarrow{KMnO_4} (RO)_2P(O)CRMeNO_2 \quad .$$
R=Me, Et

Silver salts of polynitroalkanes are obtained from other salts of these compounds by the action of silver nitrate[60,94-97].

Sterically hindered secondary aliphatic amines open the ring of a substituted nitrothiazole to give 2-dialkylamino-1-nitrovinyl thiocyanates[98]:




Several workers have postulated the formation of unstable α-nitrohetero-organic compounds. This has

been assumed in particular in the reaction between nitromethane and aluminium tribromide [99]:

$$AlBr_3 \cdot MeNO_2 + MeNO_2 \rightleftarrows \left\{ CH_2{=}N\overset{O}{\diagup\diagdown}OAlBr_2 \cdot MeNO_2 + HBr \right\}.$$

A mixture of products $(NO_2CH_2)_nSnCl_{4-n}$ ($n = 1-3$) is supposed to be formed when nitromethane acts on tin tetrachloride in a primary amine [100]. Formation of the radical-anions

$$O_3SCH_2NO_2^{\cdot-}, SCH_2NC_2^{\cdot-}$$

$$O_3PCH_2NO_2^{\cdot-}, O_2P(H)CH_2NO_2^{\cdot-}, O_2AsCH_2NO_2^{\cdot-}.$$

has been recorded [101] when certain radicals add to the anion of aci-nitromethane.

### 6. Synthesis of α-Nitro-ylides

α-Nitro-ylides of triphenylarsenic have been obtained by the reactions [102,103]

$$\begin{aligned} &Ph_3AsCl_2 + PhCH_2NO_2 \xrightarrow[C_6H_6]{Et_3N} Ph_3As{=}C(NO_2)Ph \\ &Ph_3AsO + MeNO_2 \longrightarrow \begin{cases} \xrightarrow{Ac_2O} Ph_3As{=}C(NO_2)Ac \\ \xrightarrow[P_2O_5]{Et_3N} Ph_3As{=}CH(NO_2) \end{cases} \end{aligned} \qquad (5)$$

for which the mechanism

$$Ph_3AsO + Ac_2O \rightarrow [Ph_3As^+OAc] \xrightarrow{CH_2NO_2^-} [Ph_3As^+CH_2NO_2] + OAc^- \xrightarrow{-H^+} Ph_3As^+{-}\bar{C}HNO_2 \leftrightarrow Ph_3As{=}CHNO_2$$

has been suggested. The corresponding α-nitro-ylides of phosphorus were unstable compounds [102]. The product of the decomposition of trimethylsilyl dinitromethanenitronate $[C(NO)NO_2]$ has been detected as the ylide with triphenylphosphine [16]:

$$Ph_3P + [C(NO)NO_2] \rightarrow Ph_3P^+[C(NO_2)NO]^-.$$

When dimethyl sulphoxide was treated with dinitromethane in the presence of acetic anhydride, the corresponding αα-dinitro-ylide of sulphur $(CH_3)_2S^+{-}C^-(NO_2)_2$ was obtained [104].

## III. ESTABLISHMENT OF STRUCTURE

Elementotropism is now known in many classes of organic compounds. Therefore any α-nitrohetero-organic compound can in principle exist as an equilibrium tautomeric mixture:

$$\underset{\text{"O-form"}}{\diagup C{=}N\overset{O}{\diagdown}OElR_n} \text{ or } \underset{\text{"O-form"}}{-N{=}N\overset{O}{\diagdown}OElR_n} \rightleftarrows \underset{\text{"C" or "N-form"}}{\diagup C(NO_2)ElR_n} \text{ or } \underset{\text{"C" or "N-form"}}{-N(NO_2)ElR_n} \qquad (6)$$

$$\diagup C(NO_2)^- ElR_n^+ \text{ or } [-N(NO_2)]^- ElR_n^+$$

The presence of a particular form and the position of the equilibrium (6) are, of course, determined both by the nature of the element and by the structure of the nitro-containing group. Furthermore, it must be borne in mind that the compound isolated may be either kinetically or thermodynamically preferred. In most cases the nature of the product has not been firmly established¶.

¶Products of the sulphenylation of mono- and polynitro-compounds are kinetically preferred, since their structure depends on the nature of the sulphenylating reagents as well as on the process conditions [2,7].

In view of the above considerations neither the chemical reactions nor the method of preparation can be a criterion in establishing the structure of α-nitrohetero-organic compounds, but at best merely enable one form to be identified. Therefore only a combined study by physicochemical methods will establish the structure. Confirmation of a structure is obtained by comparing spectroscopic characteristics with corresponding properties of model compounds. However, such correspondence must be approached extremely cautiously, since the introduction of an element in the α position with respect to a nitro-group may itself distort appreciably the properties of the model. The choice of method for proving the structure is, of course, determined by the nature of the element adjacent to the nitro-group. Much published information on this question appears to be incorrect, and requires critical review.

### 1. Physicochemical Methods

Papers have appeared during recent years on the use of ultraviolet, infrared, and nuclear magnetic resonance spectroscopy to investigate the structure of α-nitrohetero-organic compounds. Reports of the use of Mössbauer spectroscopy, mass spectrometry, or nuclear quadrupole resonance are considerably less frequent.

*(a)* Electronic absorption spectra

Polynitro-compounds and functionally α-substituted nitro-compounds exhibit marked differences in the ultraviolet spectra of anions, *O*-derivatives (alkyl esters of the corresponding nitronic acids), and true nitro-compounds [105,106], which may be used to determine the structure of α-nitrohetero-organic compounds derived from them. Nevertheless, the differences between the ultraviolet spectra of anions and *O*-derivatives have largely levelled off with mononitroalkanes and nitramines, so that it is difficult to use ultraviolet spectroscopy to determine the structure of α-nitrohetero-organic compounds obtained from them.

Kharasch and Cameron [3] regarded 2-chloroethyl and *p*-tolyl 1-nitroethyl sulphones as true nitro-compounds, having shown that their far ultraviolet spectra were similar to the ultraviolet spectrum of nitroethane. The intense absorption maximum in the range 290–320 nm, characteristic of alkyl esters of substituted nitromethanenitronic acids, is absent from the ultraviolet spectra of sulphides of general formula $RC(NO_2)_2SR'$ (R = H, $CH_3$, $NO_2$ and R' = H, $CH_3$, 2,4-$(NO_2)_2C_6H_3$, *p*-$CH_3OC_6H_4$, *p*-$NO_2C_6H_4$) [6,7], which indicates that the above polynitroalkyl sulphides are *C*-nitro-derivatives. When the sulphenylating agent was changed, however, other products were isolated, regarded as *O*-derivatives on the basis of their ultraviolet spectra [7].

Electronic absorption spectra have been used to investigate trialkylsilyl derivatives of aliphatic nitro-compounds. These products can be regarded as nitronic esters, since the ultraviolet spectra of $RR'C{:}NO.OSi(CH_3)_3$ contain a characteristic absorption maximum ($\lambda_{max}$ = 240 nm for R, R' = H, Alk [17,52] and 265–315 nm for R, R' = $COOCH_3$, $NO_2$, CN [14-16,50], with lg $\epsilon$ = 3.7–4.0), coinciding with a maximum in the corresponding standard alkyl nitronates [107-109].

The ultraviolet spectra of diethylboryl derivatives of nitroalkanes contain a maximum at $\lambda$ = 228–235 nm ($\epsilon$ = 10200–10700), [23,73] which is consistent with their suggested structure as dialkylboron nitronates.

Degrees of ionisation in solution have been determined for several α-nitrohetero-organic compounds from their molar extinction coefficients. It has been shown in particular that bistrinitromethylmercury has a covalent structure in solvents of low polarity[110,111]. Its complexes may be either *C*-derivatives or ionic compounds depending on the nature of the ligand[112,113]. Bisfluorodinitromethylmercury is almost completely unionised in solvents of various polarities (dimethylformamide, acetonitrile, acetone, alcohol).[111] Silver salts of polynitroalkanes are assumed[60,114,115] also to be covalent in several aprotic solvents†

Trinitromethyl derivatives of diethylthallium are completely ionised both in protic and in aprotic solvents. However, equilibrium between ionic and covalent forms is assumed[67] for diethylthallium derivatives of *gem*-dinitroalkanes in weakly ionising solvents:

$$Et_2Tl^+A^- \rightleftarrows Et_2Tl{-}A$$
$$A{=}CH(NO_2)_2,\quad C(NO_2)_2Me.$$

Ultraviolet spectra have been determined[103] for α-nitro-ylides of triphenylarsenic. The ultraviolet spectrum of $(C_6H_5)_3As:CHNO_2$ contains three maxima—at 223 nm (lg ε = 4.39), 265 nm (3.76), and 298 nm (3.81)—and that of $(C_6H_5)_3As:C(NO_2).COCH_3$ has two maxima—at 222 nm (4.40) and 315 nm (4.06).

(*b*) Infrared and Raman spectra

The method of infrared and Raman spectroscopy enables the structure of an α-nitrohetero-organic compound to be established not only in solution but also in the crystalline state. A rigorous choice between true nitro-compounds and anions or nitronic esters can be based on the infrared spectra of derivatives of nitroalkanes[109,117-119]. In true nitroalkanes the $\nu_{as}$ band of the nitro-groups lies in the range 1530–1560 $cm^{-1}$, whereas the C=N stretching vibration lies between 1585 and 1620 $cm^{-1}$‡. In the Raman spectra of nitroalkanes the $\nu_{as}$ vibration of the nitro-group is usually apparent as a weak depolarised line, whereas $\nu_{C:N}$ is seen as a strong polarised band. From this it may be concluded that infrared spectroscopy permits *C*-derivatives of α-nitrohetero-organic compounds to be distinguished from nitronic esters or ionic compounds§. Nevertheless, it is difficult on the basis of the infrared spectra to choose between hetero-organic *O*-derivatives of nitroalkanes and ionic structures.

Introduction of an electronegative functional substituent (including a nitro-group) in an α position with respect to the nitro-group in a nitroalkane shifts the $\nu_{as}$ band of the latter group to higher frequencies[119,120], while the C:N stretching vibration in an *O*-alkyl derivative may move to lower frequencies[14]. As a result the $\nu_{as,NO_2}$ and $\nu_{C:N}$ ranges overlap, and sharp demarcations can no longer be made from the infrared spectra between *C*- and *O*-derivatives of such nitro-compounds (including α-nitro-hetero-organic compounds). It may be supposed that the Raman spectra preserve the difference between these structures, but this question has not yet been examined experimentally. With functionally substituted α-nitro-hetero-organic compounds, on the other hand, infrared spectroscopy enables a clear choice to be made between ionic and covalent structures, since very significant differences are evident in the infrared and Raman spectra of corresponding nitro-compounds and their salts[117].

In the infrared spectra of silyl alkanenitronates the $\nu_{C:N}$ band is located in the range 1617–1622 $cm^{-1}$, which differs by 40–60 $cm^{-1}$ from $\nu_{as}$ for the nitro-group in the corresponding nitroalkanes. The $\nu_{C:N}$ band is strongly developed also in the Raman spectra of the products[17,52]. The introduction of electronegative substituents into methanenitronic acid shifts the $\nu_{C:N}$ band to shorter wavelengths (1595–1605 $cm^{-1}$), where it almost coincides with $\nu_{as,NO_2}$ in the corresponding nitro-compounds. Several silyl derivatives of functionally substituted nitro-compounds exhibit an intense $\nu_{C:N}$ band in the Raman spectra[14,15,17,50].

The infrared and Raman spectra of trialkylmetal nitronates of general formula $R'R''C:NO.OMR_3$ (where $R = CH_3$, $C_2H_5$, n-$C_4H_9$; $R' = R'' = H$, $CH_3$; $R' = H$, $R'' = CH_3$; and M = Sn, Pb) are almost identical with those of salts of the corresponding nitro-compounds[121], so that the structure of *C*-derivatives was rejected for these products. Analysis of the spectra of compounds in which $R = CH_3$ established[121] that the $MC_3$ group has $D_{3h}$ symmetry.

In the infrared spectra of diethylboron dialkylated methanenitronates the C:N stretching band appears at 1630–1645 $cm^{-1}$.[23,73] The infrared spectrum of the diethylboron derivative of methyl α-nitropropionate indicates that the boron atom is attached to the carbonyl oxygen atom by a donor–acceptor bond[24], which moves $\nu_{C:O}$ by more than 150 $cm^{-1}$ to lower frequencies. Yet coordination of boron with the carbonyl group is probably absent from diethylboron derivatives of amides of α-nitro-acids, the boron being coordinated with the amide nitrogen atom[24].

Bands characteristic of anions of nitro-compounds are absent from the infrared spectra of the mercury salts of nitromethane[122] and trinitromethane[110,123,124] and from those of many complexes of the mercury salt of trinitromethane[112]; all these products are regarded as *C*-derivatives. Yet the infrared spectra of crystalline polynitromethyl derivatives of thallium[66,67] and silver[60,114,115] are almost identical with those of the potassium salts, which indicates that the products have an ionic structure. However, infrared spectroscopic data suggest that the silver salts of polynitroalkanes are not ionised in certain solvents[60].

Bands characteristic of covalent true nitro-compounds are present in the infrared spectra of α-nitroalkyl sulphones[40,43,84,125] and poly-α-nitroalkyl sulphides[6]. Bands due to the nitro-group and to carbonyl have shifted to lower frequencies in the infrared spectra of nitro-ylides of arsenic having the general formula $(C_6H_5)_3As:CR.NO_2$ (where $R = H$, $COCH_3$): $\nu_{s,NO_2}$, $\nu_{as,NO_2}$, and $\nu_{C:O}$ are respectively 1208, 1395, and 1595 $cm^{-1}$.[103] Spectral data are available also for trichloromercapto-derivatives of arylhydrazones of nitroformaldehyde[8] and for thiocyanates of general formula $R'RNCH:C(NO_2)SCN$ in which R, R' = n-$C_3H_7$, iso-$C_3H_7$, $C_6H_5CH_2$, $[CH_2]_5$, $[CH_2]_7$, etc.[98].

For alkylnitramine derivatives infrared spectroscopy in principle enables a choice to be made between *O*-forms, *N*-forms, and ionic compounds. The infrared spectra of primary and secondary nitramines contain $\nu_{s,NO_2}$ bands at

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†Nielsen[116] cites several references to the preparation of covalent salts of heavy metals, but these results cannot be regarded as entirely reliable.

‡This conclusion cannot be extended to derivatives of nitromethane[117].

§It may be assumed that, under the influence of electropositive elements—boron, silicon, tin, etc.—the $\nu_{as}$ vibration of the nitro-group will undergo further displacement to lower frequencies, which should facilitate identification of the α-nitrohetero-organic compound.

1310–1340 $cm^{-1}$ and $\nu_{as,NO_2}$ bands at 1570–1590 and 1510–1550 $cm^{-1}$ respectively[117,126,127]. Furthermore, those of *O*-alkyl derivatives of alkylnitramines are characterised by two intense bands at 1240–1260 $cm^{-1}$ and 1545–1570 $cm^{-1}$.[128] The presence of two stereoisomers splits the shorter-wavelength band, whose shorter-wavelength shoulder corresponds to the *cis*-isomer of the *O*-derivative[129]. Anions of alkylnitramines are characterised by the $\nu_{s,NNO_2}$ band in the range 1400–1500 $cm^{-1}$.[127] It is thus obvious that ionic structures of derivatives of nitramines are easily distinguished by means of the infrared spectra from covalent structures, and a choice between *O*- and *N*-forms can be based on the $\nu_s$ band of the nitro-group. It must be remembered, however, that the positions of characteristic bands in the infrared spectra of nitramine derivatives depend significantly on the conditions under which the spectra are determined¶, so that special attention must be paid to comparing the spectra of specimens recorded under closely similar conditions.

It may be expected from general considerations that the characteristic bands of the *O*-forms and ionic structures of α-nitrohetero-organic compounds will not differ significantly from the corresponding bands in the analogous alkyl derivatives, whereas the introduction of a heteroatom α to the nitro-group in the *N*-form may produce considerable shifts in the $\nu_s$ and $\nu_{as}$ bands of the nitro-group.

In conformity with this the *O*-trialkylsilyl derivatives of methylnitramine exhibit intense bands at 1250–1270 and 1550–1560 $cm^{-1}$.[20,130] In the *N*-trialkylsilyl derivatives, however, the $\nu_{as,NO_2}$ band appears in the range 1500–1510 $cm^{-1}$: i.e. it has undergone a low-frequency shift of $>70$ $cm^{-1}$ in comparison with methylnitramine†. The low-frequency shift of $\nu_{s,NO_2}$ in these compounds is considerably smaller: in trialkylsilyl derivatives of methylnitramine this band appears around 1300 $cm^{-1}$.[20,130] Similarly, in the pyridine complex of diethylborylmethylnitramine the $\nu_{as}$ band of the nitro-group has been displaced to lower frequencies than in methylnitramine by about 100 $cm^{-1}$.[25]

Organotin derivatives of alkylnitramines of general formula $R'N(NO_2)SnR_3$ (R = Alk, $C_6H_5$, and R′ = Alk) are assumed[27] to have the structure of *N*-derivatives with the tin atom coordinated with an oxygen atom of the nitro-group. The infrared spectra of these compounds do not contain in the region of 1550 $cm^{-1}$ bands due to N=N(→O).O–vibrations, nor bands typical of alkali-metal salts of primary nitramines‡.

The structure of an *O*-derivative has been assigned to the trimethylsilyl derivative of *N*-nitrotoluene-*p*-sulphonamide, since its infrared spectrum does not contain the $\nu_{s,NO_2}$ band (1280–1290 $cm^{-1}$) characteristic of *N*-alkyl-*N*-nitrosulphonamides, while bands found with the standard *O*-isopropyl derivative of *N*-nitrotoluene-*p*-sulphonamide are present[22].

¶In solvents $\nu_{as,NO_2}$ shifts to higher frequencies, but $\nu_{s,NNO_2}$ to lower frequencies.

†The spectra of the trialkylsilyl derivatives of methylnitramine were determined in dichloromethane.

‡According to the infrared spectra data, however, an ionic structure cannot be completely excluded for these products.

(*c*) Nuclear magnetic resonance spectroscopy

This method is probably the most informative with respect to the structure of α-nitrohetero-organic compounds, but hitherto has not been sufficiently widely used, and then mainly as proton magnetic resonance. Analysis of hetero-organic derivatives of aliphatic nitro-compounds is usually based on the chemical shifts of protons $\delta_H$ attached to α- and β-carbon atoms (relative to the nitro-group), the $J_{El-H}$ constants in the El–$CH(NO_2)$– group, and also the shifts $\delta_H$ of protons attached to the heteroatom. The principal $^1H$ n.m.r. spectroscopic data for the hetero-organic derivatives of aliphatic nitro-compounds are listed in Table 1, which includes corresponding values for model nitro-compounds. The signals from protons attached to α- and β-carbon atoms in nitronic esters and nitroalkane salts exhibit down-field shifts relative to the analogous signals in the corresponding *C*-nitro-derivatives.

It may be assumed that the introduction, at an α position with respect to the nitro-group in the *C*-form, of an element of electronegativity less than that of hydrogen–lead, tin, mercury, thallium, silicon, boron—will produce an up-field shift in the signals of corresponding protons[131], whereas the introduction of such groups into the *O*-form or especially into an ionic structure should not significantly change the $\delta_H$ of the protons in comparison with the model compounds. Hence it should be easy by means of $^1H$ n.m.r. data to distinguish covalent *C*-derivatives of α-nitrohetero-organic compounds from the corresponding *O*-derivatives, provided that they contain one of the above six elements, as is confirmed by Table 1. Compounds No. 1–24 are *O*-derivatives, and therefore in most of them the signals due to protons attached to α- and β-carbon atoms are displaced down-field relative to those of the corresponding nitro-compounds§. Compound No. 4 was regarded[65] as a *C*-derivative, but the methylene proton chemical shifts and certain other criteria indicate that it is undoubtedly an *O*-derivative.

The introduction of hetero-organic groups of electronegativity exceeding that of hydrogen into an α position relative to the nitro-group should shift the signals of α or β protons down-field[131]. In agreement with this the signals of these protons in α-nitroalkyl sulphones[40,44,45,84,125] and α-nitroalkanesulphonates[43] are considerably displaced down-field relative to those of analogous protons in nitro-compounds, and almost coincide in the value of $\delta_H$ with the signals of α and β protons in *O*-alkyl derivatives of closely related nitronic acids. In the spectra of *C*-derivatives of α-nitrohetero-organic compounds containing thallium, mercury, and certain other elements a spin–spin interaction should be evident between the element and the α or β proton[138]. The absence of such an interaction for compounds No. 2, 4, 6, 11, and 13 in Table 1 finally eliminates the *C*-derivative structure for them.

Study of the dependence of $\delta_H$ for trimethylstannyl on the nature of the element with which this group is combined reveals[71] that the shift in compounds No. 2, 6, and 11 corresponds exactly with $\delta_H$ for $(CH_3)_3Sn$–O– and differs considerably from that for $(CH_3)_3Sn$–C. However, a cautious approach must be adopted towards such analogies, since the introduction of the very electronegative and anisotropic nitro-groups may distort the picture.

§The abnormally low value of $\delta_{CH_3}$ for compound No. 9 was noted by the authors themselves[71].

Table 1. Proton magnetic resonance data for α-nitrohetero-organic compounds.

| No. | Compound* | δ, ppm** CH=N or CH—$NO_2$ | δ, ppm** $CH_3C$=N or $CH_3C$—$NO_2$ | Ref. | Model cpd. | δ, ppm | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | $R_3PbON(O)$=$CH_2$; R=Me, Et | 5.4—5.5 | — | 71 | $CH_3NO_2$ | 4.28 | 133 |
| 2 | $R_3SnON(O)$=$CH_2$; R=Me, Et | 5.5—5.6 | — | 71 | $[CH_2NO_2]^-$ in $H_2O$ | 5.83 | 133 |
| 3 | $Me_3SiON(O)$=$CH_2$ | 5.55 | — | 52, 132 | | | |
| 4 | $Et_2TlCH_2(NO_2)$*** | 5.35 | — | 65 | | | |
| 5 | $R_3PbON(O)$=$CHCH_3$; R=Me, Et | 5.7 | 1.7—1.9 | 71 | $CH_3CH_2NO_2$ | 1.48 ($CH_3$); 4.38 ($CH_2$) | 134 |
| 6 | $R_3SnON(O)$=$CHCH_3$; R=Me, Et | 5.96 | 1.83 | 71 | $[CH_3CHNO_2]^-$ | 1.73 ($CH_3$); 6.14 (CH) | 135 |
| 7 | $Me_3SiON(O)$=$CHCH_3$ | 6.05 | 1.84 | 52, 132 | $CH_3CH$=N(O)$OCH_3$ | 1,9 and 1.8 ($CH_3$) | |
| 8 | $Et_2BON(O)$=$CHCH_3$**** | 6.95 | 2.0 | 24 | | 5,9 and 3.2 (CH) | 135 |
| 9 | $Me_3PbON(O)$=$C(CH_3)_2$ | — | 1.35 | 71 | $(CH_3)_2CHNO_2$ | 1.57 ($CH_3$); 4.58 (CH) | 134 |
| 10 | $Et_3PbON(O)$=$C(CH_3)_2$ | — | 1.95 | 71 | | | |
| 11 | $R_3SnON(O)$=$C(CH_3)_2$; R=Me, Et | — | 1.9 | 71 | | | |
| 12 | $Me_3SiON(O)$=$C(CH_3)_2$ | — | 1.9 | 5, 132 | | | |
| 13 | $EtHgON(O)$=$C(CH_3)_2$ | — | 1.95 | 71 | | | |
| 14 | $Et_2BON(O)$=$C(CH_3)_2$ ***** | — | 2.1 | 23 | | | |
| 15 | $Me_3SiON(O)$=CHPh | 6.74 | — | 52, 132 | | | |
| 16 | $Et_2BON(O)$=C(CH)$_3$Ph | — | 2.49 | 24 | | | |
| 17 | $Me_3SiON(O)$=CHBr | 6.96 | — | 132 | | | |
| 18 | $Me_3SiON(O)$=$CH(CO_2Me)$ | 6.33 | — | 50, 132 | $CH_2(NO_2)CO_2CH_3$ | 5.35 ($CH_2$) | 24 |
| 19 | $Et_2BON(O)$=$CH(CO_2Me)$ | 6.82 | — | 24 | $CH(CH_3)(NO_2)CO_2CH_3$ | 1.75 ($CH_3$); 5.15 (CH) | 24 |
| 20 | $Et_2BON(O)$=$C(CH_3)(CO_2Me)$ | — | 2.1 | 24 | $CH(NO_2)(CH_3)CONH_2$ | 1.7 ($CH_3$); 5.45 (CH) | 24 |
| 21 | $Et_2BON(O)$=$CH(CONH_2)$ | 6.85 | — | 24 | $CH(CO_2Me)$=N(O)$OCH_3$ | 6.43 and 6.79 (CH) | 136 |
| 22 | $Et_2BON(O)$=$C(CONH_2)CH_3$ | — | 2.13 | 24 | | | |
| 23 | $Me_3SiON(O)$=$CHNO_2$ | 8.25 | — | 50, 132 | $CH_2(NO_2)_2$ | 6.1 | 134 |
| 24 | $Me_3SiON(O)$=$C(CH_3)NO_2$ | — | 2.55 | 132 | $CH_3CH(NO_2)$ | 2.18 ($CH_3$); 6.28 (CH) | 134 |
| 25 | $Ph_3As$=$CH(NO_2)$ | 7.6 | — | 103 | $CH_2$=$CH(NO_2)$ | 7.12 (CH) | 137 |

*Solution in tetrachloromethane at 20 or 35°C.

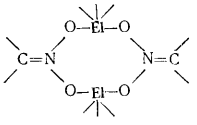
**Here and subsequently chemical shifts are given on the δ scale in all n.m.r. spectra. The standards adopted were tetramethylsilane for $\delta_H$, $\delta_{13C}$, and $\delta_{29Si}$; nitromethane for $\delta_{14N}$ and $\delta_{15N}$; and boron trifluoride–diethyl ether for $\delta_{11B}$.

***Solution in acetonitrile; structure according to Ref. 65.

****Solution in dichloromethane at −20°C; the product has a dimeric structure.

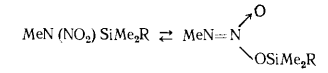
*****The product has a dimeric structure.

It is interesting that the α-nitrohetero-organic compounds listed in Table 1 do not exhibit non-equivalence of protons in α and β positions relative to the C=N(→O).O group, although such non-equivalence is very strongly developed in the corresponding *O*-alkyl derivatives. The averaging of the signals of α and β protons is attributed in trialkylsilyl derivatives to rapid exchange of the trialkylsilyl group between the two oxygen atoms of the O–N → O group[132,139], but in trialkyl-tin and -lead nitronates[71] it is due to the formation of symmetrical dimeric structures.



(see further in this subsection and also under *d*). In diethylboryl derivatives of nitroalkanes the averaging of the signals is also due to the formation of stable dimers[23,73], but in dialkylboryl methoxycarbonyl- and carbamoylmethanenitronates only the *cis*-isomer of the nitronic ester is present in the reaction mixture, owing to coordination of the boron atom with the functional group[24]. In diethylboryl dimethoxycarbonylmethanenitronate rapid intramolecular transfer of the diethylboryl radical from one methoxycarbonyl group to the other has been established by proton magnetic resonance, and several kinetic parameters of the process have been determined[24].

The proton magnetic resonance spectra of α-nitrohetero-organic derivatives of nitramines do not permit a choice between *O*- and *N*-forms, since the $\delta_H$ ranges in the corresponding model compounds overlap[37]. However, use of this method to study dynamic processes in such compounds has established the presence of tautomerism in trialkylsilyl derivatives of methylnitramine[20,130]:



Appreciable displacement of this equilibrium in favour of the *O*-form is produced by rise in temperature and by the substituents R in the sequence t-$C_4H_9$ ≫ iso-$C_3H_7$ > $CH_3$ > H.

Heteronuclear magnetic resonance has hitherto been used mainly to analyse organosilyl and diethylboryl derivatives of nitro-compounds and nitramines. Table 2 shows that the α-carbon-13 signals are located in higher fields in aliphatic mononitro-compounds than in corresponding salts and *O*-alkyl derivatives. Published data suggest that, as in the $^1H$ n.m.r. spectra, replacement of a proton α to a nitro-group by an element of lower electronegativity should produce a diamagnetic shift in the α-carbon-13 signal[142], whereas the replacement of alkyl in an *O*-derivative by a hetero-organic group should not affect significantly the chemical shift $\delta_\alpha$-$^{13}C$. The signal from the α-carbon atom will then distinguish covalent *O*- and *C*-derivatives of α-nitrohetero-organic compounds (it is more difficult to distinguish *O*-derivatives from ionic structures). It is evident that this holds for compounds 1–9 in Table 2. However, the α-carbon-13 signal from compound No. 10, which according to ultraviolet spectral data is a *C*-derivative[112,113], is located considerably down-field from the signals for trinitromethane and trinitroethane. This suggests that the proposed criterion cannot be used to interpret the structures of α-nitrohetero-organic derivatives of polynitro-compounds.

Among other peculiarities of the $^{13}C$ n.m.r. spectra of α-nitrohetero-organic compounds is firstly their temperature dependence determined e.g. for compound No. 4, which indicates rapid exchange of the trimethylsilyl group

Table 2. Carbon-13 n.m.r. data (at 20°C).

| No. | Compound | $\delta^{13}C$, ppm | | | | Ref. | Model cpd. | $\delta^{13}C$, ppm. | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Me—Si or BEt | $\alpha_C$ | $\beta_C$ | other signals | | | $\alpha_C$ | $\beta_C$ | |
| 1 | $MeCH{=}N(O)OSiMe_3$ | −0.9 | 109.8 | 11.4 | — | 132 | $CH_3CH_2NO_2$ | 69.3 | 11.5 | 140 |
| 2 | $Me_2C{=}N(O)OSiMe_3$ | −0.2 | 118.3 | 18.0 | — | 132 | $[CH_3CH(NO_2)]^-$ | 115.7 | — | 139 |
| 3 | $MeC(NO_2){=}N(O)OSiMe_3$ | −0.7 | wide | 14.7 | — | 132 | $(CH_3)_2CHNO_2$ | 78.4 | 20.0 | 141 |
| 4 | $(MeO_2C)_2C{=}N(O)OSiMe_3$ * | −1.7 | 114.2 | 158.8 | 51.9 | 132, 139 | $CH_3CH(NO_2)_2$ | 109 | 14.1 | 140 |
| 5 | $MeO_2CC{=}N{\rightarrow}O$ <br> $MeO$ (C, O) $O{\cdots}BEt_2$ | — | 111.7 | 170.1 <br> 158.1 | 57.4 <br> 52.9 | 24 | $(CH_3OCO)_2CHNO_2$ | 88.2 | 160.7 | 139 |
| 6 | $HC{=}N{\rightarrow}O$ <br> $MeO$ (C, O) $O{\cdots}BEt_2$ | 8.1 | 103.0 | 171.8 | 56.0 | 24 | $(CH_3OCO)_2C{=}N(O)OCH_3$ | 111.8 | 158.5 <br> 159.5 | 139 |
| 7 | $MeC{=}N{\rightarrow}O$ <br> $MeO$ (C, O) $O{\cdots}BEt_2$ | 8.0 | 111.5 | 170.9 | 55.8 <br> 10.2 | 24 | $[(CH_3OCO)_2C(NO_2)]^-$ | 111.7 | 164.6 | 139 |
| 8 | $CH{=}N{\rightarrow}O$ <br> $CONH_2{\cdots}BEt_2$ | 8.7 | 105.8 | 168.9 | | 24 | $CH_3OCOCH_2NO_2$ | 74.9 | 161.4 | 24 |
| 9 | $MeC{=}N{\rightarrow}O$ <br> $CONH_2{\cdots}BEt_2$ | 8.7 | 112.4 | 167.2 | 10.2 | 24 | $CH_3OCOCH(CH_3)NO_2$ | 80.4 | 164.2 | 24 |
| 10 | $(O_2C_6H_4)_2Hg[C(NO_2)_3]_2$ | — | 151.8 | — | — | 112, 113 | $CH_2(NO_2)CONH_2$ | 78.8 | 168.7 | 24 |
| 11 | $MeN(NO_2)SiMe_2R$ | 0 (−3) | 34—35 | — | — | 130 | $CH_3CH(NO_2)CONH_2$ | 80.4 | 164.2 | 24 |
| 12 | $MeN{=}N(O)OSiMe_2R$ | 0 (−3) | 39—40 | — | — | 130 | $HC(NO_2)_3$ | 113.5 | — | 141 |
| 13 | $MeN(NO_2)BEt_2$ ** | 8.4 | 38.2 | — | — | 25 | $[C(NO_2)_3]^-$ | 149 | — | 140 |
| 14 | $MeN{=}N(O)OBEt_2$ ** | 7.2 <br> 6.9 | 40.0 <br> 40.2 | — | — | 25 | $CH_3C(NO_2)_3$ | 128 | — | 133 |
| 15 | $MeN(NO_2)BEt_2{\cdot}C_5H_5N$ | 8.7 | 36.5 | — | 125.3 <br> 140.4 <br> 143.7 | 25 | $CH_3NHNO_2$ | 31.7 | — | 133 |

*At −80°C the carbonyl carbon atom gives two signals differing in δ values by 1.45 ppm, and the methoxy-carbon atom two signals differing by 0.73 ppm.
**In dichloromethane at −60°C.

between the two oxygen atoms of the O–N → O group. Secondly, analysis of the spectra of diethylboryl derivatives of nitro-compounds shows that in compounds 5–7 the boron atom is coordinated with the carbonyl oxygen atom. This produces a paramagnetic shift in the $^{13}C{=}O$ signal exceeding 10 ppm. In compounds 8 and 9, in which boron is coordinated with an amino-nitrogen atom, the paramagnetic shift is considerably smaller.

The $^{13}C$ n.m.r. spectra for silyl and diethylboron derivatives of methylnitramine show a sharp difference between the $^{13}CH_3{-}N$ signals for *N*- and *O*-derivatives[25,130]. The $^{14}N$ n.m.r. spectra of α-nitrohetero-organic derivatives of nitroalkanes and functionally substituted nitro-compounds usually permit reliable differentiation between covalent *C*- and *O*-products: firstly the signals from the O–N → O group in *O*-derivatives are considerably broader than the signals from the nitro-group in *C*-products, and secondly they are appreciably displaced up-field. However, comparison of the nitrogen-14 and nitrogen-15 chemical shifts in $Hg[C(NO_2)_3]_2$ (a *C*-product) and in $(^{15}NO_2)_2C{=}^{15}N(\rightarrow O).O.COCH_3$ shows that the accumulation of nitro-groups tends to level off this difference in chemical shifts[93]. It must be noted that, in the case of α-nitrohetero-organic derivatives of nitroalkanes, it is difficult to distinguish *O*-derivatives from ionic structures by means of the nitrogen-14 spectra without additional investigations.

Table 3 shows appreciable differences between nitrogen-14 chemical shifts for the nitro-group and for O–N → O in *O*- and *N*-hetero-organic derivatives of methylnitramine, without any significant influence of the nature of the heteroatom on the chemical shifts. The half-width of the line due to the nitro-group is considerably smaller than that for the O–N → O group. It is advisable to use $^{15}N$ n.m.r. at a low temperature in order to analyse labile compounds. Trimethylsilyl and diethylboron derivatives of *N*-nitrotoluene-*p*-sulphonamide are assumed to be *O*-products because the nitrogen-14 signal from the O–N → O group is very broad in their spectra.

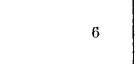
Analysis of n.m.r. spectra on nuclei of the heteroatoms may prove extremely fruitful in elucidating the structure of α-nitrohetero-organic compounds. Such studies have hitherto been made on trialkylsilyl and diethylboron derivatives of nitro-compounds and nitramines. Comparison of the silicon-29 n.m.r. spectra of silyl nitronates (compounds 2 and 3 in Table 4) with those of trialkylsilyl derivatives of the corresponding oximes confirms that silicon is not five-coordinated in nitronic esters. Compounds 5 and 6 show that the ranges of $\delta^{29}Si$ values for *N*- and *O*-forms are sharply delimited in the case of trialkylsilyl derivatives of nitramines. The boron-11 n.m.r. spectra for a series of α-nitrohetero-organic compounds (Table 5) indicate that the boron atom in them is hybridised. Fluorine-19 n.m.r. spectral data have been published[145] for several complexes of bisfluorodinitromethylmercury.

### (*d*) Mass spectrometry

The mass spectra of α-nitro-sulphones of general formula $p\text{-}CH_3C_6H_4SO_2C(NO_2)RR'$ have been investigated with R = H, $CH_3$ and R′ = H, $CH_3$, $C_2H_5$, $C_6H_5$, $p\text{-}ClC_6H_4$, $p\text{-}CH_3OC_6H_4$.[12,84] If R or R′ = H, the mass spectrum contains an intense peak having *m/e* 172 ($C_7H_8SO_3^{+}\cdot$). The fragmentation of nitromethyl *p*-tolyl sulphone is given as example:

$$\left(p\text{-}MeC_6H_4SO_2CH_2N\begin{matrix}O\\O\end{matrix}\right)^{+} \xrightarrow{-HCNO} \underset{m/e\ 172}{(p\text{-}MeC_6H_4SO_3H)^{+}} \begin{cases} \xrightarrow{-SO_2} C_7H_8O^{+} \ m/e\ 108 \\ \xrightarrow{-HSO_3} C_7H_7^{+} \ m/e\ 91 \end{cases}$$

**Table 3.** Nitrogen-14 n.m.r. data.

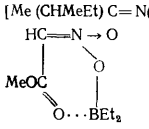
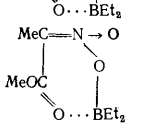
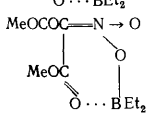
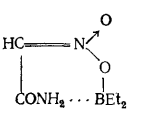
| No. | Compound | $\delta^{14}N$, ppm $NO_2$ or NO.O (half-width, Hz) | Ref. | Model cpd. | $\delta^{14}N$, ppm $NO_2$ or NO.O (half-width, Hz) | Ref. |
|---|---|---|---|---|---|---|
| 1 | $MeCH{=}N(O)OSiMe_3$ | −83±5 (270±20) | 132 | $EtNO_2$ | 12±1 (30) | 143 |
| 2 | $Me_2C{=}N(O)OSiMe_3$ | −97± (550±30) | 132 | $[MeCHNO_2]^-$ | −60.5±20 | 140 |
| 3 | $(MeOCO)_2C{=}N(O)OSiMe_3$ | broadened | 132 | $Me_2CHNO_2$ | 24 (38) | 143 |
| 4 | $MeC(NO_2){=}N(O)OSiMe_3$ | −12±2 ($NO_2$)<br>−74±8 (350±50) | 132 | $[Me_2CNO_2]^-$ | −79±5 | 140 |
| | | | | $[MeOCO]_2CHNO_2$ | −16±4 (220±15) | 139 |
| 5 | $Hg[C(NO_2)_3]_2$ | −25±1 (24±2) | 112,113 | $[(MeOCO)_2CNO_2]^-$ | −31±5 (230±20) | 139 |
| 6 |  | −23.6±1 (67±3) | 112,113 | $(MeOCO)_2C{=}N(O)OMe$ | −70±5 (290±20) | 139 |
| | | | | $Me_2CH(NO_2)_2$ | −11±1 (28) | 144 |
| 7 | $MeN(NO_2)SiMe_2R$ | −25.0 | 130 | $[MeC(NO_2)_2]^-$ | −22.5±1 | 140 |
| 8 | $MeN{=}N(O)OSiMe_2R$ | −55.0 | 130 | $HC(NO_2)_3$ | −33.5 (11) | 143 |
| 9 | $MeN(NO_2)BEt_2$ * | −20±3 | 25 | $CH_3C(NO_2)_3$ | −26.0 | 133 |
| 10 | $MeN{=}N(O)OBEt_2$ * | −49±1 | 25 | $[C(NO_2)_3]^-$ | −28±1 | 133 |
| 11 | $MeN(NO_2)BEt_2{\cdot}C_5H_5N$ | −21±1,5 | 25 | $C(^{15}NO_2){=}{}^{15}N(O)OAc$ | −35.6 and −31.8 | 93 |
| | $MeN(NO_2)BEt_2{\cdot}C_5H_5N$ * | −15.8 | 25 | $MeNHNO_2$ | −23.2±0.5 | 133 |
| 12 | $n\text{-}MeC_6H_4SO_2N{=}N(O)OSiMe_3$ | broadened | 22 | $[MeN(NO_2)]^-$ | −26.3±1.0 | 133 |
| 13 | $n\text{-}MeC_6H_4SO_2N{=}N(O)OBEt_2$ | broadened | 22 | $p\text{-}MeC_6H_4SO_2NRNO_2$ R=H, Alkyl | −40±2 (60±10) | 22 |
| | | | | $p\text{-}MeC_6H_4SO_2N{=}N(O)OPr\text{-}iso$ | broadened | 22 |

*Nitrogen-15 n.m.r. data at −50°C, with $^{15}NO_2NHCOOC_2H_5$ ($\delta$ = −41 ppm) as standard.

**Table 4.** Silicon-29 n.m.r. data [132].

| No. | Compound | $\delta^{29}Si$, ppm | No. | Compound | $\delta^{29}Si$, ppm |
|---|---|---|---|---|---|
| 1 | $MeCH{=}N(O)OSiMe_3$ | 22.6 | 6 | $MeN{=}N(O)OSiMe_2R$ (R=Me, t-Bu) | 28—30 |
| 2 | $Me_2C{=}N(O)OSiMe_3$ | 21.1 | | model cpd. | |
| 3 | $(MeOCO)_2C{=}N(O)OSiMe_3$ | 32.7 | | $Me_2C{=}NOSiMe_3$ | 21.2 |
| 4 | $Me(NO_2)C{=}N(O)OSiMe_3$ | 32.2 | | $(MeOCO)_2C{=}NOSiMe_3$ | 33.8 |
| 5 | $MeN(NO_2)SiMe_2R$ (R=Me, t-Bu) | 13—15 | | | |

**Table 5.** Boron-11 n.m.r. spectral data.

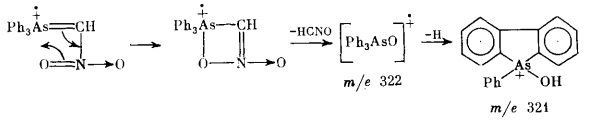
| No. | Compound | $\delta^{11}B$, ppm | Ref. |
|---|---|---|---|
| 1 | $[Me_2C{=}N(O)OBEt_2]_2$ | 12.0 | 23 |
| 2 | $[Me(CHMeEt)C{=}N(O)OBEt_2]_2$ | 13.6 | 23 |
| 3 |  | 15.8 | 24 |
| 4 |  | 16.7 | 24 |
| 5 |  | 15.9 | 24 |
| 6 |  | 12.8 | 24 |
| 7 | $MeNBEt_2 \rightleftarrows MeN{=}N(O)OBEt_2$ *  | 54 | 25 |
| 8 | $MeN(NO_2)BEt_2{\cdot}C_5H_5N$ | 5.0 | 25 |
| 9 | $p\text{-}MeC_6H_4SO_2N{=}N(O)OBEt_2$ * | 43.0 | 22 |

*At −20°C.

The tropylium cation has been identified in the mass spectrum of benzyl $\alpha$-nitrobenzyl sulphone [12].

In the opinion of Lorberth and Lange [71] the mass spectra of trialkyltin, trialkyl-lead, and alkylmercury derivatives of nitroalkanes confirm the suggested nitronic ester structure, since the $NO_2$ and NO peaks are absent. The mass spectra of trialkyl-lead, trialkyltin [71], and diethylboryl [23,73] derivatives of nitroalkanes indicate that these compounds are dimeric, which eliminates the possibility of salt structures.

$\alpha$-Nitro-ylides of arsenic on electron bombardment undergo the fragmentation [103]




(*e*) Nuclear $\gamma$-ray and quadrupole resonance spectroscopy

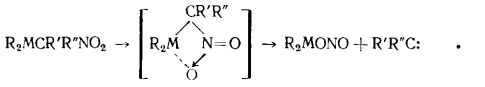
Mössbauer spectroscopy enables the structure of solid specimens containing tin to be elucidated. Lorberth et al. [121] have shown that trialkylstannyl alkanenitronates have a trigonal bipyramidal structure with five-coordinated tin. *N*-Trialkylstannyl derivatives of alkylnitramines also contain tin coordinated to the nitro-group [27].

Chlorine-35 and indium-115 nuclear quadrupole resonance data for the diethylthallium derivative of chloronitromethane and for dialkylindium derivatives of nitroalkanes respectively were regarded [66,68] as showing that these compounds are *C*-derivatives, with intramolecular coordination of the metal to oxygen of the nitro-group. However, this conclusion is not supported by the investigation of organothallium derivatives of certain nitro-compounds by other physicochemical methods—see (*c*) above.

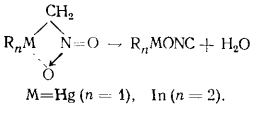
2. Establishment of Structure by Chemical Reactions

Several chemical reactions of α-nitrohetero-organic compounds may give information on their structure. Firstly mention must be made of 1,3-dipolar cycloaddition, by means of which several alkyl nitronates had earlier been detected[146]. However, *O*-acyl nitronates do not undergo this reaction[93], so that it cannot be regarded as common to all *O*-derivatives of nitro-compounds. Only trialkylsilyl nitronates have yet been subjected to such addition with alkenes, and therefore the possibility of detecting in this way *O*-derivatives of α-nitrohetero-organic compounds has so far been examined very roughly. (This reaction will be considered in detail in Section IV.)

The possibility of intramolecular coordination has been suggested[65,66,68] for *C*-derivatives of α-nitrohetero-organic compounds in which the heteroatoms have vacant *d* orbitals, leading to elimination of the corresponding carbene and formation of a nitrite:



However, the formation of carbenes in this process has not been rigorously confirmed, and the structure of the initial nitro-derivatives (especially the diethylthallium derivative of nitromethane) arouses great doubt. Therefore the isolation of nitrites of the type $R_2MONO$ cannot serve as a strict proof of the existence of the corresponding α-nitrohetero-organic compounds in the *C*-form. All the above considerations apply also to the formation of fulminates from hetero-organic derivatives of nitromethane. This reaction has been assumed[54,68] to be characteristic of *C*-derivatives of nitro-compounds and to involve intramolecular coordination of a mercury or an indium atom:



M=Hg ($n = 1$), In ($n = 2$).

Yet Lorberth and Lange[71] observed that methylmercury fulminate is readily formed also by the methylmercury derivative of nitromethane, which is a nitronic ester¶.

It is assumed[2] that the reaction of salts of primary nitroalkanes with 2,4-dinitrobenzenesulphenyl chloride forms *O*-derivatives, which then rearrange into *C*-products or else undergo a series of chemical reactions. The following tests have been suggested[1] for distinguishing α-nitro-sulphides from the corresponding *O*-derivatives — (i) treatment with alkali followed by oxidation, when α-nitro-sulphides undergo no changes, whereas the corresponding nitronic esters should decompose, and (ii) oxidation, which converts α-nitro-sulphides into the corresponding sulphones, whereas *O*-derivatives should be cleaved at the sulphur–oxygen bond (more detailed information on the reactions of *O*- and *C*-derivatives will be found in Section IV, 3 and 6*c*).

¶Theoretically the above hetero-organic derivatives of nitro-compounds may exist as an equilibrium tautomeric mixture, with one form present in such minute quantity that it cannot be reliably detected by physicochemical methods. In the equilibrium mixture, however, this particular form may well be responsible for conversion into nitrite or fulminate.

Chemical reactions enabling the *N*-form to be distinguished from *O*-derivatives are unknown for α-nitrohetero-organic compounds derived from nitramines. Among possible reactions of this type, mention may be made of the Franchimont test[147], which has been successfully used for the qualitative detection of various nitramines. Furthermore, the action of 40% sulphuric acid on certain *O*-alkyl derivatives of nitramines results in rapid evolution of nitrous oxide[148]. However, it is not clear how effective and specific this reaction is for the *O*-forms of α-nitrohetero-organic compounds.

In the identification of α-nitrohetero-organic compounds by means of chemical reactions it must be borne in mind that many of them are hydrolytically extremely unstable (Section IV, 2), so that reagents having a mobile hydrogen atom cannot be used for their analysis.

Several general conclusions on the structure of α-nitrohetero-organic compounds derived from aliphatic nitro-compounds and nitramines can be drawn from the above discussion. The structure depends on the nature of the element and the residue containing the nitro-group. Derivatives of mercury, phosphorus, and sulphur are usually true nitro-compounds, whereas those of boron and especially silicon are often nitronic esters. Contrary to published views[65-68] thallium and indium derivatives of nitroalkanes are also nitronic esters. The overwhelming majority of α-hetero-organic derivatives of mononitro-compounds exist in the *O*-form. The contribution of ionic structures is increased by the attachment of electronegative substituents to the carbon atom bearing the nitro-group.

Since the majority of α-nitrohetero-organic compounds are most probably not kinetically favoured products, their structure cannot be related to the direction of attack by the heteroatomic group on the ambident nitro-anion. Information on the structure of hetero-organic derivatives of nitramines and nitroamides is insufficient for any significant generalisations to be made, but even in these cases the compounds isolated are thermodynamically favoured products.

It is interesting that trialkylsilyl and diethylboron derivatives of alkylnitramines[20,25,130] are tautomeric mixtures of *N*- and *O*-forms containing the two structural isomers in comparable quantities. However, the pyridine complex of the diethylboryl derivative of methylnitramine is the pure *N*-form[25].

## IV. CHEMICAL PROPERTIES

We shall first discuss the properties common to most α-nitrohetero-organic compounds.

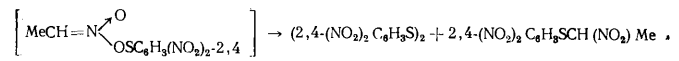
1. Thermal Decomposition

On the whole these compounds are less thermostable than the corresponding nitro-compounds or their salts; *O*-derivatives are usually thermally less stable than their *C*- or *N*-analogues.

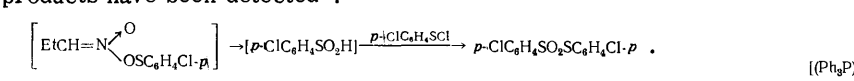
(*a*) Thermal decomposition of *O*-derivatives

The modes of decomposition of the *O*-forms of α-nitrohetero-organic compounds differ from the rearrangements of alkyl nitronates[108]. The character of the former process and the final products depend on the nature of the nitro-component and the heteroatom. The way in which nitronic esters of the type RCH : N(→O).O.SAr

breakdown is supposed[2] to be determined by the structure of the aryl radical. Thus if Ar = 2,4-$(NO_2)_2C_6H_3$ or $m$-$NO_2C_6H_4$, the $O$-derivatives rearrange into aryl nitroalkyl sulphides and decompose into bisnitroaryl disulphides: e.g.

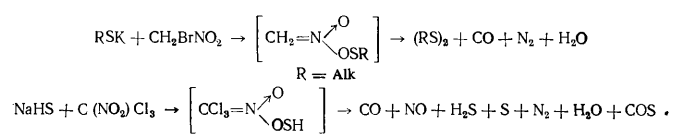


If, however, Ar = $p$-$ClC_6H_4$, quite different decomposition products have been detected[2]:

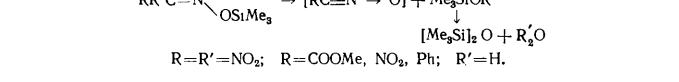


$O$-Thienyl derivatives of polynitroalkanes are also thermally unstable[7].

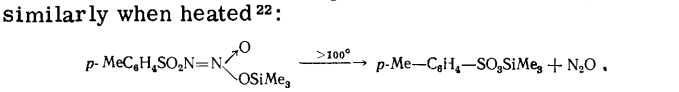
In the reactions of potassium and sodium salts of thols or of sodium hydrogen sulphide with halogenonitromethanes[76-80] unstable $O$-alkylthio- or $O$-mercapto-derivatives of alkanenitronic acids are obviously formed, which decompose to give mixtures of products:



Trialkylsilyl nitronates break down in a different way[15-17,50]:

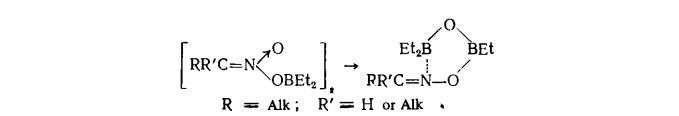


If R′ = H, parallel hydrolysis of the nitronic esters by trimethylsilanol takes place. The $O$-trimethylsilyl derivative of $N$-nitrotoluene-$p$-sulphonamide decomposes similarly when heated[22]:



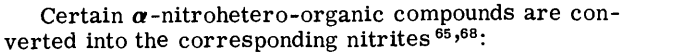
Trialkylsilyl derivatives of methylnitramine are unstable at room temperature, but the way in which they decompose has not been studied[20].

Diethylboron derivatives of alkanenitronic acids, whether in solid form or in solution, undergo rearrangement into a new heterocyclic system, a 4-alkylidene-2,5,5-triethyl-1,3-triethyl-1,3-dioxa-4-aza-2,5-diborolidine[23,24]:



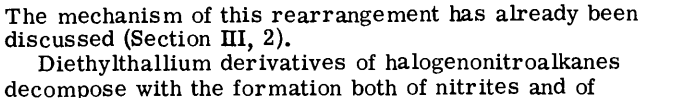
### (*b*) Conversion into nitrites or fulminates

Certain $\alpha$-nitrohetero-organic compounds are converted into the corresponding nitrites[65,68]:



The mechanism of this rearrangement has already been discussed (Section III, 2).

Diethylthallium derivatives of halogenonitroalkanes decompose with the formation both of nitrites and of diethylthallium halides[66]. In particular, chloro (and fluoro)nitromethyldiethylthallium pass rapidly into diethylthallium nitrite, whereas difluoronitromethyldiethylthallium forms diethylthallium fluoride[66]. Alkylmercury and dialkylindium derivatives of nitromethane are similarly converted into the corresponding fulminates†:



Beck and Schorpp[63,64] assume that in the reaction

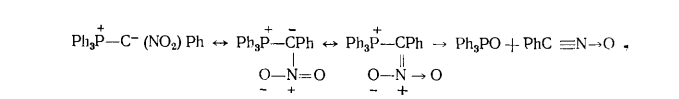


platinum derivatives of nitromethane and of nitroalkanes are formed, and then pass rapidly into the corresponding fulminates or nitrites.

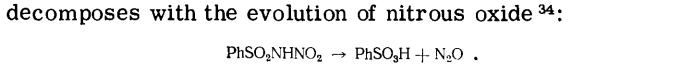
### (*c*) Decomposition of hetero-organic *C*-derivatives of nitro-compounds and *N*-derivatives of nitramines

Compounds whose structure as $C$-derivatives has been firmly established are usually stable at ordinary temperatures.

Thermal changes undergone by $\alpha$-nitro-ylides of phosphorus closely resemble the Wittig reaction[102]:



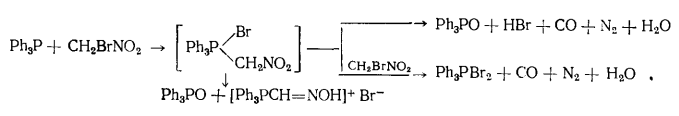
The thermal decomposition of hetero-organic $N$-derivatives of nitramines remains almost uninvestigated. Organotin derivatives of nitramines are stable below 150°C.[27] $N$-Nitrobenzenesulphonamide when heated decomposes with the evolution of nitrous oxide[34]:



### (*d*) Decomposition of hypothetical $\alpha$-nitrohetero-organic compounds

Here we consider reactions of $\alpha$-nitrohetero-organic compounds whose formation has been postulated in studies of the chemical changes undergone by nitroproducts.

The oxidation of triphenylphosphine by bromonitromethane is assumed to involve formation of an unstable triphenylnitromethylphosphonium bromide[80,86-89]‡:



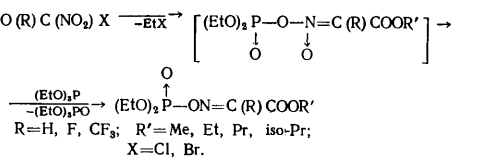
Dibromonitromethane reacts similarly with triphenylphosphine[80]. Nevertheless, the action of trialkyl

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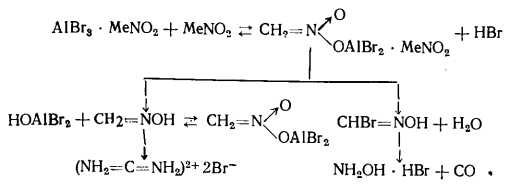
†A review on nitronic acids and esters[116] gives two references[149,150] reporting decomposition of the mercury salt of nitromethane into mercury fulminate. However, it has been shown more recently[122] that the former salt is stable up to 180°C.

‡The corresponding alkanonitriles have been detected in reactions of $\alpha$-halogenonitroalkanes with triphenylphosphine, and are obviously formed by reduction of the nitrile oxides by the triphenylphosphine[87].

phosphites on α-halogenonitro-compounds gives[90] unstable nitronic esters, which rapidly oxidise the phosphite:

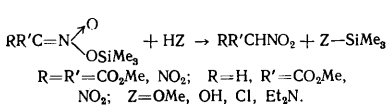


The reaction of nitromethane with aluminium bromide can be represented by the scheme[99]

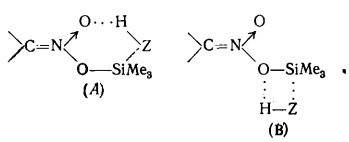


## 2. Reaction with Compounds containing a Mobile Hydrogen Atom

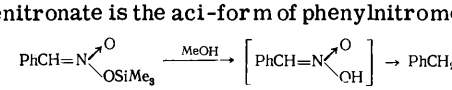
The resistance of α-nitrohetero-organic compounds to hydrolysis or solvolysis is governed by the nature of the heteroelement, the structure of the nitro-group, and in several cases also the form of the hetero-organic compound. Among the relatively thermostable α-nitrohetero-organic compounds the most sensitive to hydrolysis and solvolysis are α-organosilicon derivatives of nitro-compounds, which react readily with water, alcohols, acids, and primary and secondary amines[14,16,17,50,52]:



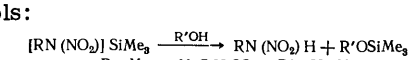
The reaction probably involves a multicentre transition state of type (*A*) or (*B*)[14]



In agreement with this it has been shown that the primary product of the methanolysis of trimethylsilyl phenylmethanenitronate is the aci-form of phenylnitromethane



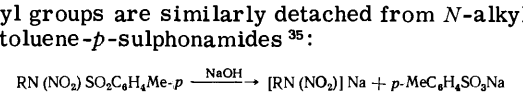
Trimethylsilyl derivatives of methylnitramine[20] and *N*-nitrotoluene-*p*-sulphonamide[22] also react with water and alcohols:



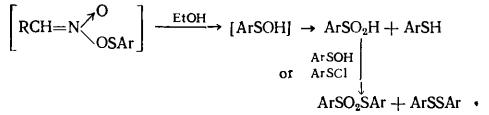
However, the rate of alcoholysis of hetero-organic compounds of this type is significantly retarded by the presence of a t-butyl radical in the trialkylsilyl group[20].

Diethylboryl derivatives of alkanenitronic acids[23,24,73] (including functionally substituted compounds), as well as diethylboryl derivatives of methylnitramine[25] and *N*-nitrotoluene-*p*-sulphonamide[22] are very readily hydrolysed by water, and they react with alcohols. Organotin derivatives of alkylnitramines are perfectly stable in air, but break down fairly slowly on treatment with water[27].

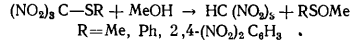
Diethylthallium derivatives of α-nitroalkanes readily undergo solvolysis in protic solvents, but on the addition of hydrochloric acid or a salt thereof the nitroalkyl group is replaced by the halogen:



*O*-Alkylthio-derivatives of nitro-compounds are extremely unstable in alcohols[2]:



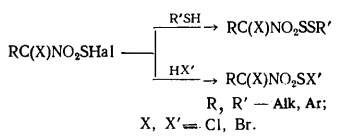
Nevertheless, α-nitroalkyl[1] and αα-dinitroalkyl[6,7] sulphides are unaffected by proton-containing solvents. In trinitromethyl sulphides, on the other hand, the sulphur–carbon bond is labile towards protic solvents[6]:



α-Nitro-sulphones and *N*-nitrosulphonamides are inert towards water and alcohols[1,2,34].

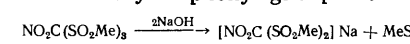
α-Nitroalkylphosphonates of general formula $NO_2CR'(CH_3).PO(OR)_2$ (where R, R′ = $CH_3$, $C_2H_5$) give the corresponding acids $NO_2CR'(CH_3).PO(OH)_2$ on treatment with an acid§[49]. With dialkyl nitromethylphosphonates the course of this reaction is complicated and involves the nitro-group.

α-Halogeno-α-nitroalkanesulphenyl chlorides react with acids and thiols at the sulphur–halogen bond[11,151]:

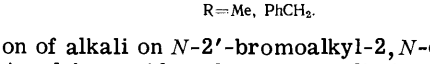


## 3. Reaction with Nucleophilic Reagents

The action of alkalis or alkali-methyl alkoxides on certain α-nitrohetero-organic compounds results in the formation of salts of the corresponding nitro-compounds[17,24,73] or nitramines[20,22,25]. With α-organosulphur derivatives of nitro-compounds[1,6,40,45,47,48,82] and with *N*-nitrosulphonamides[34,35], in particular, these alkaline reagents yield the nitronate salts. If an α-nitrohetero-organic compound of this type does not contain a mobile hydrogen atom, other reactions may occur. Thus, under the influence of alkali, trismethylsulphonylnitromethane loses one of its methylsulphonyl groups[39]:



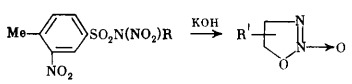
Sulphonyl groups are similarly detached from *N*-alkyl-*N*-nitrotoluene-*p*-sulphonamides[35]:



The action of alkali on *N*-2′-bromoalkyl-2,*N*-dinitrotoluene-4-sulphonamides also causes elimination of the sulphonyl group, with intramolecular alkylation of anions

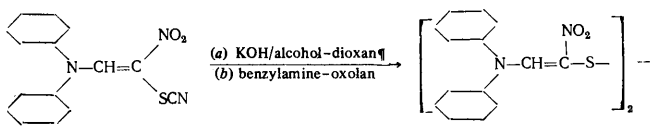
§Nitroalkylphosphonic chlorides are formed by the action of phosphorus pentachloride.

of the nitramines with formation of the 2-oxides of 4,5-dihydro-1,2,3-oxadiazoles [37]:

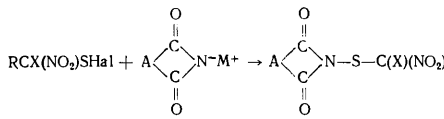


R=$CH_2CH_2Br$, CH(Me)$CH_2Br$, $CH_2CHBrMe$; R′=Me.

Certain α-nitro-organosulphur compounds undergo greater breakdown under the influence of alkalis [98]:



α-Nitroalkane-sulphenyl and -sulphonyl chlorides react with nucleophilic reagents at the sulphur–halogen bond:



Hal and X = Br, Cl; M=Na, K;

R= Alk ($C_1$—$C_6$); R′=H, Alk ($C_1$—$C_6$);

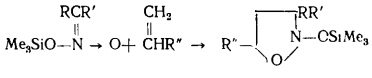
R″=H, Alk [10];

$R_2NH + R'R''C(NO_2)SO_2Cl \rightarrow R'R''C(NO_2)SO_2NR_2$

R=H, Me; R′ and R″=H, Alk, cyclo Alk, or N, O, or S heterocycle [44,75].

## 4. 1,3-Dipolar Cycloaddition

Among all the α-nitrohetero-organic compounds that exist as the *O*-esters only the silyl nitronates have been studied in this reaction. Styrene and methyl acrylate have been used as model compounds, and in isolated cases ethylene. Silyl nitronates undergo cycloaddition to selected alkenes to give good yields of the corresponding cycloadducts:



for R″=$CO_2$Me: R=H, Me, Et, R′=H, Me [52];

R=R′=$CO_2$Me; R=H, $CO_2$Me, R′=H, $NO_2$ [14,50];

for R″=Ph: R=H, Me, Et, R′=H, Me [52];

R=R′=$CO_2$Me [14], $NO_2$ [15,16,152], R=$CO_2$Me, H,

R′=H, $NO_2$ [50];

for R″=H: R=$CO_2$Me, R′=H [50,153];

R=R′=$NO_2$ [16].

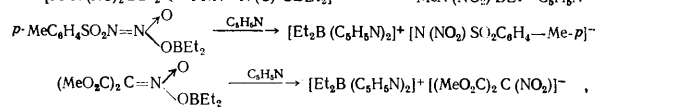
This reaction exhibits strict structural and in most cases also steric regiospecificity.

Silyl nitronates are rather less reactive than their alkyl analogues, but their enhanced thermal stability extends significantly the possibility of using nitro-compounds in the synthesis of heterocyclic structures by 1,3-dipolar cycloaddition. It is noteworthy that silyl dinitromethanenitronates $(NO_2)_2C:NOOSi(CH_3)_n(C_6H_5)_{3-n}$ ($n$ = 0, 1, 3) with methyl acrylate undergo direct silylation, not 1,3-cycloaddition [15,16].

¶Alcoholic hydrogen chloride acts on the starting material of this reaction to give dicyclohexylamine hydrochloride.

## 5. Complexes of α-Nitrohetero-organic Compounds

Bistrinitromethylmercury [112] and bisfluorodinitromethylmercury [145] readily form complexes with many organic ligands (ethers, dioxan, dimethyl sulphoxide, etc.). Both neutral complexes [25] and boronium salts [22,24,26] have been isolated from the action of pyridine on diethylboryl derivatives of nitro-compounds and nitramines: e.g.



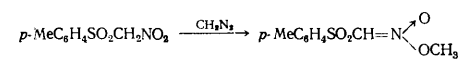
Below we shall discuss reactions undergone only by individual types of α-nitrohetero-organic compounds. The most detailed studies have been made, of course, on the most stable compounds, which include organosulphur and organomercury derivatives of mononitro- and polynitro-compounds.

## 6. Reactions of α-Organosulphur Derivatives of Nitro-compounds

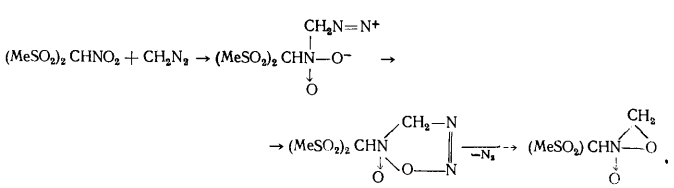
Many reactions well known in the chemistry of aliphatic nitro-compounds have been reported for α-nitroalkyl and α-nitramine derivatives of organosulphur compounds.

### (*a*) Alkylation

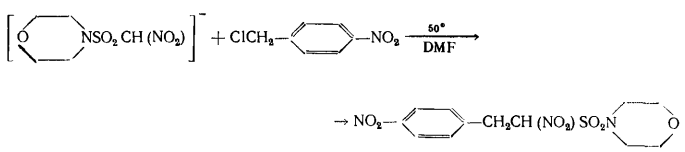
The direction of alkylation depends on the nature of the nitro-component, the alkylating reagent, and the solvent. Thus nitromethyl *p*-tolyl sulphone is alkylated by diazomethane at an oxygen atom in the nitro-group [47]:



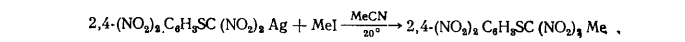
The alkylation of dimethylsulphonylnitromethane by diazomethane follows a completely different course [154]:



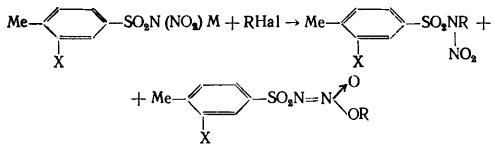
Anions of α-nitroalkanesulphonamides do not react with benzyl chloride, but with *p*-nitrobenzyl chloride they give *C*-alkylated products [45]:



This reaction was regarded as having a radical-anion mechanism. The alkylation of salts of αα-dinitroalkyl sulphides by methyl iodide gives *C*-substituted products [6]:



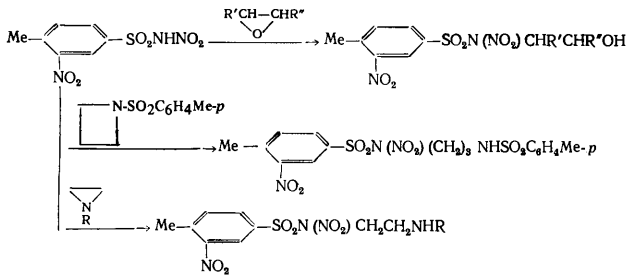
The alkylation of salts of *N*-nitroarenesulphonamides by alkyl halides gives a mixture of *N*- and *O*-alkylated products:



X=H, R=$C_6H_5CH_2$; M=Ag, Hal=Cl[35];
X=H, $NO_2$, R=Alk, $C_1$—$C_3$, adamantyl,
M=Ag, Na, Hal=Br, I[155].

The accumulation of alkyl groups in the alkylating reagent increases the proportion of the *O*-product, while the quantity of the *N*-alkylated product increases in the sequence of solvents—hexane < ether < ethyl acetate < diglyme < acetonitrile < dimethylformamide < acetone < methanol.

Silver and potassium salts of 2,*N*-dinitrotoluene-4-sulphonamide give with methyl iodide only the *N*-alkylated product[35,156]. Diazomethane, adamantyldiazoketone, and triethyloxonium tetrafluoroborate also alkylate nitrosulphonamides at the amino-nitrogen atom[155]. 2,*N*-Dinitrotoluene-4-sulphonamide reacts with oxirans and with aziridines and azetidine containing electronegative *N*-substituents to form *N*-2-hydroxyalkylated and *N*-2-amidoalkylated *N*-nitrosulphonamides[157]†:



R=$COC_6H_4NO_2$-*p*, $SO_2C_6H_4Me$-*p*; R′, R″=H or Alk.

(*b*) Halogenation

Nitro-derivatives of sulphones, sulphonamides, and sulphides in which the nitro-group is accompanied by a mobile hydrogen atom are readily halogenated either in the presence or in the absence of a base. In particular, dimethylsulphonylnitromethane and its sodium salt react in aqueous solution with bromine and chlorine[39]:

$$O_2NCR(SO_2Me)_2 + X_2 \rightarrow O_2NC(X)$$

X=Cl, Br; R=H, Na.

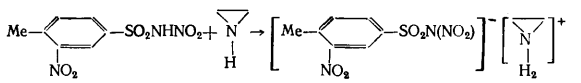
The bromination of α-nitro-sulphones may lead to isolation of the corresponding monobrominated[40,82] or dibrominated[40] derivatives:

$$RCH(NO_2)SO_2R' \xrightarrow[2.\ Br_2]{1.\ R''O^-} RCBr(NO_2)SO_2R'$$

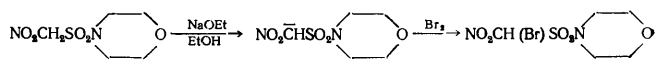
$$CH_2(NO_2)SO_2Me \xrightarrow[2.\ Br_2/CCl_4]{1.\ R''O^-} MeSO_2C(NO_2)Br_2$$

R=Bu, Ph; R′=Ph, $CH_2Ph$, $CH_2CH_2Me$;
R=H, R′=*p*-$MeC_6H_4$; R″=Alk.

†Reaction of 2,*N*-dinitrotoluene-4-sulphonamide with aziridine itself results merely in the formation of an aziridinium salt[157]:



The bromination of primary α-nitro-sulphonamides has been described[45]:



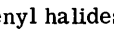
Bis-1-nitroalkyl disulphides are converted by halogens into 1-halogeno-1-nitroalkanesulphenyl halides[10,11]:

$$RCH(NO_2)S—SC(NO_2)RH \xrightarrow{X_2} 2RCX(NO_2)SX$$

R=Alk, Ar; X=Cl, Br.

Salts of dinitromethyl sulphides give 70–95% yields of chloro-derivatives[6]:

$$[RSC(NO_2)_2]^-M^+ + Cl_2 \rightarrow RSC(NO_2)_2Cl + MCl$$

R=Me, 2,4-$(NO_2)_2C_6H_3$; M=K, 

Alkyl 1-nitroalkanesulphonates have been identified by conversion into the corresponding brominated products[43]:

$$RCH(NO_2)SO_2R' \xrightarrow[2.\ Br_2,CCl_4]{1.\ KOH—EtOH} RC(NO_2)BrSO_2R'$$

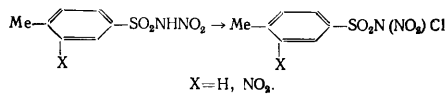
R,R′ = — Alk.

In some cases the halogenation of sulphonyl derivatives is hindered by the presence of a nitro-group. Thus the conversion of α-nitro-sulphonate salts into the acid chlorides requires more severe conditions than does preparation of the unsubstituted sulphonyl chlorides[44,75]:

$$RCH(NO_2)SO_2Na \xrightarrow{PCl_5,POCl_3} RCH(NO_2)SO_2Cl$$

R=H, Alk, cycloAlk, Ar.

*N*-Chloro-*N*-nitroarenesulphonamides are obtained by the action of t-butyl hypochlorite on the corresponding *N*-nitrosulphonamides[158]:



X=H, $NO_2$.

(*c*) Oxidation and reduction

Oxidation of the sulphur atom in α-mono- and αα-di-nitroalkyl sulphides has been reported:

$$RSC(NO_2)R'R'' \xrightarrow[AcOH]{H_2O_2} RSO_2CR'R''(NO_2)$$

R=Me, R′=R″=H[48]; R=*p*-$MeC_6H_4$,
R′=R″=H[47]; R=$ClCH_2CH_2$, 3-$NO_2C_6H_4$,
R′=H, R″=Me[3]; R=Me, Ar, R′=$NO_2$,
R″=H, Me[7].

The corresponding oximes can be isolated from the reduction of certain α-nitro-sulphides by lithium tetrahydroaluminate[3]:

$$p\text{-}MeC_6H_4SCH(NO_2)Me \rightarrow p\text{-}MeC_6H_4SC(Me)=NOH.$$

Yet the action of this reductant on a sulphone of similar structure is accompanied by cleavage of the carbon–sulphur bond and formation of toluene-*p*-sulphinic acid (in 80% yield)[3]. Reduction of the same sulphone by hydrogen over Raney nickel gives a mixture of products[3]:

$$p\text{-}MeC_6H_4SO_2CH(NO_2)Me \xrightarrow[Ni/Re]{H_2} p\text{-}MeC_6H_4SO_2C(Me)=NOH + p\text{-}MeC_6H_4SO_2NH_4 + p\text{-}MeC_6H_4SO_2H.$$

Dimethylsulphonylnitromethane is reduced by lithium tetrahydroaluminate with the evolution of ammonia[39]:

$$NO_2CH(SO_2Me)_2 \xrightarrow{LiAlH_4} CH_2(SO_2Me)_2 + NH_3.$$

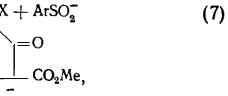
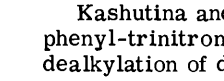
In the catalytic or electrolytic hydrogenation of certain α-nitro-organosulphur compounds the nitro-group may be reduced to amino[75]:

$$RR'C(NO_2)SO_2NR''R''' \rightarrow RR'C(NH_2)SO_2NR''R'''$$
R, R', R'', R'''=H, Alk, cycloAlk, etc.

(*d*) Other reactions

Several anions act on α-nitroalkyl sulphones with elimination of the sulphonyl group[125,159]:

$$RR'C(NO_2)SO_2Ar + X^- \rightarrow RR'C(NO_2)X + ArSO_2^- \quad (7)$$

$X^- = [Me_2C(NO_2)]^-$,  ,  ,

$MeC^-(CO_2Me)_2$, $p$-$MeC_6H_4SO_2^-$,
$p$-$ClC_6H_4S^-$.
R, R' = Alk, cycloAlk.

The reaction is accomplished under mild conditions at room temperature. It takes place by a radical-anion mechanism:

$$TosCMe_2(NO_2) + [Me_2C(NO_2)]^- \rightarrow [TosCMe_2(NO_2)]^{\cdot-} + Me_2C(NO_2)^{\cdot}$$
$$[TosCMe_2(NO_2)]^{\cdot-} \rightarrow Tos^- + Me_2C(NO_2)^{\cdot}$$
$$Me_2C(NO_2)^{\cdot} + [Me_2C(NO_2)]^- \rightarrow [Me_2C(NO_2)-C(NO_2)Me_2]^{\cdot-}$$
$$[Me_2C(NO_2)-C(NO_2)Me_2]^{\cdot-} + TosCMe_2(NO_2) \rightarrow [Me_2C(NO_2)]_2 + [TosCMe_2(NO_2)]^{\cdot-},$$

In addition to the products indicated in Eqn. (7) potassium salts of α-nitroalkyl sulphones and iodine are isolated from the reaction of the potassium salt of 2-nitropropane with α-iodo-α-nitroalkyl sulphones[125].

Sodium nitrite acts on α-nitroalkyl sulphones under mild conditions[41]:

$$RSO_2CH(NO_2)R' + NaNO_2 \rightarrow RSO_2C(NO_2)(NO)R' \xrightarrow{B^-} \rightarrow [RSO_2\bar{C}(NO)R' \leftrightarrow RSO_2CR'(=N\bar{O})] \xrightarrow{-H_2O} RSO_2CR'(=NOH)$$
R=$p$-$MeC_6H_4$, $C_6H_5CH_2$; R'=H, Me, Et, Ph,
$p$-$MeOC_6H_4$, $p$-$ClC_6H_4$.

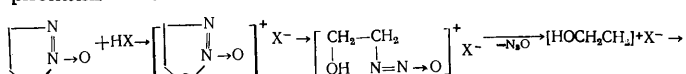
An α-bromo-α-nitroalkyl sulphone reacts with potassamide[40]:

$$PrC(NO_2)(Br)SO_2CH_2Pr \xrightarrow[NH_3]{KNH_2} PrCH=C(SO_2NH_2)Pr.$$

With benzenediazonium salts α-nitro-sulphones of general formula $RSO_2CH_2NO_2$ (R = $C_6H_5$, $p$-$BrC_6H_4$) form hydrazones $RSO_2C(NO_2):NHC_6H_5$. Analogous hydrazones can be obtained also by the interaction of an arenediazonium chloride and nitromethyl trichloromethyl sulphide[8,9]:

$$[RC_6H_4N\equiv N]^+Cl^- + CH_2NO_2(SCCl_3) \xrightarrow{AcONa} RC_6H_4NH-N=C(NO_2)SCCl_3$$
R=H, $p$-Me, $p$-MeO, $m$- and $p$-$NO_2$, $p$-Cl, etc.

An interesting reaction takes place between 4,5-dihydro-1,2,3-oxadiazole 2-oxide and 2,*N*-dinitrotoluene-4-sulphonamide[37]:



$\rightarrow HOCH_2CH_2X$ or $AcH + HX$
X=$Me(NO_2)C_6H_3SO_2N(NO_2)$.

The addition of *N*-chloro-*N*-nitrosulphonamides to unsaturated compounds gives mixtures of *O*- and *N*-halogenoalkylated products[159]:

$$p\text{-}MeC_6H_4SO_2N(Cl)NO_2 + RCH=CHR' \rightarrow p\text{-}MeC_6H_4SO_2N(NO_2)CHRCHR'(Cl) +$$
$$+ p\text{-}MeC_6H_4SO_2N=N(O)OCHRCHR'Cl$$
R=H, Me, Ph; R'=H; R and R'=$(CH_2)_4$.

With butadiene *N*-chloro-*N*-nitrotoluene-$p$-sulphonamide forms the 1,4(*N*)-adduct $p$-$CH_3C_6H_4SO_2N(NO_2)CH_2CH:CHCH_2Cl$, and from its reaction with diphenylacetylene $p$-$CH_3C_6H_4SO_2N(NO_2)C(C_6H_5):CCl.C_6H_5$ is isolated in low yield[159].

## 7. Reactions of Polynitroalkylmercury Derivatives

The main chemical reactions of trinitromethylmercury derivatives and of bisfluorodinitromethylmercury have been reviewed in detail[112,146,160,161], and only a few additional results will be given here.

Kashutina and Okhlobystin[54] have shown that butyl- and phenyl-trinitromethylmercury can be obtained by the dealkylation of dibutyl- and diphenyl-mercury respectively:

$$Hg[C(NO_2)_3]_2 + R_2Hg \rightarrow 2RHgC(NO_2)_3$$
R=Bu, Ph.

Reaction of bitrinitromethylmercury with vinyltrimethylsilane in solvents varying polarity—water, alcohol, benzene, tetrachloromethane—yields bis-3,3,3-trinitro-1-trimethylsilylpropylmercury[162]:

$$2Me_3SiCH=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow Hg[Me_3SiCHCH_2C(NO_2)_3]_2.$$

A similar reaction occurs with but-3-enyltrimethylsilane[162]. A product of the reaction of bistrinitromethylmercury with allyltrimethylsilane is 2,2-bistrinitromethyl-1,3-bistrinitromethylmercurypropane (VI)[162]:

$$Me_3SiCH_2CH=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow Me_3SiCH_2CH[C(NO_2)_3]CH_2Hg[C(NO_2)_3] \xrightarrow{-Me_3SiH} \rightarrow CH_2=C[C(NO_2)_3]CH_2HgC(NO_2)_3 \xrightarrow{Hg[C(NO_2)_3]_2} [(NO_2)_3CHgCH_2]_2C[C(NO_2)_3]_2$$
(VI)

The reactions of (VI) with halogens and with hydrogen chloride can be represented by the scheme

$$(VI) \begin{cases} \xrightarrow{Br_2} (BrHgCH_2)_2C[C(NO_2)_3]_2 \xrightarrow[(PhCO_2)_2]{Br_2} (BrCH_2)_2C[C(NO_2)_3]_2 \\ \xrightarrow{HCl} [ClHgCH_2]_2C[C(NO_2)_3]_2 + 2HC(NO_2)_3 \end{cases}$$

## 8. Other Reactions of α-Nitrohetero-organic Compounds

Nitrotriphenylarsenylmethylide reacts with aromatic aldehydes to form the corresponding alkenes—*trans*-β,4-dinitrostyrene with $p$-nitrobenzaldehyde, and ω-nitrostyrene with benzaldehyde[103]:

$$Ph_3As=CH(NO_2) + RCHO \rightarrow RCH=CH(NO_2) + Ph_3AsO$$
R=Ph, $p$-$NO_2C_6H_4$.

While the Review was being prepared for press, communications have appeared on the preparation and properties of organosulphur derivatives of nitro-compounds[163,164,176], various nitro-ylides[165-167,172], organophosphorus derivatives of aliphatic nitro-compounds[173-175], and also the mechanism of silatropic rearrangements in trialkylsilyl derivatives of nitramines[168-170] and *N*-nitrourethanes[171], as well as the problem of the structure of various hetero-organic derivatives of nitromethane[177].

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# New Data on the Chloromethylation of Aromatic and Heteroaromatic Compounds

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The fundamental methods and applications of the chloromethylation of aromatic and hetero-aromatic compounds as well as ideas concerning the reaction mechanism are considered on the basis of data published mainly during the last ten-fifteen years. The bibliography includes 285 references.

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## I. CHLOROMETHYLATION METHODS AND APPLICATIONS OF THE REACTION

Chloromethylation is a specific and most important instance of halogenoalkylation. It consists of the direct substitution of a hydrogen atom by the chloromethyl group. Hydrogen atoms linked not only to carbon but also to heteroatoms may be substituted (see, for example, Refs. 1–5), but chloromethylation at a carbon atom in an aromatic or heteroaromatic ring is of greatest importance, and this in fact will be considered below.

Chloromethylation of aromatic compounds was achieved for the first time in 1898 by Grassi and Maselli[6], who succeeded in obtaining benzyl chloride by the reaction of benzene with trioxymethylene and hydrogen chloride in the presence of zinc chloride. Nowadays chloromethylation is one of the important synthetic methods in organic chemistry.

The studies of the last ten–fifteen years will be mainly considered below, since the fundamental achievements in this field approximately up to 1962 have already been described in a number of reviews[7-9]. As regards the use of chloromethylation methods which have already become classical, we shall as a rule confine ourselves merely to references to the corresponding papers and patents published after 1962. The treatment of studies in which the reaction mechanism is considered as well as certain specific examples of chloromethylation methods which have developed recently will be relatively detailed. These are the chloromethylation of deactivated aromatic and heteroaromatic compounds, particularly the reactions using chloromethyl ethers.

Judging from the data presented in reviews[7-9], the result of the reaction under consideration depends greatly on the nature of the chloromethylating agent, the catalyst, and the process conditions. Effective chloromethylating agents are formaldehyde, paraformaldehyde or trioxymethylene with hydrogen chloride, and monochloromethyl and $\alpha\alpha'$-bischloromethyl ethers. The reaction is carried out in the presence of $ZnCl_2$, $SnCl_4$, $AlCl_3$, $BF_3$, $FeCl_3$, $TiCl_4$, as well as protic acids—HCl (taken in excess and behaving simultaneously as a reactant), $H_2SO_4$, $H_3PO_4$, $ClSO_3H$, and $CH_3COOH$. Zinc chloride is used most frequently. To increase its activity, it is often used with a small amount of aluminium chloride. However, the employment of $AlCl_3$ as a catalyst can entail the formation of a side product—a diarylmethane derivative—so that aluminium chloride is used mainly for compounds with deactivating substituents for which zinc chloride may be insufficiently effective. The water evolved in chloromethylation in the presence of metal halides hydrolyses the catalyst. In order to remove the water, the chlorides of inorganic acids are sometimes added to the reaction mixture, for example thionyl chloride[10,11]. Chloromethylation may be carried out under both heterogeneous and homogeneous conditions. $CH_3COOH$, $CCl_4$, $CHCl_3$, $CH_2Cl_2$, $CS_2$, as well as an excess of the chloromethyl ether are widely used as solvents.

The chloromethyl group, which has a mobile chlorine atom, can be converted into a methyl, hydroxymethyl, cyanomethyl, formyl, dialkylaminomethyl, and other functional groups. It is possible to obtain in this way many compounds otherwise difficult to synthesise, particularly biologically active compounds and substances used as intermediates in various syntheses, for example benzene[12-15], biphenyl[16], thiophen[17-24], furan[25], benzofuran[26], isoxazole[27], oxazine[28], benzoxazine[29], benzopyrimidine[30], and xanthotoxin[31] derivatives, as well as chromones[32] and flavones[33,34]. The interaction of bischloromethyl derivatives with various nucleophiles can lead not only to bifunctional compounds but also to complex bicyclic and polycyclic systems (see, for example, Refs. 35–41). Certain chloromethylated aromatic compounds have found industrial applications. Isothiuronium and pyridinium salts of anthraquinone-acridones[42], obtained from chloromethylderivatives, are used as dyes. Technical syntheses of pyromellitic dianhydride, trimellitic anhydride[43], terephthalic acid[44], phthalic and benzenepolycarboxylic acids[45], surfactants[46], etc. have been developed on the basis of mono- and bis-chloromethyl derivatives of aromatic hydrocarbons. The use of the chloromethylation reaction in the manufacture of ion-exchange resins has assumed significant importance recently[47-49].

## II. CHLOROMETHYLATION BY TREATMENT WITH FORMALDEHYDE AND HYDROGEN CHLORIDE

Chloromethylation is usually carried out with the aid of formaldehyde (normally in the form of formalin or paraformaldehyde) and hydrogen chloride in aqueous or non-aqueous media. Chloromethylation with formaldehyde in HCl was extensively redeveloped at one time by Blanc[50],

which led to his name being given to this reaction [7,51], although the process conditions do not differ from those described by Grassi and Maselli [6]. Zinc chloride is usually employed as the catalyst [52-58], more rarely tin(IV) chloride [59] or aluminium chloride [57]. However, when the $CH_2Cl$ group is introduced into aromatic compounds containing activating substituents, hydrogen chloride may serve as the catalyst [44,60-69]; in certain cases the reaction is carried out under pressure [43]. Other protic acids are also used successfully as catalysts—sulphuric [70], phosphoric [56,57], and perchloric [58]. The chloromethylation method considered here is applicable also to the compounds containing simultaneously activating and deactivating substituents, for example to hydroxybenzoate esters [71-74] and dimethoxybenzaldehydes [75]. Studies on the chloromethylation of the benzene rings of the condensed and partly hydrogenated 2-benzofuranone and 3,4-dihydrocoumarin [76,77] as well as phenoxathiin [78] systems are related to the above investigations. The reactions of pyromucic acid esters [79], 2,5-dimethylthiophen [80], 2-phenylbenzofuran [81], 1,2,5-thiadiazole [82], substituted $\alpha$-pyridone [83], and a derivative of tetrahydrocorrin [84] may be quoted as examples of the chloromethylation of heterocycles by treatment with formaldehyde and HCl.

The chloromethylation of deactivated aromatic compounds by treatment with formaldehyde and HCl is frequently carried out in concentrated sulphuric acid [85-88]. In some cases, the reaction is performed in the absence of HCl; the chloromethylating mixture is then prepared from paraformaldehyde, chlorosulphonic acid, and concentrated sulphuric acid [89,90].

Specific difficulties arise in the chloromethylation of alkyl aryl ketones. In the absence of activating substituents in the benzene ring, as in the case of dialkyl ketones (see, for example Dermer and Newcombe [91]), the $\alpha$-position in the side chain is substituted. For example the chloromethylation of acetophenone in the side chain is carried out by treatment with paraformaldehyde and HCl in glacial acetic acid at 100°C in the presence of phosphoric or sulphuric acid [92-95]. The use of paraformaldehyde and concentrated hydrochloric acid in acetic acid, in the presence of 70% $HClO_4$, makes it possible to introduce two $CH_2Cl$ groups into the methyl group of acetophenone [96].

It is quite likely that chloromethylation of the side chain proceeds via the mechanism of the Prins reaction [97-99]—the condensation of formaldehyde with olefins in the presence of acid catalysts. As a result of the interaction of formaldehyde with the catalyst, the hydroxymethyl cation is produced in this reaction and then attacks the double bond of the olefin. The chloromethyl derivative may be formed in the presence of HCl—for example, on treatment with paraformaldehyde and HCl in acetic acid, 1,1-diphenylethylene is converted into 3-chloro-1,1-diphenylprop-1-ene [100].

We believe that, in the reaction involving alkyl aryl ketones, the $(CH_2OH)^+$ cation attacks the enolic form of the ketone, after which the newly formed cation is stabilised by the elimination of a proton, this being followed by the substitution of the hydroxy-group by chlorine. This process may be represented schematically as follows:

$$CH_2O + HX \rightleftarrows HO\overset{+}{C}H_2 + X^- ,$$

$$RC(=O)-CH_3 \rightleftarrows R-C(OH)=CH_2 ,$$

$$R-C(OH)=CH_2 + \overset{+}{C}H_2OH \rightarrow R-\overset{+}{C}(OH)-CH_2CH_2OH ,$$

$$R-C(OH)(\overset{+}{C})-CH_2CH_2OH \xrightarrow{-H^+} R-C(OH)=CHCH_2OH ,$$

$$R-C(OH)=CHCH_2OH + HCl \rightarrow R-C(=O)-CH_2CH_2Cl .$$

It is important to note that the introduction of electron-donating substituents into the benzene ring of an alkyl aryl ketone alters the mode of chloromethylation—the $CH_2Cl$ group enters the aromatic ring and not the side chain [92,101-106]. It therefore becomes understandable why acyl derivatives of activated heteroaromatic systems (furan [107], thiophen [108-114], and selenophen [115]) are also chloromethylated in the ring.

Chloromethylation is a typical electrophilic substitution reaction. Nazarov and Semenovskii [116] have shown that the amount of the *meta*-chloromethyl derivative increases in the following sequence in chloromethylation, as in other electrophilic substitution reactions (nitration and halogenation):

$$C_6H_5CH_3 < C_6H_5CH_2COOC_2H_5 < C_6H_5CH_2Cl .$$

In the chloromethylation of halogenobenzenes, a gradual increase of the amount of *o*-isomers is observed on passing from fluorobenzene to iodobenzene [116]. A similar variation of the proportions of the isomers occurs, for example, in the nitration of halogenobenzenes [117]. The study of the proportions of the isomers obtained in the chloromethylation of alkylbenzenes [116,118,119] has shown that they fully obey the rules established for other electrophilic substitution reactions. The chloromethyl group enters mainly the *para*- and *ortho*-positions. Substitution in the *meta*-position is observed to only a slight extent and the fraction of the *meta*-isomer increases for alkylbenzenes with increase in the bulk of the alkyl group in the sequence $CH_3 < C_2H_5 <$ iso-$C_3H_7 <$ t-$C_4H_9$. For example, the chloromethylation of toluene results in the formation of only traces of the *meta*-chloromethyl derivative, while t-butylbenzene gives rise to 6.1% of *meta*-t-butylbenzyl chloride [119].

Comparison of the results of the chloromethylation [116,120] of toluene, ethylbenzene, cumene, and other hydrocarbons differing in the bulk of the alkyl substituent established that the amount of *o*-isomer decreases from 51.7% to 0% in the series of $C_6H_5Alk$ derivatives, where Alk = $CH_3$, $C_2H_5$, n-$C_3H_7$, n-$C_4H_9$, iso-$C_4H_9$, cyclo-$C_6H_{11}$, iso-$C_3H_7$, or t-$C_4H_9$†. This phenomenon is due to the increasing steric hindrance in the *o*-position on passing from toluene to t-butylbenzene. The same type of regular decrease of the amount of *o*-isomer is characteristic of other electrophilic substitution reactions [121].

It is noteworthy that the available quantitative literature data for the relative rates of chloromethylation of aromatic hydrocarbons are extremely contradictory at first sight. Thus the observed ratio of the rates of chloromethylation of toluene and benzene ($k_t/k_b$) varies within very wide limits—from 3 [122,123] to 30 [124] and even to 112. [125] Incidentally, one should note that in the above studies [122-125] the reactions were carried out under different conditions and different chloromethylating agents were used. Furthermore, we believe that some of the workers [122,123] employed an inadequate analytical method and it is quite likely that errors might have been made in the determination of the concentration of chloride ions.

† Traces of *o*-t-butylbenzyl chloride have been detected [119].

Vavon et al.[122] used for chloromethylation a monochloromethyl ether in glacial acetic acid at 100°C and measured the rate of reaction on the basis of the amount of HCl evolved on hydrolysis of the ether which failed to react. Szmant and Dudek[123] carried out the reaction by treatment with paraformaldehyde and HCl in glacial acetic acid at 85°C. The kinetics were followed from the change in the concentration of chloride ions during the reaction. Brown and Nelson[125] were unable to reproduce the results of Vavon et al.[122] and Szmant and Dudek[123] and carried out the reaction under other conditions, namely they used trioxymethylene and gaseous HCl in the presence of zinc chloride as the catalyst in solution in glacial acetic acid at 60°C. The ratio $k_t/k_b$ was found by the method of competition kinetics, by a quantitative determination of the corresponding hydrocarbons, isolated after the reduction of the chloromethyl derivatives with lithium tetrahydroaluminate‡. For the chloromethylation rate constant ratio $k_t/k_b = 112$ obtained by Brown and Nelson[125], a linear relation is observed between the logarithms of the partial rate factors for substitution in the *p*-position ($\lg f_p$) and the selectivity factors $F_S = \lg(f_p/f_m)$, where $f_m$ is the partial rate factor for substitution in the *m*-position, as for other electrophilic substitution reactions.

The fact that chloromethylation is an electrophilic substitution reaction is consistent also with the reaction constant $\rho$, which has been determined[124,126] and found to be of the order of $-5$. In the above studies, paraformaldehyde with hydrochloric acids were used as the chloromethylating agent. The reaction mixture was analysed for hydrochloric acid and formaldehyde at specified time intervals. The isomeric composition of the chloromethylated derivatives was determined after their catalytic reduction to the corresponding polymethylbenzenes. The experimental relative rates agree satisfactorily with data calculated by Condon's method[127] from the partial rate factors for substitution in the *o*-, *m*-, and *p*-positions in toluene.

Attempts to elucidate the mechanism of chloromethylation by treatment with formaldehyde and HCl have been made frequently. Darzens[128] believed that chloromethyl acetate $ClCH_2OOCCH_3$ is the chloromethylating agent when the reaction is carried out in acetic acid:

$$CH_2O + CH_3COOH + HCl \rightarrow ClCH_2OOCCH_3 + H_2O\,,$$
$$ArH + ClCH_2OOCCH_3 \rightarrow ArCH_2Cl + CH_3COOH\,.$$

However, Brown and Nelson[125] showed that the reaction of benzene with this ester at 75–80°C for 16 h without catalysts and for 4 h in the presence of zinc chloride does not give rise to benzyl chloride. Chloromethyl acetate can be used for the chloromethylation of benzene if the mixture is allowed to stand for 100 h.

The reaction of $CH_2O$ and HCl may lead to the formation of $CH_2Cl_2$, but the latter is not a chloromethylating agent: the attempt to chloromethylate benzene by methylene chloride in the presence of zinc chloride was unsuccessful[129]. It was believed[130] that the chloromethylating agent is $\alpha\alpha'$-bischloromethyl ether formed in the reaction between $CH_2O$ and HCl. In fact, as will be shown in the next section, the formation of the bischloromethyl ether is most likely in the chloromethylation of relatively inactive compounds under severe conditions. On the other hand, in chloromethylation under mild conditions, particularly in aqueous solutions, other possibilities must be considered.

Together with the mechanism presented above, two ionic mechanisms have also been put forward for the chloromethylation reaction. The first[131] presupposes that the attacking species is $[CH_2Cl]^+$, which may be formed in the first stage in conformity with the following reaction scheme:

$$CH_2O + HCl + H^+ \overset{K_1}{\rightleftarrows} CH_2OHCl + H^+ \overset{K_2}{\rightleftarrows} \overset{+}{C}H_2Cl + H_2O\,,$$
$$ArH + \overset{+}{C}H_2Cl \overset{k}{\rightarrow} ArCH_2Cl + H^+\,.$$

According to this scheme, the rate of reaction should be described by the equation

$$\frac{dx}{dt} = k\,[ArH][\overset{+}{C}H_2Cl] = kK_1K_2\frac{[ArH][CH_2O][HCl][H^+]}{[H_2O]}\,,$$

where $K_1$ and $K_2$ are the equilibrium constants and $k$ is the rate constant.

However, the above mechanism conflicts with experimental data[132]: when the reaction is carried out in $H_2SO_4$ in the absence or presence of chloride ion (LiCl), the rate constant is virtually the same, i.e. the chloride ion does not affect the rate and yet if the reaction involves the mechanism under consideration such an effect should have been observed, because the rate equation includes the concentration of HCl. On the basis of this mechanism, the rate of the chloromethylation reaction should be described by the equation for third-order kinetics, which also conflicts with experimental data[133].

Another mechanism which postulates the formation of the hydroxymethyl cation $[CH_2OH]^+$ and subsequent attack by the latter on the aromatic compound appears to be most justified at the present time; in the next stage, the hydroxy-group is substituted by a chlorine atom, which leads to the formation of the final compound[132,134,135]. The conclusion that the attacking species is the hydroxymethyl cation was reached[124] particularly on the basis of the finding that the formation of *o*- and *p*-isomers in identical proportions is observed in the bromomethylation and chloromethylation of toluene, ethylbenzene, and cumene. This shows that in both cases the same attacking species is active, consisting of the protonated form of formaldehyde, namely $[CH_2OH]^+$§. If the reaction involved the halogenomethyl ion, then bromomethylation should have produced a greater amount of the *p*-isomer than chloromethylation, since the bulk of the bromomethyl group is significantly greater than that of the chloromethyl group. Furthermore, it has been shown[134] that, under the chloromethylation conditions, the hydroxy-group in the benzyl alcohol is fully substituted by chlorine.

This conclusion has been confirmed by the kinetic studies of Ogata and Okano[132] on the chloromethylation of mesitylene by treatment with formaldehyde and HCl in 90% aqueous acetic acid and by Farberov and coworkers[135] on the chloromethylation of xylenes and pseudocumene by

‡ According to recently published data[284], the analytical method employed by Brown and Nelson[125] leads to an unduly high value of $k_t/k_b$. It is possible to infer from the results obtained by gas–liquid chromatography directly for mixtures of the chloromethyl derivatives formed under the conditions of competing reactions[284] that this quantity is about 30 (cf. Mironov et al.[124]).

§ In this connection, it is interesting to note that at equilibrium in acid media (pH < 2.6) formaldehyde is present in the form of the hydroxymethyl cation[136].

treatment with formaldehyde and hydrochloric acid. The following chloromethylation mechanism was proposed[135]:

$$CH_2O + H^+ \underset{K}{\overset{\text{fast}}{\rightleftharpoons}} \overset{+}{C}H_2OH ,$$

$$ArH + \overset{+}{C}H_2OH \xrightarrow{\text{slow}} [\overset{+}{Ar}HCH_2OH] ,$$

$$[\overset{+}{Ar}HCH_2OH] \rightarrow ArCH_2OH + H^+ ,$$

$$ArCH_2OH + HCl \xrightarrow{\text{fast}} ArCH_2Cl + H_2O .$$

If it is postulated that the rate-limiting stage is the addition of the protonated form of formaldehyde to the molecule of the aromatic hydrocarbon, then kinetic analysis leads to the following expression for the rate of reaction:

$$\frac{dx}{dt} = k[ArH][\overset{+}{C}H_2OH] = kK[ArH][CH_2O][H^+] = K_F[ArH][CH_2O] ,$$

where $k$ is the rate constant, $K$ the equilibrium constant, and $K_F = kK[H]^+$.

After taking logarithms in this equation, we obtain the relation

$$\lg K_F = -H_0 + \text{const} ,$$

where $H_0$ is the Hammett acidity function.

Experimental data confirm the proposed mechanism, since it has been observed that the rate of reaction is directly proportional to the product $[ArH][CH_2O]$. A linear relation has been obtained[135] between the logarithm of the rate constant and the Hammett acidity function for the monochloromethylation of *m*-xylene and pseudocumene by treatment with formaldehyde and hydrochloric acid. The concentration of hydrochloric acid and the molar ratios of hydrochloric acid, the hydrocarbon, and formaldehyde have a considerable influence on the rate of chloromethylation, which confirms the acid-catalysed reaction mechanism.

Detailed studies have shown that the monochloromethylation of *m*-xylene and pseudocumene by treatment with $(CH_2O)_n$ and HCl for a constant acidity function $H_0$ is described by a second-order kinetic equation, which confirms the last mechanism[135]. When the reaction was carried out in different solvents—formic, acetic, and propionic, and butyric acids and dioxan—it was observed that the rate of chloromethylation in the presence of aliphatic acids is much higher than in dioxan and water[137]. According to the authors, this phenomenon can be accounted for by the formation of the protonated form of the aliphatic acid, which exhibits a high proton-donating capacity. This results in an increase of the concentration of $[CH_2OH]^+$ and of the rate of the rate-limiting stage of reaction (2). If the reaction is performed in acetic acid in the presence of zinc chloride, the latter forms with acetic acid the complex acid $H_2[ZnCl_2(OCOCH_3)_2]$, which is just as strong as inorganic acids[138]. The acceleration of the process can be explained by the increase of acidity of the medium, leading to an increase of the concentration of $[CH_2OH]^+$ ions[139].

The mechanism of chloromethylation by treatment with $CH_2O$ and HCl in the presence of zinc chloride in the absence of a catalyst can be represented as follows[8]:

$$CH_2O + HCl + ZnCl_2 \rightleftharpoons [CH_2OH]^+ ZnCl_3^- ,$$

$$ArH + [CH_2OH]^+ ZnCl_3^- \rightleftharpoons \text{(arenium ion, R, } CH_2OH\text{)} \quad ZnCl_3^- \xrightarrow{HCl} ArCH_2Cl + ZnCl_2 + H_2O ,$$

or

$$\overset{\delta+}{CH_2O} \rightarrow \overset{\delta-}{ZnCl_2} + \text{(C}_6\text{H}_6\text{)} \rightleftharpoons Cl_2Zn{-}O{-}C(H)(H){-}\text{(arenium ion)} \xrightarrow[-H^+]{HCl} \text{(C}_6\text{H}_5\text{)}{-}CH_2Cl + H_2O + ZnCl_2 .$$

Together with the formation of monochloromethyl derivatives, bischloromethyl derivatives are produced as an admixture. By carrying out the reaction with a specific reactant ratio, it is possible to drive it towards the formation of bischloromethyl derivatives. For example, the bischloromethylation of xylene and pseudocumene[135] at 95° requires a considerable excess of hydrochloric acid, (8–10 moles) and paraformaldehyde (4–6 moles) relative to the stoichiometric amount. Very few studies have been made on the kinetics and mechanism of the formation of bischloromethyl derivatives. According to Ishii and Yamashita[140], the chloromethylation of monochloromethylxylene is not described by the equation for zero-order kinetics. However, on the basis of a study of the kinetics of the formation of the products of the bischloromethylation of *m*- and *p*-xylenes, Mironov et al.[141] proposed for this reaction the same mechanism as for monochloromethylation; the observed kinetic relations were interpreted in terms of the second-order equation for acid-catalysed reactions.

The most important side reaction in the chloromethylation process is the formation of diarylmethanes as a result of the further condensation of the initial compounds and the chloromethyl derivative obtained. It has been reported that the formation of diarylmethane may be inhibited by employing arsenic(III) chloride or arsenic(III) oxide as the catalyst[142]. In some cases, this reaction may be of independent interest, since it gives rise to polymethylbenzenes (as a result of the hydrocracking of the corresponding diarylmethanes[143]), benzophenonepolycarboxylic acid, and their anhydrides[144]. It has been shown by studying the kinetics of the chloromethylation of pseudocumene and *m*-xylene and the subsequent synthesis of diarylmethanes in the presence of toluene-*p*-sulphonic acid that the condensation reaction is described by the equation for second-order kinetics[133] (first order with respect to $CH_2O$ and first order with respect to HCl). The slowest stage, determining the overall rate of reaction, is the addition of the hydroxymethyl cation to the aromatic hydrocarbon molecule, as in chloromethylation[133].

It has been suggested recently[145] that the active chloromethylating species is the protonated form of the hypothetical chloromethanol ($ClCH_2\overset{+}{O}H_2$). The overall mechanism may be represented by a scheme[145] similar to that proposed previously[146]:

$$CH_2O + 2HCl + ZnCl_2 \rightleftharpoons ClCH_2\overset{+}{O}H_2ZnCl_3^- ,$$

$$H_2\overset{+}{O}CH_2Cl + \text{(C}_6\text{H}_5\text{)}{-}R \rightleftharpoons \text{(arenium ion, R, } ClH_2C,\ H\text{)} \xrightarrow{-H^+} \text{(C}_6\text{H}_4\text{)}(R)(CH_2Cl) .$$

This mechanism does not conflict with the kinetic data discussed above (first order with respect to $CH_2O$ and ArH), but it gives rise to a number of objections. In the first place, the authors who proposed it[145] established themselves that the $ClCH_2\overset{+}{O}H_2$ species exists only below −65 °C even in a very acid medium. Chloromethylation is possible in principle at such temperatures (see, for example, Ref. 147), but the reaction is usually carried out at a higher temperature. On the other hand, the above mechanism presupposes the direct introduction of the $CH_2Cl$ group, and not $CH_2OH$, into the aromatic ring. A number of arguments against this view were examined above. Furthermore, there is direct experimental evidence in support of the primary formation of hydroxymethyl derivatives, which are converted into chloromethylation products only in later stages[106,148].

## III. CHLOROMETHYLATION BY TREATMENT WITH CHLOROMETHYL ETHERS

### 1. Conditions and Characteristic Features of the Use of the Reaction

Another important group of chloromethylating agents are chloromethyl ethers, mainly monochloromethyl (MCME) and $\alpha\alpha'$-bischloromethyl (BCME) ethers. Chloromethylation by alkyl chloromethyl ethers was described for the first time by Sommelet[149]. By treating benzene with $\alpha$-monohalogenoalkyl ethers in the presence of $AlCl_3$ in $CS_2$, he obtained a mixture of the benzyl ether and benzyl chloride. He believed[149] that the primary product is an ether which is readily converted into the chloromethyl derivatives under the influence of the HCl liberated during the reaction:

$$ArH + ClCH_2OR \xrightarrow[CS_2]{AlCl_3} ArCH_2OR,$$
$$ArCH_2OR \xrightarrow{HCl} ArCH_2Cl.$$

Apart from $AlCl_3$, the catalysts used for this reaction were $ZnCl_2$, $SbCl_5$, and $SnCl_4$; the author believed that $SnCl_4$ was the most suitable catalyst. Aluminium chloride usually gives rise to further condensation reactions with formation of diphenylmethane and high-molecular-weight products.

Vavon and Bolle[150] suggested that aromatic hydrocarbons be chloromethylated under homogeneous conditions, namely by treatment with MCME in acetic acid without a catalyst. However, under these conditions the reaction is much slower than in the presence of a catalyst. Presumably, on treatment with MCME in acetic acid, chloromethylation may be accompanied by acetoxymethylation, since solutions of MCME in acetic acid contain methoxymethyl acetate[151]. However, the product of the acetoxymethylation of mesitylene was not isolated. As stated above, the substituted benzyl acetate formed is readily cleaved by the HCl evolved or MCME.[151] Lock[129] showed that the optimum conditions for chloromethylation by treatment with MCME are the use of zinc chloride as the catalyst in a heterogeneous medium with an excess of the aromatic compound as the solvent.

The chloromethylation with $\alpha\alpha'$-bischloromethyl ether was also carried out for the first time in the synthesis of benzyl chloride and related compounds[130]. The chloromethylating agent was the unpurified product obtained by treating paraformaldehyde or an aqueous formaldehyde solution with hydrogen chloride; Tishchenko[152] showed that it contains mainly BCME¶. A certain amount of MCME is also present in this mixture, because formaldehyde usually contains an admixture of methanol[156,157] and the interaction of $CH_3OH$, $CH_2O$, and HCl is known to be a preparative method for synthesising MCME.[158-160]

It has been shown[161] that the mixture obtained when HCl is passed into formalin contains, apart from MCME, and BCME, the bischloromethyl acetal of formaldehyde $CH_3(OCH_2Cl)_2$, which can also serve as a chloromethylating agent. This conclusion was reached in a study of the chloromethylation of selenophen and its homologues. It is of interest to note that, according to Yur'ev et al.[161] treatment in acetic acid with BCME, specially prepared and purified by a standard method[162], failed to yield chloromethylselophens. We believe that this finding can be explained by the fact that the reaction mixture does not contain HCl, which usually plays the role of the catalyst. Furthermore, BCME obtained by the standard method[162] contains paraformaldehyde and, according to Pesin and D'yachenko[163], bases and pseudobases (urotropine, dimethylformamide and paraformaldehyde) inhibit chloromethylation with BCME. It must be emphasised that the mixture of MCME and BCME usually used for chloromethylation always contains an admixture of HCl, since it is obtained by passing HCl into formalin and is used in the reaction without preliminary purification.

The data presented permit the conclusion that the chloromethylation by treatment with $CH_2O$ and HCl may result in the formation of BCME and MCME. It may be that, in the chloromethylation of comparatively reactive aromatic compounds in an aqueous medium, the rate of formation of the ethers is low. On the other hand, the chloromethylation of deactivated aromatic compounds with paraformaldehyde and hydrogen chloride in the presence of $H_2SO_4$, oleum, or $HSO_3Cl$ actually proceeds under conditions in which BCME is formed on a preparative scale[162]. The chloromethylation of deactivated aromatic compounds takes place fairly slowly and the rate of reaction may therefore be comparable to the rate of formation of BCME in the reaction medium. Evidently, under such conditions the reaction mechanism must reflect the involvement of the chloromethyl ethers. The problem of the mechanism of chloromethylation by BCME and MCME is discussed below. Examples of the employment of chloromethyl ethers for the synthesis of the corresponding substituted aromatic and heteroaromatic derivatives are also given.

Chloromethyl ethers are used as chloromethylating agents for a wide variety of compounds differing greatly in their reactivities. The reactivity of BCME is higher than that of MCME;[130] furthermore, it depends significantly on the catalysts employed and also on different impurities and additives. The chloromethylation of reactive aromatic compounds (hydrocarbons with *ortho–para* directing substituents and heterocycles) is usually carried out by treatment with MCME in acetic acid[164-166] or in carbon disulphide in the presence of tin(IV) chloride at 0°C.[167,168] Compounds containing simultaneously activating and deactivating substituents, for example nitrophenols, are chloromethylated by treatment with MCME or BCME when heated in the presence of catalysts—usually zinc chloride[169,170]. Under the same conditions, it is possible to chloromethylate also fairly stable aromatic compounds[171]. Deactivated compounds are normally acted upon by chloromethyl ethers in sulphuric acid or oleum, sometimes in the presence of chlorosulphonic acid[172-174].

Chloromethylation with chloromethyl ethers has come to be widely used in the manufacture of ion-exchange resins. Polystyrene[175-183]†, the copolymers of styrene with divinylbenzene[185-193], *NN'*-arylenedimethacrylamides[194,195], 9-alkyl-3-vinylcarbazoles[196], divinylbenzene, acrylonitrile[48], and ethylene terephthalate[197], polyphenylisoprene[198], poly-(*p*-phenylene-ethylene)[199], and other polymers have been chloromethylated for this purpose. The chloromethyl group usually enters the *p*-position and to a small extent the *o*-position in the aromatic ring. The reaction is frequently accompanied by side processes—the polymer chains are cross-linked by methylene bridges[185,187]. The nature of the catalyst

¶ It has been found that, when formaldehyde and HCl interact in the gas phase, BCME is also formed[153-155].

† Chloromethylated polystyrene can also be obtained by the polymerisation of *p*-chloromethylstyrene[184].

has a significant influence on the rate of reaction and the degree of conversion of the copolymer, i.e. the average number of chloromethyl groups per benzene ring in the polymer molecule. Comparison of the degrees of conversion of the copolymer over a specified period, the effective rate constants, and the activation energies made it possible to arrange the catalysts investigated in the following sequence in terms of their activities [200]:

$$SnCl_4 > ZnCl_2 > AlCl_3 > SnCl_2 > FeCl_3 .$$

The introduction of various additivites into the reaction mixture ($SiCl_4$ [201] and $ZrCl_4$ [202]) increases significantly the degree of conversion of the copolymer. These additives apparently regenerate the catalyst during the reaction.

The use of chloromethyl ethers instead of formaldehyde and HCl in the examples considered here is due to the fact that the diffusion of the reactants into the polymer is of decisive importance for these reactions, which take place in a heterogeneous medium. At the same time the fact that under comparable conditions the chloromethyl ethers are apparently more reactive chloromethylating agents than formaldehyde and HCl may also play a role in other instances. For example, when an unpurified mixture of MCME and BCME in acetic acid was used, the chloromethylation of 2-pyrones was achieved for the first time [203,204]. On the other hand, chloromethylpyrones could not be obtained by treatment with paraformaldehyde in the presence of HCl or zinc chloride.

Substituents influence the rate of reaction of chloromethyl ethers in the same way as that of formaldehyde and HCl. In particular, substituents with the $+I$ effect accelerate the reaction; for example, the rate of chloromethylation of mesitylene with MCME is much higher than that of benzene [149]. As shown for isoxazole derivatives [205,206], the reaction is facilitated by the presence in the ring of substituents such as methyl or phenyl and in all cases the chloromethyl group is directed to the 4-position of the isoxazole ring, similarly to other electrophilic substitution reactions, for example, nitration and halogenation [207].

Similar results were obtained also in the chloromethylation of 2,1,3-thia- and selena-diazoles and their homologues [208-211]. The chloromethyl group enters the 4-position, as in chlorination [212,213]; the reaction is facilitated by the introduction of electron-donating groups and is hindered in the presence of electron-accepting substituents. The activating influence of the alkyl substituent has also been observed for a series of *N*-aryl-*N*-methylsulphonylanilides [214-217].

Phenols and alkylphenols are chloromethylated readily, but immediately undergo further condensation reactions [218, 219]. For this reason, it has so far been impossible to isolate chloromethylphenols. Romadane and coworkers [220,221] chloromethylated *p*-alkoxybenzenes by various methods and showed that the main reaction product is 2-alkoxy-5-alkylbenzyl chloride (96–99%), while a second isomer, 5-alkoxy-2-alkylbenzyl chloride, is formed in a yield of 1–4%.

When 4-alkylphenyl methyl carbonates are chloromethylated by MCME in the presence of $SbCl_5$ as the catalyst, a mixture of isomers with the chloromethyl group in the 2- and 3-positions is formed, with the former isomer predominating [222,223]. It was possible to obtain bischloromethyl derivatives of these compounds only by treatment with BCME and in the presence of $SbCl_5$ as the catalyst [224]. The introduction into the ring of substituents with the $-I$ effect and even more so the introduction of substituents with the $-I$ and $-M$ effects (for example, using $CH_2O$ + HCl) [150] hinders further chloromethylation. Thus dichlorobenzenes are chloromethylated with much greater difficulty than monosubstituted derivatives [225-229]. The attempts to introduce the chloromethyl group into 5-nitrosalicylaldehyde by the usual methods were unsuccessful. The reaction proceeds only when an excess of $AlCl_3$ and MCME is used [230].

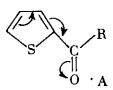
The chloromethylation of nitrobenzenes is carried out under severe conditions—by treatment with strong chloromethylating agents such as BCME and MCME and in the presence of strong inorganic acids. For example, when nitrobenzene is treated with BCME in 96% sulphuric acid (at 45–50°C for a week!), a 35% yield of *m*-nitrobenzyl chloride is obtained [231]. Berezovskii et al. [232] investigated the interaction of *p*-nitrotoluene with BCME and showed that, when the reaction is carried out in chlorosulphonic acid, or 5% oleum at a temperature not exceeding 10°C, the monochloromethyl derivative is obtained in an almost quantitative yield. An increase of temperature to 40–50°C and the use of 20–40% oleum or an excess of chlorosulphonic acid make it possible to introduce two chloromethyl groups into the *p*-nitrotoluene molecule. *p*-Ethylnitrobenzene gives 43% of 2-chloromethyl-1-ethyl-4-nitrobenzene and 10% of the corresponding 2,6-bischloromethyl derivative; *p*-isopropylnitrobenzene gives rise to monosubstituted products only, while *p*-t-butylnitrobenzene does not react at all [233]. The chloromethylation of phenols having deactivating substituents (the nitro-group or halogens) has been described in patents [234,235]. The reaction was carried out under different conditions: by treatment with bischloromethylether in sulphuric acid [234] and by treatment with mixture of 55% oleum and BCME. [235] The corresponding monochloromethyl derivatives were obtained in all instances. In the course of development of the synthesis of disubstituted tetrahydroisoquinolines, Beeby and Mann [236] obtained 2-(2-chloroethyl)-5-nitrobenzyl chloride as an intermediate, having treated 2-(*p*-nitrophenyl)ethyl chloride with BCME in the presence of 20% oleum. Under the influence of BCME in sulphuric acid, benzoic acid is converted into a mixture of *o*-, *m*-, and *p*-chloromethyl derivatives, with the *m*-isomer predominating [237] (see also Ref. 238). Under these conditions, alkylbenzoic acids give rise to bischloromethyl derivatives [239]. Chloromethyl derivatives of *N*-arylphthalimides have been obtained by treatment with BCME in concentrated sulphuric acid [240]; a patent [241] showed that indigo dyes can be mono- and di-chloromethylated. There have been a number of patents by the same investigators devoted to the chloromethylation of condensed systems deactivated by the carbonyl group [242-251]. The products of these reactions are of interest for the synthesis of dyes [244-247].

As in chloromethylation with formaldehyde and HCl (see above), on treatment with MCME the $CH_2Cl$ group can be directed to the side chains of alkyl aryl ketones; the reaction is carried out in the presence of boron trifluoride etherate as the catalyst [252,253]. However, on treatment with MCME using an excess (2.5 moles) of aluminium chloride without a solvent [254] or under the influence of BCME in the presence of 1.4 moles of $AlCl_3$ in chloroform [255], the chloromethyl group enters the *m*-position of the benzene ring. Under these conditions, acetophenone exists in the form of a complex with $AlCl_3$, [256] which is the cause of the change in the mode of substitution. In the reaction involving complexes of 2-acylthiophens with $AlCl_3$, a change in the site where the $CH_2Cl$ group is introduced into the thiophen ring is also observed. The chloromethylation of 2-acylthiophens by paraformaldehyde and HCl leads to the formation of a mixture of

4- and 5-chloromethyl derivatives in nearly equimolecular proportions [109-111]. The chloromethylation of thiophen-2-aldehyde and 2-acetothienone by MCME in the presence of 2.2 moles of $AlCl_3$ without a solvent or in chloroform yields 4-chloromethyl derivatives containing 7% and 2% of the 5-isomers respectively [110,257].

By carrying out the reaction in a solvent, it is possible to discover the essential features of the processes occurring, since there is the possibility of varying the amount of $AlCl_3$ (in experiments without a solvent, one must use more than 2 moles of $AlCl_3$ per moles of the carbonyl compound, since solid complexes are formed with small amounts of $AlCl_3$). In chloromethylation by treatment with MCME in the presence of comparatively small amounts of $AlCl_3$ in chloroform, the main reaction products are 5-substituted derivatives (70%, 90%, and up to 95% yields when 1.8, 1.3, and 0.9 moles of $AlCl_3$ are used respectively) [257]. This is undoubtedly caused by the dissociation of the complex of the carbonyl compound with $AlCl_3$ under the influence of MCME. The use of a weaker base (BCME) as the chloromethylating agent makes it possible to obtain 4-chloromethyl derivatives virtually without the 5-isomers even when the chloromethylation is carried out in the presence of 1.3 moles of $AlCl_3$. [257]

Thus, as in other electrophilic substitution reactions [258,259], the change in the mode of chloromethylation is a consequence of the formation of a 1 : 1 complex with $AlCl_3$ via the carbonyl group. By enhancing the electron-accepting capacity of the substituent, complex formation leads to such appreciable deactivation of the 5-position that the 4-position in the thiophen ring becomes the most reactive. This is confirmed by $^1H$ and $^{13}C$ NMR data for complexes of carbonyl derivatives of thiophen with $AlCl_3$. [256,260] The same effect, involving a change in the mode of electrophilic substitution, particularly in chloromethylation by chloromethyl ethers, is observed also when the carbonyl group is modified by protonation or complex formation with a strong protic acid [261,262]:




$A = AlCl_3$ or $H^+$.

One should note that the formation of a complex with aluminium chloride may influence the mode of substitution also in compounds with electron-donating substituents. Thus treatment of thioanisole with MCME in the presence of an excess of $AlCl_3$ leads to a high degree of selectivity with respect to the *p*-chloromethyl derivative. Nevertheless, in the presence of a deficiency of aluminium chloride, or when the reaction with MCME is carried out in acetic acid, or on chloromethylation by treatment with formalin and HCl, the product contains considerable amounts of the *o*-isomer (up to the equimolar ratio) together with the *p*-isomer [263].

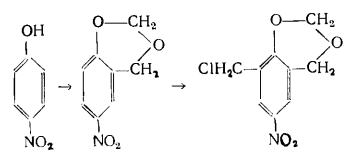
## 2. The Problem of the Mechanism of Chloromethylation by Treatment with Chloromethyl Ethers

In contrast to chloromethylation by treatment with formaldehyde and HCl, there are few kinetic data for the reactions of aromatic compounds with chloromethyl ethers in the literature. With the exception of the study [264] when the kinetics of the reaction of MCME with *p*-dichlorobenzene were investigated (however, unfortunately a detailed analysis of the mechanism in relation to the authors' kinetic data had not been carried out), the remaining investigations were devoted mainly to the study of the kinetics of the chloromethylation of polystyrene [265] or its copolymers [194,200]. The results thus obtained can be used only with important reservations, because, apart from the brief initial stage of the process, the rate of reaction is limited by the diffusion of the MCME–catalyst complex into the polymer

Two versions of the mechanism of the chloromethylation reaction involving chloromethyl ethers are possible. In the first, chloromethylation is preceded by the cleavage of the chloromethyl ether $ROCH_2Cl$ at the C–O bond under the influence of the protic or aprotic acid used as the condensing agent; the chloromethylating species is then the cation $\overset{+}{C}H_2Cl$. [261,264] In the second version the chloromethyl ether behaves as the alkylating agent, forming the cation $\overset{+}{C}H_2OR$ in the limiting case [187,257,262]. The alkoxymethyl derivatives formed are cleaved under the influence of the hydrogen chloride evolved and the aprotic acid (Verley [266]):

$$ArH \rightarrow ArCH_2OR \rightarrow ArCH_2Cl\ .$$

The reaction can proceed in principle simultaneously via two pathways or either pathway can predominate, depending on the conditions; however, the second pathway appears to be preferable. Indeed the alkylation of aromatic compounds by dialkyl ethers in the presence of Lewis acids takes place at elevated temperatures (of the order of 150–170°C), [267] i.e. under much more severe conditions than chloromethylation. Furthermore, MCME is known to be difficult to cleave by $AlCl_3$ (approximately to the extent of 3% after 100 h at 55°C), while BCME is still more stable [268]. On the other hand, chloromethyl ethers contain an exceptionally mobile halogen atom, capable of being exchanged via an $S_N1$ mechanism [269], which is probably associated with the stabilising effect of the oxygen atom on the cationic centre [270]. The formation of alkoxymethyl compounds noted above (see also Refs. 257, 263, 271, and 272) agrees with the second hypothesis. Since the alkoxymethyl derivatives are ethers of the benzyl type, they should be cleaved comparatively readily under the influence of $AlCl_3$ and HCl. [273,274] Indeed, additional treatment with hydrogen chloride and $AlCl_3$ of the reaction mixture obtained as a result of the interaction of 2-acetothienone with MCME in the presence of 1.3 moles of $AlCl_3$ lowers the content of 5-methoxymethyl-2-acetothienone approximately by a factor of two [257] (see also Belen'kii et al. [255]). When the reaction of 2-acetothienone with MCME is carried out in the presence of aluminium chloride etherate, i.e. under conditions promoting the cleavage of methoxymethyl derivatives by $AlCl_3$, the main product is a mixture of 4- and 5-methoxymethyl-2-acetothienones [257]. Topchiev and Stavrovskaya [275,276] showed that treatment of *p*-nitrophenol with BCME in the presence of $ZnCl_2$ entails initial alkylation and subsequent intramolecular ring closure and the formation of the methylene ether of 5-nitrosaligenin, which is then converted into the methylene ether of 3-chloromethyl-5-nitrosaligenin:




Thus the formation of chloromethyl derivatives when aromatic compounds are treated with chloromethyl ethers in the presence of $AlCl_3$ is the result of a multistage process, which may be represented by the following scheme:

$$ROCH_2Cl + AlCl_3 \rightleftarrows (ROCH_2)^+\ AlCl_4^-\ , \quad (1)$$

$$ArH + (ROCH_2)^+\ AlCl_4^- \rightleftarrows (ArHCH_2OR)^+\ AlCl_4^-\ , \quad (2)$$

$$(ArHCH_2OR)^+ AlCl_4^- \rightarrow ArCH_2OR + HCl + AlCl_3 , \quad (3)$$
$$ArCH_2OR + AlCl_3 \rightarrow ArCH_2Cl + RCl + AlOCl , \quad (4)$$
$$ArCH_2OR + HCl \rightarrow ArCH_2Cl + ROH . \quad (5)$$

In the reactions with MCME and BCME, R = $CH_3$ and R = $CH_2Cl$ or $CH_2Ar$ respectively.

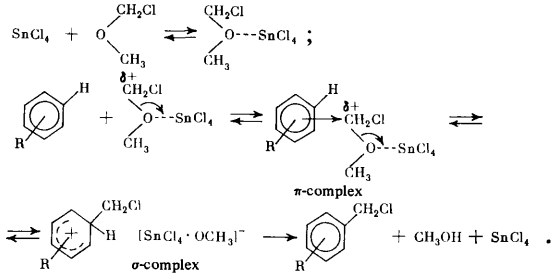
The process under consideration includes the formation of an electrophilic species [stage (1)], which is converted via a σ-complex [stage (2)] into a benzyl ether analogue $ArCH_2OR$ [stage (3)]; the latter gives rise to a chloromethyl derivative on cleavage under the influence of $AlCl_3$ [stage (4)] or HCl [stage (5)]. Nor can one rule out the possibility of the joint action of HCl and $AlCl_3$ on the ether with the intermediate formation of the protonated form $ArCH_2OHR^+.AlCl_4^-$.

The substances formed in stages (4) and (5) are the "normal" products of the cleavage of ethers by $AlCl_3$ [277] and HCl [273] (the cleavage of benzyl ethers by Lewis acids is also described by Gol'dfarb [278] and Stadnikov and Kashtanov [279]). If chloromethylation on treatment with BCME proceeds via the dibenzyl ether analogue $(ArCH_2)_2O$, then its cleavage by both an aprotic acid and by HCl should lead to the formation of two $ArCH_2Cl$ molecules [280]. The cleavage of an ether of the type $ArCH_2OCH_2Cl$ by HCl can lead to a chloromethyl derivative and the unstable chloromethanol $HOCH_2Cl$. The latter can function as a chloromethylating agent either directly or after dehydration with formation of BCME. Thus both $CH_2Cl$ groups of the initial BCME can be used in the reaction [255,257].

However, the above mechanism does not provide a complete idea about the process considered, because it does not reflect the formation of diarylmethanes and bis-chloromethyl derivatives (for further details, see Belen'kii et al. [255]). In principle, the same mechanism is also probable when the reaction is carried out in strong inorganic acids. It has been shown [145] that alkyl chloromethyl ethers are protonated at the oxygen atom in an ultra-acidic medium and the protonated forms produced are dehydrochlorinated above −60°C, being converted into alkoxy-methyl cations‡:

$$ClCH_2OR \xrightarrow[-80°]{FSO_3H-SbF_5} ClCH_2-\overset{+}{O}(H)-R \xrightarrow[-60°]{-HCl} CH_2=\overset{+}{O}R .$$

A significant argument against the mechanism under consideration, involving attack by an alkoxymethyl cation, arises from the fact that the ion may react not only via the carbon atom with formation of an alkoxymethyl derivative but can also behave as a methylating agent (with liberation of formaldehyde) [281]. One can therefore consider a chloromethylation mechanism which does not provide for the formation of alkoxymethyl or chloromethyl cations and in which the chloromethylating species is a complex of the chloromethyl ether with a protic or aprotic acid. Mechanisms of this kind have been put forward in a number of studies [282,283]. In the relevant reports, it is postulated in essence that the $CH_2Cl$ fragment from a complex of MCME and a Lewis acid enters into the aromatic ring. One of these mechanisms [283] is presented below:




If this or a similar mechanism is adopted, one cannot explain the formation of methoxymethyl derivatives discussed above. The reaction mechanism must apparently take into account both possible primary processes—chloromethylation and alkoxymethylation.

Despite the great importance of chloromethylation and its large-scale employment for preparative purposes, only partly described in this Review, many significant aspects of this reaction, associated primarily with its mechanism, have still been inadequately elucidated. This situation is apparently due to the great complexity of the process and its many pathways, as a result of which one can obtain, together with monochloromethyl derivatives, not only disubstituted derivatives but also products of another type—diarylmethanes and benzyl ethers. At the same time, the great scope of the synthesis based on chloromethyl derivatives led to the undertaking of further new investigations whose aim is both to modify the methods and to investigate the mechanism of the chloromethylation reaction.

‡ A mechanism of a similar type has also been proposed [284] for chloromethylation and bromomethylation by treatment with 1-chloro-4-[chloro(bromo)methoxy]-butanes and 1,4-bis[chloro(bromo)methoxy]butanes, which have been recently described as effective halogenomethylating agents [285]. A characteristic feature of these substances is the possibility of the intermedite formation and involvement in the reaction of chloro-(bromo) methyltetrahydrofuranonium ions, which has been confirmed by the detection [284] with the aid of $^1H$ NMR of this type of ion, formed as a result of the following reaction at −50°C in $SO_2$:

$$ClCH_2O(CH_2)_4Cl + SbCl_5 \rightarrow ClCH_2-\overset{+}{O}\!\!<\!\!\begin{matrix}CH_2-CH_2\\ |\\ CH_2-CH_2\end{matrix}\!\!> SbCl_6^- .$$

The halogenoalkylation by these reagents proceeds with high yields in the presence of $SnCl_4$ or $ZnBr_2$. An advantage of these new agents over the less active BCME is a lower volatility and hence a smaller danger to the human organism [285].

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# Oxidation by Ozone of Hetero-organic Compounds of the Silicon Subgroup

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The kinetics and the reaction products are surveyed, and the mechanism is discussed. The reactivity of the compounds towards ozone depends on the nature of the heteroatom, the attached substituent, and non-specific and specific solvation. A list of 68 references is included.

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## I. INTRODUCTION

The early publications devoted to the action of ozone on hetero-organic compounds[1-3] report only qualitative observations concerned to elucidate oxidisability. Thus Bailey et al.[1] noted that bubbling ozone through vinyltrichlorosilane in tetrachloromethane at 0°C gave a product whose hydrolysis with dilute aqueous hydrogen peroxide yielded silicon dioxide. It was suggested that an ozonide was formed as intermediate in the ozonolysis of vinyltrichlorosilane. A possible structure for the ozonide was not discussed[1]. Later Clasen[2] showed that under ordinary conditions diethylsilane is oxidised by ozone with cleavage of the alkyl–silicon bond. Barry and Beck[3] found that siloxanes are formed by the oxidation of organosilicon compounds.

More recently it has been reported that ozone is able to cleave the lead–lead bond in diplumbanes[4], which has been used to obtain triphenylplumbane hydroxide and acetate from hexaphenyldiplumbane. Enek'yanov et al.[5] utilised the high reactivity of tetraethylplumbane towards ozone in the application of this toxic organolead compound. Investigations on the ozonolysis of hetero-organic compounds of non-transition elements of Groups V and VI have been discussed in some detail[6].

Reactions of ozone with organic derivatives of transition and non-transition metals of other groups have remained almost uninvestigated. Only isolated studies have shown that ferrocene and its vinyl derivatives are readily oxidised by ozone[7,8], and that the main product of the ozonisation of phenylmagnesium bromide in an inert atmosphere at low temperatures (−78°C) is phenol[9], but products of the action of ozone on certain mercury-containing organic compounds[10,11] may be acids (if the organic group is of normal structure) or ketones and alcohols (if it is secondary or tertiary).

The ozonolysis of hetero-organic compounds of elements in the silicon subgroup has been investigated systematically since 1965 (by Spialter, Austin, Aleksandrov, et al.). The results were summarised in a review [12], but more than five years have elapsed since its publication, during which period a considerable number of

studies have been made, extending significantly our knowledge of the ozonolysis of hetero-organic compounds. This work will be surveyed in the present Review.

## II. REACTION PRODUCTS AND MECHANISM

### 1. Fully Organic Derivatives of the Elements

Information has now been published on the ozonolysis of tetraethylsilicon [13-19], tetraethylgermanium [18], tetramethyltin [20], tetraethyltin [16-23], tetrapropyltin [20], tetrabutyltin [20], tetraisobutyltin [20], tetrapentyltin [20], tetraethyllead [23,24], tetrapropyl-lead [24], diethyldimethylsilane [14], methyltriethylsilane [14], and phenyltrimethylsilane [14]. All completely organic derivatives of elements in the silicon subgroup whose reactions with ozone have been investigated are usually extremely stable in air at room temperature [25]. However, they are readily oxidised by ozone under these conditions.

The rate of ozonolysis of the tetra-alkyl derivatives is described by a kinetic equation of the first order with respect to ozone and the first order with respect to the initial hetero-organic compound [19,20]. The example of tetraethyltin in n-nonane and in the absence of a solvent shows [22] that ozonolysis of a hetero-organic compound does not initiate oxidation of the solvent. The proportions of ozone and tetra-alkyl compound that react are nearly equimolecular [22]. The composition of the ozonolysis products indicates [13-17,21-24] that the heteroatom–carbon bond is attacked.

The ozonolysis of tetraethylsilane (up to 50% and more conversion of the initial organosilicon compound) yields as hetero-organic products a mixture [13,14] of various polyethylsiloxanes of linear or cyclic structure (hexaethyldisiloxane, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, octaethyltrisiloxane). 1,1,3,3-Tetraethyl-1,3-dimethyldisiloxane has been detected as main product of the ozonolysis of methyltriethylsilane at room temperature, but under analogous conditions phenyltrimethylsilane gives hexamethyldisiloxane in theoretical yield [13]. Ozonolysis of tetraethylsilane involves formation in the early stages [15] of triethylsilyl hydroperoxide, bistriethylsilyl peroxide, hexaethyldisiloxane, hydrogen peroxide, water, acetaldehyde, and acetic acid.

A complicated mixture of products is formed by the ozonolysis of tetraethylstannane [22]: free acetaldehyde is accompanied by organotin compounds containing ethylidene, diethylstannylene, and terminal triethylstannyl groups linked by oxygen or a peroxide bond. Hydrolysis of these products gives acetaldehyde, diethyltin oxide, hydrogen peroxide, and triethylstannyl hydroxide in respective yields (hydrolysis of the reaction mixture after ozonolysis of tetraethylstannane in the absence of a solvent at 0°C) of 0.68, 0.70, 0.86, and 1.29 mole mole$^{-1}$ active oxygen. It was also established [22] that the peroxide product present in the reaction mixture is an intermediate: its rate of accumulation diminishes with rise in temperature, but at a sufficient degree of conversion of the tetraethylstannane (ozonolysis in trichlorobenzene, tetrachloromethane, and 1,1,2,2-tetrachloroethane) the rate curves for the accumulation of active oxygen are extremal in character.

It was suggested [21] that the reactions of ozone with tetraethylsilane and with tetraethylstannane have the same mechanism, but that the latter process is complicated by secondary reactions of intermediate peroxy-compounds. The oxidation of tetraethylstannane by ozone was therefore investigated in the presence of a large excess of water, i.e. under conditions of controllable secondary reactions, when triethylstannyl hydroperoxide or peroxide, if formed, would undergo hydrolysis:

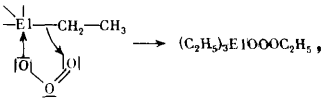
$$(C_2H_5)_3SnOOH + H_2O \rightarrow (C_2H_5)_3SnOH + H_2O_2,$$
$$(C_2H_5)_3SnOOSn(C_2H_5)_3 + 2H_2O \rightarrow 2(C_2H_5)_3SnOH + H_2O_2.$$

It would then be expected that equimolar quantities of acetaldehyde, hexaethyldistannoxane, and hydrogen peroxide would accumulate in the reaction mixture when tetraethylstannane undergoes ozonolysis in the presence of water. The main products were in fact hydrogen peroxide, acetaldehyde, and triethylstannyl hydroxide in nearly equimolecular quantities. It was shown further [21] that tetraethyldistannoxane dihydroxide is also formed, by ozonolysis of triethylstannyl hydroxide as intermediate.

Discussion of the mechanism of the ozonolysis of tetra-n-alkylated hetero-organic compounds [12,16,17] has led to the suggestion that reaction with ozone involves the sequence of stages—(1) coordination of ozone to the heteroatom by means of vacant *d* orbitals of the latter and the electron shell of the nucleophilic centre of ozone

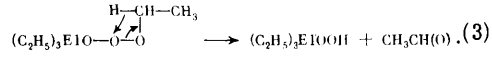
$$(C_2H_5)_4E1 + O_3 \longrightarrow (C_2H_5)_4E1 \cdot O_3, \quad (1)$$

(2) electrophilic attack by the coordinated ozone on the heteroatom–carbon bond to form an intermediate trioxide



(2)

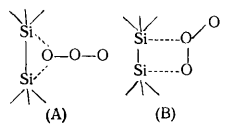
and (3) transformation of the trioxide with migration of hydrogen from the $\alpha$-carbon atom to the middle oxygen atom of the trioxide



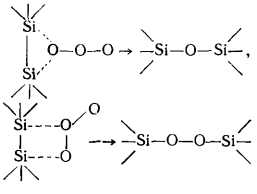
(3)

### 2. Bihetero-organic Compounds

Only three representatives of this class of compounds—hexamethyldisilane [14], hexaethyldistannane [26], and octa-t-butylstannetan [27]—have been examined. Spialter and Austin [14] showed that hexamethyldisilane reacts readily with ozone at room temperature, giving hexamethyldisiloxane as sole organosilicon product. Two possible mechanisms were discussed [14], involving intermediate formation of either a three-membered (A) or a four-membered (B) complex




subsequent conversion of which would give either hexamethyldisiloxane or bistriethylsilyl peroxide:



From the composition of the products of ozonolysis it was supposed[14] that the action of ozone on hexamethyldisilane involves a three-membered intermediate complex:

$$(CH_3)_3SiSi(CH_3)_3 + O_3 \rightarrow (CH_3)_3SiOSi(CH_3)_3 + O_2 . \quad (4)$$

The ratio of hexaethyldistannoxane formed to the quantities of hexaethyldistannane and ozone that have reacted at room temperature also corresponds to the stoichiometry of reaction (4).[26] When hexaethyldistannane is treated in isopropyl chloride with excess of ozone at −100°C, however, hexaethyldistannoxane is accompanied by an almost equimolecular quantity of bistriethylstannyl peroxide. This was attributed[26] to a different reaction mechanism from the above[14], at least at temperatures considerably lower than 0°C. It was assumed[26] that formation of an intermediate trioxide

$$(C_2H_5)_3SnSn(C_2H_5)_3 + O_3 \rightarrow (C_2H_5)_3SnOOOSn(C_2H_5)_3$$

was followed by the reaction

$$(C_2H_5)_3SnOOOSn(C_2H_5)_3 + (C_2H_5)_3SnSn(C_2H_5)_3 \rightarrow (C_2H_5)_3SnOOSn(C_2H_5)_3 + (C_2H_5)_3SnOSn(C_2H_5)_3.$$

Under these conditions (−100°C) the reaction of bistriethylstannyl peroxide with hexaethyldistannane, which occurs comparatively easily at room temperature[28], can play no significant part. On these views the observance of the stoichiometry of Eqn.(4) is attributed to the thermal instability of the trioxide at room temperature:

$$(C_2H_5)_3SnOOOSn(C_2H_5)_3 \rightarrow (C_2H_5)_3SnOSn(C_2H_5)_3 + O_2.$$

The action of ozone on hetero-organic compounds containing several heteroatom–heteroatom bonds also takes place predominantly at these bonds. Thus the oxidation of octa-t-butylstannetan involves[27] ~4 moles of ozone, in conformity with the equation

$$(t\text{-}C_4H_9)_8Sn_4 + 4O_3 \rightarrow 4(t\text{-}C_4H_9)_2SnO + 4O_2.$$

This result is consistent with the above mechanism for the action of ozone on the heteroatom–heteroatom bond[26].

## 3. Bihetero-oxanes, Alkoxy and Hydroxy-derivatives

Information on ozonolysis is available only for these derivatives of silicon and tin[13,14,16,17,21,29,30]. The main products of the oxidation of hexaethyldisiloxane by ozone at room temperature are acetic acid and a mixture of various polydiethylsiloxanes (hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, octaethyltrisiloxane)[14]. The ozonolysis of triethylsilyl hydroxide or ethoxytriethylsilane at room temperature[14] yields hexaethyldisiloxane as the main product, oxidation being more rapid with the second compound.

A detailed investigation of the ozonolysis of hexaethyldistannoxane by Aleksandrov and Sheyanov[29] showed that oxidation in n-decane at 10–60°C yields a polydiethylstannoxane $(C_2H_5)_3Sn.[O.Sn(C_2H_5)_2]_6.CSn(C_2H_5)_3$ together with acetaldehyde and triethylstannyl acetate. Estimation of the quantity of ozone consumed suggested that initiated oxidation of the initial organotin oxide either does not occur or plays no significant part in the ozonolysis of hexaethyldistannoxane.

The ozonolysis of triethylstannyl hydroxide in aqueous solution[21] is accompanied by the formation of acetaldehyde and tetraethyldistannoxane dihydroxide, whereas that of diethyldimethoxystannane in n-nonane yields acetaldehyde, acetic acid, and an organotin compound $(C_2H_5)_2Sn(OCH_3).OSn(OCH_3)_2C_2H_5$.[30] This work showed also[30] that diethyldimethoxystannane readily undergoes ozonolysis in n-decane at room temperature, but rise in temperature has little effect on the reaction velocity, as with hexaethyldistannoxane[29].

The mechanism of ozonolysis suggested earlier for tetraethyl derivatives of elements of the silicon subgroup is assumed to apply to the ethyl derivatives, alkoxides, and hydroxides of bihetero-oxanes[30,31].

## 4. Hetero-organic Halides and Hydrides

Information has been published on the ozonolysis of triethyltin chloride[16,17,30,32], diethyltin dichloride[16,17,30,33], triethyl-lead chloride[16,17,30,33], and organosilicon compounds containing various numbers of unsubstituted hydrogen atoms[13,14,34–41].

Ozone reacts readily with halides of organic derivatives of Group IV elements at room temperature and in the absence of illumination[16,17]. Under such conditions these compounds are extremely stable towards oxygen. Ozonolysis of triethylstannyl chloride in n-hexane at 0°C leads to the formation[32] of acetaldehyde and a solid product presumed to be $2(C_2H_5)_3SnCl.CSn(C_2H_5)Cl.O_3$. The same workers found[30,33] that the ozonolysis of triethylplumbyl chloride under similar conditions yields acetaldehyde, acetic acid, ethanol, and ethyl-lead chloride oxide $(C_2H_5ClPbO)_n$. The yields of these products and the quantity of ozone that reacts correspond to the stoichiometric relation

$$(C_2H_5)_3PbCl + O_3 \rightarrow 0.9 \cdot C_2H_5ClPbO + 0.9 \cdot CH_3CHO + 0.24 \cdot CH_3COOH + 0.57 \cdot C_2H_5OH .$$

The oxidation of diethyldichlorostannane under the same conditions[30,33] gives acetaldehyde, acetic acid, and an organotin product $C_2H_5Sn(COH)Cl_2.(C_2H_5)_2SnCl_2$, in the respective yields 0.1, 0.33, and 0.46 mole mole$^{-1}$ initial organotin compound.

The mechanism of the ozonolysis of hetero-organic chlorides is assumed[12] to be fundamentally the same as that of the reaction of ozone with fully organic derivatives of the elements.

Organosilicon compounds containing unsubstituted hydrogen atoms undergo ozonolysis at a silicon–hydrogen bond to form the corresponding silanols[13,14,34–41]. The mechanism is assumed[34,37,38] to involve formation of an intermediate trioxide:

$$R_3ElH + O_3 \rightarrow R_3ElOOOH \rightarrow R_3ElOH + O_2.$$

# III. REACTIVITY TOWARDS OZONE

## 1. Influence of Nature of Heteroatom

The kinetics of the ozonolysis of $(C_2H_5)_4El$[18,42,43] and $(C_2H_5)_3El.El(C_2H_5)_3$[44–46] (where El represents an element of the silicon subgroup) has been investigated in tetrachloromethane over the range 0–20°C. The results (Table 1) show that the reaction is first order with respect both to ozone and to the hetero-organic compound. The temperature dependence of the ozonolysis rate constant $k$ is described satisfactorily by the Arrhenius equation for all the compounds investigated.

It is noteworthy that the ozonolysis rate constants for hexaethyldisiloxane, hexaethyldigermanoxane, and hexaethyldistannoxane (Nos. IX–XI), representing the most reactive (towards ozone) of the corresponding reaction products[16], are significantly smaller than those for

the initial compounds. For this reason the ozonolysis rate constants obtained for compounds I–VIII can be assigned quite accurately to the primary act.

Table 1. Influence of nature of heteroatom on reactivity towards ozone [27,46].

| No. | Compound | $k_{20°C}$, $M^{-1}\,s^{-1}$ | lg $k_0$ | $E$, kcal mole$^{-1}$ | $\alpha \pm 0.01$ |
|---|---|---|---|---|---|
| I | $(C_2H_5)_4Si$ | $2.4\cdot10^{-2}$ | 4.1 | 7.6 | 3.583 |
| II | $(C_2H_5)_4Ge$ | $1.2\cdot10^{-1}$ | 7.3 | 11 | 3.574 |
| III | $(C_2H_5)_4Sn$ | 96 | 6.7 | 6.3 | 3.563 |
| IV | $(C_2H_5)_4Pd$ | 1300 | 8.5 | 7,0 | 3.559 |
| V | $(C_2H_5)_6Si_2$ | 0,7 | 6.5 | 9.0 | 3.573 |
| VI | $(C_2H_5)_6Ge_2$ | 2,1 | 6.0 | 7.5 | 3.567 |
| VII | $(C_2H_5)_6Sn_2$ | 300 | 8.0 | 7,5 | 3.549 |
| VIII | $(C_2H_5)_6Pb_2$ | 1650 | — | — | 3.542 |
| IX | $[(C_2H_5)_3Si]_2O$ | $1\cdot10^{-2}$ | — | — | — |
| X | $[(C_2H_5)_3Ge]_2O$ | $4\cdot10^{-2}$ | — | — | — |
| XI | $[(C_2H_5)_3Sn]_2O$ | 40 | 7.1 | 7.5 | — |

In the series of compounds investigated—$(C_2H_5)_4El$, $(C_2H_5)_6El_2$, and $[(C_2H_5)_3El]_2O$—which are equivalent with respect to the influence of the organic groups, steric hindrance, and the presence of vacancies in the coordination capacity of the heteroatom, there is considerable variation in the electronegativity of the heteroatom. Ozonolysis rate constants for the first two series at 20°C correlate satisfactorily with the effective electronegativities of the heteroatoms in these compounds [27]. The latter were measured by the "stability ratios" $\alpha$ of the heteroatoms, calculated from the Gordy system of electronegativities [47]:

$$\text{for } (C_2H_5)_4El,\ \lg k = 709 - 198.4\cdot\alpha,$$
$$\text{for } (C_2H_5)_6El_2,\ \lg k = 389 - 109\cdot\alpha.$$

This result indicates parallel variation in the reactivity towards ozone with the nucleophilicity of the heteroatom. In view of the suggested mechanism [30,48,49] the results indicate that the bimolecular reaction of the hetero-organic compound with ozone is limited at the stage of electrophilic attack by ozone on a heteroatom–carbon or heteroatom–heteroatom bond.

## 2. Influence of Substituent attached to Heteroatom

### (*a*) Fully organic derivatives and halides

The ozonolysis of several tetra-alkylstannanes in tetrachlorom ethane has been used [20] to investigate the influence of the inductive effect of the organic substituent in alkyl derivatives of Group IV elements. The reaction of these compounds with ozone is overall of second order, and the temperature dependence satisfies the Arrhenius equation (Table 2). The values obtained for the ozonolysis rate constant can be attributed quite accurately to reaction of the tetra-alkylstannanes with ozone [27]: i.e. the kinetics of ozonolysis of the initial compounds is not complicated by secondary reactions or by the products. Comparison of the kinetic parameters (Table 2, compounds II–VI) with the sum of the Taft inductive constants of the organic groups [50] indicates that differences in the $+I$ effects of the substituents have little influence on the reactivity of the tetra-alkyl derivative towards ozone.

When ethyl groups in tetraethylstannane and tetraethylgermane are replaced by substituents possessing powerful $-I$ effects (bromo, chloro, hydroxy), the reactivity of the compound is greatly diminished (Table 3) [51,52]. The dependence of lg$k$ on $\Sigma\sigma^*$ (Table 3) had led to the suggestion [27,51] that in this case the reaction velocity is probably influenced by at least two effects: firstly the strong inductive effect of chlorine, bromine, or hydroxyl tends to diminish the electron density on the carbon atoms adjacent to the tin atom, which hinders electrophilic attack by ozone on the tin–carbon bond; secondly, $d_\pi - p_\pi$ conjugation of the $p$ electrons of chlorine with vacant $d$ orbitals of tin tends to oppose the inductive effect and to promote such electrophilic attack. It is noteworthy that the presence of $d_\pi - p_\pi$ conjugation in the corresponding silicon compounds is convincingly supported by independent physical methods [53].

Table 2. Effect of organic radical on rate of ozonolysis of organotin compounds ($\sim10^{-3}$–$10^{-5}$ M) in tetrachloromethane [20] ([$O_3$] = $10^{-4}$–$10^{-7}$ M).

| No. | Compound | $k_{0°C}$, $M^{-1}\,s^{-1}$ | lg $k_0$ | $E$, kcal mole$^{-1}$ | $\Sigma\sigma^*$ |
|---|---|---|---|---|---|
| I | $(CH_3)_4Sn$ | $2.8\cdot10^{-2}$ | 5 | 8.2 | 0 |
| II | $(C_2H_5)_4Sn$ | 46 | 6.7 | 6.3 | 0.40 |
| III | $(p\text{-}C_3H_7)_4Sn$ | 18 | 7 | 7.3 | 0.46 |
| IV | $(p\text{-}C_4H_9)_4Sn$ | 17 | 7 | 7.2 | 0.52 |
| V | $(iso\text{-}C_4H_9)_4Sn$ | 16 | 7 | 7.2 | 0.50 |
| VI | $(p\text{-}C_5H_{11})_4Sn$ | 16 | 6.3 | 6.4 | 0.65 |

Table 3. Influence of $-I$ effect of substituent on rate of ozonolysis of hetero-organic compounds ($10^{-2}$–$10^{-5}$ M) in tetrachloromethane [51] ([$O_3$] = $10^{-4}$–$10^{-7}$ M).

| No. | Compound | $k_{20°C}$, $M^{-1}\,s^{-1}$ | lg $k_0$ | $E$, kcal mole$^{-1}$ | $\Sigma\sigma^*$ [50] |
|---|---|---|---|---|---|
| I | $(C_2H_5)_4Ge$ | $1.2\cdot10^{-1}$ | 7.3 | 11 | −0.40 |
| II | $(C_2H_5)_3GeBr$ | $1.5\cdot10^{-2}$ | 3 | 6.3 | 2.6 |
| III | $(C_2H_5)_4Sn$ | 96 | 6.7 | 6.3 | −0.40 |
| IV | $(C_2H_5)_3SnCl$ | 1.34 | 5.3 | 6.6 | 2.7 |
| V | $(C_2H_5)_2SnCl_2$ | $6.5\cdot10^{-2}$ | 3.8 | 6.6 | 5.7 |
| VI | $(C_2H_5)SnCl_3$ | $2\cdot10^{-2}$ | — | — | 8.7 |
| VII | $(C_2H_5)_3SnOH$ | 3 | — | — | 1.35 |
| VIII | $(C_2H_5)_3SnBr$ | 1.6 | — | — | 2.6 |

### (*b*) Organosilanes

A fairly long series of trisubstituted organosilicon derivatives has been used [54–56] to examine the influence of substituents attached to the heteroatom on the rate of reaction with ozone. Organosilanes provided a more convenient model to solve this problem because ozone acts bimolecularly on organosilicon hydrides and only at the silicon–hydrogen bond. The products are the corresponding silanols [13,14,34–41], which, like the organic solvents (hydrocarbons, halogenated hydrocarbons, etc.), have no appreciable chemical role in the reaction.

Relative ozonolysis rate constants for a considerable group of silanes have been correlated with the silicon–hydrogen stretching frequency $\nu_{Si-H}$ [35] or with the Hammett and Taft inductive constants [34,37–39]. These correlations were obtained on the assumption that inductive effects have a decisive influence on such frequencies [57]

and on the rate constants. Resonance effects ($d_\pi - p_\pi$ and $\sigma,\sigma$ conjugation) were disregarded, which cannot be accepted as correct[53].

Table 4. Effect of $\Sigma\sigma^*$ of substituents on ozonolysis rate constants for silanes in tetrachloromethane at 20°C.[54]

| No. | Silane | $\Sigma\sigma^*$ | $k_{exp}$ | $k_{calc}$ | $\Delta \lg k$ | $E$, cal mole$^{-1}$ | $10^{-7} k_0$, $M^{-1} s^{-1}$ |
|---|---|---|---|---|---|---|---|
| I | $(C_5H_{11})_3SiH$ | −0.486 | 107 | — | — | 7 700 | 6.3 |
| II | $(C_4H_9)_3SiH$ | −0.390 | 100 | — | — | 7 600 | 5 |
| III | $(C_3H_7)_3SiH$ | −0.345 | 94.5 | — | — | 7 700 | 4 |
| IV | $(C_2H_5)_3SiH$ | −0.300 | 80 | — | — | 8 000 | 6.3 |
| V | $(C_2H_5)(C_6H_5CH_2)_2SiH$ | 0.330 | 30 | — | — | — | — |
| VI | $(C_6H_5CH_2)_3SiH$ | 0 645 | 18.5 | — | — | 9 100 | 10 |
| VII | $(C_2H_5)_2(C_6H_5)SiH$ | 0.400 | 53 | 27.1 | 0.29 | 6 800 | 0.63 |
| VIII | $(C_2H_5)(C_6H_5)_2SiH$ | 1.100 | 40 | 8.8 | 0.65 | 8 100 | 4 |
| IX | $(C_6H_5)_3SiH$ | 1.800 | 30.5 | 2.9 | 1.03 | 10 200 | 100 |
| X | $(CH_3)(C_5H_{11})_2SiH$ | −0.324 | 63 | 86.5 | −0.13 | 7 500 | 2 |
| XI | $(CH_3)(C_4H_9)_2SiH$ | −0.260 | 60 | 78.05 | −0.11 | 7 500 | 2 |
| XII | $(CH_3)(C_3H_7)_2SiH$ | −0.230 | 56 | 74.4 | −0.12 | 6 500 | 0.31 |
| XIII | $(CH_3)(C_2H_5)_2SiH$ | −0.200 | 50.5 | 70.9 | −0.15 | 7 600 | 2 |
| XIV | $(CH_3)(C_6H_5CH_2)_2SiH$ | 0.430 | 21.5 | 25.8 | −0.08 | 8 000 | 2 |
| XV | $(CH_3)(C_6H_5)_2SiH$ | 1.200 | 29.5 | 7.5 | 0.60 | 7 100 | 0.5 |
| XVI | $(CH_3)_2(C_6H_5)SiH$ | 0.600 | 35 | 19.7 | 0.25 | 8 000 | 2.5 |

Determination of the ozonolysis rate constants for sixteen organosilanes (Table 4) has shown[54] that they all react readily with ozone at room temperature. Variation in the initial concentration of ozone or silane by factors of 5–10 has no effect on the rate constant. The stoichiometry is almost equimolecular, which indicates a first-order reaction with respect to ozone and to the initial organosilane. The equation for the rate constant is

$$M^{-1} s^{-1} = k_0 \exp(-E/RT).$$

Values of $k_0$ and $E$ are included in Table 4.

The organosilanes investigated can be divided into three groups (Table 4). Only the inductive effect of the substituents can reasonably be expected to appear in the first group (compounds I–VI), but in the second group (VII–IX) this is supplemented by $d_\pi - p_\pi$ interaction with the heteroatom. The third group of organosilanes (X to XIV and XV, XVI) is of interest in comparison with the first and second groups respectively, since the $\sigma,\sigma$-conjugation effect of methyl exceeds considerably those of other alkyl and aralkyl radicals[50].

The dependence of the ozonolysis rate constants for the organosilanes on the sum of the inductive constants of the organic substituents is described[54] by the Hammett–Taft equation

$$(\lg k = \rho\Sigma\sigma^* + \text{const}),$$

as illustrated by Fig. 1. For organosilanes of the first group at 20°C the equation is

$$\lg k = -0.696\,\Sigma\sigma^* + 1.7114. \quad (5)$$

The sensitivity to $\Sigma\sigma^*$ of the reactivity of the organosilanes (i.e. the slope $\rho$) is almost independent of temperature (Table 5). The negative slope supports a mechanism of the primary reaction of an organic compound of a non-transition Group IV element with ozone as coordination of the latter to the heteroatom followed by electrophilic attack at a heteroatom–carbon or heteroatom–hydrogen bond (depending on the nature of the hetero-organic compound). According to these views, reactivity towards ozone in a series of such compounds differing only in the total inductive effect of the substituents should increase with decrease in $\Sigma\sigma^*$. This is quantitatively consistent with experimental results[54].

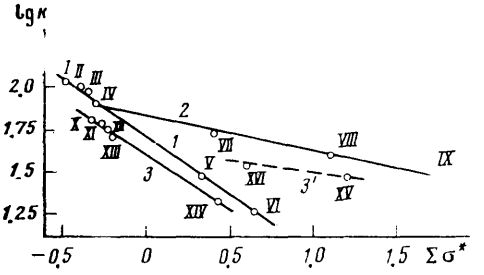



Figure 1. Dependence of $\lg k$ on $\Sigma\sigma^*$ for reaction of ozone with organosilanes in tetrachloromethane at 20°C: the numbering of the straight lines (1–3, 3′) corresponds to the groups of silanes.

Table 5. Values of $\rho$ at various temperatures of ozonolysis of the first group of organosilanes in tetrachloromethane[54].

| $t$, °C | $\rho$ | $r$ |
|---|---|---|
| 20 | −0.696 | 0 998 |
| 15 | −0.735 | 0.980 |
| 10 | −0.787 | 0.996 |
| 5 | −0.672 | 0.995 |
| 0 | −0.762 | 0.995 |

For organosilanes of the second and third groups the dependence of $\lg k$ on $\Sigma\sigma^*$ is not described by Eqn. (5), as is illustrated by Fig. 1. Rate constants $k_{calc}$ calculated by means of formula (5) from values of $\Sigma\sigma^*$ are smaller than the experimental values $k_{exp}$ for organosilanes of the second group, but larger in the third group (Table 4, compounds X–XIV). In the case of the second group this is attributed[54] to $d_\pi - p_\pi$ interaction of phenyl radicals with silicon, which opposes the negative inductive effect of this substituent and is formally equivalent to a decrease in its $-I$ effect; and for silanes of the third group to $\sigma,\sigma$ conjugation of the methyl group.

The explanation of the difference between experimental and calculated rate constants for the second group of organosilanes solely by $d_\pi - p_\pi$ interaction is supported by the linear relation (Fig. 2) between $\Delta \lg k = \lg k_{exp} - \lg k_{calc}$ for compounds VII–IX (Table 4) and values[58] of $\Delta\nu$Si–H for these compounds (where $\Delta\nu$Si–H is the contribution to the change in the silicon–hydrogen stretching frequency due solely to the $d_\pi - p_\pi$ interaction between silicon and phenyl substituents).

Quantitative comparison of the contributions by $\sigma,\sigma$ conjugation to the reactivity of the third group of organosilanes (X–XIV) could not be made[53] owing to the relatively minute differences in the values of $\Delta\nu$Si–H for these compounds. However, the "point" on Fig. 2 corresponding to the organosilanes with "unresolved" frequency differences lies satisfactorily on the general straight line.

The additivity of the effects of $d_\pi - p_\pi$ interaction and $\sigma,\sigma$ conjugation on the reactivity of the organosilanes towards ozone is confirmed by the good agreement, with the linear relation obtained between $\Delta \lg k$ and $\Delta\nu$Si–H (Fig. 2), of analogous experimental data for methyldiphenylsilane and phenyldimethylsilane (XV and XVI in Table 4), values of $\Delta\nu$ for which have been taken also from Refs. 53 and 58.

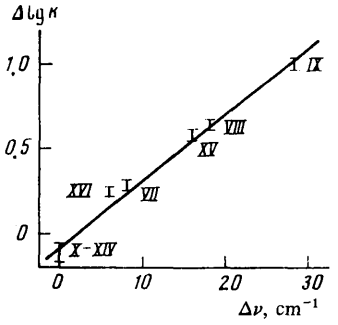



Figure 2. Relation between $\Delta \lg k$ and $\Delta\nu$ for organosilanes.

Table 6. Calculated charges and reactivity indices of reaction centre $\tau_C/\beta$ for certain organotin compounds (here and subsequently charges are given in units of the electronic charge).

| ЭОС | $q_{Sn}$ | $q_C$ | $\tau_C/\beta$ | ЭОС | $q_{Sn}$ | $q_C$ | $\tau_C/\beta$ |
|---|---|---|---|---|---|---|---|
| $(C_2H_5)SnCl_3$ | 0.78 | −0.05 | 4.05 | $(C_2H_5)_3SnCl$ | 0.68 | −0.16 | 4.16 |
| $(C_2H_5)_2SnCl_2$ | 0.73 | −0.11 | 4.11 | $(C_2H_5)_4Sn$* | 0.63 | −0.21 | 4.21 |

*The parameters $q_{Sn}$, $q_C$, and $\tau_C/\beta$ have the same values for $(n\text{-}C_3H_7)_4Sn$, $(n\text{-}C_4H_9)_4Sn$, $(n\text{-}C_5H_{11})_4Sn$, and $(iso\text{-}C_4H_9)_4Sn$ as for $(C_2H_5)_4Sn$.

Comparison of the ozonolysis rate constants with the distribution of electron density in several organotin (Table 6) and organosilicon compounds leads to extremely interesting conclusions[27,59]. The tin atom always bears the highest calculated positive charge, while the charge on the carbon atoms adjacent to the heteroatom is more negative than on the other carbon atoms, so that $\tau_C/\beta$ has its highest positive value. Comparison of the calculated charges on the reaction centre with the relative ozonolysis rate constants $k/k_0$, where $k_0$ is the rate constant for tetraethyltin (Table 3), leads to a dependence whose semilogarithmic form is almost linear (Fig. 3). The relative rate constant increases with the absolute value of the negative charge on the carbon atom of the reaction centre. These results are consistent with the above heterolytic mechanism of ozonolysis. Departure from linearity may be due to disregard of the $d_\pi - p_\pi$ interaction between chlorine and tin atoms, since such interaction tends to increase the negative charge on the carbon atom.

The analogous calculation of the distribution of electron density in a series of silanes—methyldiethyl, methyldi-n-propyl, methyldi-n-butyl, methyldi-n-pentyl, triethyl, tri-n-propyl, and tri-n-butyl—gives[27] almost the same charge density on silicon, *Si*-hydrogen, and *Si*-carbon atoms [$q$Si, $q$H(Si), and $q$C(Si) respectively +0.33, from −0.15 to −0.16, and from −0.07 to −0.09]. This result indicates that the empirical method of calculation used[27] (the Del Re method) is not sufficiently effective to "resolve" differences in the electronic structure of the silanes. However, the higher electron density on the hydrogen than on the carbon atom attached to silicon is of interest. It is consistent with the experimental observation in the ozonolysis of silanes that attack by the coordinated ozone is directed at the silicon–hydrogen bond, not at a silicon–carbon bond[13,14].

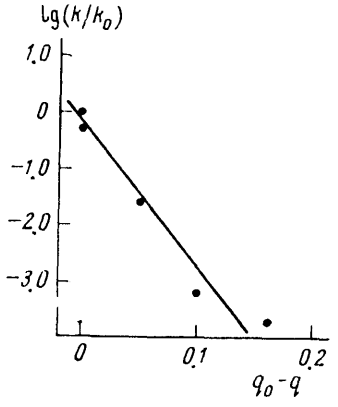



Figure 3. Dependence of logarithm of relative rate of ozonolysis of organotin compounds on variation in charge on reaction centre.

### 3. Effect of Non-specific Solvation

The influence of non-specific solvation on reactivity towards ozone has been investigated[60] on two organosilanes (tribenzyl and triethyl) and also on two biheteroorganic derivatives (hexaethyl-disilane and -digermane). Significant differences in reactivity towards ozone are present in both of these pairs of compounds (see subsection 1). In the choice of solvents preference was given to tetrachloromethane and 1,1,2,2-tetrachloroethane, which possess comparatively low dielectric constants $\epsilon$ and contain no functional groups that might have caused specific solvation of the test compounds.

The investigation has established[60] that at 25°C the dependence of the ozonolysis rate constant on the dielectric constant of the medium (for a mixed solvent the latter was calculated by means of the formula

$$\lg \varepsilon = N_1 \lg \varepsilon_1 + N_2 \lg \varepsilon_2,$$

where $N_i$ and $\epsilon_i$ are the respective component mole fractions and dielectric constants) is described by Kirkwood's equation

$$\lg k = A + B(\varepsilon - 1)/(2\varepsilon + 1) \qquad (6)$$

with the coefficients listed in Table 7 ($1 > r$ (correlation coefficient) $> 0.99$, method of least squares). The results indicate that non-specific solvation of the heteroorganic compound and of ozone enhance their mutual reactivity. In each pair of compounds the sensitivity of

ozonolysis to non-specific solvation is greater the greater the reactivity towards ozone. Such a dependence is consistent with a heterolytic mechanism of ozonolysis [12,16,17].

Table 7.

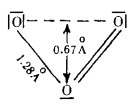
| Compound | Triethylsilane | Tribenzylsilane | Hexaethyldigermane | Hexaethyldisilane |
|---|---|---|---|---|
| *A* | 1.72 | 1.24 | −0.45 | −0.63 |
| *B* | 1.15 | 1.11 | 3.87 | 2.32 |

In the activated complex the valency electrons of the heteroatom are probably in an $sp^3d$ state owing to coordination of ozone with the quadrivalent silicon (or germanium) atom. Such hybridisation seems improbable if the test compounds are solvated in the tetrachloromethane–1,1,2,2-tetrachloroethane system. In discussing the effect of the medium, therefore, we have grounds for ignoring the formation of "diffusion pairs", and interpreting the results in terms of the greater polarity of the activated complex than of the initial reactants. On this basis the slope $B$ in Eqn.(6) is related to the dipole moment $\mu^{\ddagger}$ and the effective radius $r^{\ddagger}$ of the activated complex, as well as to the corresponding parameters of the initial reactants ($\mu_1$ and $r_1$ for the hetero-organic compound, and $\mu_2$ and $r_2$ for ozone), by the well known formula [61]

$$B = -\frac{1}{2{,}3\,kT}\left(\frac{\mu_1^2}{r_1^3} + \frac{\mu_2^2}{r_2^3} - \frac{\mu^{\ddagger 2}}{r^{\ddagger 3}}\right) \qquad (7)$$

which has been used to estimate the dipole moment of the activated complex and the relative charge $q$ on the heteroatom.

For the calculations the value $\mu_2 = 0.53$ D [62] was adopted. The choice of $r_2$ and $r^{\ddagger}$ was governed by the amphiphilic nature of ozone, with its nucleophilic centre coordinated with the heteroatom, entailed in a heterolytic reaction mechanism. The latter was therefore taken to be $r^{\ddagger} = r_{Si-O} = 1.64$ Å [63] for silanes and hexaethyldisilane, and $r_{Ge-O} = 1.85$ Å [63] for hexaethyldigermane, while $r_2$ was given the values 1.28 and 0.67 Å depending on the different steric positions




For triethylsilane and tribenzylsilane $r_1 = 1.47$ Å, while $\mu_1$ has the values 1.54 and 1.31 D respectively [65]; for hexaethyldisilane and hexaethyldigermane $r_1$ was taken to be 2.34 and 2.41 Å, while $\mu_1$ was equated to zero [63]. The above data were used to calculate $\mu^{\ddagger}$ and $q$ for the activated complex in the ozonolysis. Table 8 shows satisfactory agreement between the value of $q$ with $r_2 = 1.28$ Å and the value obtained by other investigators from spectroscopic data [65], from which it can be concluded [60] that 1.28 Å is more probable than 0.67 Å for $r_2$ in the ozonolysis of the hetero-organic compounds investigated. Hence the dipolar ozone molecule entering into reaction is preferably regarded as an amphiphilic form with the nucleophilic centre localised mainly on a single oxygen atom.

An analogous investigation was made with individual solvents [66] differing essentially in nature (and dielectric constant)—tetrachloromethane (2.23), chloroform (4.72), 1,2-dichloroethane (10.16), 1,1,2,2-tetrachloroethane (8.08), propionic acid (3.2), acetic acid (6.2), and acetic anhydride (20.5)—the test compounds being methyldi-n-propylsilane, tribenzylsilane, hexaethyldisilane, and hexaethyldigermane. This established that the dependence of the ozonolysis rate constant on the dielectric constant was also described by Kirkwood's equation, which indicated non-specific solvation of the substrates in the solvents. The coefficients in the relations (6) established at 0°C are given in Table 9 [66] (method of least squares, $0.90 < r < 0.99$).

Table 8. Calculation of $\mu^{\ddagger}$ and $q$ for ozonolysis at 25°C [60] (values of $q$ in units of the electronic charge).

| Compound | $\mu^{\ddagger}$ ($r_2$=1.28 Å) | $q$ ($r_2$=1.28 Å) | $\mu^{\ddagger}$ ($r_2$=0.67 Å) | $q$ ($r_2$=0.67 Å) | $q^{obs}$ |
|---|---|---|---|---|---|
| $(C_2H_5)_3SiH$ | 2.08 | 0.26 | 2.84 | 0.36 | 0.22 |
| $(C_6H_5CH_2)_3SiH$ | 1.85 | 0.24 | 2.55 | 0.32 | 0.18 |
| $(C_2H_5)_6Ge_2$ | 1.78 | 0.20 | 2.87 | 0.32 | — |
| $(C_2H_5)_6Si_2$ | 1.25 | 0.16 | 2.26 | 0.29 | — |

Table 9.

| Compound | Methyldipropylsilane | Tribenzyl silane | Hexaethyldigermane | Hexaethyldisilane |
|---|---|---|---|---|
| *A* | 0.91 | 0.44 | −0.60 | −1.09 |
| *B* | 1.88 | 1.35 | 2.50 | 1.45 |

Table 10. Values of $\mu^{\ddagger}$ and $q$ for hetero-organic–ozone activated complex at 0°C ($r_2 = 1.28$ Å). [66]

| Compound | $\mu^{\ddagger}$ | $q$ | Compound | $\mu^{\ddagger}$ | $q$ |
|---|---|---|---|---|---|
| $(CH_3)(C_3H_7)_2SiH$ | 2.24 | 0.32 | $(C_2H_5)_6Si_2$ | 1.08 | 0.14 |
| $(C_6H_5CH_2)_3SiH$ | 2.10 | 0.30 | $(C_2H_5)_6Ge_2$ | 1.49 | 0.20 |

The type of relations established is consistent with the results obtained in binary mixtures of tetrachloromethane and 1,1,2,2-tetrachloroethane. Substitution in Eqn.(7) of the same values for $r^{\ddagger}$, $r_1$, $r_2$, $\mu_1$, and $\mu_2$ as in the preceding case yielded calculated values of $\mu^{\ddagger}$ and $q$ for the activated complex agreeing satisfactorily with those obtained with use of the binary solvents (Table 10).

## 4. Effect of Specific Solvation

The first study of the effect of specific solvation on the ozonolysis has been made [67] on triethylstannyl chloride in tetrachloromethane in the presence of dimethylformamide, which solvates the initial hetero-organic compound specifically. The phenomenology of the reaction remains almost unchanged in the presence of dimethylformamide [67]. In this case, however, the rate constant depends significantly on its concentration (Table 11).

The observed [67] kinetic effect of the medium is explained by specific solvation of triethylstannyl chloride

by dimethylformamide, by analogy with the well known complexes formed by halides of alkylstannanes with many ligands (amides, ketones, etc.[68]). Calorimetric and spectroscopic measurements were made[67] to test this hypothesis. Determination of the heat of mixing of triethyltin chloride and dimethylformamide in the proportions 1 : 2 at 20°C gave for the enthalpy of formation of the complex the value $-5 \pm 0.5$ kcal mole$^{-1}$. The infrared spectra of a 20 : 1 mixture showed a significant low-frequency shift (by 18 cm$^{-1}$) of the carbonyl-stretching frequency (for pure dimethylformamide $\nu C:O = 1680$ cm$^{-1}$), which was accepted as proof of complex formation through the lone pair on the carbonyl oxygen atom of the amide molecule. Proofs of the specific solvation of triethylstannyl chloride by dimethylformamide were obtained[67] also on analysing the infrared spectra of the former compound.

Table 11. Effect of additions of dimethylformamide ($N = [D_0]/[A_0]$) on rate of oxidation of triethylstannyl chloride (concentration $c$, M) by ozone ($2 \times 10^{-4}$ M) in tetrachloromethane.

| $N$ | $k$, M$^{-1}$ s$^{-1}$ | $N$ | $k$, M$^{-1}$ s$^{-1}$ | $N$ | $k$, M$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| −17°C, $c=4.23\cdot10^{-3}$ | | 0° C, $c=2.82\cdot10^{-3}$ | | 20° C, $c=1.41\cdot10^{-3}$ | |
| 0 | 0.110 | 0 | 0.42 | 0 | 1.34 |
| 5.2 | 0.184 | 5.2 | 0.53 | 2.7 | 1.38 |
| 8.7 | 0.250 | 7.9 | 0.62 | 5.4 | 1.44 |
| 12.2 | 0.300 | 13.1 | 0.76 | 8.0 | 1.62 |
| 15.2 | 0.320 | 18.3 | 0.91 | 13.5 | 1.59 |
| 20.8 | 0.380 | 23.5 | 0.93 | 20.0 | 1.89 |
| 29.6 | 0.390 | 31.3 | 0.93 | 27.0 | 2.18 |
| | | 39.2 | 0.93 | 40.0 | 2 17 |

The degree of charge transfer in the dimethylformamide complex of the hetero-organic compound was 5–7% estimated for one donor–acceptor bond from the correlation[68] of the enthalpy of complex formation with the transfer of charge. From the results it was assumed[67] that the increase in the rate of reaction of triethylstannyl chloride with ozone in the presence of dimethylformamide was due to formation of a complex that was more reactive towards ozone than was the original hetero-organic compound. To analyse the kinetic results we denote triethylstannyl chloride, dimethylformamide, ozone, and the reaction products by A, D, C, and P respectively, when the process can be written

$$A + C \xrightarrow{k_1} P,$$

$$A + D \underset{k_{-2}^{(1)}}{\overset{k_2^{(1)}}{\rightleftarrows}} AD, \qquad (8_1)$$

$$AD + D \underset{k_{-2}^{(2)}}{\overset{k_2^{(2)}}{\rightleftarrows}} AD_2, \qquad (8_2)$$

. . . . . .

$$AD_{n-1} + D \underset{k_{-2}^{(n)}}{\overset{k_2^{(n)}}{\rightleftarrows}} AD_n. \qquad (8_n)$$

$$AD + C \xrightarrow{k_3^{(1)}} P,$$

$$AD_2 + C \xrightarrow{k_3^{(2)}} P,$$

. . . . . .

$$AD_n + C \xrightarrow{k_3^{(n)}} P.$$

The reaction velocity will then be

$$w = k_1[A] \cdot [C] + \sum_{i=1}^{n} k_3^{(i)}[AD_i][C].$$

When the extent of oxidation of triethylstannyl chloride is small,

$$[A] = [A]_0 - \sum_{i=1}^{n} [AD_i],$$

$$k_{exp} = \frac{w}{[A]_0[C]} = k_1 + \frac{\sum_{i=1}^{n} k_3^{(i)}[AD_i] - k_1 \sum_{i=1}^{n} [AD_i]}{[A]_0}. \qquad (9)$$

On the hypothesis[67] that the complexes formed by reactions $(8_1)-(8_n)$ differed significantly in reactivity, the mathematics was simplified by considering only the most reactive complex towards ozone (of arbitrary composition $AD_n$). With $[D]_0 \gg n[AD_n]$ Eqn.(9) then becomes

$$k_{exp} = k_1 + (k_3^{(n)} - k_1)\frac{N^n}{N^n + \frac{1}{K[A]_0^n}}, \qquad (10)$$

where $N = [D]_0/[A]_0$ and $K$ is the equilibrium constant of the overall process comprising stages $(8_1)-(8_n)$.

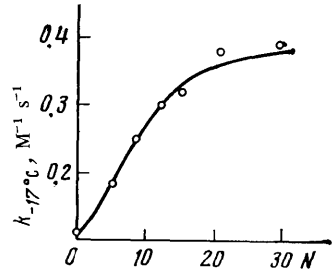



**Figure 4.** Agreement between ozonolysis rate constants $k$ obtained experimentally (points) and calculated by means of Eqn.(11) (curve).

Experimental data (Table 11) were substituted in Eqn. (10) to find the minimum standard deviation, for each temperature investigated, over the range $n = 0.5-3$ in steps of 0.5 with optimum values of $K$ estimated from the standard deviation between calculated and experimental values. The optimum value $n = 2$ was found, and the experimental results at −17°C (Table 11) were satisfactorily described by the equation

$$k_{exp} = k_1 + (k_{max} - k_1)\frac{N^2}{N^2 + 70} \qquad (11)$$

(standard deviation not exceeding 3%). Formation of a 1 : 2 complex of triethylstannyl chloride with dimethylformamide is confirmed by the good agreement between ozonolysis rate constants $k$ in the presence of dimethylformamide determined experimentally at −17°C and calculated by means of formula (11) (Fig.4).

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# The Mechanism and Stereochemistry of the Oxidation of Bicyclic Hydrocarbons with a Bridge Bond

E.A.Lazurin, V.V.Voronenkov, and Yu.G.Osokin

Reactions involving the oxidation of unsaturated bicyclic hydrocarbons with a bridge bond by oxygen, hydroperoxides, peracids, and hydrogen peroxide are examined, particular attention being devoted to the mechanism and the stereochemistry of the oxidation of norbornene hydrocarbons and their derivatives.
The bibliography includes 98 references.

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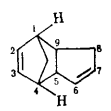

## I. INTRODUCTION

Bicyclic hydrocarbons with a bridge bond include a series of important natural compounds (terpenes). Since the beginning of the 1960s, individual representatives of hydrocarbons of this class (bicyclic olefins—mainly norbornene and its homologues) have been finding increasing practical applications as monomers[1-4] for the manufacture of high-molecular-weight compounds with valuable technical properties, obtained mainly by solution polymerisation and copolymerisation in the presence of Ziegler–Natta catalysts.

Owing to their complex steric structure, bicyclic hydrocarbons with a bridge bond are excellent objects for the study of the mechanisms and stereochemical characteristics of chemical reactions[5-7], among which the oxidation reactions are of special interest.

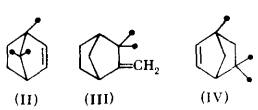
## II. AUTOXIDATION

Having autoxidised dicyclopentadiene (I), Hock and Depke[8] found that the primary reaction products are derivatives with hydroperoxy-groups in the 5- and 8-positions; the 1- and 4-positions (at the bridgehead of the bicyclic system) remain unaffected.



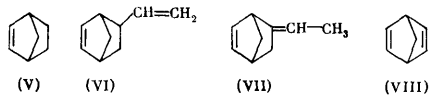
(I)

The oxidation of certain bicyclic hydrocarbons—derivatives of bicyclo[2,2,1]heptane—was described most fully for the first time by Nesmeyanov et al.,[9] who showed that bornylene (II), camphene (III), and δ-fenchene (IV), i.e.



(II) (III) (IV)

are hardly oxidised by oxygen in the presence of cobalt and manganese stearates. Similar results were also obtained when an attempt was made to oxidise norbornene (V), vinylnorbornene (VI), ethylidenenorbornene (VII), and norbornadiene (VIII)[10,11] (Fig. 1).




(V) (VI) (VII) (VIII)

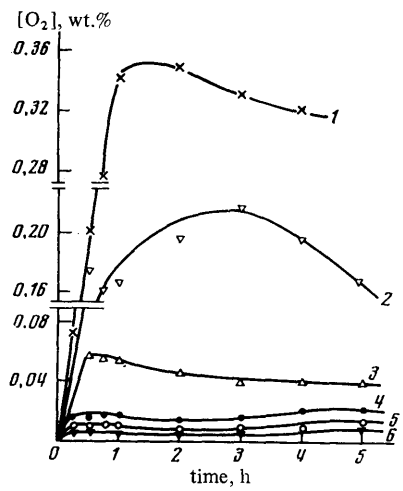



**Figure 1.** Kinetic curves for the accumulation of hydroperoxides (calculated in relation to active oxygen) at 95°C: 1) vinylcyclohexene; 2) tetrahydroindene; 3) dicyclopentadiene; 4) vinylnorbornene; 5) ethylnorbornene; 6) norbornene.

Nesmeyanov[9,12] explained the chemical passivity of the α-$C_{tert}$–H bond in the above systems as follows: the reactivity of the C–H bond in hydrocarbons depends on its strength, which diminishes in the presence of σ,π-conjugation. The latter takes place to the maximum extent only when the C–H bond and the axes of the "π-electron" clouds

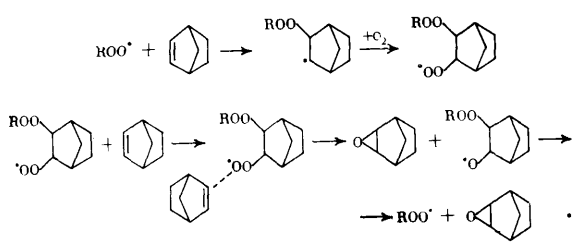
are nearly parallel; on the other hand, if they are at right angles, there is no conjugation and it has no influence on the C–H bond. In the above hydrocarbons (I)–(VIII), the $\alpha$-C$_{tert}$–H bond is firmly fixed nearly at right angles to the axes of the "$\pi$-electron" clouds, which removes the $\alpha$-C$_{tert}$–H bond from the $\sigma,\pi$-conjugation and reduces its chemical reactivity. It follows from Nesmeyanov's ideas that the axial $\alpha$-C–H bond should show the greatest tendency towards oxidation in cyclic olefins, because, in contrast to the equatorial C–H bond, it exhibits the maximum degree of $\sigma,\pi$-conjugation, which has been confirmed experimentally[11,13].

A subsequent explanation of the passivity of the $\alpha$-C$_{tert}$–H bond in bicyclo[2,2,1]heptane derivatives is associated with hypotheses concerning the structure of the transition state[14]. The hydroperoxide—the primary oxidation product—is known[15] to be formed via the mechanism

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}\,.$$

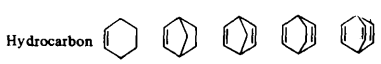
The formation of the radical R$^{\cdot}$ involves the transition of the carbon atom in the C–H bond from the $sp^3$-hybrid state to the $sp^2$-hybrid state. Since the rigid structure of bicyclo[2,2,1]heptane derivatives preclude such transition, then evidently the C–H bonds in this hydrocarbon must be chemically passive in radical reactions, in agreement with experiment[10]. It is noteworthy that the idea of taking into account the ring energy in considering the structure of the transition state has been used to explain the different rates of oxidation of $C_5$–$C_{10}$ cycloparaffins[16].

Data on the oxidation of bicyclo[2,2,1]hept-2-ene in the presence of initiators proved to be extremely interesting. Mayo[17] observed that, when bicyclo[2,2,1]hept-2-ene is oxidised by oxygen in the presence of azobisisobutyronitrile (AIBN), an epoxy-derivative is formed. It was shown subsequently[18] that the epoxide is the main product of the oxidation of bicyclo[2,2,1]hept-2-ene derivatives by oxygen in the presence of not only AIBN but also of benzoyl peroxide. The study of the mechanism of the oxidation of bicyclo[2,2,1]hept-2-ene derivatives[10,19] showed that the formation of the epoxide from norbornene is described by the following mechanism:



The mechanism agrees satisfactorily with the reaction kinetics.

The main cause of this type of oxidation of norbornene and its derivatives is the presence of a strained double bond in their ring systems. A strained double bond is understood as one involving appreciable angular distortions and therefore possessing a large potential energy. The strain of the double bond is estimated experimentally from heats of hydrogenation[20,21] (as a rule a large absolute negative heat of hydrogenation corresponds to a large strain of the double bond in the system):



| Hydrocarbon | | | | | |
|---|---|---|---|---|---|
| $-\Delta H_{hydr}$, kcal mole$^{-1}$ | 28,9 | 33,1 | 35,0 | 35,0 | 37,6 |

Comparison of the rates of initiated oxidation of cyclohexene and norbornene (Fig. 2) and also of the reaction products led to the hypothesis that the double bond of norbornene undergoes homolysis to a greater extent than that of cyclohexene[11], possibly because the $p_z$ orbitals of the norbornene double bond overlap to a lesser extent than the $p_z$ orbitals of the double bond of cyclohexene. This view has been confirmed by a comparison of the relative rates of autoxidation of hydrocarbons of different classes[22] (Table 1). Table 1 shows that olefins are oxidised much more readily than aromatic alkylhydrocarbons. The explanation is probably that the degree of conjugation in the allyl group is greater than in the benzyl group. The products of the oxidation of olefins (as well as cyclo-olefins) are hydroperoxides, unsaturated alcohols, and ketones, i.e. the products of oxidation involving C–H bonds in the $\alpha$-position relative to the double bond. High rates of autoxidation are also characteristic of norbornene hydrocarbons, but here the ring double bond is oxidised and not the $\alpha$-C–H bond.

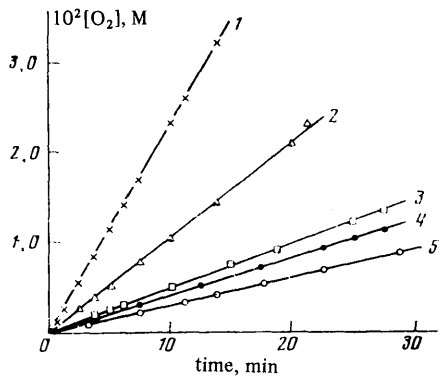
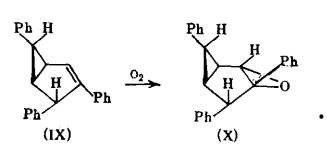



**Figure 2.** Kinetic curves for the absorption of oxygen at 50°C in the presence of AIBN (0.0304 M): 1) tetrahydroindene; 2) ethylidenenorbornene; 3) cyclohexene; 4) vinylnorbornene; 5) norbornene.

**Table 1.** The relative rates of autoxidation of hydrocarbons[22].

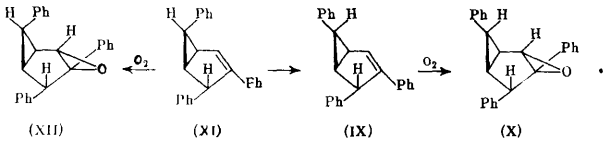
| Hydrocarbon | $k_{rel}$ | Hydrocarbon | $k_{rel}$ | Hydrocarbon | $k_{rel}$ |
|---|---|---|---|---|---|
| Cyclohexene | 10.15 | 2-Methylbut-1-ene | 6.54 | Isopropylbenzene | 1.00 |
| Cyclopentene | 9.34 | Indan | 4.30 | Ethylbenzene | 0.83 |
| 2-Methylbut-2-ene | 8.50 | *p*-Ethyltoluene | 1.30 | *p*-Xylene | 0.73 |
| Dicyclopentadiene | 8.21 | *p*-Isopropyltoluene | 1.27 | *m*-Xylene | 0.67 |
| Norbornene | 7.82 | *o*-Ethyltoluene | 1.05 | Toluene | 0.28 |

A study of the oxidation of the stereoisomers of 3,4,6-triphenylbicyclo[3,1,0]hex-2-ene in xylene[23] showed that the *exo*, *exo*-isomer (**IX**) gives rise to the *exo*,*exo*-epoxide (**X**):




(IX) (X)

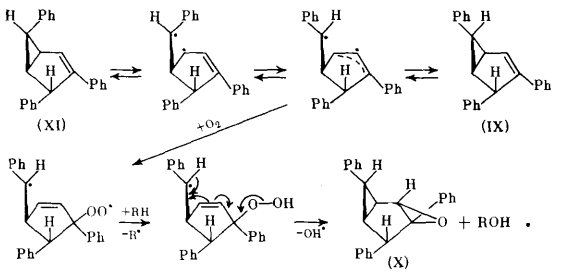
On the other hand, the oxidation of *exo,endo*-3,4,6-triphenylbicyclo[3,1,0]hex-2-ene (**XI**) results in the formation of *exo,exo*-2,4,6-triphenylbicyclo[3,1,0]hex-2-ene (**IX**) and its *exo,exo*-epoxide (**X**) together with the corresponding *exo,endo*-epoxide (**XII**):



(XII) (XI) (IX) (X)

Evidently, in this case hydrocarbon (**XI**) is not only converted into the epoxide (**XII**) but also isomerises to hydrocarbon (**IX**), which is oxidised to compound (**X**). To demonstrate the occurrence of the isomerisation process, the authors[23] heated hydrocarbon (**IX**) or (**XI**) in nitrogen and obtained an equilibrium mixture of hydrocarbons (**IX**) and (**XI**) in proportions of 16 : 1.

A mechanism for the formation of products (**IX**) and (**X**) from compound (**XI**), according to which the rupture of the cyclopropane ring of the bicyclo-olefin leads to an intermediate biradical which then interacts with oxygen to form a peroxy-radical, was proposed on the basis of literature data[24,25]. The subsequent reactions of the peroxy-radical lead to products (**IX**) and (**X**):

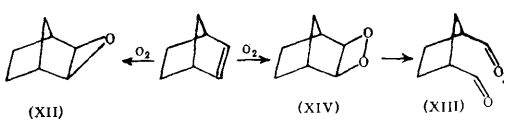


A study of the sensitised photochemical oxidation of norbornene by singlet oxygen at room temperature in different solvents showed[26] that a mixture of the *exo*-epoxide of norbornene (**XII**) and *cis*-cyclopentane-1,3-dialdehyde (**XIII**) is formed in all cases (Table 2).

**Table 2.** The composition of the products of the photochemical oxidation of norbornene by singlet oxygen in various solvents at room temperature.

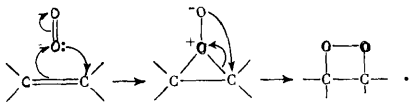
| Solvent | Composition of products, % | |
|---|---|---|
| | (XII) | XIII) |
| $CH_3CN$ | 39 | 61 |
| $CH_3COC(CH_3)_3$ | 53 | 47 |
| $CH_3COCH_3$ | 65 | 35 |

The authors[26] believe that the dialdehyde is formed via a dioxetan (**XIV**) stage,

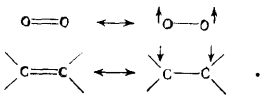


(XII) (XIV) (XIII)

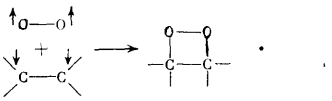
the mechanism of the formation of which can be represented as follows[27,28]:



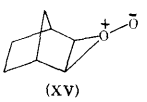
However, we believe that dioxetan can be formed in a different way. In the presence of a sensitiser, the carbon and oxygen double bond systems pass to excited triplet and singlet states[29-31]:



Since the species formed are paramagnetic, the synthesis of dioxetan can be regarded as a homolytic and not a polar interaction:

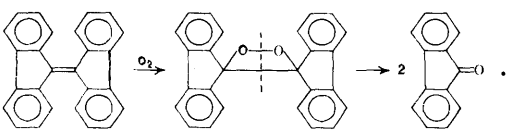


The mechanism of the formation of the norbornene *exo*-epoxide was not finally elucidated[26], but the authors suggest that dioxetan (**XIV**) or the perepoxide (**XV**) may serve as precursors of the epoxide:



(XV)

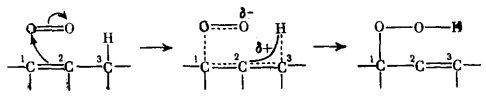
It is noteworthy that the sensitised oxidation of a strained double bond is a general reaction. If the allylic hydrogen atom is inactive and the double bond is highly strained, the dioxetan formed on oxidation may be isolated as a product[27,32,33]. For example, the photochemical oxidation of 9,9'-difluorenylidene, which has a strained double bond, proceeds with formation of fluorenone via an intermediate dioxetan stage[34] in accordance with the following mechanism:



Jefford and Boschung[35] also investigated the photochemical oxidation by singlet oxygen of 2-methylnorborn-2-ene, 2-methylenenorbornane, and their 7,7-dimethyl derivatives in the presence of a sensitiser. They showed that the primary reaction products are not epoxides but unsaturated hydroperoxides. Table 3 lists the relative rates of photochemical oxidation of certain cyclic and bicyclic olefins. The ratios of the rates of *exo*- and *endo*-attack by oxygen on the double bond were calculated for certain bicyclic hydrocarbons from the relative yields of the *exo*- and *endo*-products (Table 4).

The data presented in Tables 3 and 4 indicate a high sensitivity of the photochemical oxidation to steric hindrance: the *endo*-attack by singlet oxygen on the double bond of 2-methylnorborn-2-ene is 1000 times slower than in the reaction involving 1-methylcyclopentene, while the rate of *exo*-attack is reduced approximately by a factor of 250 following the introduction of two methyl substituents in the 7.7-position of 2-methylnorborn-2-ene.

Jefford and Boschung[35] proposed the following mechanism, taking into account the geometry of the transition state in the formation of the hydroperoxide:



(XVI)

and concluded that the transition state (**XVI**) has a dipolar structure.

**Table 3.** The relative rates of photochemical oxidation and partial rates of *exo*- and *endo*-attack by singlet oxygen on the double bonds in cyclo- and bicyclo-olefins.

| Hydrocarbon | Relative rate of photochemical oxidation | Partial rates | |
|---|---|---|---|
| | | of *exo*-attack | of *endo*-attack |
|  | 2.3 | 1.15 | 1.15 |
|  | 115.0 | 57.5 | 57.5 |
|  | 9.5 | 4.5 | 4.5 |
|  | 1.0 | 0.97 | 0.03 |
|  | 3.2 | 3.15 | 0.05 |
|  | 0.262 | 0.108 | 0.154 |
|  | 0.077 | 0.012 | 0.065 |

**Table 4.** The ratios of the rates of *exo*- and *endo*-attack ($v_{exo}/v_{endo}$) by singlet oxygen on the double bond in bicyclic hydrocarbons[35].

| Hydrocarbon |  |  |  |  |
|---|---|---|---|---|
| $v_{exo}/v_{endo}$ | 66.0 | 0.19 | 28.0 | 0.67 |

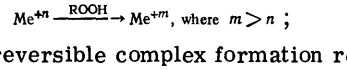
The addition of an oxygen atom to the first carbon atom of the double bond leads to the appearance on the central carbon atom of the allyl fragment of a positive charge δ+, which is delocalised via hyperconjugation with a C–H bond in the α-position relative to the C–C bond. The formation of the hydroperoxide is completed by the transfer of the conjugated γ-hydrogen atom to the $O^-$ centre and the migration of the double bond. The displacement of the double bond in hydrocarbons has been demonstrated with the aid of a deuterium label[35].

## III. INTERACTION WITH HYDROPEROXIDES

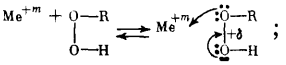
The epoxidation of olefins by reaction with hydroperoxides proceeds in the presence of catalysts. It is recommended that metals whose ions must possess the following fundamental properties be used as catalysts[36]: a high positive charge; vacant electronic orbitals (*d* orbitals) capable of accommodating pairs of electrons; a tendency towards the formation of unstable complexes with the reactants. Such metals are molybdenum, chromium, tungsten, vanadium, manganese, cobalt, niobium, tantalum, titanium, rhenium, selenium, etc.[37] Molybdenum, tungsten, vanadium, and chromium compounds, which may be used as such or with added iron, nickel, manganese, and cobalt are the most common catalysts[38]. The proposed catalysts may be homogeneous and heterogeneous. The most active homogeneous systems comprise molybdenum and vanadium carboxylates and acetylacetonates, alkyl molybdates, and $MoO_3$ and $WO_3$ complexes with organic oxygen, nitrogen, and sulphur compounds, etc.[39] Among the catalysts enumerated above, preference is given to molybdenum compounds, which ensure a high selectivity of the epoxidation process[40-42].

A mechanism for the epoxidation of olefins by hydroperoxides in the presence of variable-valence metals has been proposed by Gould et al.[36] and has been confirmed in many investigations[43-50]. On the basis of the above studies, the mechanism of the liquid-phase epoxidation of olefins by hydroperoxides can be represented as follows:

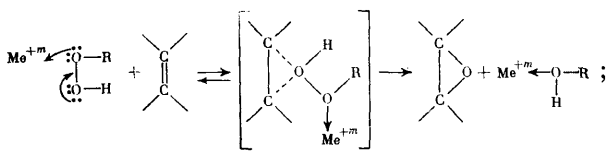
(1) rapid and irreversible activation of the catalyst:



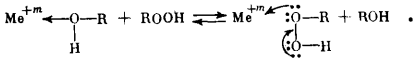
(2) rapid and reversible complex formation reaction:

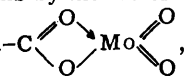


(3) reaction of the complex with the olefin (the stage limiting the rate of the entire process):



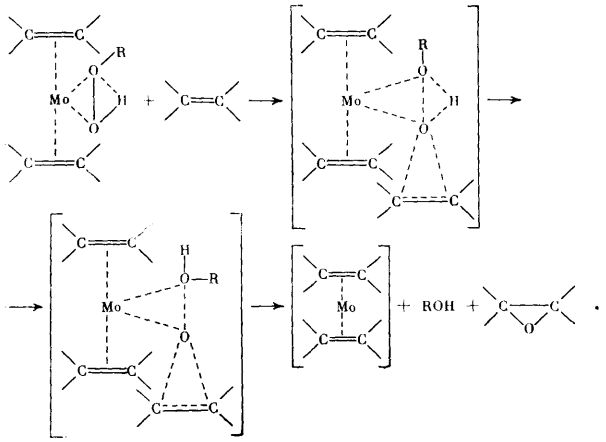
(4) rapid reversible exchange of ligands:



It has been shown[51] that, when ethylphenyl hydroperoxide is added in the oxidation of olefins by the latter in the presence of molybdenum resinate  , the valence of the metal changes: molybdenum(V) is converted into molybdenum(VI) and compounds of molybdenum in the +5 and +6 oxidation states (*n* and *m* respectively in the mechanism) exist simultaneously during the epoxidation reaction, and the proportions of the two types of compounds are influenced by the concentration of the epoxidising agent.

In a detailed study of the individual stages of the epoxidation of cyclohexene by ethylphenyl hydroperoxide in the presence of the molybdenum catalyst, it was suggested[52] that the formation of the epoxide proceeds via the reaction

of the hydroperoxide bound in a complex with a new olefin molecule:



It has been found in studies [53,54] by NMR and ESR of the epoxidation of olefins by t-butyl hydroperoxide in the presence of dioxobis(cyclohexane-1,2-diolo)molybdenum that stable paramagnetic free radicals are formed during the reaction and give rise at the beginning to a complex of the catalyst–t-butyl peroxy-radical type and, after the addition of the olefin, a catalyst–t-butylperoxy-radical–olefin complex is formed.

It was shown above that an olefin with a high negative heat of hydrogenation is oxidised at a high rate. In a study of the catalytic epoxidation of individual isomeric butenes by t-butyl hydroperoxide, Farberov and coworkers [55] found that *cis*-but-2-ene is the most reactive. This is consistent with the negative heats of hydrogenation of the relevant hydrocarbons [21] (Table 5).

**Table 5.** The negative heats of hydrogenation and the reactivities of isomeric butenes in the epoxidation reaction in the presence of molybdenum acetylacetonate (epoxidation temperature 50°C, hydrocarbon concentration 4.0 M, catalyst concentration $1.0 \times 10^{-4}$ M).

| Olefin | $-\Delta H_{hydr}$, kcal mole$^{-1}$ | Rate constant for epoxidation reaction, litre mole$^{-1}$ s$^{-1}$ | Relative rate of epoxidation |
|---|---|---|---|
| But-1-ene | 26.8 | $0.08 \cdot 10^{-3}$ | 1.0 |
| *trans*-But-2-ene | 27.6 | $1.08 \cdot 10^{-3}$ | 14.2 |
| *cis*-But-2-ene | 28.6 | $2.74 \cdot 10^{-3}$ | 36.0 |

It has been shown similarly [56,57] that in the series of cyclic olefins the carbon atom involved in the most strained bond is epoxidised most readily (Table 6). Furthermore, it has been shown by $^1$H NMR and infrared spectroscopy that, in all cases of the epoxidation of cyclic olefins having double bonds in the ring and in the side chain (vinylnorbornene and vinylcyclohexene), the products are in all cases monoepoxy-derivatives formed on the ring double bond, which indicates a high degree of strain of the latter compared with that of the double bond in the side chain.

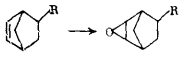
It has been found in the oxidation of norbornene, vinylnorbornene, cyclopentene, cyclohexene, and camphene by t-butyl hydroperoxide in the presence of the molybdenum catalyst [58] that the relative rates of epoxidation of the above hydrocarbons are in the ratios 6.5 : 6.0 : 5.0 : 2.0 : 1 respectively. The opposite dependence of the rate of epoxidation of hydrocarbons on the stretching vibration frequency of the ring C–C bond in the infrared spectra was observed.

**Table 6.** Degree of conversion of t-butyl hydroperoxide in the epoxidation of cyclo-olefins in the presence of molybdenum acetylacetonate (temperature 0°C, molar ratio olefin : hydroperoxide = 3:1, catalyst concentration 0.001 mole of Mo per mole of hydroperoxide, reaction time 30 min).

| Hydrocarbon | Camphene | Vinylcyclohexene | Vinylnorbornene |
|---|---|---|---|
| Conversion of hydroperoxide, wt.% | 4.0 | 21.0 | 26.5 |

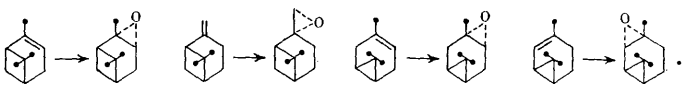
The epoxidation of olefins by hydroperoxides in the presence of catalysts has an electrophilic mechanism [59,60]. Consequently in a series of norbornene derivatives the rate of oxidation should vary as a function of the electronegativity of the substituent. This has been confirmed in a study [61] where it was found that, in the epoxidation of norbornenes by t-pentyl hydroperoxide in the presence of $MoCl_5$, compounds with electron-donating substituents are oxidised at higher initial rates than compounds containing electron-accepting substituents (Table 7).

**Table 7.** The rates of oxidation of 6-substituted norbornene derivatives by t-pentyl hydroperoxide [61]:



| R | $CO_2CH_3$ | $CH_2OCO_2CH_3$ | $OCO_2CH_3$ | OH | *exo*-CN | *endo*-CN | Cl | $CH_2OH$ | H | $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^7W$, mole litre$^{-1}$ s$^{-1}$ | 2 | 5 | 6 | 7 | 8 | 9 | 15 | 23 | 35 | 116 |

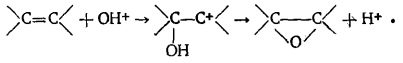
The stereochemistry of the catalytic epoxidation of bicyclic olefins by hydroperoxides has been investigated [60,62] and it has been established that $\alpha$- and $\beta$-pinenes as well as $\Delta^3$- and $\Delta^4$-carenes, which have a markedly hindered double bond, give rise only to the *endo*-epoxides on oxidation by t-pentyl hydroperoxide in the presence of $MoCl_5$, because in all cases there is *endo*-attack on the reactant:



Methods for the determination of the conformations of terpene epoxides by $^1$H NMR have been developed by Arbuzov et al. [63]

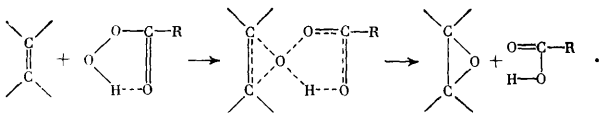
## IV. OXIDATION BY PERACIDS

The oxidation of olefins by peracids has been investigated in detail; together with reports containing data on the kinetics and mechanisms of individual reactions, a number of reviews[47,64-66] and monographs[67,68] devoted to the Prilezhaev reaction have appeared in recent literature. It was suggested previously[68,69] that the epoxidising species is the free hydroxyl cation $OH^+$, which attacks the olefin via the reaction



However, it was found that the Prilezhaev reaction does not undergo general acid catalysis.

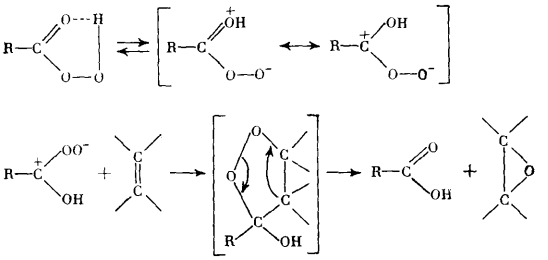
In later studies of the kinetics of the epoxidation of various olefins by peracids[70-73], it was suggested that the epoxide is formed via a $\pi$-complex:



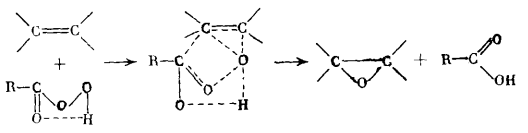
The formation of an intramolecular hydrogen bond in peracids was noted and demonstrated for the first time by Emanuel' et al.[74]

The mechanism of the epoxidation of olefins proposed by Bartlett[70] and Lynch and Pausacker[71] in general agrees satisfactorily with the fundamental process characteristics[67,75]. It explains readily the irreversibility of the reaction and the energetic process characteristics, because the formation of a complex reduces the energy required to abstract an oxygen atom from the peracid and to transfer it to the C=C bond.

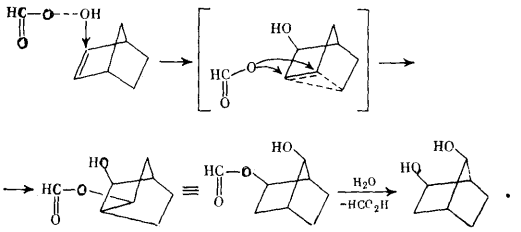
In highly polar solvents, epoxidation via a mechanism involving dipolar 1,3-addition is possible[67,76]:



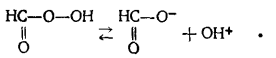
or



A characteristic feature of the Prilezhaev reaction is high stereospecificity leading to pure *cis*-addition of the oxygen atom with retention of the configuration of the substituents at the double bond[67]. However, the bridge structure of bicyclic olefins leads in many instances to an anomalous epoxidation reaction. Thus it was found in one of the early studies[77] that, in the oxidation of norbornene by performic acid, the only product is *cis*-norcamphane-2,7-diol. The authors suggested that the reaction proceeds with a Wagner–Meerwein rearrangement via a stage involving the formation of 2-formyl-7-hydroxynorbornane:

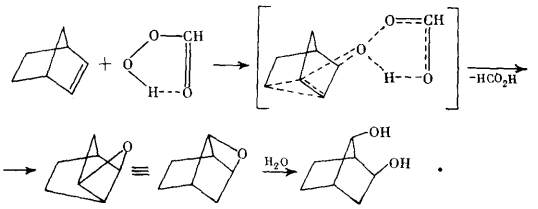


The proposed mechanism is based on the dissociation of performic acid into ions via the reaction



However the $HO^+$ cation should have a high energy[47] and its formation is not very likely under the given conditions. The intermediate—2-formyl-7-hydroxynorbornane—was not isolated either.

According to modern ideas[67], the oxidation of norbornene by performic acid probably involves a stage in which 2,7-epoxynorbornane is formed:



A study of the epoxidation of norbornene and *exo*-dihydrobicyclopentadiene by perbenzoic acid[78] showed that the reaction proceeds without a Wagner–Meerwein rearrangement and the consequent formation of *exo*-2,3-epoxynorbornane and *exo*-2,3-epoxy-*exo*-5,6-cyclopentanonorbornane respectively (the yield was 80% in both cases). These results were confirmed by Gassman and Pape[79], who oxidised bicyclo[2,2,1]hept-2-ene-7-one and bicyclo[2,2,1]-hept-2-*anti*-7-ol by perbenzoic acid and established that in both cases the reaction also proceeds without a Wagner–Meerwein rearrangement and the consequent formation of *exo*-products: *exo*-2,3-epoxybicyclo[2,2,1]heptan-7-one and *exo*-2,3-epoxybicyclo[2,2,1]heptan-*anti*-7-ol.

*endo*-Products are formed in the oxidation of norbornadiene by peracids[80-82]. It was shown in the studies quoted that the *endo*-2,3-epoxynorbornene formed undergoes a partial rearrangement which results in the formation of *endo*-bicyclo[3,1,0]hex-2-en-6-al[80,81] or *endo*-9-formylbicyclo[3,1,0]hex-2-ene[82]. The *endo*-pathway of the oxidation of norbornadiene and its homologue is most likely because double bond between the $C_{(5)}$ and $C_{(6)}$ carbon atoms is not shielded by hydrogen atoms[83].

In a study of the stereochemistry of the epoxidation of norbornene and its homologues with subsequent reduction of the products by lithium in ethylenediamine, Brown et al.[84] found that a mixture of *endo*- and *exo*-hydroxy-derivatives is formed in all cases (Table 8). They also demonstrated[84] that the presence of the 7,7-dimethyl substituents in the norbornene molecule decreases the overall rate of epoxidation by a factor of 100 and the rate of *exo*-attack by a factor of 1000; in such cases, the epoxidation proceeds mainly via *endo*-attack on the reactant (Table 8).

A study of the stereoselectivity of the oxidation of olefin double bonds by peracids showed[85] that peroxybenzimidic acid is the least stereoselective reagent in relation to double bonds among other peracids (for example $CH_3COOOH$). Table 9 presents the relative rates of epoxidation of olefins by peroxybenzimidic and peracetic acids (the rates of reaction of the above acids with cyclohexene were assumed to be unity).

**Table 8.** The ratio of the amounts of *endo*- and *exo*-products obtained in the epoxidation of norbornene and its homologues by *m*-chloroperbenzoic acid.

| Hydrocarbon | Composition of products, % | |
|---|---|---|
| | *exo*-form | *endo*-form |
| Norbornene | 99.0 | 1.0 |
| 7,7-Dimethylnorbornene | 12.0 | 88.0 |
| 1-Methylnorbornene | 99.0 | 1.0 |
| 2-Methylnorbornene | 99.5 | 0.5 |
| 1,7,7-Trimethylnorbornene | 5.0 | 95.0 |

**Table 9.** The rates of epoxidation of olefins by peracids.

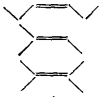
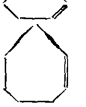
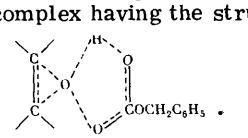
| Hydrocarbon | Relative rate of epoxidation | | Hydrocarbon | Relative rate of epoxidation | |
|---|---|---|---|---|---|
| | by peroxybenzimic acid | by peracetic acid | | by peroxubenzimic acid | by peracetic acid |
|  | 0.4 | 0.039 |  | 1.46 | — |
| | 0.9 | 1.0 | | | |
| | 1.3 | 1.0 | | | |
|  | 2.1 | 7.95 |  | 0.92 | 1.43 |
|  | 3.5 | — | | | |
|  | 1.0 | 1.0 |  | 2.03 | 1.36 |
| | | |  | 3.8 | 1.2 |

**Table 10.** The yields of *endo*-epoxides in the epoxidation of R-5-norbornenes.

| R | Yield of epoxide, % |
|---|---|
| $COOCH_3$ | 39 |
| $(CH_2)_2OCOCH_3$ | 53 |
| $(CH_2)_3OCOCH_3$ | 39 |

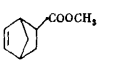
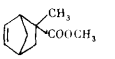
In a study of the oxidation of 5-substituted norbornenes by *o*-benzylmonoperoxycarbonic acid—an extremely effective epoxidising agent yielding mainly *endo*-epoxides—it was found[86] that the reaction gives rise to an intermediate olefin–peracid complex having the structure



(XVII)

This fact constitutes direct confirmation of the mechanism[70,74] of the epoxidation of olefins by perbenzoic acids described above.

**Table 11.** The oxidation of norbornene derivatives by peracetic acid at 20°C.

| Compound | Yield of epoxide, % |
|---|---|
|  | 80 |
|  | 72 |
|  | 55* |
|  | 51 |

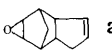
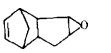
*Under these conditions, dicyclopentadiene gives rise to 30% of the epoxide  and 25% of the epoxide 

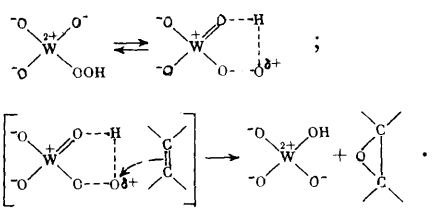
Table 10 presents the yields of the *endo*-epoxides of 5-substituted norbornenes obtained by the reaction of the corresponding hydrocarbons with *o*-benzylmonoperoxycarbonic acid.

The oxidation of norbornene derivatives by peracetic acid takes place mainly via *exo*-attack on the double bond[87]. The yields of the resulting *exo*-epoxides are listed in Table 11.

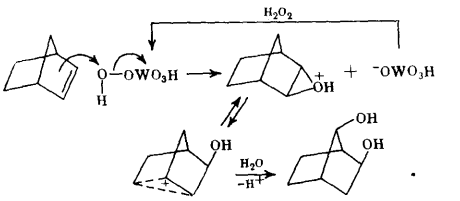
## V. REACTIONS WITH HYDROGEN PEROXIDE

The oxidation of olefins by hydrogen peroxide has been investigated in detail[47]. The reaction is accelerated in the presence of tungstic acid and tungstates. The epoxidation mechanism can be represented as follows[88-90]:

$$HWO_4^- + H_2O_2 \rightleftarrows HWO_5^- + H_2O\ ;$$



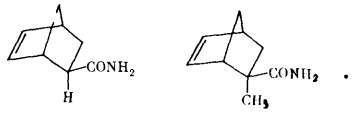
In one of the early papers[91], it is stated that the interaction of norbornene with a solution of hydrogen peroxide in t-butyl alcohol in the presence of tungstic acid yields *exo*, *syn*-norbornane-2,7-diol and not the epoxide. However, the mechanism proposed by the authors includes an epoxide-formation stage:



The occurrence of the rearrangement, caused by the structure of the epoxidised hydrocarbon, constitutes evidence for the cationic mechanism of the addition reaction catalysed by tungstic acid, since the rearrangement is not observed when the corresponding bicyclic radical is formed[92].

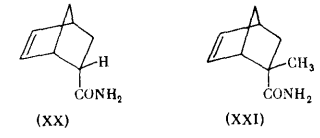
The epoxidation of norbornene hydrocarbons containing functional groups proceeds anomalously. It has been shown[93,94] that, when the functional groups are in the *exo*-positions, the only reaction product is an epoxide. The *endo*-configuration of the carboxy-[93,95], hydroxymethyl[94,96], and methoxycarbonyl[97] groups leads to the complete or partial formation of tricyclic structures containing a heteroatom.

The oxidation of stereoisomeric carbonamides of the norbornene series was investigated in a later study[98]. The authors showed that the oxidation of *endo*-carboxamides (XVIII) and (XIX), containing a strained double bond, proceeds readily with formation of the corresponding epoxides having the *exo*-configuration:

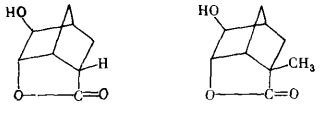


(XVIII) (XIX)

The epoxidation of the stereoisomeric *endo*-carboxamides (XX) and (XXI) leads to the formation of the lactones (XXII) and (XXIII), by virtue of the nucleophilic attack on the carbon atom of the carbonyl group directed towards the positively charged carbon atom in the intermediate complex, formed as a result of the electrophilic attack by the peracid on the norbornene double bond.



(XX) (XXI)



(XXII) (XXIII)

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The review of the literature data on the oxidation of bicyclic hydrocarbons with a bridge bond shows that the oxidation reaction is of theoretical interest, particularly from the standpoint of stereochemistry. Presumably some of these reactions will be used in future in the chemical industry.

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# Polarographic Study of the Reactions of Carbonyl Compounds with Ammonia and Its Derivatives and Their Application in Polarographic Analysis

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The theoretical principles and the experimental results of the application of polarography to the study of equilibria in single- and multi-stage reactions of carbonyl compounds with ammonia and its derivatives and of the acid-base properties of their products are examined. A comparison is made with data obtained by other research techniques. More than 100 reactions are analysed taking into account the nature of the carbonyl compound and the nucleophile.
The mechanism of the polarographic electrochemical reduction of the reaction products, including aminocarbinols, is considered. The analytical application of the reactions in the indirect polarographic determination of carbonyl and nitrogen compounds is discussed.
The bibliography includes 207 references.

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## I. INTRODUCTION

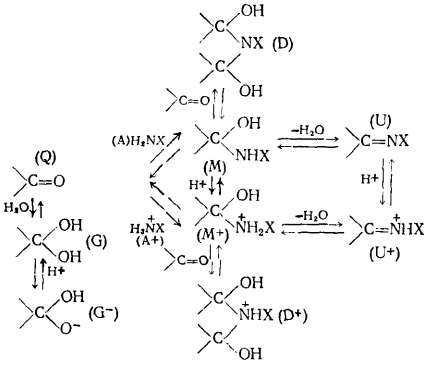
The use of the reactions of carbonyl compounds with ammonia and its derivatives in polarography makes it possible to investigate the physicochemical parameters of these reactions [1-3] and to achieve in many instances important indirect determinations of the substances involved. The latter is very important for the understanding of the mechanism of the nucleophilic interaction [4,5], which is widely used in other branches of analytical chemistry [6,7].

Among the physicochemical parameters of the reactions of carbonyl compounds with ammonia and its derivatives, the equilibrium constants and the acid–base dissociation constants of the products have been most widely investigated with the aid of polarography. These applications of the polarographic method are examined in the present review together with the mechanism of the reduction of the reaction products and the analytical applications.

## II. REACTION EQUILIBRIA AND ACID–BASE PROPERTIES OF PRODUCTS

An extensive application of polarography in the study of the reactions of carbonyl compounds with ammonia and its derivatives was achieved for the first time by Zuman [8-11] and by Zuman and Březina [12,13]. However, in the majority of the early studies [8-21] the polarographic method was used to investigate the simpler single-stage interaction and Matoušek [22] was the first to use polarography to characterise quantitatively the multistage interaction on the basis of the reactions with formaldehyde. This research was developed further [23-29] and now involved the determination of quantitative reaction parameters. The development of the theoretical and experimental principles of the application of polarography to the study of single-stage and partly multistage interactions was continued in other studies [30-35].

Among the reactions involved in the given equilibrium, it is possible to isolate the main and side reactions. The main reactions, which are observed in aqueous solution, can be described by the following general mechanism [36-38]:

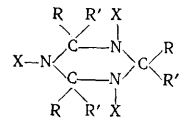



(1)

where Q, G, and G′ are respectively the carbonyl compound, its hydrated form, and its anion, A and $A^+$ are ammonia or an ammonia derivative and its form protonated at the nitrogen atom, M, D, and $D^+$ are adducts—hydroxyalkyl- and bishydroxyalkylamines (there is also a possibility of trishydroxyalkylamines T and $T^+$ in the reaction between HCHO and $NH_4^+$ [28])—and the corresponding forms protonated at the nitrogen atom, and U and $U^+$ represent the dehydration products—an unsaturated compound and its form protonated at the nitrogen atom.

The reaction of secondary amines HNXX′ with formaldehyde leads to the formation, apart from M($M^+$), of the corresponding cation of the quaternary amino-derivative [39-41] $X'X\overset{+}{N}(CH_2OH)_2$. A similar reaction is also characteristic [39] of tertiary amines $XX'X''\overset{+}{N}CH_2OH$, although according to Matoušek [22] there is also a possibility of the formation of the compound $XX'X''\overset{+}{N}CH_2O^-$ under these conditions.

Together with the main reactions (1), numerous side reactions have been noted[36], among which those involving the formation of the cyclic trimer



(2)

and the diamine $\diagdown C(HNX)_2$ are the most important[38,39].

We shall use the following notation for the equilibrium constants of the main reactions:

$$L_G = [G]/[Q], \quad (3)$$
$$L_M = [M]/[A][Q], \quad (4)$$
$$L_{M^+} = [M^+]/[A^+][Q], \quad (5)$$
$$L_D = [D]/[A][Q]^2, \quad (6)$$
$$L_{D^+} = [D^+]/[A^+][Q]^2, \quad (7)$$
$$L_T = [T]/[A][Q]^3, \quad (8)$$
$$L_{T^+} = [T^+]/[A^+][Q]^3, \quad (9)$$
$$L_U = [U]/[A][Q], \quad (10)$$
$$L_{U^+} = [U^+]/[A^+][Q], \quad (11)$$

and for the acid dissociation constants:

$$K_G = [G^-][H^+]/[G], \quad (12)$$
$$K_{A^+} = [A][H^+]/[A^+], \quad (13)$$
$$K_{M^+} = [M][H^+]/[M^+], \quad (14)$$
$$K_{D^+} = [D][H^+]/[D^+], \quad (15)$$
$$K_{T^+} = [T][H^+]/[T^+], \quad (16)$$
$$K_{U^+} = [U][H^+]/[U^+]. \quad (17)$$

If the reaction involves the anion of the carbonyl compound (for example, the anion of pyruvic acid) or with the anion of the nucleophile (for example, the anion of an aminoacid), then $L_M$, $L_D$, $K_{M^+}$, $K_{D^+}$, and $K_{U^+}$ are replaced by $L_{M^-}$, $L_{D^-}$, $K_{M^\pm}$, $K_{D^\pm}$, and $K_{U^\pm}$. For the reaction of the anion of the carbonyl compound with the nucleophile anion, we have $L_M$ = and $K_{M^\pm}$. In a fairly acid pH range, Eqns.(5), (7), and (13)–(15) hold also for aminoacids. Here it is necessary to bear in mind that the constant $K_{A^+}$ has not been determined experimentally and is usually assumed[42] to be equal to the acid dissociation constant of the methyl or ethyl ester of the aminoacid. On the other hand, the acid dissociation constants of the carboxy-group in the protonated form of the aminoacid $K'_{A^+}$ as well as the acid dissociation constants $K_{A^\pm}$ of the protonated nitrogen atom in the aminoacid dipolar ion have been determined experimentally[42]. Some of the above constants are interrelated:

$$K_{M^+} = K_{A^+}L_M/L_{M^+}, \quad (18)$$
$$K_{D^+} = K_{A^+}L_D/L_{D^+}, \quad (19)$$
$$K_{T^+} = K_{A^+}L_T/L_{T^+}, \quad (20)$$
$$K_{U^+} = K_{A^+}L_U/L_{U^+}. \quad (21)$$

In view of the insignificant influence[42] of the carbonyl compound undergoing the addition reaction on the constant $K'_{A^+}$, we obtain a similar relation also for aminoacids:

$$K_{M^\pm} = K_{A^\pm}L_{M^-}/L_{M^+}. \quad (22)$$

We shall now consider equations for the determination of equilibrium constants from the average limiting polarographic current $\bar{i}_{lim}$ for the reduction of the reaction products. If $G^-$, D, and $D^+$ are neglected in mechanism (1) for $c_Q$ = const. ($c$ is the overall concentration, the subscript indicates the substance involved, and the square brackets represent the equilibrium concentration), we obtain the equation[32]:

$$L_e = \frac{[M]+[M^+]+[U]+[U^+]}{([Q]+[G])([A]+[A^+])} = (L_{M^+}+L_{U^+})\frac{K_{A^+}\{(L_M+L_U)/(L_{M^+}+L_{U^+})\}+[H^+]}{(1+L_G)(K_{A^+}+[H^+])} =$$
$$= \frac{\bar{i}_{lim}\cdot\bar{i}^0_{lim}}{(\bar{i}^0_{lim}-\bar{i}_{lim})(c_A\bar{i}^0_{lim}-c_Q\bar{i}_{lim})}. \quad (23)$$

The sums of the constants $L_M + L_U$ and $L_{M^+} + L_{U^+}$ (for the reaction between HCHO and $NH_2NH_2$)[33] were determined from the dependence of the effective equilibrium constant $L_e$ on pH and the individual equilibrium constants were found with the aid of additional investigations[33,34]. In Eqn.(23), $\bar{i}^0_{lim}$ is the limiting current in the presence of an excess of nucleophile such that a further increase of $c_A$ does not lead to an increase of $\bar{i}_{lim}$, i.e. under these conditions virtually the entire carbonyl compound is converted into products which can be polarographed; $\bar{i}_{lim}$ and $\bar{i}^0_{lim}$ can have both diffusional and kinetic origins[30,32]. The dehydration product $U^+$ is reduced[1,32,34] and, if a diffusion current obtains, the stages involving the protonation of M and U and the $M(M^+)$ dehydration stages are fairly rapid and there is insufficient time for the equilibrium in the stages involving the formation of the adduct $M(M^+)$ to be appreciably displaced at the surface of the dropping electrode. The latter condition should also be observed in the presence of a kinetic current[30–35], which is due to slow stages involving either the protonation of U or the dehydration of $M^+$ (see below).

If the study is performed with $c_A$ = const., $\bar{i}_{lim}$ is determined in the presence of an excess of the carbonyl compound and Eqn.(23) then has the same form, but $c_A$ and $c_Q$ must be interchanged.

Under the conditions such that $L_U \gg L_M$ and $L_{U^+} \gg L_{M^+}$ (M and $M^+$ may be neglected), Eqn.(23) assumes a simpler form when account is taken of Eqn.(21):[32]

$$L'_e = \frac{[U]+[U^+]}{([Q]+[G])([A])+[A^+])} = L_{U^+}\frac{K_{U^+}+[H^+]}{(1+L_G)(K_{A^+}+[H^+])} =$$
$$= \frac{\bar{i}_{lim}\cdot\bar{i}^0_{lim}}{(\bar{i}^0_{lim}-\bar{i}_{lim})(c_A\bar{i}^0_{lim}-c_Q\bar{i}_{lim})}. \quad (24)$$

The equilibrium constants for the individual stages can now be found directly from Eqn.(24) (for the reactions of various carbonyl compounds with $NH_2NH_2$, with the exception of HCHO).[31,33,35]

A further simplification of Eqn.(24) is achieved when $c_A \gg c_Q$:[12,13,17,30,34]

$$L'_e = L_{U^+}\frac{K_{U^+}+[H^+]}{(1+L_G)(K_{A^+}+[H^+])} = \frac{\bar{i}_{lim}}{(\bar{i}^0_{lim}-\bar{i}_{lim})c_A}. \quad (25)$$

When $c_Q \gg c_A$ ($c_A$ = const.), it is necessary to replace $c_A$ by $c_Q$ in Eqn.(25). Eqn.(25) has been used in a number of studies[12,13,17] but without taking into account the hydration of the carbonyl compound. Furthermore, the limiting diffusion current $\bar{i}_d$ for the carbonyl compound was used in some investigations[8,10–13] instead of $\bar{i}^0_{lim}$, which is less accurate, because the constants of the $U(U^+)$ and Q diffusion currents may differ. On the other hand, in the case of the kinetic current the replacement of $\bar{i}^0_{lim}$ by $\bar{i}_d$ is altogether inadmissible.

If $L_M \gg L_U$ and $L_{M^+} \gg L_{U^+}$ (i.e. U and $U^+$ may be neglected), then [U], $[U^+]$, $L_{U^+}$, and $K_{U^+}$ in Eqns.(24) and (25) must be replaced by [M], $[M^+]$, $L_{M^+}$, and $K_{M^+}$ respectively. $M^+$ may then be reduced at the electrode instead of $U^+$.

Retaining M, $M^+$, D, and $D^+$ in Eqn.(1), introducing T and $T^+$ (for the reaction between HCHO and $NH_4^+$),[28] and

neglecting A, $G^-$, U, and $U^+$, the present author and Cheremukhina [28] obtained the equation

$$\frac{\bar{i}_{\lim}}{\bar{i}^0_{\lim}-\bar{i}_{\lim}} = L_{M^+}\frac{K_{M^+}[H^+]}{(1+L_G)[H^+]}c_Q + L_{D^+}\frac{K_{D^+}[H^+]}{(1+L_G)^2[H^+]}c_Q^2 + L_{T^+}\frac{K_{T^+}+[H^+]}{(1+L_G)^3[H^+]}c_Q^3, \quad (26)$$

but no account was taken of the hydration of Q. In the derivation of Eqn.(26), it was assumed that $c_Q \gg c_A$ ($c_A$ = const.) and that the sum of the products $M^+ + D^+ + T^+$ is reduced. The current $\bar{i}^0_{\lim}$ was determined in the presence of a large excess of Q. If A is also involved in mechanism (1), then $[H^+]$ in the denominators of all the terms on the right-hand side of Eqn.(26) must be replaced by $K_{A^+} + [H^+]$. When $[H^+] \gg K_{A^+}(K_{M^+}, K_{D^+}, K_{T^+})$ or $[H^+] \ll K_{A^+}(K_{M^+}, K_{D^+}, K_{T^+})$, then Eqn.(26) and the corresponding equation with $K_{A^+} + [H^+]$ in the denominators can be greatly simplified [23,24,26,41]. Furthermore, the trishydroxyalkyl derivative $T(T^+)$ was not involved in the equilibrium [reactions of formaldehyde with aminoacids [24,25], $\overset{+}{N}H_3OH$, [26] and $(CH_3)_2\overset{+}{N}H_2$ [40,41]] and the third term in Eqn.(26) (with $c_Q^3$) was eliminated. The equilibrium constants were found with the aid of equations of type (26) [23-26,28,41] using a graphical method analogous to the methods of determining the equilibrium constants for stepwise complex-formation reactions based on the study of potentials [43] (potentiometry) or half-wave potentials [44] (polarography).

Eqn.(25) can be used to describe the equilibrium in the reactions involving $NH_2NHCONH_2$ [17,30] without any changes (because $U + U^+$ predominates). On the other hand, in the studies [8,10-13] of the reactions involving $NH_3$, $NH_2RCOO^-$, and $NH_2CH_2CH_2OH$ in the presence of an excess of the nucleophile, the adduct M [8,10,11] or $M + M^+$ [12,13] was the dominant species and $L_{M^+}(L_M)$ and $K_{M^+}$ were apparently determined from Eqn.(25) [8,10-13] rather than $L_{U^+}(L_U)$ and $K_{U^+}$, as believed by the authors [8,10-13]. We shall return to this problem later.

The single-stage interaction (the dominance of $M^+$ in the reactions of formaldehyde with aminoacids in an acid medium [29] and of M in the reaction of formaldehyde with $NH_2CH_2CH_2OH$ [45,46] in the presence of an excess of the latter) has been investigated polarographically using Eqns. (26), in which only the first term (the aminoacid term) was retained and (25) in which $L_{U^+}$ and $K_{U^+}$ were replaced by $L_{M^+}$ and $K_{M^+}(NH_2CH_2CH_2OH)$ respectively. The insignificant concentration of $D^+$ in the reactions involving aminoacids with a primary amino-group in an acid medium [29] is apparently due to the relatively low value of $L_{D^+}$, which has been confirmed by data obtained using kinetic [24,29] and other methods [47].

It is noteworthy that, in a polarographic study [24] of the reactions of formaldehyde with aminoacids in an alkaline medium, samples were polarographed in an acid medium in order to increase $\bar{i}_{\lim}(\bar{i}^0_{\lim})$. Under these conditions, the limiting current decreased with time $t$ and values of $\bar{i}_{\lim}(\bar{i}^0_{\lim})$ extrapolated by $t = 0$ were used in the calculations. The extrapolation was facilitated by the fact that the kinetic equation relating $\bar{i}_{\lim}(\bar{i}^0_{\lim})$ to time was of first order [24], which can be explained by the rapid and almost complete decomposition of $D^+$ to $M^+$ and the reduction of $M^+(L_{D^+}/L_{M^+} \ll L_{M^+})$. Thus, although only the $M^+$ wave was observed in the acid solution, its height corresponded to the sum of the concentrations of the adducts [M] + [D] formed in the alkaline medium.

In contrast to these reactions, the $HCHO-\overset{+}{N}H_3OH$ [26] and $HCHO-\overset{+}{N}H_4$ [28] equilibria in an acid medium, i.e.

$$Q + A^+ \underset{k_{-1}}{\overset{k_{+1}}{\rightleftarrows}} M^+ + Q \underset{k_{-2}}{\overset{k_{+2}}{\rightleftarrows}} D^+, \quad (27)$$

which were also investigated by the polarographic method, are characterised by the opposite relation: $L_{D^+}/L_{M^+} \gg L_{M^+}$, which is probably due to the much smaller influence of steric hindrance than in the reactions with aminoacids. When account is taken of the relation $k_{-1} \gg k_{+2}$, [27] which is most likely to be characteristic of aminoacids (steric effect), the decomposition reaction between $M^+$ and $D^+$ (aminoacids) involving the reformation of the initial substances via a first-order mechanism cannot be accounted for by postulating the attainment of equilibrium in the $D^+ \rightleftharpoons M^+ + Q$ stage. As stated above, here it is necessary to assume (bearing in mind the very low value of $L_{D^+}/L_{M^+}$, so that $k_{-2} \gg k_{+2}$) a rapid and almost complete decomposition of $D^+$ to $M^+$ and a slow decomposition of $M^+$ into the initial substances Q and $A^+$ in accordance with a first-order kinetic equation [24]. It is noteworthy that, when the reactions between formaldehyde and aminoacids were carried out in an alkaline medium and samples were polarographed in an acid medium [24] in the presence of an excess of formaldehyde, the currents $\bar{i}^0_{\lim}$ were readily attained. On the other hand, when the reactions were carried out in the acid medium used in the polarographic experiments [29], $\bar{i}^0_{\lim}$ could not be attained even in the presence of a very large excess of formaldehyde, because of the low value of $L_{M^+}$. The values of $\bar{i}^0_{\lim}$ obtained by carrying out the reactions in an alkaline medium [24] were therefore used to calculate $L_{M^+}$. [29]

Equilibria (1) can be investigated polarographically also on the basis of the wave of the carbonyl compound [14,16,19], but the scope of the method is then limited: (1) the use of only an excess of the nucleophile hinders the study of the equilibrium involving the formation of D($D^+$) and even more so of $T(T^+)$; (2) the wave of the carbonyl compound may be distorted by the superposition of the reduction of the reaction product [22].

Since either the reaction products or the starting material are consumed at the electrode during the polarographic experiment, there is a possibility of a shift of the equilibrium at the electrode surface. This results in exaltation of the limiting current [48] and the values of $\bar{i}_{\lim}$ are no longer suitable for a sufficiently accurate determination from the latter of the equilibrium constants for the reactions investigated. The degree of such exaltation of $\bar{i}_{\lim}$ is greater the larger are the rate constants for the first stages of reactions of type (27) under conditions corresponding to the reduction of M, D, and T ($M^+$, $D^+$, and $T^+$). It has been shown [48] that the above influence cannot introduce a major error if $k_{-1} \leq 0.1-0.2\ s^{-1}$, while in the reduction of the initial substance Q and in the presence of only the stage involving the formation of M, [14,16] we have $k_{+1}[A] \leq 0.1-0.2\ s^{-1}$. This rule holds [48] in the reduction (and also oxidation) of substances subject to both diffusional and kinetic limitations, but in the latter case the limitations should not be associated with the displacement of the equilibria in the test reactions at the electrode surface. The kinetic limitation may be caused either by the slow protonation of the adducts M (D, T) [28] or of the dehydration product [31-35] (the adducts D and T are absent and U is reduced or hydrogen is evolved catalytically under the influence of $U^+$ [30]). This conclusion can be extended to the limiting kinetic current due to the slow dehydration of the adduct M (U is reduced) [32,33].

We may note that the rate constants for the decomposition of the adducts $M^+$ into the initial substances (the reactions between formaldehyde and aminoacids), which have been investigated by the polarographic method [24], remained sufficiently low in an acid solution (Table 1) to cause the undesirable exaltation of $\bar{i}_{\lim}$ in the study of the

equilibrium [24]. Under these conditions, the constants $k_{+1}$ and $k_{-1}$ depended appreciably on the nature of the amino-acid and the observed increase of $k_{-1}$ with increase of both the $-I$ and $+I$ effects of the substituent X (Table 1) can be explained on the basis of the kinetic scheme of Cordes and Jencks [56]:

$$X\overset{+}{N}H_2CH_2OH \overset{-H^+}{\rightleftarrows} X\overset{+}{N}H_2CH_2O^- \xrightarrow[slow]{} HCHO + NH_2X \overset{H^+}{\rightleftarrows} \overset{+}{N}H_3X. \qquad (28)$$

The substituent X with a $-I$ effect accelerates the slow stage (the inductive effect facilitating the dissociation of the $C-\overset{+}{N}$ bond predominates); the acceleration of the reaction with increase of the $+I$ effect of the substituent X is due to the dominance of the steric factor, which is manifested by the displacement of the initial equilibrium stage to the right. The steric effect also predominates in glycine and, since it is smaller, the result is a relatively low value of $k_{-1}$ (Table 1). The correlation between $k_{-1}$ and $K'_{A^+}$ (Table 1) confirms the above role of the inductive and steric factors. It is also possible to follow the influence of the steric factor on $k_{+1}$ (Table 1). With the exception of glycine, this effect predominates at the equilibrium stage involving the deprotonation of the nucleophile (the increase of $k_{+1}$ with increase of the $+I$ effect). The reduced steric hindrance in glycine is apparently manifested to a greater extent in the slow stage involving interaction with formaldehyde, which in fact leads to a relatively larger value of $k_{+1}$ (Table 1). Mechanism (28) also makes it possible to understand the reason why $k_{-1}$ increases with pH [24] without the need to take into account the appreciable amount of the doubly protonated $M^{2+}$ species [24] (protonated at the nitrogen and oxygen atoms).

Table 1. The limiting current constants ($I^0_{lim}$, $\mu A\ mmole^{-1}\ mg^{-2/3}\ s^{1/2}$) for the reduction of the adduct $CH_2(OH)\overset{+}{N}H_2X$, [24] the rate constants for the formation of the adduct from formaldehyde monohydrate and an amino-acid ($k_{+1}$), [29] the rate constants for its decomposition ($k_{-1}$) [24] into the initial substances, and the dissociation constants of the carboxy-groups of the corresponding aminoacids ($K_{A^+}$) [49] (the rate constants were determined at pH ~ 1 and 25°C).

| Aminoacid | X | $I^0_{lim}$ | $10^4 k_{+1}$, litre mole$^{-1}$ s$^{-1}$ | $10^3 k_{-1}$, s$^{-1}$ | $pK'_{A^+}$ |
|---|---|---|---|---|---|
| β-Alanine | $CH_2CH_2COOH$ | 0.55 | — | 0.19 | 3.55 |
| Glycine | $CH_2COOH$ | 0.91 | 5.6 | 3.0 | 2.35 |
| α-Alanine | $CH(COOH)CH_3$ | 1.5 | 0.68 | 3.4 | 2.35 |
| Norvaline | $CH(COOH)(CH_2)_2CH_3$ | 2.7 | 1.4 | 3.8 | — |
| Norleucine | $CH(COOH)(CH_2)_3CH_3$ | 2.5 | 1.1 | 4.5 | 2.34 |
| Leucine | $CH(COOH)CH_2CH(CH_3)_2$ | 2.5 | — | 5.2 | 2.33 |
| α-Aminoadipic acid | $CH(COOH)(CH_2)_3COOH$ | 2.4 | — | 6.7 | — |
| Valine | $CH(COOH)CH(CH_3)_2$ | (3.1) | 2.9 | 8.8 | 2.29 |
| Glutamic acid | $CH(COOH)(CH_2)_2COOH$ | 2.5 | — | 12.8 | 2.30 |
| β-Phenyl-α-alanine | $CH(COOH)CH_2C_6H_5$ | 2.7 | — | 17.6 | 2.11 |
| Aspartic acid | $CH(COOH)CH_2COOH$ | 2.7 | — | 26.0 | 1.99 |

The reaction between formaldehyde and $\overset{+}{N}H_3OH$ is also fairly slow because the limiting current has a diffusional origin [51]. Only the rate constant for the decomposition of $D^+$ into $M^+$ and Q ($k_{-2} = 2 \times 10^{-4}\ s^{-1}$) has been obtained for this reaction (by the polarographic method) [26,27].

With increase of pH, the rate of formation of M (D, T) and U increases appreciably. Thus, on the basis of kinetic data (polarographic method) [10] for the reaction between $CH_3COCOO^-$ and $NH_3$ (pH 9.25), one may assume [48] that the author [10] worked under the conditions corresponding to the limit of a fairly reliable application of the method to the study of the equilibrium in this reaction on the basis of the values of $\bar{i}_{lim}$. The rate of formation of the adduct M in the reaction between pyridine-4-aldehyde and methylamine at pH 10.5 is so high that the kinetics are controlled in this case by the carbonyl dehydration step [52]. $k_{-1} = 58\ s^{-1}$ was obtained [52] for this dehydration stage (by the stopped-flow method), which implies that, during the polarographic reduction of M, there is an appreciable exaltation of $\bar{i}_{lim}$ and the polarographic method becomes unsuitable for the investigation of the equilibrium in the formation of this adduct.

The pH dependence of the rates of the reactions $Q + A(A^+) \rightarrow U(U^+)$ is more complex because these reactions proceed via the formation and dehydration of $M(M^+)$ and involve a change in pH, as shown by Jencks [37,53]; there is also a change in the rate-determining stage. However, here too the problem of the degree of the distorting influence of the reactions involving the formation of an intermediate aminocarbinol (the reduction of U [17,31-35]) at the electrode surface can be in many instants solved comparatively simply. The point is that, in the majority of reactions of this kind, the equilibrium concentrations of $M(M^+)$ may be neglected compared with the concentrations of $U(U^+)$ and in the calculations one must therefore use the overall equilibrium constant and the effective rate constant for the reaction $Q + A(A^+) \rightarrow U(U^+)$ and not the equilibrium and kinetic parameters of the individual stages. The maximum value of $k_{-1}$ is obtained [37] for the reaction between $(CH_3)_2CO$ and $NH_2OH$. .($\overset{+}{N}H_3OH$) under fairly acid conditions (the value of $L_{U^+}$ for the calculations was taken from Conant and Bartlett [54]), but this value too ($k_{-1} = 3.5 \times 10^{-3}\ s^{-1}$) is much lower than the lowest permissible limit [48]. This conclusion can probably be extended also to reactions of aliphatic carbonyl compounds with hydrazine (the formation and reduction of hydrazones) [31-35], although no direct kinetic measurements have been made. This is indicated by the invariance of the equilibrium constants over a wide range of nucleophile concentrations [31-35].

The equilibrium constants for the side reactions between nucleophiles and carbonyl compounds [the formation of a cyclic trimer (2) and a diamine], found in a number of studies [38,39,47,55,56], show that the concentrations of these products are insignificant under the conditions of the polarographic study [24,29]. Only the glycinate anion gives rise to an appreciable concentration of the trimer under the given conditions (alkaline solution) [24], but here too it does not exceed 9%.

The acid dissociation of the hydrated form of the carbonyl compound is also indicated in mechanism (1), but in the majority of studies $[H^+] \gg K_G$, so that this process may be neglected. On the other hand, polarographic data [24] for the reactions of formaldehyde with aminoacids in an alkaline medium were recently revised [25] taking into account the acid dissociation of $CH_2(OH)_2$.

It is noteworthy that, under the conditions of the polarographic study at ordinary temperatures and relatively low concentrations of the carbonyl compound, the influence of the additional (apart from hydration) deactivation of the carbonyl compound (for example owing to polycondensation [57], aldol condensation, or the Cannizzaro reaction [58]) can also be usually neglected, at any rate for the usual accuracy of the equilibrium constants (±10–30%). In the determination of $\bar{i}^0_{lim}$, the concentration of formaldehyde reached [28] a fairly high value in some cases (7.0 M), but under these conditions the side reactions of

Table 2. The equilibrium constants ($L_M$) for the reactions RR'CO + $H_2NX \rightleftharpoons$ RR'C(OH)NHX at 20–30°C.

| $H_2NX$ | | $NH_3$ ($pK_{A+}$=9,25) | | | α-Alanine $CH_3CH(NH_2)COO^-$ ($pK_{A\pm}$=9,87) | | | Glycine $H_2NCHNCOO^-$ ($pK_{A\pm}$=9,88) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RR'CO | $L_G$ | $L_M$, litre mole$^{-1}$ | method | references | $L_M^c$, litre mole$^{-1}$ | method | references | $L_M^d$, litre mole$^{-1}$ | method | references |
| Cyclopentanone | — | $1.6\cdot10^{-3}$ | P | 13 | $8.0\cdot10^{-2}$ | P | 13 | 0.190 | P | 13 |
| α-Methylcyclohexanone | — | $4.5\cdot10^{-3}$ | P | 13 | — | — | — | $2.4\cdot10^{-2}$ | P | 13 |
| $(CH_3)_2CO$ | $2.0\cdot10^{-3}$ | $4.0\cdot10^{-3}$ | P | 12 | — | — | — | $6.8\cdot10^{-2}$ | P | 12 |
| Cyclohexanone | — | $9.8\cdot10^{-3}$ | P | 13 | $3.0\cdot10^{-2}$ | P | 13 | $7.2\cdot10^{-2}$ | P | 13 |
| $C_6H_5COCOO^-$ | — | $L_{M^-}$=0.10 | P | 8 | — | — | — | — | — | — |
| $C_6H_5CHO$ | — | 0.15 | P | 8 | — | — | — | — | — | — |
| $CH_3COCOCH_3$ | 2,0 | 0.15 | P | 8 | — | — | — | — | — | — |
| $CH_3COCOO^-$ | $5.4\cdot10^{-2}$ | $L_{M^-}$=0.26 | P | 8, 10 | $L_{M^{2-}}$=0.98 | P | 8, 11 | $L_{M^{2-}}$=2.6 | P | 8, 11 |
| $CH_3(CH_2)_2CHO$ | 0.48 | 11.6 | S | 59 | — | — | — | — | — | — |
| $CH_3CH_2CHO$ | 0.72 | 18.1 | S | 59 | — | — | — | — | — | — |
| $CH_3CHO$ | 1.4 | $1.1\cdot10^{2}$ | S | 59 | 26 | Pt, Su | 38 | 47 | Pt, Su | 38 |
| » | » | 8.9[a] | Pt | 38 | — | — | — | — | — | — |
| » | » | 1.3 | P | 8 | — | — | — | — | — | — |
| HCHO | $2.0\cdot10^{3}$ | $1.5\cdot10^{3}$[b] | P | 28 | $4.8\cdot10^{4}$ | Pt | 60 | $3.2\cdot10^{5}$ | Pt | 60 |
| » | » | — | — | — | $4.4\cdot10^{4}$ | Pt | 61 | $1.2\cdot10^{5}$ | Pt | 61 |
| » | » | — | — | — | $4.6\cdot10^{4}$ | Pt | 62 | $1.3\cdot11^{5}$ | P | 24, 25 |
| » | » | — | — | — | $4.8\cdot10^{4}$ | P | 24, 25 | $1.8\cdot10^{5}$ | Su, Pt, I | 47 |
| » | » | — | — | — | $4.2\cdot10^{4}$ | Pt | 39 | — | — | — |
| » | » | — | — | — | $4.4\cdot10^{4}$ | Su, I, Pt | 47 | — | — | — |

Methods: P = polarographic; S = spectrophotometric; Pt = potentiometric (pH); Su = sulphite; I = iodometric. [a] $L_D = 1.9\times10^{2}$ from Ref. 38; [b] $L_D = 5.2\times10^{9}$ and $L_T = 1.4\times10^{13}$ from Ref. 28; [c] $L_{M^-}$ for HCHO and $L_{D^-} = (1.4-3.0)\times10^{8}$ from Refs. 24, 25, 39, 47, 60, and 61; [d] $L_{M^-}$ for HCHO and $L_{D^-} = (1.2-4.4)\times10^{9}$ from Refs. 24, 25, 47, and 61.

Table 3. The equilibrium constants ($L_M$) for the reactions RR'CO + $H_2NX \rightleftharpoons$ RR'C(OH)NHX at 20–25°C.

| $H_2NX$ | | Leucine $(CH_3)_2CHCH_2CH(NH_2)COO^-$ ($pK_{A\pm}$=9,74) | | | Aspartic acid $-OOCCH_2CH(NH_2)COO^-$ ($pK_{A\pm}$=10,00) | | | $CH_3NH_2$ ($pK_{A+}$=10,62) | | | $(CH_3)_2CHNH_2$ ($pK_{A+}$=10,63) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RR'CO | $L_G$ | $L_M^d$, litre mole$^{-1}$ | method | References | $L_M^e$, litre mole$^{-1}$ | method | References | $L_M$, litre mole$^{-1}$ | method | References | $L_M$, litre mole$^{-1}$ | method | References |
| $(CH_3)_2CO$ | $2.0\cdot10^{-3}$ | — | — | — | — | — | — | 0.22 | S | 63 | $4.9\cdot10^{-2}$[c] | T | 65 |
| $(CH_3)_2CHCHO$ | 0.44 | — | — | — | — | — | — | $1.3\cdot10^{2}$[b] | S, Pt | 64 | 48[b] | S, Pt | 64 |
| $CH_3CHO$ | 1.4 | 55 | Pt, Su | 38, 56 | 47 | Pt, Su | 38, 56 | — | — | — | — | — | — |
| HCHO | $2.0\cdot10^{3}$ | $3.4\cdot10^{4}$ | Pt | 60 | $3.1\cdot10^{4}$ | P | 24, 25 | $3.0\cdot10^{6}$ | Cr, Su, I | 55 | — | — | — |
| » | » | $4.0\cdot10^{4}$ | Pt | 62 | $3.0\cdot10^{4}$ | Pt, Su | 47 | — | — | — | — | — | — |
| » | » | $4.8\cdot10^{4}$ | P | 24, 25 | $5.2\cdot10^{4}$[a] | P | 61 | — | — | — | — | — | — |
| » | » | $4.2\cdot10^{4}$ | Pt, Su | 47 | — | — | — | — | — | — | — | — | — |

Methods: Cr = cryoscopic; T = acid–base titration; the remaining symbols have the same significance as in Table 2. [a] 30°C; [b] 35°C; [c] in $C_2H_5OH$; [d] $L_{M^-}$; $L_{D^-} = (1.2-1.8)\times10^{8}$ for HCHO was taken from Refs. 24, 25, 47, 60, and 62; [e] $L_{M^{2-}}$; $L_{D^{2-}} = (0.92-2.2)\times10^{8}$ for HCHO was taken from Refs. 24, 25, 47, and 61.

Table 4. The equilibrium constants ($L_M$) for the reactions RR'CO + $H_2NX(HNXX') \rightleftharpoons$ RR'C(OH)NHXRR'C(OH)NXX' at 20–25°C.

| $H_2NX(HNXX')$ | | $n$-$C_4H_9NH_2$ ($pK_{A+}$=10,60) | | | $NH_2OH$ ($pK_{A+}$=5,97) | | | $H_2NC_2H_4OH$ ($pK_{A+}$=9,50) | | | Morpholine O(CH$_2$–CH$_2$)NH(CH$_2$–CH$_2$) ($pK_{A+}$=8,7) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RR'CO | $L_G$ | $L_M$, litre mole$^{-1}$ | method | references | $L_M$, litre mole$^{-1}$ | method | references | $L_M$, litre mole$^{-1}$ | method | references | $L_M$, litre mole$^{-1}$ | method | references |
| $(CH_3)_2CO$ | $2.0\cdot10^{-3}$ | $8.4\cdot10^{-2}$ | P | 20 | 1.0[c] | S | 37 | — | — | — | — | — | — |
| $CH_3COCOO^-$ | $5.4\cdot10^{-2}$ | — | — | — | 60[d] | S | 37 | 3.3[d] | P | 8 | — | — | — |
| $(CH_3)_2CHCHO$ | 0.44 | $1.0\cdot10^{2}$[a] | S, Pt | 64 | — | — | — | — | — | — | — | — | — |
| $CH_3CHO$ | 1.4 | — | — | — | — | — | — | — | — | — | 25 | Pt | 38 |
| HCHO | $2.0\cdot10^{3}$ | $1.2\cdot10^{3}$[b] | Pt | 39 | — | — | — | $5.8\cdot10^{4}$ | P | 45, 46 | $1.6\cdot10^{6}$ | Pt | 38, 39 |
| Cyclohexanone | — | — | — | — | 6.5 | S | 37 | — | — | — | — | — | — |
| $C_6H_5CHO$ | — | — | — | — | 11.3 | S | 37 | — | — | — | — | — | — |

For the significance of the symbols designating the methods, see Table 2. [a] 35°C; [b] reaction with $t$-$C_4H_9NH_2$; [c] $L_U = 1.1\times10^{6}$ and $L_{U^+} = 63$;[54] [d] $L_{M^-}$.

the carbonyl group were disregarded, since the aim of the experiments was merely to achieve a virtually complete conversion of the nucleophile into the polarographed products.

Table 5. The equilibrium constants $L_U$ for the reactions $RR'CO + H_2NX \rightleftharpoons RR'C{=}NX + H_2O$ at 25 °C.

| $H_2NX$ | | $NH_2NHCONH_2$ ($pK_{A^+}$=3.43) | | | $NH_2NH_2$ ($pK_{A^+}$=8.1) | | |
|---|---|---|---|---|---|---|---|
| RR'CO | $L_G$ | $L_U$, litre mole$^{-1}$ | method | references | $L_U$, litre mole$^{-1}$ | method | references |
| Glucose | — | 16 | P, I, S | 21 | — | — | — |
| $(C_2H_5)_2CO$ | — | 38 | I | 66 | — | — | — |
| $CH_3(OH)COCH_2OH$ | — | $1.4\cdot10^2$ | P | 30 | — | — | — |
| Cyclopentanone | — | $6.8\cdot10^2$ | I | 66 | — | — | — |
| » | — | 56 | P | 17 | — | — | — |
| Cyclohexanone | — | $5.0\cdot10^2$ | I | 54 | — | — | — |
| » | — | $4.9\cdot10^2$ | I | 66 | — | — | — |
| » | — | $1.9\cdot10^2$ | P | 17 | — | — | — |
| $CH_3COC_2H_5$ | — | — | — | — | $1.3\cdot10^8$ | P | 33 |
| $(CH_3)_2CO$ | $2.0\cdot10^{-3}$ | $3.2\cdot10^2$ | I | 54 | $2.4\cdot10^8$ | P | 33 |
| » | — | $3.1\cdot10^2$ | I | 66 | — | — | — |
| » | — | 76 | P | 17 | — | — | — |
| $C_6H_5COCH_3$ | — | $3.8\cdot10^2$ | P | 17 | — | — | — |
| $CH_3CO(CH_2)_2COO^-$ | — | — | — | — | $3.5\cdot10^8$ | P | 35 |
| $CH_3COCOO^-$ | — | $2.1\cdot10^{5a}$ | I | 54 | b | — | — |
| $CH_3CH_2CHO$ | 0.72 | — | — | — | $2.5\cdot10^5$ | P | 33 |
| $CH_2(OH)CHO$ | — | $4.0\cdot10^4$ | P | 30 | — | — | — |
| $CH_3(OH)CH(OH)CHO$ | — | $4.0\cdot10^4$ | P | 30 | — | — | — |
| $CH_3CHO$ | 1.4 | $7.7\cdot10^4$ | I | 54 | $1.9\cdot10^8$ | P | 31, 33 |
| » | » | $9.1\cdot10^4$ | P | 17 | — | — | — |
| $(CH_3)_3CCHO$ | 0.24 | $6.2\cdot10^4$ | I | 54 | — | — | — |
| Furfural | — | $1.3\cdot10^{5c}$ | I | 54 | — | — | — |
| $C_6H_5CHO$ | — | $3.2\cdot10^5$ | I | 54 | — | — | — |
| » | — | $>5\cdot10^4$ | P | 17 | — | — | — |
| » | — | $4.5\cdot10^{5d}$ | S | 67 | — | — | — |
| HCHO | $2.0\cdot10^3$ | $1.2\cdot10^7$ | Pt | 52 | $5.8\cdot10^{8e}$ | P | 33, 34 |

For the significance of the symbols designating the method, see Table 2.
[a] $L_U$, $L_{M^-} = 10.5$ from Ref. 37; [b] $L_{M^-} = 25.5$ from Ref. 37; [c] $L_M = 1.1$ from Ref. 37; [d] $L_M = 1.3$ from Ref. 68; [e] $L_M = 1.9 \times 10^9$ from Ref. 34.

Tables 2–7 present the equilibrium constants, including those obtained by nonpolarographic methods, for the reactions of nucleophiles with various carbonyl compounds. A fairly complete compilation of equilibrium constants (Tables 6 and 7) is available for protonated species, since the polarographic method is particularly promising, because of its high sensitivity, for the investigation of equilibria of this kind. It is noteworthy that the study of the equilibria involving the protonated forms of the nucleophile and the products, carried out for the first time in polarographic investigations [12,17,25], makes it possible to eliminate to a considerable degree the distorting influence of the cyclisation of the product [39,47]. In order to take into account the hydration of carbonyl compounds (which has been done in only a few studies; the effective equilibrium constants are more difficult to compare), the present author selected the most reliable values for $L_G$ [69] (Tables 2–7). In the calculations for carbonyl compounds those values of $L_G$ have not been determined, it was assumed that $L_G \ll 1$, although this was not apparently valid in all cases [for example, in the reactions involving $CH_2(OH)COCH_2OH$, $CH_2(OH)CH(OH)CHO$, and $CH_2(OH)CHO$ in Tables 5 and 7]. Tables 1–7 also list the acid dissociation constants of the initial nucleophiles taken from Ref. 49. Furthermore, the values of $K_{A^+}$ are indicated for certain aminoacids in an acid medium; as mentioned above, they were assumed equal to the values of $K_{A^+}$ for the methyl or ethyl esters of the corresponding aminoacids [70–72].

Table 6. The equilibrium constant $L_{M^+}$ for the reactions $RR'CO + H_3\overset{+}{N}X(H_2\overset{+}{N}XX') \rightleftharpoons RR'C(OH)\overset{+}{N}H_2X[RR'C(OH)\overset{+}{N}HXX']$ at 20–25 °C.

| RR'CO | | HCHO, $L_G$=2.0·10$^3$ | | | $CH_3CHO$, $L_G$=1.4 | | |
|---|---|---|---|---|---|---|---|
| $H_3\overset{+}{N}X(H_2\overset{+}{N}XX')$ | $pK_{A^+}$ | $L_{M^+}$, litre mole$^{-1}$ | method | references | $L_M$, litre mole$^{-1}$ | method | references |
| $\overset{+}{N}H_3OH$ | 5.97 | $(1.7–1.8)\cdot10^{4a}$ | P | 26 | — | — | — |
| Aspartic acid | — | $8.0\cdot10^2$ | Pt, Su, I | 47 | 0.34 | Pt, Su | 38, 56 |
| Leucine | 7.57 | $1.8\cdot10^3$ | Pt, Su | 47 | 0.41 | Pt, Su | 38, 56 |
| Glycine | 7.64 | $5.0\cdot10^2$ | P | 29 | — | — | — |
| » | » | $1.3\cdot10^3$ | Pt, Su, I | 47 | 0.72 | Pt, Su | 38, 56 |
| α-Alanine | 7.74 | 60 | P | 29 | — | — | — |
| » | » | $2.8\cdot10^2$ | Pt, Su, I | 47 | 0.17 | Pt, Su | 38, 56 |
| Norvaline | — | 90 | P | 29 | — | — | — |
| Norleucine | — | 90 | P | 29 | — | — | — |
| Valine | — | 96 | P | 29 | — | — | — |
| » | — | 72 | Pt, Su, I | 47 | — | — | — |
| Morpholine | 8.7 | $(3.8–4.2)\cdot10^3$ | Cr, Su, M | 55 | 0.17 | Pt, Su | 38 |
| » | » | $1.8\cdot10^3$ | Pt | 39 | — | — | — |
| β-Alanine | 9.06 | — | — | — | 0.65 | Pt, Su | 38, 56 |
| $NH_4^+$ | 9.25 | 26[b] | P | 28 | $\leqslant 2.4\cdot10^{-2}$ | Su | 38 |
| γ-Aminobutyric acid | 9.71 | — | — | — | 0.62 | Pt, Su | 38, 56 |
| ε-Aminocaproic acid | 10.30 | — | — | — | 0.65 | Pt, Su | 38, 56 |
| Sarcosine | — | $4.4\cdot10^2$ | Pt | 39 | — | — | — |
| Proline | — | $1.0\cdot10^3$ | Pt | 39 | — | — | — |
| $CH_3\overset{+}{N}H_3$ | 10.62 | $2.6\cdot10^3$ | Cr, Su, M | 55 | — | — | — |
| $(CH_3)_2\overset{+}{N}H_2$ | 10.71 | $(3.2–4.0)\cdot10^3$ | Cr, Su, M | 50 | — | — | — |
| » | » | $3.4\cdot10^3$ | Pt | 39 | — | — | — |
| » | » | $6.0\cdot10^3$ | P | 40, 41 | — | — | — |
| Piperidine | 11.12 | $3.0\cdot10^3$ | Pt | 39 | — | — | — |
| Pyrrolidine | 11.27 | $2.8\cdot10^3$ | Pt | 39 | — | — | — |

Method: M = mercurimetric; for the significance of the remaining symbols designating the methods, see Tables 2 and 3.
[a] $L_{D^+} = (6–12) \times 10^3$ from Refs. 26; [b] $L_{D^+} = 7.2 \times 10^4$; $L_{T^+} = 1.6 \times 10^9$ from Ref. 28.

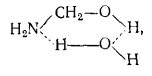
Table 7. The equilibrium constant $L_{U^+}$ for the reaction $RR'CO + H_3\overset{+}{N}X \rightleftharpoons RR'C{=}\overset{+}{N}HX + H_2O$ at 25 °C.

| $H_3\overset{+}{N}X$ | | $\overset{+}{N}H_3NHCONH_2$ ($pK_{A^+}$=3.4) | | $\overset{+}{N}H_3NH_2$ ($pK_{A^+}$=8.19) | |
|---|---|---|---|---|---|
| RR'CO | $L_G$ | $L_{U^+}$, litre mole$^{-1}$ | references | $L_{U^+}$, litre mole$^{-1}$ | references |
| $C_6H_5COCH_3$ | — | 0.38 | 17 | — | — |
| Cyclopentanone | — | 0.40 | 17 | — | — |
| $CH_3COC_2H_5$ | — | — | — | 0.63 | 33 |
| $(CH_3)_2CO$ | $2.0\cdot10^{-3}$ | 1.5* | 54 | 1.1 | 33 |
| » | — | 0.55 | 17 | — | — |
| Cyclohexanone | — | 1.04 | 17 | — | — |
| $CH_2(OH)CHO$ | — | 5.0 | 30 | — | — |
| $CH_3CO(CH_2)_2COO^-$ | — | — | — | 1.6** | 35 |
| $CH_3CO(CH_2)_2COOH$ | — | — | — | 2.3 | 35 |
| $CH_3(OH)CH(OH)CHO$ | — | 6.6 | 30 | — | — |
| $CH_3CH_2CHO$ | 0.72 | — | — | 86 | 33 |
| $CH_3CHO$ | 1.4 | $3.2\cdot10^2$* | 54 | $4.3\cdot10^2$ | 31, 33 |
| » | » | 42 | 17 | — | — |
| $C_6H_5CHO$ | — | $6.7\cdot10^2$* | 54 | — | — |
| » | — | >40 | 17 | — | — |
| Furfural | — | $8.3\cdot10^2$* | 54 | — | — |
| $CH_3COCOOH$ | 2.4 | $1.0\cdot10^3$* | 54 | — | — |
| HCHO | $2.0\cdot10^3$ | — | — | $7.4\cdot10^4$*** | 33, 34 |

*Measured by the iodometric method; in the remaining cases, the polarographic method was used.
**$L_{U^+}$.
***$L_{M^+} = 2.4 \times 10^5$ from Ref. 33.

The reproducibility of the equilibrium constants in various studies using polarographic and other methods is quite satisfactory in many instances: the reactions of formaldehyde with α-alanine and glycine (Table 2), with leucine and aspartic acid (Table 3), and dimethylamine (Table 6). On the other hand, in some cases it is so far

difficult to regard the constants as reproducible within one order of magnitude, this being particularly true of the equilibrium constants $L_D$ (Tables 2 and 3). The values of $L_M$ for reactions between RR'CO and $NH_3$ taken from Ogata and Kawasaki[59] (Table 2) are probably too high owing to failure to take into account, as suggested by Gaux and Le Henaff[38], the cyclisation of the adduct. The value of $L_M$ (Table 2) found from $L_{M^+}$ and $K_{M^+}$ for the reaction between formaldehyde and ammonia also appears too high[28]. However, the stoichiometry of the reactions in an acid medium, established by the present author and Cheremukhina[28], rules out the likelihood of the cyclisation of the adduct, particularly since one of the possible cyclisation products (hexamethylenetetramine) is polarographically inactive[73]. The hypothesis of the formation in the reaction between formaldehyde and $NH_4^+$ of a similar cyclisation product with several nitrogen atoms of type (2) or of hexamethylenetetramine must be rejected also because of the observation of two titration jumps corresponding to strong and weak ($pK_{A^+} \simeq 5$ for the reaction product) acids. On the other hand, one cannot assume the similarity of the $pK_{A^+}$ for several groups in the cyclisation product, protonated at the nitrogen atom, because of the strong inductive effect (for example $pK_{A^{2+}} = 5.57$ and $pK = 9.81$ for piperazine). However, the formation of mono-, bis-, and tris-hydroxymethyl derivatives of ammonia with similar $pK_{A^+}$ values in the range 4.3 to 4.5 in the reaction between formaldehyde and $NH_4^+$ [28] fully justifies the single-stage titration of the adducts as acids whose strength is close to that of acetic acid. Another possible factor causing an unduly high value of $L_M$(HCHO + $NH_3$) [25] is the formation of the dehydration product $NH{=}CH_2$ and not the adduct $NH_2CH_2OH$. However, the existence of $NH{=}CH_2$ in solution is hardly possible in an appreciable concentration owing to the marked tendency of this compound to cyclise[36]. The formation of the fairly stable cyclic hydrate



(29)

on the basis of the adduct appears more probable, which leads to an increase of $L_M$.

Other nucleophiles (Table 2) as well as other carbonyl compounds form less stable cyclic hydrates of type (29) owing to steric hindrance, and an anomalously high value of $L_M$ is therefore characteristic of such compounds (Table 2). This can also be said of the protonated form of the adduct, including the adduct obtained in the reaction between formaldehyde and $NH_4^+$.[28] The enhanced overall hydration of both the initial protonated nucleophile and of the protonated adduct under these conditions rules out a significant influence of the formation of the cyclic hydrate on $L_{M^+}$. The values of $L_{M^+}$ for the reaction between formaldehyde and $NH_4^+$ and other analogous reactions are therefore fairly comparable (Table 6). Admittedly, the cause of the lower values of $L_{M^+}$ for the reactions of formaldehyde with $\overset{+}{N}H_3CH_2COOH$ and $CH_3CH(\overset{+}{N}H_3)COOH$, taken from the study of Zhantalai and the present author[29], compared with the data of Feraud and Le Henaff[47] is not altogether clear, particularly since the values of $L_{M^+}$ in these studies are similar for the reactions involving valine (Table 6). It is noteworthy that the reliability of the data from Ref. 29 was also confirmed by kinetic measurements (Table 1).[24,29].

The relation between the reactivity and the nature of the carbonyl compound in reactions with the same nucleophile was considered on the basis of the Hammett equation (aromatic carbonyl compounds[67]) and the Taft equation (aliphatic carbonyl compounds[33,59]). An increase of the equilibrium constants with increase of the positive charge on the carbonyl carbon was demonstrated (Tables 2–7).

In the reactions of aliphatic carbonyl compounds with ammonia, primary amines, aminoalcohols, and amino-acids, the concentrations of the dehydration products U($U^+$) can usually be neglected. When aliphatic aldehydes are considered, the main cause of the low capacity of the adducts M($M^+$) formed under these conditions for dehydration is due to the overall electron-accepting effect of the substituents at the carbonyl group[4], which hinders the protonation of the oxygen of the hydroxy-group in M and even more so in the $M^+$ species protonated at the nitrogen atom. It would appear that aliphatic ketones should have led to a shift of the equilibrium towards dehydration products, which has in fact been suggested[8-13,63]. However, here too (probably owing to the insufficient electron-donating effect) the equilibrium involves the preferential formation of the adducts M($M^+$), as shown by a comparison with other equilibrium constants (Tables 2 and 6).

The values of $L_M$ and $L_U$ have been found separately[37] for the reactions involving $NH_2OH$. The higher values of $L_M$ for $NH_2OH$, $NH_2NHCONH_2$, and $NH_2NH_2$ compared with other nucleophiles are noteworthy, which has been explained[37] by the stabilisation of the adduct in the former case owing to an intramolecular hydrogen bond. The lower values under these conditions of $L_M$ for furfural and benzaldehyde (Table 5) are caused[37] by the conjugation of the carbonyl group and the aromatic ring. The influence of the intramolecular hydrogen bond in the initial carbonyl compound on the kinetics of reactions with $NH_2CH$ was noted by Knorre and Emanuel'.[74]

There are many reactions (Tables 5 and 7) where the equilibrium between M($M^+$) and U($U^+$) is almost completely displaced towards the dehydration product U($U^+$), which is characteristic of nucleophiles containing nitrogen or oxygen next to the $NH_2$ group (the compounds $NH_2NH_2$, $NH_2NHCONH_2$, and $NH_2OH$). In these reactions, with the exception of those between formaldehyde and $NH_2NH.CONH_2$ ($NH_2NH_2$, $\overset{+}{N}H_3NH_2$, $\overset{+}{N}H_3OH$),[26,32,33,52] the relation $L_U \gg L_M$ or $L_{U^+} \gg L_{M^+}$ holds (Tables 5 and 7). Under these conditions, the thermodynamic stabilisation of the dehydration products owing to the presence of conjugated systems in the latter apparently has the main influence[5,53]. The higher values of $L_U$ for furfural and benzaldehyde (Table 5) have been explained[37] by the additional stabilisation of the dehydration product as a result of the conjugation of the azomethine group with the aromatic ring. On the other hand, in the reactions of formaldehyde with $NH_2NHCONH_2$ ($NH_2NH_2$, $\overset{+}{N}H_3NH_2$, $\overset{+}{N}H_3OH$), the electron-accepting effect of the two hydrogen atoms at the carbon atom of the $CH_2OH$ group of the aminocarbinol to a large extent prevents the protonation of the oxygen in the hydroxy-group and hence hinders the dehydration of the aminocarbinol. For example, $L_U/L_M \simeq L_{U^+}/L_{M^+} = 0.31$ for $NH_2NH_2(\overset{+}{N}H_3NH_2)$.[33] Since the values of $L_M$ and $L_U$ may be expected to be similar also for the reaction of formaldehyde with $NH_2NHCONH_2$, the observed[52] equilibrium constant, which the authors[52] believed to be $L_M$, was included in Table 5 (see $L_U$).

The problem of the relation between reactivity and the nature of the nucleophile is more complex. Apart from the effects of the intramolecular hydrogen bond and conjugation discussed above ($NH_2NH_2$, $NH_2NHCONH_2$, $NH_2OH$), attention was directed[37] to the absence of any correlation between $L_M$($L_U$) and $K_{A^+}$ (Tables 2–7). Jencks[37] and Kallen and Jencks[39] explained the latter by the similarity

of the values of σ* for the hydrogen atom and the RR'COH group substituting it, as a result of which the polar effects of the substituents in the nucleophile should not influence $L_M(L_U)$ appreciably. This is the difference [39] between the reactions under consideration and those of carbonyl compounds with nucleophiles such as CH acids [75-77]. Nevertheless the problem of the role of the polar effect of substituents in nitrogen-containing nucleophiles is apparently more complex. Thus the relations $L_M \gg L_{M^+}$ and $L_U \gg L_{U^+}$ (Tables 2 and 7), the increase of $L_M$ [38,56] in the series of aminoacids $NH_2(CH_2)nCOO^-$ with increase of $n$, and the influence of the nature of the substituents in amides on the rates of reaction with formaldehyde [78] can be explained [38,78] by the polar effect. Furthermore, a distinct correlation between $L_{M^+}$ and $K_{A^+}$ (Table 6) and between $L_{M^+}$ and σ* for the substituent X in $\overset{+}{N}H_3X$ has been observed for several nucleophiles ($\overset{+}{N}H_4$, $\overset{+}{N}H_3CH_2COOH$, $\overset{+}{N}H_3OH$) with a primary amino-group in the protonated state [79]. For reasons which are obscure, $CH_3\overset{+}{N}H_3$ deviates significantly from this correlation (Table 6). Protonated secondary amines and also aminoacids of the type $H_3\overset{+}{N}(CH_2)nCOOH$ likewise failed to show a correlation between $L_{M^+}$ and $K_{A^+}$ (Table 6).

Sander and Jencks [52] obtained a correlation (also confirmed by Hine and Redding [80]) between the reactivity and the nature of the nucleophile using a set of constants expressing the ratios of the equilibrium constants for the given series to the equilibrium constant for a standard nucleophile (methylamine). However, these data are insufficient for reactions involving aliphatic carbonyl compounds, particularly since formaldehyde exhibits an appreciable deviation from the correlation [52].

The reactivity of the nucleophile depends appreciably on steric factors [36,38,39]. This is manifested in the series of aminoacids [36], for example, on passing from glycine to α-alanine, and also in the relation $L_{M^-} > L_{D^-}/L_{M^-}$ (Tables 2 and 3). It is noteworthy that the relation $L_{M^+} < L_{D^+}/L_{M^+}$ holds for protonated forms (Table 6), which is most probably due to the dominant influence of the decrease of the degree of hydration on passing from $A^+$ to $M^+$. However, the dominance of steric factors may also be expected for aminoacids ($L_{M^+} \gg L_{D^+}/L_{M^+}$), since the formation of $D^+$ could not be observed experimentally [29,47,56]. It has been noted [38] that the steric factors of nucleophiles are manifested to a lesser extent in the reactions of acetaldehyde compared with those of formaldehyde. Apparently for this reason we have $L_M < L_D/L_M(CH_3CHO)$ (Table 2).

On the basis of Eqns. (18)-(22) and using the equilibrium constants $L_M$, $L_U$, $L_{M^+}$, and $L_{U^+}$, the acid dissociation constants of adducts protonated at the nitrogen atom (Table 8) and of the dehydration products (Table 9) were found in a number of studies. Some of the results have been revised using the average equilibrium constants (when different equilibrium constants are quoted in the literature for the same reaction). Furthermore, Tables 8 and 9 present some of the results of direct measurements of $K_{M^+}$ and $K_{U^+}$. It is necessary to consider the considerable discrepancies between the results [54,67] (see $K_{U^+}$ for $C_6H_5CH{=}\overset{+}{N}NH_2CONH_2$; Table 9) and also the considerable variation of $K_{M^+}$ for the adduct obtained in the reaction between RR'CO and $\overset{+}{N}H_4$ as a function of the nature of the carbonyl compound (Table 8). In contrast to other nucleophiles, in the latter case the formation of a cyclic hydrate of type (29) and the sensitivity of this factor to the nature of the carbonyl residue (the steric effect) show a more significant influence; the sensitivity is lowest for formaldehyde. On the other hand, a somewhat low value of $K_{M^+}$ for $\overset{+}{N}H_3C(CH_3)_2CH$ was apparently found [12] (Table 8). Nucleophiles which themselves introduce an appreciable steric hindrance (for example α-aminoacids) form adducts for which the difference between the $K_{M^+}$ as a function of the nature of the carbonyl compound are small (Table 8). The dependence of $K_{U^+}$ for the dehydration product on the nature of the carbonyl compound (reactions with $NH_2NH_2$ and $\overset{+}{N}H_3NH_2$) is described by the Taft equation [33].

**Table 8.** The acid dissociation constants of the nucleophiles $H_3\overset{+}{N}X(H_3\overset{+}{N}\overset{-}{X}; H_2\overset{+}{N}XX')$ ($K_{A^+}$) and the adducts ($K_{M^+}$) in reactions with RR'CO at 20-25 °C.

| RR'CO | $H_3\overset{+}{N}X(H_3\overset{+}{N}\overset{-}{X}; H_2\overset{+}{N}XX)$ | $pK_{A+}$ | $pK_{M+}$ | References |
|---|---|---|---|---|
| HCHO | Morpholine | 8.7 | 6.0 | 38,39,55 |
| $CH_3CHO$ | » | » | 6.5 | 38 |
| HCHO | $NH_4^+$ | 9.25 | 4.5 | 28 |
| $CH_3CHO$ | » | » | 6.9 | 8,38 |
| $(CH_3)_2CO$ | » | » | 9.0 | 12 |
| HCHO | Valine | 9.72[a] | 7.0[b] | 24,25,29,47,60,61 |
| HCHO | Leucine | 9.74[a] | 7.4[b] | 24,25,47,60,62 |
| $CH_3CHO$ | » | » | 7.6[b] | 38,56 |
| HCHO | α-Alanine | 9.87[a] | 7.4[b] | 24,25,29,39,47,60—62 |
| $CH_3CHO$ | » | » | 7.7[b] | 38,56 |
| $(CH_3)_2CO$ | » | » | 8.4[b] | 12 |
| HCHO | Glycine | 9.88[a] | 8[b] | 42 |
| HCHO | » | » | 7.6[b] | 24,25,29,47,60,61 |
| $CH_3CHO$ | » | » | 8.1[b] | 38,56 |
| HCHO | Aspartic acid | 10.00[c] | 8.4[d] | 24,25,47 |
| $CH_3CHO$ | Ditto | » | 7.9[d] | 38,56 |
| $CH_3CHO$ | β-Alanine | 10.24[a] | 7.5[b] | 38,56 |
| $CH_3CHO$ | γ-Aminobutyric acid | 10.56[a] | 7.7[b] | 38,56 |
| HCHO | $CH_3\overset{+}{N}H_3$ | 10.62 | 7.5 | 55 |
| HCHO | Proline | 10.64 | 7.9 | 39,60 |
| HCHO | Sarcosine | 10.7 | 7.7[b] | 39,60 |
| HCHO | $(CH_3)_2\overset{+}{N}H_2$ | 10.71 | 8.0 | 39 |
| HCHO | Piperidine | 11.12 | 8.1 | 39 |
| HCHO | Pyrrolidine | 11.27 | 8.6 | 39 |

[a] $pK_{A^\pm}$; [b] $pK_{M^\pm}$; [c] $pK_{A^\pm}$; [d] $pK_{M^\pm}$.

**Table 9.** The acid dissociation constants of the nucleophiles $H_3\overset{+}{N}X$ ($K_{A^+}$) and the dehydration products ($K_{U^+}$) in the interaction of the nucleophiles with RR'CO at 25 °C.

| RR'CO | $pK_{U+}$ | References |
|---|---|---|
| $\overset{+}{N}H_3NHCONH_2$; $pK_{A+} = 3.43$ = | | |
| $CH_2(OH)CHO$ | −0.5 | 30 |
| $CH_2(OH)CH(OH)CHO$ | −0.4 | 30 |
| $CH_3CHO$ | 0.8 | 17,54 |
| $C_6H_5CHO$ | 0.8[a] | 54 |
| $C_6H_5CHO$ | −1.05 | 67 |
| Furfural | 1.2[a] | 54 |
| $(CH_3)_2CO$ | 1.2 | 17,54,66 |
| Cyclopentanone | 1.3 | 17 |
| Cyclohexanone | 0.9 | 17,54,66 |
| $(CH_3)_2CO$ $\overset{+}{N}H_3OH$; $pK_{A+} = 5.97$ | 1.7[b] | 54 |
| HCHO $\overset{+}{N}H_3NH_2$; $pK_{A+} = 8.15$ | 4.21 | 33,34 |
| $CH_3CHO$ | 4.45 | 31,33 |
| $CH_3CH_2CHO$ | 4.64 | 33 |
| $CH_3CO(CH_2)_2COO^-$ | 4.76 | 35 |
| $(CH_3)_2CO$ | 4.76 | 33 |
| $(CH_3)_2CO$ | 5.1[c] | 81 |
| $CH_3COC_2H_5$ | 4.79 | 33 |

[a] Adjusted for $pK_{A^+} = 3.43$; [b] adjusted for $pK_{A^+} = 5.97$; [c] in methanol; [d] $pK_{A^+} = 8.19$ was used in Refs. 31, 33, and 35; here the values of $pK_{U^+}$ have been adjusted to $pK_{A^+} = 8.1$.

The main conclusion which can be drawn from Tables 8 and 9 is the occurrence of the relations $K_{M^+} \gg K_{A^+}$ and $K_{U^+} \gg K_{A^+}$, which is very important for the acid–base titration of the reaction products [6,7]. Under these conditions, $K_{M^+}$ ($K_{M^\pm}$) is greater by 1.5–3.0 orders of magnitude than $K_{A^+}$ ($K_{A^\pm}$), while $K_{U^+}$ is greater than $K_{A^+}$ by 2.0–4.0 orders of magnitude. Whereas the higher values of $K_{U^+}$ compared with $K_{A^+}$ can be readily explained (by the polar effect of the azomethine group), the reason for the appreciably higher values of $K_{M^+}$($K_{M^\pm}$) is still insufficiently clear, because, as stated by Kallen and Jencks [39], polar effects do not change very greatly when the hydrogen atom is replaced by the C(OH)RR′ group. The above authors' hypothesis of the significant role in this case of the common hydration factor is quite justified (by analogy with amines [82]), but the formation under these conditions of a cyclic hydrate of type (29), particularly for the adduct involving HCHO and $NH_4^+$, which causes an additional enhancement of the acid function of the protonated nitrogen, is probably also important. Aminocarbinols where the amino-group is not in the 1-position apparently form less stable hydrates (with more than 6 units) and the role of this factor is reduced. Naturally, the direct electron-accepting effect of the R″C(OH)RR′ group in such aminocarbinols is less pronounced, which also reduces their acid properties.

## III. THE MECHANISM OF THE POLAROGRAPHIC REDUCTION OF REACTION PRODUCTS

The mechanism of the reduction of the dehydration products (hydrazones, oximes, etc.) has been investigated in greater detail (Lund [83,84], Kitaev and coworkers [85–87]). This mechanism was recently considered in Kitaev and Buzykin's review [88] and will be only briefly described in the present review, with the exception of the problem of the kinetics of the limiting current which has not been dealt with adequately. The possible mechanisms of the electrochemical reduction of adducts (aminocarbinols) have been considered in the literature in less detail, particularly since their reduction via the formation of the usual dehydration product U (the adduct of a nucleophile with a secondary or tertiary amino-group) is frequently ruled out.

As stated in Section II, the presence of conjugated systems [5] is characteristic of the dehydration product U having the structure RR′C=NYR″, where Y is either a nitrogen atom (hydrazones) or an oxygen atom (oximes), which, together with protonation, facilitates the dissociation of the N–Y bond during their reduction. Under these conditions, four-electron reduction is usually observed in an acid solution [83–87]:

$$\begin{aligned} RR'C{=}N{-}YR'' \xrightarrow{H^+} (RR'C{=}N{-}YR'')^+ H \xrightarrow{2\bar{e};2H^+} \\ \rightarrow R''YH + RR'C{=}\overset{+}{N}H_2 \xrightarrow{2\bar{e};2H^+} RR'CH\overset{+}{N}H_3. \end{aligned} \qquad (30)$$

It has recently been shown [34] that unsubstituted hydrazones of aliphatic carbonyl compounds also undergo a four-electron reduction reaction at pH ≤ 8. Since hydrazones of this kind are to a large extent hydrolysed, a microcoulometric study has been carried out [34] in the presence of a very large excess of hydrazine.

If Y is a carbon atom in the compounds RR′C=NYR″ (azomethines), only the double bond is reduced (a two-electron process) [83]:

$$RR'C{=}NYR'' \xrightarrow{2\bar{e};\,2H_2O} RR'CHNHYR'' + 2OH^-. \qquad (31)$$

The mechanism of the generation of the kinetic limiting current in the reduction of hydrazones when the solution contains the corresponding adducts has been considered [34] on the basis of the scheme

$$\begin{array}{ccccc} M & \xrightarrow{\text{diff.}} & M & & \\ \uparrow\downarrow & & \uparrow\downarrow k'_{-1}\ k'_{+1} & & \\ & & H^+;\,k''_{+1} & & \\ U & \xrightarrow[\text{diff.}]{} & U & \underset{k''_{-1}}{\rightleftharpoons} & U^+ \xrightarrow{\text{red.}} \end{array}, \qquad (32)$$

which takes into account both the slow protonation of U and the slow dehydration of M. A kinetic equation has been derived (in the presence of a large excess of the nucleophile when virtually the entire carbonyl compound is converted into M and U): [34]

$$\lg \frac{\bar{i}^0_{lim}}{(\bar{i}^0_{lim})_d - \bar{i}^0_{lim}} = \lg \frac{k''_{+1}[k'_{+1}(L_M + L_U) + \bar{\varkappa} L_U]}{\bar{\varkappa}\,(k'_{+1}(L_{M^+}L_U) + (k'_{-1} + \bar{\varkappa})(L_M + L_U) + k''_{+1}L_M[H^+]\}} - pH, \qquad (33)$$

where $(\bar{i}^0_{lim})_d$ is the limiting diffusion current and $\bar{\varkappa}$ is the Ilkovič constant. Since under these conditions $k'_{-1} \gg k'_{+1}[H^+]$ and $k'_{-1} \gg \bar{\varkappa}$ or $k'_{-1} \gg k''_{+1}[H^+]$ and $k'_{+1} \gg \bar{\varkappa}$ (enhancement of base catalysis at the hydration–dehydration stages) [89,90], Eqn.(33) assumes the following form [34] with increase of pH ($L_U/L_M = k'_{+1}/k'_{-1}$):

$$\lg \frac{\bar{i}^0_{lim}}{(\bar{i}^0_{lim})_d - \bar{i}^0_{lim}} = \lg \frac{k''_{+1}\,L_U}{\bar{\varkappa}\,(L_M + L_U)} - pH; \qquad (34)$$

when $L_U \gg L_M$, whereupon the dehydration product predominates {[U] ≫ [M]}, we obtain

$$\lg \frac{\bar{i}^0_{lim}}{(\bar{i}^0_{lim})_d - \bar{i}^0_{lim}} = \lg \frac{k''_{+1}}{\bar{\varkappa}} - pH. \qquad (35)$$

It is noteworthy that Eqns.(33)–(35) are applicable to both bulk-phase and surface protonation processes [91] when the Henry adsorption isotherm holds. Eqns.(34) and (35) correspond to mechanism (32) with a fairly rapid adduct dehydration stage. Here kinetic inhibition is due solely to the stage involving the protonation of the dehydration product U.

Eqn.(33) has been confirmed [34] for the reduction of the products of the reaction of formaldehyde with $NH_2NH_2$. .($\overset{+}{N}H_3NH_2$) in the pH range 5.5–8.0. Thus formaldehyde hydrazone is reduced even in the acid pH range with considerable kinetic limitation owing to the slow dehydration of the adduct present in a considerable amount (Table 5). With increase of pH, the retardation of the process at the protonation stage was also observed. This inhibition predominated at pH ≥ 7.0 [see Eqn.(34)]. [34] Since the concentration of the adduct was extremely low, the limiting current for the hydrazones of other aliphatic carbonyl compounds at pH ≤ 6.5 had a diffusional origin, while at pH > 6.5–7.0 kinetic process inhibition, due to the retardation of the stage involving the protonation of the dehydration product, was manifested. The applicability of the usual equation for the polarographic dissociation curve [Eqn.(35)] to these hydrazones has been demonstrated [34], this being characteristic also of thiosemicarbazones [92].

In order to find the true rate constants from Eqns. (33)–(35), the Koutecký equation has been used [34,92]. For the formaldehyde adduct, the true dehydration rate constant $k' = 0.4\ s^{-1}$ at pH ~ 6, which is close to the result obtained from a chronopotentiometric study [93]. The rate constants for the protonation reaction are listed in Table 10. Surface protonation [34,87,91,92] with participation of adsorbed species is characteristic of the majority of these compounds, as shown by the unduly high rate constants (Table 10). The rate constant for the bulk-phase process may have been

found only for the anions of levulinic acid owing to the insignificant adsorption of the hydrazone anion at $E = -1.3 - -1.6$ V (here and henceforth potentials relative to the normal calomel electrode are quoted) (Table 10). Surface protonation is also characteristic of oximes [94]. The semicarbazonium ion may participate in the protonation reaction [95,96].

Table 10. The true ($K_{U^+}$) and apparent (polarographic) ($K'_{U^+}$) acid dissociation constants of the dehydration products and the rate constants $k$ (based on the Koutecky equation with a coefficient of 0.886) for their protonation at 25°C.

| Dehydration product | $pK_{U+}$ | $pK'_{U+}$ | $k$, litre mole$^{-1}$ s$^{-1}$ | Refs. |
|---|---|---|---|---|
| Acetophenone thiosemicarbazone | 0.92 | 7.5 | $5 \cdot 10^{13}$[a] | 92 |
| Cyclohexanone thiosemicarbazone | 1.04 | 7.0 | $4 \cdot 10^{12}$[a] | 92 |
| Acetaldehyde semicarbazone | 0.8 | 6.5 | $6 \cdot 10^{11}$[a] | 92 |
| Benzaldehyde semicarbazone | 0.8 | 7.2 | $2 \cdot 10^{13}$[a] | 92 |
| Formaldehyde hydrazone | 4.21 | 6.7 | $2 \cdot 10^{10}$[b] | 34 |
| Acetaldehyde hydrazone | 4.45 | 7.8 | $6 \cdot 10^{10}$ | 34 |
| Propionaldehyde hydrazone | 4.64 | 7.8 | $5 \cdot 10^{10}$ | 34 |
| Acetone hydrazone | 4.76 | 7.8 | $3 \cdot 10^{10}$ | 34 |
| Ethyl methyl ketone hydrazone | 4.79 | 7.8 | $3 \cdot 10^{10}$ | 34 |
| Hydrazone of levulinate anion | 4.76 | 7.4 | $5 \cdot 10^{9}$ | 35 |

[a] The dropping period of the dropping mercury electrode was $t_1 = 3.0$ s; [b] Eqn.(34), $L_M = 1.9 \times 10^9$ and $L_U = 5.8 \times 10^8$ (Table 5).

The plot of $\bar{i}_{lim}$ against pH for the limiting current corresponding to the equilibrium $Q + A(A^+) \rightleftharpoons M(M^+) \rightleftharpoons U(U^+)$ passes [30,34] through a maximum, which has been explained [30,34], on the one hand, by the increase of the concentration of the reaction products with increasing pH (because $L_M \gg L_{M^+}$ and $L_U \gg L_{U^+}$) and, on the other hand, by the opposed effect due to the enhancement of inhibition at the product U protonation stage. The calculated $\bar{i}_{lim}$–pH curves obtained with the aid of Eqn.(23) (for $c_A \gg c_Q$) are close to the experimental curves [34]. Expressions have also been found [34] for $pH_{max}$ {subject to the condition $d\bar{i}_{lim}/d[H^+] = 0$} at which $\bar{i}_{lim}$ reached a maximum value. The expression for $pH_{max}$ corresponding to reactions involving the appreciable formation of M (formaldehyde) together with U is [34]

$$pH_{max} = -\frac{1}{2} \lg \frac{(L_M + L_U)(k'_{+1} + k'_{-1} + \bar{\varkappa})\bar{\varkappa} c_A}{k''_{+1}(k'_{+1} + \bar{\varkappa})(1 + L_G)}. \quad (36)$$

The following expression has been obtained for reactions where the concentration of M compared with U may be neglected [34]:

$$pH_{max} = -\frac{1}{2} \lg \frac{K_{A+}(1 + L_G + c_A L_U)\bar{\varkappa}}{k''_{+1}(1 + L_G)}. \quad (37)$$

The values of $pH_{max}$ have been calculated [34] with the aid of Eqns.(36) and (37) and the maximum limiting currents $(\bar{i}_{lim})_{max}$ have been obtained with the aid of Eqn.(22) for $c_A \gg c_Q$ using the values of $\bar{i}^0_{lim}$ and $[H^+]_{max}$. $pH_{max}$ and $(\bar{i}_{lim})_{max}$ are close to the experimental values for a series of hydrazones (Table 11) (the values of $L_G$ were taken from Tables 2–7).

The influence of the nature of the hydrazones of aliphatic carbonyl compounds on the half-wave potential $E_{1/2}$ is determined to a large extent (Table 12) by the inductive effects of the substituents in the carbonyl compound, as shown by the shift of $E_{1/2}$ towards negative values with increase of the electron-donating effect of the substituents. A similar conclusion follows also from the correlation analysis of the half-wave potentials for many other compounds with the azomethine group [97]. With the exception of formaldehyde hydrazone, the limiting current constants in the acid pH range (Table 12) correspond to a diffusion process.

Table 11. Comparison of the experimental and calculated values of $pH_{max}$ and $(\bar{i}_{lim})_{max}$ [34] ($c_Q = 1.0 \times 10^{-4}$ M; $c_A = 1.0 \times 10^{-3}$ M).

| Hydrazone | $pH_{max}$ | | $(\bar{i}_{lim})_{max}$, μA | |
|---|---|---|---|---|
| | expt. | calc. | expt. | calc. |
| Of formaldehyde | 6.0 | 6.1 | 1.18 | 1.17 |
| Of acetaldehyde | 6.6 | 6.6 | 2.26 | 2.27 |
| Of propionaldehyde | 6 9 | 7.1* | 1.75 | 1.77* |
| Of acetone | 7.8 | 7.9 | 0.60 | 0.49 |

*It was assumed in the calculations that $L_G = 0.72$, which is more accurate than the value adopted in Ref. 34.

Table 12. The half-wave potentials ($E_{1/2}$, pH = 7.4) and the limiting current constants ($I^0_{lim}$, μA mmole$^{-1}$ mg$^{-2/3}$ s$^{1/2}$; pH = 3.5–5.5) for the reduction of $RR'C{=}NH_2$.

| R | R' | $-E_{1/2}$, V | $I^0_{lim}$ | R | R' | $-E_{1/2}$, V | $I^0_{lim}$ |
|---|---|---|---|---|---|---|---|
| $CH_2{=}CH$ | H | 1.05 | — | $CH_3CH_2$ | H | 1.30 | 9.8 |
| $CH_2{=}C(CH_3)$ | H | 1.15 | — | $CH_3$ | $CH_3$ | 1.47 | 9.6 |
| $CH_3CH{=}CH$ | H | 1.22 | — | $CH_3$ | $C_2H_5$ | 1.46 | 9.4 |
| H | H | 1.17 | 6.4 | $CH_3$ | $(CH_2)_2COO^-$ | 1.49* | 10.5* |
| $CH_3$ | H | 1.32 | 9.8 | | | | |

Data from Ref. 35; in the remaining cases, data from Ref. 93 were used.

We shall now proceed to the consideration of the mechanism of the polarographic reduction of adducts–aminocarbinols. For the formation of aminocarbinols with participation of formaldehyde, Matoušek [22] proposed a mechanism involving the reduction of the adduct M with dissociation of the C–O bond (first wave):

$$\text{>NCH}_2\text{OH} \xrightarrow{H^+} \text{>NCH}_2\overset{+}{\text{O}}\text{H} \rightarrow H_2O + \text{>N}\overset{+}{\text{C}}\text{H}_2 \xrightarrow{2\bar{e};\ H^+} \text{>NCH}_3, \quad (38)$$

and reduction with dissociation of the N–C bond (second wave, which coincides with the formaldehyde reduction wave):

$$\text{>NCH}_2\text{OH} \xrightarrow{H^+} \text{>N}\overset{+}{\text{H}}\text{CH}_2\text{OH} \rightarrow \text{>NH} + \overset{+}{\text{C}}\text{H}_2\text{OH} \xrightarrow{2\bar{e};\ H^+} CH_3OH. \quad (39)$$

These mechanisms are based [22] on data concerning the nature of the chemical reduction of the corresponding hydroxymethyl derivatives and also pulse volt-amperometric data at different frequencies. In addition to reaction (38), attention should also be directed to the possibility of the intermediate formation and reduction of an ammonium derivative:

$$\text{>NCH}_2\text{OH} \xrightarrow{H^+} \text{>NCH}_2\overset{+}{\text{O}}\text{H} \rightarrow H_2O + \text{>}\overset{+}{\text{N}}\text{=CH}_2 \xrightarrow{2\bar{e};\ H^+} \text{>NCH}_3. \quad (40)$$

The occurrence of a two-electron process of type (38) or (40) was demonstrated[26] by a microcoulometric study of the sum of the products of the reaction between formaldehyde and $\overset{+}{N}H_3OH$. Since this reaction gives rise[26] to the mono- and bis-hydroxymethyl derivatives $HO\overset{+}{N}H_2.CH_2OH$ and $HO\overset{+}{N}H(CH_2OH)_2$, the reduction of only one hydroxymethyl group in both the mono- and bis-hydroxymethyl derivative should correspond to the two-electron process:

$$HO\overset{+}{N}H(CH_2OH)_2 \xrightarrow{H^+} HO\overset{+}{N}H(CH_2OH)\,CH_2\overset{+}{O}H \rightarrow H_2O + HO\overset{+}{N}H(CH_2OH)\,\overset{+}{C}H_2 \xrightarrow{2e;H^+} \rightarrow HO\overset{+}{N}H(CH_2OH)\,CH_3. \quad (41)$$

This is most probably associated with the fact that there is insufficient time for the product of the two-electron reduction, namely $HO\overset{+}{N}H(CH_2OH)CH_3$ to undergo a repeated dehydration stage with further reduction at the electrode surface.

Presumably the reduction with dissociation of the C–O bond [reaction (38)] or the C–N bond [reaction (39)] is activated by the formation of a six-membered cyclic hydrate of type (29). Although protonation is inhibited under these conditions, the enhancement of the mutual inductive effect of the RR'N and OH groups facilitates the reduction. This probably constitutes the main difference in the electrochemical behaviour of aminocarbinols with the amino-group in the 1-position compared with other aminocarbinols, which are incapable of being electrochemically reduced.

Table 13. Polarographic characteristics of the hydroxymethyl derivatives of aminoacids[100] at 25°C ($I$lim, μA mmole$^{-1}$ mg$^{-2/3}$ s$^{1/2}$).

| Aminoacid | $K_{A\pm}$ | $pK_{M\pm}$ | $c_{HCHO}$=0,6M | | $c_{HCHO}$=6,0M | | $c_{HCHO}$=2,0M pH=7,8 |
|---|---|---|---|---|---|---|---|
| | | | $pH_{max}$ | $(I_{lim})_{max}$ | $pH_{max}$ | $(I_{lim})_{max}$ | $-E_{1/2}$, V |
| β-Phenyl-β-alanine | 5.4 | — | 7.6 | 1.4 | 5.8 | 1.8 | 1.13 |
| β-Alanine | 10.24 | — | 7.4 | 0.60 | 4.7 | 1.7 | 1.18 |
| β-Phenyl-α-alanine | 8.6 | — | 7.8 | 1.4 | 6.2 | 2.9 | 1.16 |
| Valine | 9.72 | 7.0 | 8.2 | 1.0 | 6.8 | (1.9) | 1.17 |
| Leucine | 9.74 | 7.4 | 7.9 | 0.92 | 6.3 | 2.6 | 1.18 |
| Norleucine | 9.83 | — | 8.2 | 0.86 | 6.4 | 2.4 | 1.18 |
| Norvaline | — | — | 8.2 | 0.80 | 6.4 | 2.4 | 1.18 |
| α-Alanine | 9.87 | 7.4 | 8.0 | 0.57 | 6.0 | 1.6 | 1.19 |
| Glycine | 9.88 | 7.6 | 6.8 | 0.60 | 4.4 | 2.2 | 1.20 |
| α-Aminoadipic acid | — | — | 8.0 | 0.38 | 6.3 | 1.2 | 1.22 |
| Glutamic acid | 9.95* | — | 7.8 | 0.45 | 6.2 | 1.2 | 1.25 |
| Aspartic acid | 10.00** | 8.4 | 8.0 | 0.32 | 6.4 | 1.3 | 1.26 |

* $pK_{A\pm}$; $pK_{A\pm}$=4,51.
** $pK_{A\pm}$; $pK_{A\pm}$=3,9

In an acid medium (pH ≤ 2), where the adduct M(D, T) is almost completely protonated at the nitrogen atom, the dehydration stage preceding the electrochemical reduction process is either catalysed by repeated protonation (at the oxygen atom[24]) or there is intramolecular catalysis owing to a hydrogen bond:

$$RR'C(HO\cdots H)-N^+HX \rightleftarrows RR'C(HO-H^+)-NHX. \quad (42)$$

Since the limiting kinetic current is independent of pH in this range of the latter for many hydroxymethyl derivatives of aminoacids[24], intramolecular catalysis appears to be more likely. The independence of $\bar{i}$lim of pH in fairly acid solutions also shows that the kinetic current is caused by inhibition at the dehydration stage [mechanism (38)],[22] while the stage involving the protonation of the oxygen atom [mechanism (42)] is fairly rapid (is close to equilibrium). The nature of the substituent X in the nucleophiles (Table 1) has an effect under these conditions, manifested mainly by displacement of equilibrium (42) [the distance from the dissociating $C-\overset{+}{C}$ bond than in the decomposition of the adduct into the initial substances is greater]. An increase of the $-I$ effect of the substituent X (the inductive and steric influences) as well as an increase of the $+I$ effect (the dominance of steric influences) displaces equilibrium (42) to the right; hence follows an increase of $\bar{i}$lim and its correlation with the constants $k_{-1}$ and $K'_{A^+}$ (Table 1). Starting with norvaline, $\bar{i}$lim approaches the diffusion value (Table 1).

Table 14. The half-wave potentials for the reduction of $RR'C(OH)\overset{+}{N}H_2X$.

| R | R' | X | pH | $-E_{1/2}$, V | References |
|---|---|---|---|---|---|
| H | H | OH | ~0 | 0.49* | 26,51 |
| H | H | H | 2.5 | 0.84* | 28,99 |
| H | H | H | 7.8 | 1.11 | 99 |
| $C_6H_5$ | $COC_6H_5$ | H | 9.25 | 0.58 | 8 |
| $CH_3$ | $COCH_3$ | H | 9.25 | 0.66 | 8 |
| $C_6H_5$ | $COO^-$ | H | 9.25 | 0.88 | 8 |
| $CH_3$ | $COO^-$ | H | 9.25 | 1.04 | 8 |
| $CH_3$ | H | H | 9.25 | 1.44 | 8 |
| $CH_3$ | $CH_3$ | H | 9.25 | 1.56 | 8 |
| $CH_3$ | $COO^-$ | $CH_2COO^-$ | 9.88 | 1.09 | 8 |
| $CH_3$ | $CH_3$ | $CH_2COO^-$ | 9.88 | 1.50 | 8 |
| $CH_3$ | $COO^-$ | $CH(CH_3)COO^-$ | 9.87 | 1.10 | 8 |
| $CH_3$ | $COO^-$ | $CH_2CH_2OH$ | 9.50 | 1.04 | 8 |
| H | H | $CH_2CH_2OH$ | 10.0 | 1.3 | 73 |

* $RR'C(OH)\overset{+}{N}H_2X$.

Over a wide range of pH values with $c_Q$ = const. and $c_A$ = const., $\bar{i}$lim passes through a maximum as a function of pH,[22,28,73,95,96,98-101] as in the reduction of semicarbazones[30] and hydrazones[34] in an equilibrium mixture. This is caused by the increase of the concentrations of the adducts ($L_M \gg L_{M^+}$, $L_D \gg L_{D^+}$, $L_T \gg L_{T^+}$) with increasing pH, the opposite effect due to the decrease of the concentrations of the forms of the adducts protonated at the nitrogen atom, and inhibition either at stage (42) or at the stage involving the protonation of the adduct at the nitrogen atom. The occurrence of one of the above inhibiting effects with increasing pH is indicated by the confirmation of the validity[28] of Eqn.(35) for the reduction of M + D + T (for the reaction of formaldehyde with $NH_4^+$). Under these conditions, the $\bar{i}$lim–pH curve is described by Eqn.(26) when account is taken of Eqn.(35). As for hydrazones[34], $pH_{max}$ was found from the condition $d\bar{i}lim/d[H^+] = 0$ [28] and it was shown theoretically that $pH_{max}$ should shift towards lower pH values with increasing $c_Q$, which agrees with experimental data[99]. This is also characteristic[100] of the adducts obtained by the reaction of formaldehyde with aminoacids (Table 13). In the presence of a not unduly large excess of formaldehyde, the changes in $(\bar{i}lim)_{max}$ and in $E_{1/2}$ at a constant pH (Table 13) are caused mainly by the inductive and steric effects of substituents in similar (α- or β-) aminoacids, which leads to a correlation between $(\bar{i}lim)_{max}$ and $E_{1/2}$ and between $K_{A\pm}$ and $K_{M\pm}$ (Table 13). The influence of the inductive effect on $E_{1/2}$ at a constant pH (the displacement of $E_{1/2}$ towards positive values with increasing $-I$ effect) is also illustrated by the data in Table 14.

## IV. ANALYTICAL APPLICATIONS

The reactions under consideration are widely used for the indirect polarographic determination of carbonyl and nitrogen compounds. Distinct polarographic waves are observed, while under the usual conditions the reduction of many compounds is either partly or fully masked by the discharge of the supporting electrolyte. This applies particularly to nitrogen compounds and many aliphatic and cyclic carbonyl compounds. Even when the carbonyl compound is reduced relatively readily (formaldehyde, etc.), a valuable feature of the reaction is that the reduction wave of the product M(D, T) or U occurs at potentials much more positive than the reduction potentials of the carbonyl compounds, which makes it possible to use a large excess of the latter and hence increase the sensitivity of the determination of the nitrogen compounds. On the other hand, in the determination of the carbonyl compounds, a large excess of the nitrogen compound (ammonia, semicarbazide, hydrazine, etc.) is also permissible, because the nucleophile employed is frequently polarographically completely inactive under the given conditions.

It must be emphasised that, in the selection of the concentration of the reactant, one need not endeavour to ensure the complete conversion of the component being analysed into the polarographed product. It is sufficient to obtain an equilibrium mixture, because the limiting current in the presence of an excess of the reactant at a constant concentration of the latter and a constant pH is proportional to the concentration of the substance analysed [Eqns. (25) and (26)]. Naturally, in the analysis it is important to achieve reaction equilibrium rapidly, which is usually done by selecting the optimum pH in the solution. For this purpose and also in order to increase the sensitivity of the determination of the carbonyl compound, a supporting electrolyte buffer solution was used with a pH close to the $pK_{A^+}$ of the nucleophile present in excess [8,12,13]. The optimum pH of the supporting electrolyte corresponding to the maximum limiting current is frequently selected for analysis [98-101]. In order to attain equilibrium rapidly and increase the sensitivity of the determination, the reaction has been carried out [102,103] in an alkaline medium and the polarographic measurements have been made in an acid solution. This method is suitable only when the reaction products are very slowly decomposed in the acid solution into the initial substances (aminoacids with the amino-group not in the $\alpha$-position) [24,102,103]. It has been shown [104] that the rate of equilibration in the carbonyl–amine interaction increases sharply in anhydrous acetic acid, which is probably due mainly to catalytic factors.

The selectivity of the methods is achieved either by selecting appropriate reagents (*N*-alkylhydroxylamines [105], hydrazine [106]) or by altering the pH of the supporting electrolyte [107,108].

From the analytical point of view, it is also important that, with the aid of the reactions under consideration, it is possible to trap easily the component analysed in the gas phase [109,110] or extract it fairly completely from a non-aqueous solution [106,111]. One should also note that suitable direct analytical reactions with carbonyl compounds have not been found for many nitrogen compounds [51,73,98,102,112-117], because of their weak nucleophilic properties, so that it has been suggested (see below) that the nitrogen compounds be subjected to preliminary hydrolysis with subsequent conversion of the hydrolysis products in the presence of the carbonyl compound into the polarographed substances. Preliminary hydrolysis has also been used [118] for vinyl acetate with conversion of the resulting acetaldehyde (reaction with hexamethylene-1,6-diamine) into the polarographed product. The conversion of organic nitrogen compounds into the inorganic ammonium ion with its subsequent polarographic determination in the presence of formaldehyde has been achieved [119] in order to improve the familiar Kjeldahl method. The nitrogen-containing reagent (an aminoacid) to be used for the determination of a carbonyl compound has been obtained [120] by the hydrolysis of the substance to be analysed—polycaproamide.

Analytical determinations are usually based on cathodic waves, but anodic waves for the products of the interaction of carbonyl compounds with *o*-phenylenediamine have also been used [121-124].

### 1. Determination of Carbonyl Compounds

Reactions with Girard reagents (the formation of hydrazones) have been used [101,125-132] to determine aliphatic and cyclic ketones, ketosteroids, terpenes, and other carbonyl compounds. Analytical reactions belonging to an analogous class have been carried out on the basis of hydrazine [15,21,106,114,133-142], phenylhydrazine [143], semicarbazide [17,21,109,110,144-150], maleic acid monohydrazide [151], aminoguanidine [151], and 2,4-dinitrophenylhydrazine [152-155] (either an excess of the reagent [153] was determined [153,154] or an amperometric titration was carried out [154]). It is noteworthy that, whereas the use of hydrazine for the determination of aliphatic carbonyl compounds was unsuccessful owing to the use of an unduly acid supporting electrolyte [133] (in contrast to the determination of sugars [134]), starting with the work of Baranova et al. [114] and Yuan-Hsiao Lin and Chen-Ya Wang [135] the problem has been solved successfully (determination of carbonyl compounds in the wash water from the manufacture of isoprene [114] and determination of acetone in vinyl acetate [135]; supporting electrolytes at pH 6.3 [114] and 7.2 [135] have been used).

This application has been developed in other investigations [106,136-142] and included the separate determination of a series of aliphatic aldehydes and ketones in the manufacture of synthetic rubber monomers [106,136,139], formaldehyde has been determined in cellulose ethers [140,141], and a highly sensitive method has been developed for the determination of acetaldehyde in commercial ethanol without the need for the preliminary concentration (distillation) of the former [142]. The use [156] of reactions based on semicarbazide, thiosemicarbazide, and phenylhydrazine for the adsorption concentration of aliphatic and aromatic aldehydes on a stationary mercury drop, which permitted an appreciable increase of the sensitivity of the determination (oscillographic polarography), is of interest. An increase of the sensitivity of the determination with the aid of similar reagents has also been achieved by using oscillographic difference polarography [157].

The reactions with hydroxylamine and its alkyl derivatives (the formation of oximes) have been used for the polarographic determination of carbonyl compounds: the determination of aliphatic aldehydes [105], aldoses [21,144], pyridoxals [158], vanillin [159,160], furfural [161,162], crotonaldehyde [163], and acetone [164].

The reactions with ammonia [8,12,13,165-167], glycine [8,12,13,168], methylamine [13], n-butylamine [20], isobutylamine [124], ethylenediamine [169], 1,6-hexamethylenediamine [118,169-172], monoethanolamine [73,173], and *o*-phenylenediamine [121,124,174-178] are also of definite importance in the polarographic determination of carbonyl compounds. Nevertheless, in many cases preference must be given to substituted and

unsubstituted hydrazines and hydroxylamines as reagents because of the much larger reaction equilibrium constant (see Section II).

## 2. Determination of Nitrogen Compounds

The possibility, in principle, of the polarographic determination of an aminoacid on the basis of its reactions with pyruvic acid or acetone was already demonstrated in earlier investigations [11,12]. Subsequently methods were developed for the determination of methylamine in the presence of dimethylamine (reaction with piperonal) [179], aminoacids and ammonium ions (reactions with phthalic anhydride) [180,181], hydrazine and its derivatives (reactions with benzaldehyde) [182], and primary amines (reaction with isobutyraldehyde) [183].

Starting with the work of Matoušek [22] and Tur'yan and coworkers [38,102], formaldehyde has found extensive applications as a reagent in the indirect polarography of nitrogen compounds. It is used to determine aminoacids [98,100,102,103,107,108,184,185], caprolactam [98,102,103,186,187] (hydrolysis to $\epsilon$-aminocaproic acid), $N$-methylpyrrolidinone [116] (hydrolysis to $N$-methylaminobutyric acid), ammonium ions [28,99,108,119,188], hexamethylenetetramine [73,113] (hydrolysis to ammonium ions, but is can also be determined from the formaldehyde formed—reaction with monoethanolamine [73])†, acetonitrile [40,115] (hydrolysis to ammonium ions), primary and secondary amines [40,114,190-195], dimethylformamide [40,114] (hydrolysis to methylamine), hydroxylamine [26,51,196,197], cyclohexanone oxime [26,51,112,197] and other oximes [117] (hydrolysis to hydroxylamine), hydrazine, and formylhydrazine [138]. The successful employment of formaldehyde is due, firstly, to the high equilibrium constants for the reactions (Section II) combined with the possibility of creating a relatively high concentration of the reagent in the supporting electrolyte and, secondly, the fact that, in the presence of an excess of formaldehyde, several polarographically active products are formed (in the general case, mono-, bis-, and tris-hydroxymethyl derivatives), which also increases the sensitivity of the methods. Even in a very acid medium, where the nucleophile is almost completely protonated, formaldehyde behaves as a fairly active reagent [26,51,112,196].

Certain nitrogen compounds (diamines [198,199], hydrazine and its derivatives [200], semicarbazide [200], and hydrazides [201,202]) have been determined successfully using acetone as the reagent. Other carbonyl compounds have also been employed to determine hydrazides [203-205] and thiosemicarbazides [206].

The determination of 2,2'-bis-(3-amino-4-hydroxyphenyl)propane in polymers on the basis of its reaction with benzaldehyde has been reported [207].

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† The products of the interaction of ammonium ions with formaldehyde, formed on hydrolysis of hexamethylenetetramine, were apparently also polarographed in a study [189] where a very acid supporting electrolyte was used in the determination of hexamethylenetetramine.

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# Arynes and Carbenes Derived from Organoelement Compounds

O.M.Nefedov, A.I.D'yachenko, and A.K.Prokof'ev

The literature data on the methods for the synthesis of unstable intermediate species (arynes and carbenes) from organoelement compounds, mainly from *o*- and α-halogeno-derivatives, are surveyed and examined critically. It is shown that the ease of decomposition of the initial compound is determined by the possibility of the formation in the transition state of the coordinate bond between the groups or atoms eliminated and the theoretical proof of this mechanism is given. The bibliography includes 322 references.

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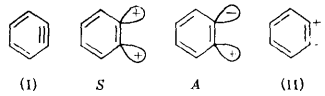

## I. INTRODUCTION

The chemistry of the reactive molecules having two electrons and two non-bonding orbitals in one carbon atom (carbenes) or two electrons and two weakly bonding orbitals in neighbouring carbon atoms (arynes, cycloalkynes) has been recently transformed into an independent field of organic chemistry, the development of which has been reflected in a number of monographs[1-6] and reviews[7-9]. Organoelement compounds, which are important and sometimes the only precursors of many of the above unstable species, play an extremely important role in the chemistry of arenes and carbenes.

The aim of this review is to survey the available literature data on the decomposition reactions of organoelement compounds which result in the formation of arynes and carbenes. Since the methods of generation of the unstable species from organic derivatives of alkali metals, magnesium, zinc, and mercury have already been considered in detail in fundamental monographs[2-6] and reviews[7-9], the present review includes only the main achievements in this field, and also the results obtained in recent years (1968–1974). The data on the organic derivatives of other metals are treated in detail. For a more complete understanding of the available results, the review presents the fundamental information about the structures and reactivities of dehydrobenzene (DHB) and carbene.

## II. THE STRUCTURE AND REACTIVITY OF DEHYDROBENZENE (DHB)

DHB (I), postulated for the first time by Wittig in 1942[10] as an unstable intermediate in the reaction of fluorobenzene with phenyl-lithium, is the simplest aromatic hydrocarbon, one of the C–C linkages of which is formally a triple bond:



(I) *S* *A* (II)

The steric strain arising following the introduction of a triple bond into the rigid aromatic system of benzene is responsible for such a high reactivity that DHB, like other arynes, is a short-lived intermediate product under the conditions of the usual chemical reactions, the involvement of which in the reaction is usually inferred from various indirect features. However, as a result of the application of special methods to the investigation of unstable species, it has become possible to achieve the direct spectroscopic detection of DHB. Thus the ultraviolet and mass spectra of DHB, recorded using flash photolysis, have now been investigated[11-13], and the infrared spectrum of DHB stabilised in a solid argon matrix has been described[14]. The possibility of the stabilisation of DHB by chemical methods has been demonstrated by synthesising a stable complex with nickel carbonyl[15]. The observed spectroscopic characteristics of DHB agree with the theoretical ideas about structure and thus provide the final evidence for the actual existence of arynes.

Qualitative ideas about the electronic structure of DHB can be readily derived by considering the results of the hypothetical reaction involving the homolytic dehydrogenation of benzene. Evidently, when the $H_2$ molecule is abstracted from neighbouring carbon atoms in benzene, the residual fragment $C_6H_4$ must have a pair of degenerate hybrid σ orbitals ($\sigma_1$ and $\sigma_2$) in which two electrons are accommodated. The interorbital interaction between $\sigma_1$ and $\sigma_2$ removes the degeneracy, leading to a pair of molecular orbitals (MO), the lower orbital (*S*), of the type $\sigma_1 + \sigma_2$, being symmetrical relative to the $C_2$ axis and the upper orbital (*A*), of the type $\sigma_1 - \sigma_2$, being antisymmetric. Depending on the relation between the energy of repulsion of the electrons in the *S* orbital and the energy of the promotion of an electron from *S* to *A*, the ground state of DHB can be either the singlet $c_1(S)^2 + c_2(A)^2$ ($c_1 > c_2 \geq 0$) or the triplet $(S)^1(A)^1$. Naturally, when only qualitative hypotheses are used, it is impossible to assign correctly the ground and first excited states, although one must bear in mind that, for orbitals of the type $\sigma_1 + \sigma_2$, the electron correlation energy is small ($\leq 1$ eV) and the splitting between the *S* and *A* levels is considerable, despite the rigidity of the ring. On the other hand, it is already clear from the above discussion that the structure of the dipolar ion (II), frequently discussed when the reactivity of DHB is described, cannot correspond either to the ground or to the first excited state of the molecule.

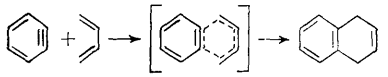
Theoretical calculations on DHB using modern quantum-chemical methods have shown that the molecule has a singlet ground state. Thus, according to calculations based on the extended Hückel method (EHM),[16] the energy of the singlet–triplet splitting ($E_{ST}$) is 35 kcal mole$^{-1}$ for the DHB molecule, the skeleton of which has the geometry of the benzene molecule. The use for the calculation on the DHB molecule of the semi-empirical SCF INDO/2 method, assuming the same geometry, led accordingly to a lower value of $E_{ST}$ (12.5 kcal mole$^{-1}$), although a somewhat higher value (20 kcal mole$^{-1}$) has been postulated for the real molecule[17]. Calculation on the molecule with the same non-equilibrium geometry by the semiempirical LCAO-MO SCF method led to $E_{ST}$ = 17 ± 5 kcal mole$^{-1}$ and the calculated parameters of the ultraviolet spectrum obtained in the same study[18] agreed satisfactorily with the experimental data[12].

The optimum geometrical parameters of the DHB molecule have been calculated by the MINDO/2[19] and MINDO/3 methods taking into account the configuration interaction[20]. According to these calculations, the molecule has the shape of an irregular hexagon with a markedly shortened distance between the C$_{(1)}$ and C$_{(2)}$ atoms; the bond lengths calculated by the two methods are in satisfactory agreement: $r_{1-2}$ = 1.256, $r_{2-3}$ = 1.344, $r_{3-4}$ = 1.399, and $r_{4-5}$ = 1.402 Å in the first set[19] and $r_{1-2}$ = 1.291, $r_{2-3}$ = 1.384, $r_{3-4}$ = 1.417, and $r_{4-5}$ = 1.419 Å in the second set[20]. One should note that the heat of formation of DHB (114.3 kcal mole$^{-1}$),[20] calculated by the most effective of the modern semiempirical methods (SCF MINDO/3), agrees extremely well with the experimental value 118 ± 5 kcal mole$^{-1}$,[21] which suggests that the geometrical and energetic parameters found for the molecule by Dewar and Li[20] ($E_{ST}$ = 12.4 kcal mole$^{-1}$, ionisation potential of 8.5 eV) are close to the real values. The low value of $E_{ST}$ is indicated by the extremely rapid conversion of the triplet DHB molecule into the singlet molecule[22].

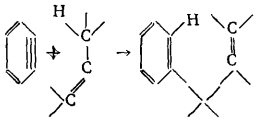
Thus, according to quantum-chemical calculations, the DHB molecule, which is in the singlet ground state, is characterised by a high energy of the highest occupied molecular orbital (HOMO), which is unique for hydrocarbons, and a low energy of the lowest vacant molecular orbitals (LVMO), the boundary orbitals being centred between the C$_{(1)}$ and C$_{(2)}$ atoms and being formed from weakly overlapping σ orbitals of the two atoms. As a consequence of this, the molecule should exhibit a high electrophilic reactivity in relation to unsaturated systems and also an ability to enter into reactions characteristic of both singlet biradicals and unsaturated compounds.

The available data on the reactivity of DHB are fully consistent with this conclusion: it readily reacts as a dienophile in the Diels–Alder reaction, enters into many other cycloaddition reactions, and is capable of being inserted into single C–H, C–metal, and other bonds[2,3].

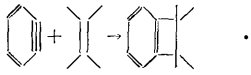
The mechanism of the interaction of DHB with planar conjugated *cis*-dienes is consistent with a concerted 2*s* + 4*s* cycloaddition reaction[23-25]:



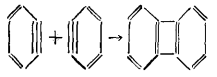
The reaction involving the 1,4-cycloaddition of DHB to aromatic systems proceeds via the same mechanism[26]. The above reactions with non-planar cyclic polyenes, for which the 2*s* + 4*s* cycloaddition reactions are not so energetically favourable, compete with the so called ene addition[27,28], which is also characteristic of the reactions of DHB with olefins:



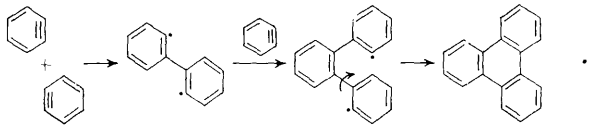
The simultaneous formation of benzocyclobutene is also usually observed under these conditions:



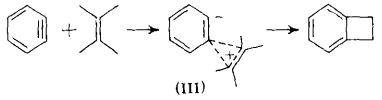
Judging from the dependence of its stereoselectivity on the nature of the olefin[24,25,29], this reaction can proceed as concerted 2*s* + 2*s* cycloaddition when $E_{ST}$ for the transition state is small[30]. In view of the evidently low value of $E_{ST}$ for the transition state, this mechanism should also operate in the dimerisation of DHB to biphenylene, which is usually formed as the main product in the gas-phase generation of DHB[2]:



The formation of terphenylene—another product of these reactions—proceeds either via the concerted 2*s* + 2*s* + 2*s* cycloaddition or, more probably, via a stepwise biradical process due to the transoid approach of the reactants:

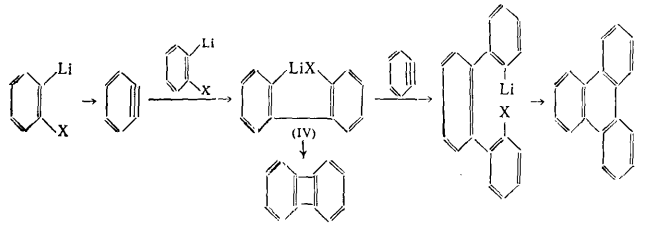


Analogous cyclodimerisation and cyclotrimerisation reactions are characteristic of cycloalkynes[31,32], and higher cycloalka-1,2-dienes[34], which also have a singlet ground state[35]. In the absence of acceptors, cyclohexa-1,2-diene in the triplet ground state[35] forms a tetramer[36]. According to calculated data[37], the addition of DHB to ethylene can proceed with the intermediate formation of a dipolar phenonium ion (III):



(III)

During its generation from organometallic compounds, DHB is readily inserted in the C–metal bond of the initial compound, which also leads to biphenylene and terphenylene, but naturally via a different pathway:



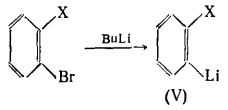
(IV)

In contrast to the majority of thermolytic gas-phase reactions, the main product here is usually terphenylene,

while biphenylene is formed in trace amounts. Since the cyclisation of compound (IV) requires the flattening of the biphenyl molecule, the yield of biphenylene under these conditions may be greatly increased by carrying out the reaction in the presence of aromatic hydrocarbons or adsorbents promoting such flattening[39].

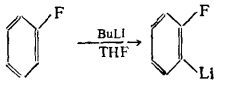
## III. ARYNES DERIVED FROM ORGANOMETALLIC COMPOUNDS

Among the organometallic precursors of DHB and its substituted derivatives, *o*-halogenolithiobenzenes (V, X = F, Cl, or Br) have been most thoroughly investigated. The first representatives of compounds of this class were synthesised as early as 1956, by the low-temperature reaction of aliphatic organolithium compounds with the corresponding *o*-dihalogenobenzenes in ether or tetrahydrofuran (THF)[40]:

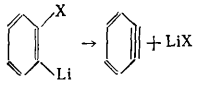


(V)

A large number of organolithium aryne precursors, the information about the thermal stability of which is presented in Table 1, have now been synthesised. Together with the exchange of a halogen atom for lithium, the H-metallation reaction is used in the synthesis of compound (V), for example[2]:



Compounds (V, X = F, Cl, or Br) without other substituents are labile, exist in solution only at low temperatures, and readily split off LiX with formation of DHB:



It follows from cryoscopic and NMR data[41-44] that in ether–hydrocarbon solutions *o*-fluorophenyl-lithium is a tetrameric tetraetherate, $(o\text{-}FC_6H_4Li)_4(R_2O)_4$, whose structure is analogous to that of the etherates of aliphatic organolithium compounds[45]. According to the results of differential thermal analysis, the stability of this compound, determined like that of other compounds (V), by the decomposition temperature $T_d$ in solution, depends on the nature of the ether $R_2O$ (Table 1), while in media without ethers, the compounds decompose at the instant of their formation[41,44]. Judging from the $^1H$ and $^{19}F$ NMR data, the carbon–lithium bond in the *o*-fluorolithiobenzene molecule is not appreciably polarised under the influence of the neighbouring fluorine atom, although both atoms [lithium and fluorine?] interact appreciably through space[39]. The influence of the lithium atom on the mobility of halogen atoms linked to the benzene ring under conditions ensuring the stability of halogenolithiobenzenes is in its turn apparently also small, since in some cases polylithio-compounds can be obtained by treatment with an excess of a lithium alkyl under extremely mild conditions, for example[46,47,48]:

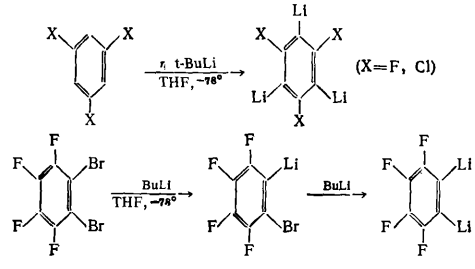
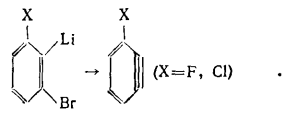


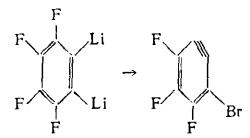
**Table 1.** Thermal stabilities of organolithium aryne precursors.

| Compound | Solvent | Stability characteristic | References |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| *o*-Fluorolithiobenzene | acyclic ethers | $T_d = -48° \text{--} -50°C$ | 41, 42 |
| | cyclic ethers | $T_d = -19° \text{--} -21°C$ | 41, 42 |
| *o*-Chlorolithiobenzene | acyclic ethers | $T_d = -70° \text{--} -73°C$ | 41, 42 |
| | cyclic ethers | $T_d = -50° \text{--} -52°C$ | 41, 42 |
| *o*-Bromolithiobenzene | acyclic ethers | $T_d = -83° \text{--} -85°C$ | 41, 42 |
| | cyclic ethers | $T_d = -73° \text{--} -75°C$ | 41, 42 |
| 2,6-Difluorophenyl-lithium | THF | stable at -65°C | 54 |
| 2,4,6-Trifluorophenyl-lithium | THF | stable at -70°C | 47 |
| 3,4,5,6-Tetrafluorophenyl-lithium | THF, $Et_2O$ | stable at -55°C | 55 |
| 2,4,5,6-Tetrafluorophenyl-lithium | $Et_2O$ | stable at -75°C | 56 |
| 2,3,5,6-Tetrafluorophenyl-lithium | THF | stable at -55°C | 55 |
| Pentafluorophenyl-lithium | THF | polymerises at 0°C | 57 |
| Pentafluorophenyl-lithium | $Et_2O$ | decomposes at 15°C, partly stable at 20°C | 51 |
| 2-Fluoro-1-lithionaphthalene | THF | $T_d = -30°C$ | 58 |
| Octafluoro-4,4'-dilithio-biphenyl | THF, $Et_2O$ | decomposes at -5° -0° | 59 |
| Octafluoro-2,2'-dilithio-biphenyl | $Et_2O$ | decomposes at 0°C | 60 |
| Pentafluorophenylpenta-fluoro-4-lithiophenyl ether | THF | decomposes via the aryne mechanism at -30°C | 61 |
| 4,4'-difluoro-3,3'-dilithio-biphenyl | THF, $Et_2O$ | stable at -78°C | 62 |
| 2-Bromo-3,4,5,6-tetra-fluorophenyl-lithium | $Et_2O$ | decomposes in 8 h at 0°C | 48 |
| 2,4,6-Trifluoro-1,3-dilithio-benzene | THF | stable at -78°C | 47 |
| Tetrafluoro-1,2-dilithio-benzene | THF, $Et_2O$ | stable at $T \leqslant -55°C$ | 55 |
| Tetrafluoro-1,4-dilithio-benzene | THF, $Et_2O$ | stable at $T \leqslant -65°C$ | 54 |
| Tetrafluoro-1,3-dilithio-benzene | $Et_2O$ | stable at $T \leqslant -75°C$ | 56 |
| 3,5-Dichloro-2,4,6-trifluoro-phenyl-lithium | $Et_2O$ | stable at $T \leqslant -75°C$ | 56 |
| 5-Chloro-2,4,6-trifluoro-1,3-dilithiobenzene | $Et_2O$ | stable at $T \leqslant -75°C$ | 56 |
| 3-Chloro-2,4,5,6-tetrafluoro-phenyl-lithium | $Et_2O$ | stable at $T \leqslant -75°C$ | 56 |
| 2,4,6-Trifluoro-1,3-trilithio-benzene | THF | $T_d \approx -60°C$ | 47 |
| 2,4,6-Trichlorophenyl-lithium | THF | stable at -65°C | 46 |
| 2,3,5,6-Tetrachlorophenyl-lithium | $Et_2O$ | stable at -10°C | 63 |
| 2,3,4,5-Tetrachlorophenyl-lithium | $Et_2O$ | stable at -20°C | 63 |
| Pentachlorophenyl-lithium | $Et_2O$ | decomposes slowly in the presence of furan at ~ 20°C; | 52 |
| ditto | | stable in crystalline state at 20°C in air | 53 |
| Nonachlorolithiobiphenyl | THF | stable at -30°C | 64 |
| Octachlorodilithiobiphenyl | THF | stable at -30°C | 64 |
| 2,4,6-Trichloro-1,3-dilithio-benzene | THF | stable at -65°C | 46 |
| 2,4,6-Trichloro-1,3,5-trilithio-benzene | THF | stable at -65°C | 46 |
| Tetrachloro-4-lithiopyridine | $Et_2O$ | stable at ~ 20°C | 65 |
| 2,3,6-Trichloro-4-lithio-pyridine | $Et_2O$ | stable at -20°C | 63 |
| Pentabromophenyl-lithium | $Et_2O$ | stable at -15°C | 52 |
| | benzene | stable at 80°C | |
| 2'-Bromo-2-lithiobiphenyl | $Et_2O$ | stable at 20°C | 53 |

In the majority of known cases, the ease of decomposition of compounds (V) with formation of arynes increases with decrease of the C–X bond energy, so that the decomposition temperatures of compounds of the type *o*-$XC_6H_4Li$ decrease in the following series of X : F > Cl > Br. The same relation has been observed for 2,6-dihalogenolithiobenzenes with different halogen atoms[2]:

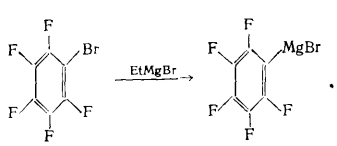



However, the accumulation of fluorine atoms in the molecule of the initial polyhalogenolithiobenzene alters the mode of elimination of LiX. For example, the only product of the decomposition of 2-bromo-3,4,5,6-tetrafluorophenyl-lithium is bromotrifluorodehydrobenzene (VI),[49] which may be attributed to thermodynamic control of the reaction[50,51]:

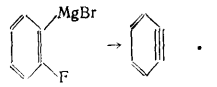



An interesting feature of pentahalogenolithiobenzenes, usually obtained by the reaction of lithium alkyls with penta- or hexa-halogenobenzenes, is their high thermal stability, compared with *o*-halogenolithiobenzenes (V), which is usually attributed[2] to stabilisation of the corresponding phenyl anions by the halogen atoms. However, comparison of the decomposition temperatures of $C_6X_5Li$ and the corresponding compounds (V) shows that this explanation is not exhaustive. Thus pentafluorophenyl-lithium, the anion of which should be the most stable species of this kind, decomposes slowly in an ethereal medium at 0°C, i.e. at a temperature only slightly higher than for *o*-fluorophenyl-lithium ($T_d$ = −20°C in THF). On the other hand, pentachlorophenyl-lithium is entirely stable under the usual conditions and can be stored at 20°C and even higher temperatures in the crystalline state, while *o*-chlorophenyl-lithium decomposes in THF at −50°C.[41,53] A similar difference between stabilities has also been noted for the corresponding bromo-derivatives ($T_d$ = 0°C for pentabromophenyl-lithium compared with −75°C for *o*-bromophenyl-lithium in THF).[52] It is noteworthy that the decomposition of pentahalogeno-derivatives of phenyl-lithium with formation of arynes is appreciably complicated by reactions of the $S_N2$ type, which are much less common for monohalogenolithiobenzenes[2].

Together with halogeno-derivatives of organolithium compounds, the analogous *o*-halogenophenylmagnesium halides behave as common organometallic precursors of arynes. Compounds of this type are obtained either by the reaction of dihalogenobenzenes with metallic magnesium in ether or THF or by an exchange interaction between aromatic halogeno-derivatives and aliphatic organomagnesium compounds[66,67]:



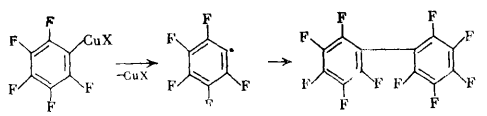

Halogeno-derivatives of aromatic organomagnesium compounds are more stable than the corresponding organolithium compounds[68,69] and in most cases decompose at a moderate rate only at the boiling point of the solvent (ether or THF):




Like the analogous lithium compounds, pentahalogenophenylmagnesium halides are more stable than the corresponding monohalogenophenyl derivatives. However, the main pathway in the reactions of these compounds in ethereal media involves intermolecular reactions of the $S_N2$ type, as a result of which they are widely used to introduce pentahalogenophenyl groups into various compounds. The aryne decomposition of pentahalogenophenyl magnesium halides is achieved in a hydrocarbon medium at extremely high temperatures (approximately 200°C)[52,70].

*o*-Iodophenylmercury iodide or bis-2-iodophenylmercury decompose at approximately 200°C, which leads to DHB according to Hoffmann[2]. On the other hand, bis-pentachlorophenyl- and bis-pentafluorophenyl-mercury are stable at higher temperatures[2] and even bis-(2-bromo-3,4,5,6-tetrafluorophenyl)mercury enters into various reactions at 230°C without undergoing the aryne decomposition[71].

Numerous pentahalogenophenyl derivatives of many other elements (Zn, Cu, Ag, B, Al, In, Tl, Si, Ge, Ti, Co, Fe) have been synthesised from pentahalogeno-derivatives of lithium and magnesium, but the thermolysis products of these compounds were not investigated, although in most of the known cases they exhibit a thermal stability characteristic of the analogous phenyl derivatives or higher[2,72], which apparently indicates their low tendency to undergo the aryne decomposition. For the less stable halogenophenyl compounds of copper, silver, cobalt, and titanium, the most probable thermolytic pathway is homolytic rupture of the carbon–metal bond with formation of free radicals[33,73–76], for example:




Pentafluorophenyl derivatives of boron, aluminium, and indium, among which $(C_6F_5)_3B$ and $(C_6F_5)In$ are fully stable and can be readily synthesised by the exchange reaction between pentafluorophenyl-lithium and the corresponding halides, possess interesting properties[77]. On the other hand, trispentafluorophenylaluminium can only be obtained in the form of the etherate, which decomposes explosively when any attempt is made to remove the ether even at a relatively low temperature (approximately 20°C). The attempt to synthesise $(C_6F_5)_3Al$ in an ether-free medium leads to the same result and the product of the decomposition of this compound is presumably the corresponding aryne.

On heating $(C_6F_5)_2TlBr$ with various elements, pentafluorophenyl derivatives of the type $(C_6F_5)_nM$ (where M = S, Se, Te, P, As, Sb, Sn, Zn, or Cd) were obtained, being fully stable at approximately 200°C.[78]

$W(C_6F_5)_5$[79] as well as compounds of the type $C_6F_5HgX$ (where X represents iron, manganese, and molybdenum carbonyls) are also resistant to aryne decomposition[80].

## IV. THE STRUCTURE AND REACTIVITY OF CARBENES

Like other molecules containing carbon atoms with an incomplete shell, the carbenes CRR′ exhibit an enhanced reactivity and are involved in chemical reactions as short-lived intermediates. Nevertheless, the use of special physical and physicochemical methods has now made it possible not only to demonstrate reliably the involvement of carbenes in many reactions (particularly in the decomposition of halogeno-derivatives of organometallic compounds[81,82]) but also to determine the thermodynamic and structural parameters of many of them[83,84].

Since the central atom of the carbene has two non-bonding orbitals accommodating two electrons, the CRR′ molecule may exist in singlet or triplet states characterised by parallel and antiparallel spins of the free electrons. The spin state of the carbene determines to a large extent its reactivity, since compounds in the triplet state have a reactivity close to that of free radicals, and those in the singlet state can exhibit properties of both compounds with a free electron pair as well as compounds having a vacant orbital, i.e. they can behave as nucleophiles or electrophiles, depending on the nature of the substituents R and R′. For this reason, the main theoretical problem of the chemistry of carbenes is the relation between the structural parameters and the spin state of the molecule.

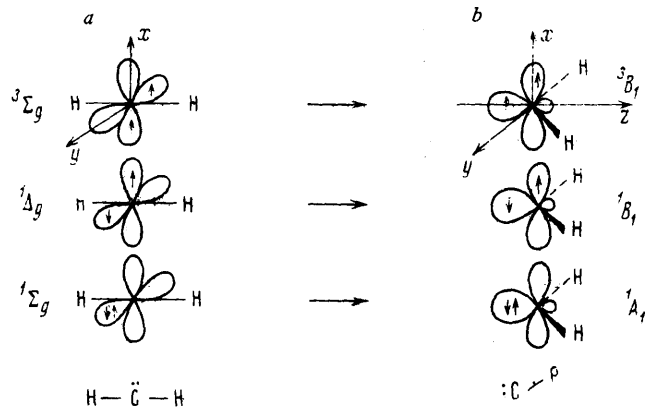



Figure 1. The spin states of methylene: *a*) linear form; *b*) bent form.

In broad outline, this problem may be examined even in relation to the simplest carbene—methylene[85]. Evidently the carbon atom of the linear $CH_2$ molecule can have two *sp* hybrid orbitals involved in the formation of C–H bonds and two non-bonding *p* orbitals ($p_x$ and $p_y$) accommodating two electrons. According to the Pauli principle, the possible states of this molecule ($D\infty h$ symmetry point group) should be arranged in the following sequence in terms of their energies: $^3\Sigma_g < {}^1\Delta_g < {}^1\Sigma_g$, so that the linear $CH_2$ molecule should have a triplet ground state. A decrease of the H–C–H valence angle, i.e. the bending of the molecule, for example in the *yz* plane, as shown in Fig. 1, removes the degeneracy of the $p_x$ and $p_y$ orbitals, since the former, being symmetrical relative to the *yz* plane, remains a pure *p* orbital under these conditions, while the latter acquires some *s* character, being converted into a hybrid $\sigma$ orbital. This change in the shape of the molecule alters its symmetry point group to $C_{2v}$ with the possible states $^3B_1$, $^1B_1$, and $^1A_1$. Evidently, on transition from the $^3\Sigma_g$ and $^1\Delta_g$ states to the corresponding $^3B_1$ and $^1B_1$ states, the energy of one of the free electrons is reduced. When this effect is greater than the decrease of the energy of the C–H bond owing to the reduction of the amount of *s* character of the corresponding hybrid atomic orbitals, the $^3B_1$ and $^1B_1$ states will be energetically more favourable than the $^3\Sigma_g$ and $^1\Delta_g$ states respectively. The molecule will therefore "strive" to increase the valence angle until the associated energy gain is compensated by the energy of repulsion between the hydrogen atoms. Since the analogous transition between the $^1\Sigma_g$ and $^1A_1$ singlet states is associated with approximately twice as great an energy gain as the transition between the first two states, presumably the equilibrium valence angle in the molecule in the $^1A_1$ state should be smaller than in the molecule in the $^3B_1$ or $^1B_1$ state.

Thus, general considerations arising from valence theory lead to the conclusion that the methylene molecule must have a triplet ground state in which it is bent and an excited singlet state with the same or smaller valence angle. On passing from methylene to other carbenes, which naturally have more bulky substituents, one must expect an increase of the valence angles in any state of the molecule. It is also evident that the interaction of the occupied orbitals of the substituents R and R′ of the CRR′ molecule with the $p_x$ orbital of the central atom should lead to a specific stabilisation of the $^1A_1$ singlet state (or another state of the $\sigma^2$ type), and the existence of carbenes in a singlet ground state should therefore be caused by a fairly strong interaction of this type[86].

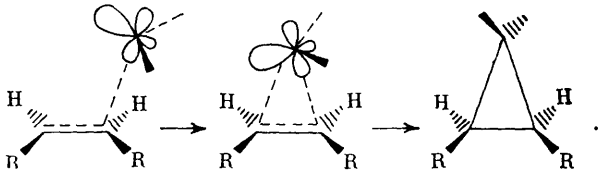
The results of many experimental[5,84] and theoretical[5,85–88] studies devoted to the problem of the structure of carbenes are in full agreement with these considerations. It has now been established that methylene and its alkyl alkenyl, alkynyl, and aryl derivatives have triplet ground states and singlet first excited states. On the other hand, singlet ground and triplet first excited states have been found for dihalogenocarbenes, the maximum value of *E*ST (39–47 kcal mole$^{-1}$[88,89]) corresponding to the $CF_2$ molecule, where the extent of the interaction of the *p* electrons of the substituents and the $p_x$ orbital of the carbon atom is greatest. In all known cases, the experimental R–C–R′ valence angles vary in the range 130–180° for triplet molecules and 100–115° for singlet molecules[5,84]. In particular, the formation of singlet dichlorocarbene with a Cl–C–Cl angle of approximately 106° in the decomposition of $LiCCl_3$[81] and $PhHgCCl_3$[82] has been demonstrated by infrared spectroscopy using the technique of matrix isolation of unstable molecules.

The majority of the known methods for the generation of carbenes are based on the decomposition of stable initial molecules in the ground electronic state. In those cases where the decomposition of the precursor is a single-stage reaction, the carbene is therefore formed in a singlet state owing to spin conservation regardless of whether it is the ground or an excited state. Thus the reactivity of carbenes in the triplet ground state is determined to a large extent by the possibility of a singlet–triplet transition under the conditions of their generation—in the absence of such transition, they react in an excited singlet state.

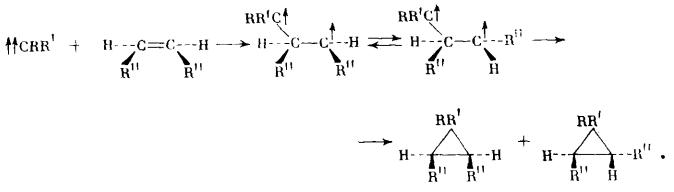
Like arynes, singlet carbenes have a low-lying LCMO. Accordingly, the reactivity of singlet carbenes is to some extent analogous to that of arynes, which was discussed

above: they are active electrophiles in relation to unsaturated organic compounds with which they readily form adducts—compounds of the cyclopropane or cyclopropene series. Furthermore, a characteristic feature of carbenes as a whole is their ability to undergo reactions involving insertion in various single bonds and also dimerisation to the corresponding olefins.

The reaction of carbenes which is most important in practice—addition to the double bonds of olefins—is stereospecific for singlet CRR′ with retention of the configuration of the initial olefin in the cyclopropane formed. Such a reaction, which is undoubtedly a single-stage process, is allowed by the orbital symmetry conservation rules in the form of a non-linear cheletropic process[90]. According to calculations[91-93], a reaction of this kind begins with electrophilic attack by the $p_X$ orbital in the carbene on one of the carbon atoms of the $\pi$-system of the olefin and further mutual approach of the reactants is accompanied by the rotation of the carbene fragment about the axis passing through its central carbon atom at right angles to the plane of the three-membered ring being formed:

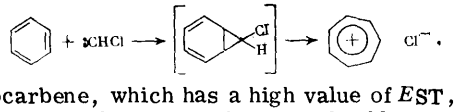


In contrast to singlet carbenes, triplet carbenes add to multiple bonds in the course of the two-stage reaction involving the intermediate formation of a triplet trimethylene biradical. The cyclisation of the latter to the corresponding cyclopropane is caused by the possibility of spin inversion and, according to Skell's postulate[94], such a biradical has a lifetime sufficiently long for the attainment of the conformational equilibrium, which entails the loss of stereoselectivity:



Thus Skell's postulate makes it possible to determine the spin state of the reacting carbene from the stereochemical result of the conversion of olefins into cyclopropanes, which is widely used in the study of carbene reactions.

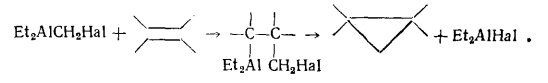
Since carbenes manifest properties of electrophiles in cycloaddition to unsaturated systems, their reactivity is determined by the energy of the LUMO and is greater the lower the energy level of this orbital. Accordingly, carbenes whose singlet state has been stabilised as a result of the raising of the LUMO level show the least reactivity in these reactions. Thus dichlorocarbene is incapable of adding to benzene[95], although this reaction does proceed with methylene[96] and monochlorocarbene[95,97,98], for example:



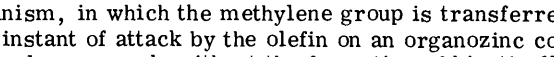
Difluorocarbene, which has a high value of $EST$, shows altogether little tendency to undergo cycloaddition reactions.

Like cycloaddition to olefins, the dimerisation of singlet carbenes begins, according to calculations[99], with electrophilic attack by the $p_X$ orbital of one :CRR′ molecule on the $\sigma$ orbital of another, as a result of which further mutual approach of the molecules involves the rotation of at least one of them. Further, one may expect that both reactions (dimerisation and conversion of olefins into cyclopropanes) proceed via the shortest pathway as a result of configuration interaction in the transition state[30], because the values of $EST$ for the majority of singlet carbenes are small (for example 1–1.5 eV or $:CCl_2$).[86]

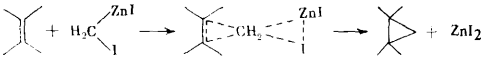
However, the above considerations concerning the mechanism of the formation of cyclopropanes and olefins are by no means applicable to all reactions in which labile organometallic compounds are used as carbene precursors. Thus organoaluminium compounds of the type $Et_2AlCH_2Hal$ exhibit, according to Hoberg's data[100], a greater tendency towards the addition of olefins to the C–Al bond than towards the elimination of methylene, as a result of which the cyclopropanes are formed in this case via a $\gamma$-elimination mechanism:



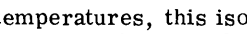
In the decomposition of certain halogenolithiomethanes, for example $LiCH_2Cl$ or $LiCHCl_2$,[101] the main reaction pathway appears to be the insertion of the carbene formed in the C–Li bond, occurring within the cage formed by the association complex of the initial organolithium compound[39,102,103]. As a consequence of this, the reaction product is a formal carbene dimer formed via $\beta$-elimination, for example:



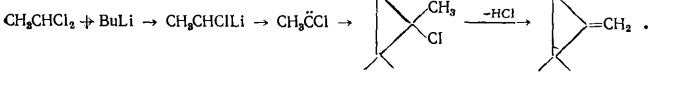
According to Blanchard and Simmons[104], the conversion of olefins into cyclopropanes via the Simmons–Smith mechanism, in which the methylene group is transferred at the instant of attack by the olefin on an organozinc compound, also proceeds without the formation of kinetically independent methylene:



The presence of a low-lying LUMO and a high HOMO determines the ability of carbenes, containing more than one carbon atom, to undergo various intramolecular rearrangements. The commonest reaction of this type is the so called carbene–olefin isomerisation, which is one of the examples of symmetry-allowed sigmatropic rearrangements[90,105]†:

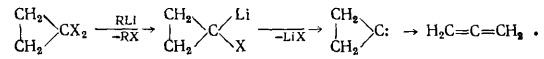


At low temperatures, this isomerisation can be avoided in certain cases. The recently proposed method for synthesising methylenecyclopropanes is in fact based on this finding[106]:

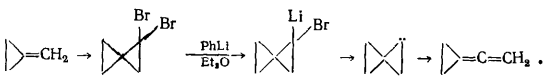


† According to calculations by the MINDO/2 method[109], the isomerisation of ethylidene to ethylene proceeds without activation energy.

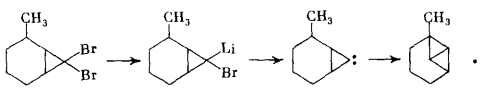
The carbene–olefin isomerisation of cyclopropylidene and a wide variety of its substituted derivatives proceed with ring opening, which results in the formation of the corresponding allenes[107]:



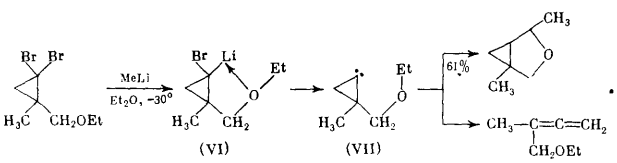
In view of the availability of *gem*-dihalogenocyclopropanes, this reaction constitutes a convenient general method for the synthesis of allenes, many of which cannot be obtained by other methods, for example[108]:



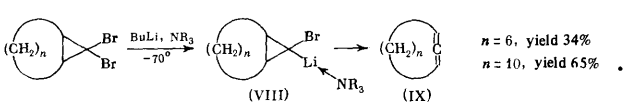
According to calculated data[110], the rearrangement of cyclopropylidenes to allene proceeds with a somewhat higher activation energy than the addition of the carbene to the double bond. Accordingly, in certain cases it is possible to observe also carbene reactions of cyclopropylidenes, for example the addition to olefins with formation of the corresponding spiropentanes[111]. Norcarylidene, which is formed by the reaction of 7,7-dibromonorcarane with metallic lithium in THF between −20° and −60°C, reacts with the solvent without a rearrangement, giving rise to 7-(α-tetrahydrofuryl)norcarane[112]. It is interesting to note that the analogous reaction of 3-methylnorcarylidene leads to a bicyclobutane derivative[113], with a 90% yield:



The formation of substituted bicyclo[1,1,0] butanes, which competes with the cyclopropylidene–allene isomerisation, has been noted also for certain di- and tetra-alkylcyclopropylidenes[114,115], the ratio of the bicyclic and allene reaction products being determined by the positions and nature of the substituents. The preferential insertion of the carbene centre of cyclopropylidene in the C–H bond has also been noted for compound (VII), where the proximity of the reaction centres is apparently ensured by the intramolecular coordinate bond Li ← O in the organometallic precursor (VI)[116]:

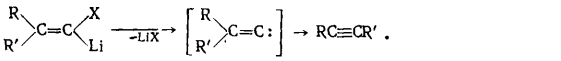


Accordingly, the use in this type of reaction of an optically active amine, (-)-sparteine, which forms a chiral complex with the intermediate bromolithio-derivative (VIII), leads to optically active cyclic allenes (IX), albeit with a low optical purity[117]:



It evidently follows from these data that the cyclopropylidene generated from a halogeno-derivative of an organolithium precursor rearranges at the instant of formation.

Another interesting example of the isomerisation of a carbene, synchronised with the decomposition of the organometallic precursor, is the Frisch–Buttenberg–Wieche rearrangement:

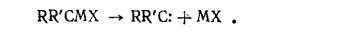


Judging from the process selectivity (only the aryl or cyclopropyl group R′ in the *trans*-position relative to the halogen atom migrates[118,119]), the rearrangement apparently takes place at the instant of the decomposition of the halogeno-derivative of the organometallic compound, which is accelerated by the interaction of the π-orbital of the migrating group with the σ*-orbital of the C–X group.

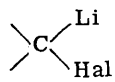
## V. CARBENES DERIVED FROM ORGANOMETALLIC COMPOUNDS

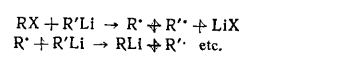
### 1. Halogenoalkyl Derivatives of Alkali Metals

Aliphatic organometallic compounds containing in the α-position a halogen atom or another group tending to be split off in the form of an anion exhibit in many instances a capacity for thermal α-elimination with formation of carbenes:



The ease of this reaction is determined mainly by the nature of the eliminated M and X groups. In particular, many compounds of this type, capable of generating carbenes at low or moderate temperatures (between −100° and +100°C), which are particularly convenient for liquid phase reactions, are known. The comparative availability of numerous compounds of the type RR′CMX together with the ease of their decomposition make them important and widely used sources of carbenes.

Halogenolithiomethanes and related compounds containing the  group are the most thoroughly investigated compounds of this type. Halogenomethyl derivatives of lithium are usually obtained by treating the corresponding halogenomethanes with lithium alkyls or phenyl-lithium at low temperatures. The ease of exchange of the substituents at the carbon atom for lithium in an ethereal medium diminishes in the sequence I > Br > H > Cl.[120,121] It follows from the observation of the effects of the chemically induced polarisation of nuclei observed in NMR spectra that the exchange reaction in lithium alkyl–alkyl halide systems[122,123] proceeds at least partially with intermediate formation of free radicals:



Exchange reactions are catalysed by Lewis bases forming complexes with organolithium compounds (ethers and amines)[45,124] and in some cases the nature of the solvent influences also the mode of reaction. Thus, when methyl-lithium is allowed to react with benzylidene bromide in ether, the bromine atom is substituted and the product is α-lithiobenzyl bromide, which decomposes subsequently with formation of phenylcarbene. However, the analogous reaction in THF proceeds as H-metallation,

leading to α-lithiobenzylidene bromide and further to bromophenylcarbene[125,126]:

$$PhCHBr_2 \begin{cases} \xrightarrow[Et_2O]{} PhCHLiBr \xrightarrow[-LiBr]{} :CHPh \\ \xrightarrow[THF]{} PhCLiBr_2 \xrightarrow[-LiBr]{} :CBrPh \end{cases}.$$

Benzylidene chloride is metallated by methyl-lithium in ether preferentially at the hydrogen atom[127]:

$$PhCHCl_2 \xrightarrow{MeLi} PhCLiCl_2 \xrightarrow[-LiCl]{} :CClPh .$$

A mixture of similar amounts of $LiCBr_3$ and $LiCHBr_2$ is formed in an analogous manner as a result of the reaction of butyl-lithium with bromoform in THF[128,129], whereas in a hydrocarbon medium the exchange of bromine for lithium takes place exclusively[129]:

$$CHBr_3 + BuLi \begin{cases} \xrightarrow[-BuH]{} LiCBr_3 \xrightarrow[-LiBr]{} :CBr_2 , \\ \xrightarrow[-BuBr]{} LiCHBr_2 \xrightarrow[-LiBr]{} :CHBr , \end{cases}$$

$$CHBr_3 + BuLi \xrightarrow[-BuBr]{hexane} LiCHBr_2 \xrightarrow[-LiBr]{} :CHBr .$$

The analogous reaction of chloroform in ether leads to $LiCCl_3$,[130] the decomposition of which results in the formation of dichlorocarbene, and, when the reaction is carried out in a hydrocarbon medium, the product is a mixture of $LiCCl_3$ and $LiCHCl_2$.[129]

Under the influence of lithium alkyls, dihalogenomethanes $CH_2X_2$ (X = Cl, Br, or I) in hydrocarbons exchange only halogen atoms for lithium[102,103,131], with subsequent formation of methylene. However, in an ethereal medium, $CH_2Cl_2$ undergoes exclusively H-metallation, being converted into $LiCHCl_2$—a precursor of monochlorcarbene[132,133]:

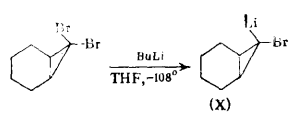
$$CH_2Cl_2 + BuLi \xrightarrow[-BuH]{Et_2O} LiCHCl_2 \xrightarrow[-LiCl]{} :CHCl .$$

This change in the mode of metallation on passing from a hydrocarbon medium to an ethereal medium can be explained[129] by a weakening of the C–H bond owing to the formation of complexes of the type $X_3C...H...OR_2$.

The reaction of phenyl-lithium and its substituted derivatives with $CH_2Cl_2$ in ether, which also leads to the intermediate formation of monochlorcarbene, constitutes the basis of a convenient method for the generation of arylcarbenes[134]:

$$CH_2Cl_2 + ArLi \xrightarrow[-ArH]{} LiCHCl_2 \xrightarrow[-LiCl]{} HClC: \xrightarrow{ArLi} ArCHLiCl \rightarrow ArHC: .$$

Bicyclic *gem*-dibromo-derivatives, namely 7,7-dibromonorcarane, 7,7-dibromo-2-oxanorcarane, and related compounds, exchange the *endo*-halogen preferentially for lithium in the reaction with lithium alkyls[135]:




(X)

On the other hand, 7,7-dichloronorcarane forms under analogous conditions (THF, −115°C) a mixture of *endo*- and *exo*-lithio-derivatives with the *exo*-isomer predominating appreciably[136].

A simple general method for the generation of halogenocarbenes is based on the reactions of di-, tri-, and tetra-halogenomethanes and similar compounds with metallic lithium or sodium in THF[137] at temperatures between −40° and +40°C, i.e. under conditions where the majority of α-halogenolithiomethanes are unstable:

$$RR'CXX' \xrightarrow[THF]{Li} RR'CLiX \xrightarrow[-LiX]{} RR'C: \rightarrow \text{(norcarane)}(R)(R') ,$$

where X and X′ are halogens and R,R′ = H, halogen, aryl, alkyl, etc.

It has been shown[127] that $PhCHCl_2$ reacts with lithium in THF even at −90°C; heating of the reaction mixture in the presence of cyclohexene leads to a high yield of 7-chloro-7-phenylnorcarane, which undoubtedly demonstrates the intermediate involvement of $PhCLiCl_2$. It is interesting to note that $CH_2Cl_2$, $CHCl_3$, $PhCHCl_2$, and $CHBr_3$ react with lithium only via the hydrogen atom under these conditions, whereas the reaction with $CH_2Br_2$ involves bromine[112,138]. In contrast to lithium alkyls and metallic lithium, lithium amides are capable of exchanging lithium only for hydrogen atoms in polyhalogenomethanes. Thus, when dibromomethane is treated with lithium di-isopropylamide in THF, the following reaction takes place unambiguously[139]:

$$CH_2Br_2 + iso\text{-}Pr_2NLi \rightarrow LiCHBr_2 + iso\text{-}Pr_2NH .$$

Such selectivity is evidently proof that the reaction is thermodynamically controlled, since the exchange of the halogen should have led in this case to labile *N*-halogenoamines.

The halogenolithiomethanes formed via H- or X-metallation reactions at low temperatures (at approximately −100°C) in an ethereal medium undergo intermolecular reactions involving not only the C–Li bond but also the exchange of halogen atoms[140]:

$$LiCBr_3 + LiCCl_3 \rightarrow LiCBrCl_2 + LiCBr_2Cl .$$

The exchange reactions of halogenolithiomethanes with lithium halides have also been reported[141]. Numerous halogenolithiomethanes and their substituted derivatives have now been synthesised by the methods examined above (Table 2).

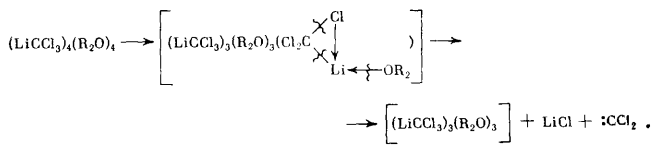
Table 2. Thermal stabilities of halogenolithiomethanes.

| Compound | Solvent* | $T_d$, °C | References |
|---|---|---|---|
| $LiCF_3$ | $Et_2O$ | −75 to −50 | 142 |
| $LiCH_2Cl$ | THF | −110 | 101 |
| $LiCHCl_2$ | THF | −30 | 143 |
| | $Et_2O$ | −100 | 133 |
| $LiCCl_3$ | THF and other cyclic ethers | −65 | 42, 130 |
| | $Et_2O$ and other acyclic ethers | −84 to −88 | 42 |
| | monoglyme, TMEDA | −75 | 42 |
| $LiCHBr_2$ | THF | −73 | 144 |
| $LiCBr_3$ | THF | −77 | 144 |
| $LiCH_2I$ | THF | −110 | 145 |
| $LiCHI_2$ | THF | −110 (slow) | 145 |
| $LiCHI_2$ | THF | −95 | 146 |

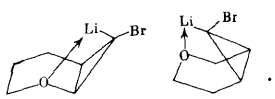
Table 2 shows that halogenolithiomethanes are relatively stable, like halogenolithiobenzenes, only in solutions containing ethers or trialkylamines. According to D'yachenko and Nefedov[147], trichloromethyl-lithium exists, like lithium alkyls and other aliphatic organolithium compounds[124], in the form of the tetrameric complex $(LiCCl_3)_4 \cdot (R_2O)_4$ in an ether–hydrocarbon medium. It follows from the results of two investigations[102,131] that

there is also a possibility of the existence of mixed association complexes of butyl-lithium with monohalogenolithiomethanes. The complex of trichloromethyl-lithium with tetramethylethylenediamine having the composition $LiCCl_3.(CH_3)_2NCH_2CH_2N(CH_3)_2$ has been obtained in a crystalline state[148].

Association and the formation of complexes by halogenolithiomethanes in solution have a significant influence, as for halogenolithiobenzenes, on the stability and reactivity of these compounds. Thus the study of the thermal stability of trichloromethyl-lithium in various solvents showed that this compound decomposes with formation of dichlorocarbene as a consequence of a synchronous reaction, the rate of which is determined by the strength of the Li ← $OR_2$ coordinate bond[42]:



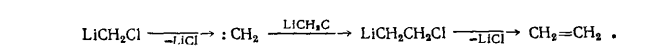
A similar conclusion follows also from the comparison of the stabilities of cyclic and *gem*-bromolithio-compounds, namely *endo*-7-bromo-7-lithionorcarane (X) and its 2-oxa-analogue (XI). According to Seyferth and Lampert[135], compound (X) is unstable in THF above −90°C, while compound (XI), where there is a possibility of the formation of the relatively stable Li ← O intramolecular coordinate bond owing to the proximity of the oxygen and lithium atoms, does not decompose in ether even at −20°C, being one of the most stable of the α-halogeno-derivatives of organolithium compounds. *endo*-7-Bromo-7-lithio-3-oxanorcarane (XII), in certain conformations of which the Li–O distance is shorter by 0.2–0.3 Å than in compound (XI), is still more stable. One should note in this connection that compound (XII) is the only known halogeno-derivative of an organolithium compound which is stable in a hydrocarbon medium[149]:



(XI) (XII)

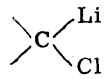
On the other hand, trichloromethyl-lithium obtained by the reaction of $CCl_4$ with atomic lithium in a solid argon matrix, which is known to be monomeric and not bound in a complex, proved to be unstable even at −230°C,[81] while in THF solutions, for example, it is stable up to approximately −70°C.[41,42]

The association of halogenolithiomethanes has a definite influence also on their reactivity. While the majority of compounds of this type are thermolysed to carbenes and are capable of undergoing their characteristic reactions (the formation of the kinetically independent dichlorocarbene from $LiCCl_3$ was demonstrated by the method of competition kinetics[148,150]), certain halogenolithiomethanes, for example $LiCH_2Cl$ or $LiCHCl_2$, give rise to the formal dimers ($CH_2{=}CH_2$, CHCl=CHCl) on thermal decomposition in solution instead of the kinetically independent carbenes[101,143]. This type of reaction is apparently associated with the rapid insertion of the highly reactive carbene (:$CH_2$, :CHCl) in the carbon–lithium bond of the initial compound within the cage of the initial association complex, for example, $(LiCH_2Cl)_4(R_2O)_4$:

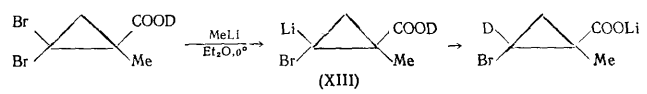


This was confirmed by the observation[147] that even the much less reactive dichlorocarbene formed on decomposition of the mixed association complex $LiCCl_3.(PhLi)_3.(THF)_4$ reacts almost completely with phenyl-lithium (forming $PhCLiCl_2$ and then tolane[127]) without emerging from the cage of the initial association complex.

It follows from the data in Table 2 that the stability of halogenolithiomethanes depends on the nature of the halogen. Evidently, as for halogenolithiobenzenes, there is a tendency for the stability of halogenolithiomethanes and related compounds to decrease with increase of the atomic number of the halogen, but in many instances this type of dependence is masked by other factors and it is extremely difficult to trace it on the basis of the available literature data. According to Talalaeva and Kocheshkov[142], $LiCF_3$ in ethereal solution has $T_d$ = −50–75°C and certain fluorolithiomethanes decompose in the same temperature range[151]. Perfluoroisopropyl-lithium is stable in ether only at −78°C.[152]

Trifluoromethyl-lithium decomposes in THF at −65°C[42]. Similar values of $T_d$ (−65–75°C) are characteristic of αα-dichlorobenzyl-lithium, a series of its substituted derivatives, and many other compounds containing the  group[136,153,154]. However, $LiCHCl_2$ is a much more stable compound ($T_d$ = 30°C in THF) and *exo*-7-chloro-7-lithionorcarane and $LiCH_2Cl$ are more labile ($T_d$ = 110°C). According to Kobrich[7], the lability of chloromethyl-lithium is caused by its high basicity, which ensures its autocatalytic decomposition via an *Elcb* mechanism.

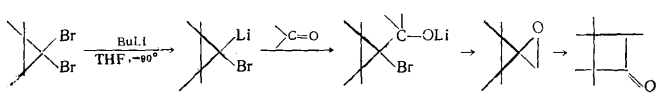
Bromo-derivatives of methyl-lithium, i.e. $LiCHBr_2$ and $LiCBr_3$, have decomposition temperatures $T_d$ close to those of $LiCCl_3$ and the majority of other chloro-derivatives; however, slow decomposition of these compounds is observed at much lower temperatures (approximately −100°C).[144] The acid (XIII), formed when equimolar amounts of methyl-lithium and of the corresponding dibromo-acid react in ether, exhibits some stability even at 0°C. The rate of exchange of bromine for lithium exceeds the rate of the corresponding salt formation reaction to such an extent that the latter is an intramolecular process[155]:



(XIII)

The exact values of $T_d$ for the two known iodolithiomethanes $LiCH_2I$ and $LiCHI_2$[145,146] have not been determined, but it has been shown that these compounds are relatively stable between −90° and −100°C.

Owing to the development of simpler (particularly hydrolytic[156]) methods for the generation of carbenes from halogenomethanes, the decomposition reactions of halogenomethyl derivatives of lithium are nowadays rarely used for the conversion of olefins into cyclopropanes. On the other hand, complex carbenes, mainly different substituted cyclopropylidenes (see above), are still generated almost exclusively by methods of organolithium chemistry. In some cases halogeno-derivatives of organolithium compounds are used at low temperatures also as organolithium reagents, for example[157]:



Many halogenolithiomethanes with different organoelement groups have been synthesised and characterised by the exchange reactions of organolithium compounds with organoelement derivatives (particularly halogen-containing derivatives). However, the majority of these compounds, particularly the trimethylsilyl and trimethylstannyl derivatives of chlorolithio- and bromolithio-methanes, are readily involved in intermolecular reactions of the $S_N2$ type instead of undergoing the carbene decomposition[158,159]. On the other hand, the decomposition of $Ph_3PbCCl_2Li$, formed when $(Ph_3Pb)_2CCl_2$ is treated with butyl-lithium, apparently proceeds with the intermediate formation of extremely interesting metallocarbenes[160]:

$$Ph_3PbCCl_2Li \begin{cases} \longrightarrow Ph_3PbCl + Li\ddot{C}Cl, \\ \longrightarrow Ph_3Pb\ddot{C}Cl \rightarrow Ph_3PbCl + :C: . \end{cases}$$

The available data about the halogenomethyl derivatives of other alkali metals are so far limited to the report of the synthesis of several sodium and potassium compounds, which are readily formed when halogenomethanes are treated with the corresponding bistrimethylsilylamides, for example[161]:

$$(Me_3Si)_2NNa + HCBr_3 \rightarrow NaCBr_3 + (Me_3Si)_2NH .$$

In contrast to lithium compounds, the analogous sodium and potassium derivatives proved to be more stable in ether than in THF. Furthermore, contrary to expectation, they are more stable in the majority of cases than the corresponding lithium and even magnesium compounds (Tables 2–4).

**Table 3.** Thermal stabilities of halogenomethyl derivatives of sodium and potassium in ether[161].

| Compound | $T_d$, °C |
|---|---|
| NaCClBrH | −30 (slow decomp.) |
| $NaCHBr_2$ | −30 (slow) |
| $NaCBr_3$ | −77 (slow) |
| $KCHBr_2$ | −65 (very fast) |
| $KCBr_2SiMe_3$ | −25 (fast) |
| $KCBr_3$ | ←120 |

**Table 4.** Thermal stabilities of halogenomethyl derivatives of Grignard reagents.

| Compound | $T_d$, °C | | References |
|---|---|---|---|
| | THF | THF + 20% HMP | |
| $CF_3MgCl$ | decomposes at instant of formation at −115°C | decomposes at instant of formation at −115°C | 164 |
| $CCl_3MgCl$ | −65 (very fast) | −65 (very fast) | 164 |
| $CBr_3MgCl$ | — | −75 (very fast) | 164 |
| $CHBr_2MgCl$ | −55 | −45 | 164 |
| $CH_2BrMgCl$ | −55 (slow) | — | 164 |
| $CH_2IMgCl$ | −55 | −45 | 164 |
| $CHI_2MgCl$ | −85 | | 146 |

A general method for the synthesis of monobromocyclopropanes has been developed on the basis of the decomposition of $NaCHBr_2$:[162]

$$(Me_3Si)_2NNa + CH_2Br_2 \xrightarrow[-(Me_3Si)_2NH]{} NaCHBr_2 \xrightarrow[-NaBr]{} :CHBr \longrightarrow \text{(Br, H)} \quad (30-50\%) .$$

## 2. Halogenomethyl Derivatives of Magnesium

Like their lithium analogues, compounds of the type $CX_3MgX$ are obtained by the exchange reaction of the corresponding halogenomethanes with stable Grignard reagents at low temperatures in an ethereal medium[163,164]. Owing to their extremely low basicity, Grignard reagents are not involved in H-metallation reactions and are capable of substituting only halogen atoms in halogenolithiomethanes[164]:

$$CHBr_3 + \text{iso-PrMgCl} \rightarrow CHBr_2MgCl + \text{iso-PrBr},$$
$$CHBr_2Cl + \text{iso-PrMgCl} \rightarrow CHBrMgCl + \text{iso-PrBr} .$$

Like the analogous lithium compounds, halogenomethyl derivatives of organomagnesium compounds are stable only in solution and at extremely low temperatures (Table 4), decomposing on heating with formation of the corresponding carbenes:

$$CX_3MgX \rightarrow :CX_2 + MgX_2 .$$

The decomposition of $CCl_3MgBr$, formed when $CCl_4$ is treated with EtMgBr or PhMgBr at relatively high temperatures (20–60°C), proceeds not only via the carbene pathway but also via a free-radical pathway[165]. It follows from the data in Table 4 that halogenomethyl Grignard reagents have thermal stabilities very similar to those of the corresponding lithium compounds. Thus the decomposition temperatures $T_d$ of $CCl_3MgCl$ and $CBr_3MgCl$ correspond to those of $LiCCl_3$ and $LiCBr_3$ (Table 2). On the other hand, $CHBr_2MgCl$ is somewhat more stable than $LiCHBr_2$, while $CF_3MgCl$ is characterised by a much lower stability than $LiCF_3$, being in general one of the least stable halogeno-derivatives of organometallic compounds. An increase of the polarity of the medium [the replacement of THF by 20% solution of hexamethylphosphoramide (HMP)] leads to an increase of the stability of certain halogenomethyl derivatives of cadmium, which is believed[164] to indicate intramolecular halogen–magnesium coordination. However, the stabilisation may also be a consequence of the strengthening of the $Mg \leftarrow OR_2$ coordinate bond, the dissociation of which must precede the carbene decomposition according to some of the present authors' data[41,42].

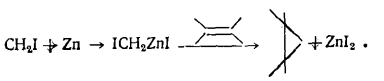
Like the corresponding organolithium compounds, Grignard reagents of the type $R_3MCHXMgX$ (M = Si or Sn; X = halogen) do not tend to undergo the carbene decomposition, forming readily in solution products of reactions of the $S_N2$ type[159].

## 3. Organozinc and Organocadmium Compounds

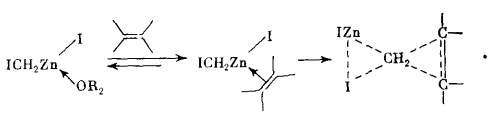
Organozinc compounds are widely used as reagents for the introduction of the methylene group, the so called Simmons–Smith reaction[8,166,167], based on the employment of methylene halides (usually $CH_2I_2$) and activated zinc powder, being of greatest preparative value. In view of the lower activity of the metal, halogenomethyl derivatives of zinc of the type $XCH_2ZnX$ show a higher thermal stability than the corresponding derivatives of alkali metals and magnesium. It has been shown[104] that $ICH_2ZnI$, formed by the reaction of methylene iodide with activated zinc in ether, is completely stable in solution at 0–20°C, decomposing slowly with liberation of ethylene at the boiling point of the solvent.

In the presence of olefins, the decomposition of this compound leads to the corresponding cyclopropanes. The Simmons–Smith reaction, usually carried out by refluxing

a mixture of methylene iodide and an olefin with the zinc–copper couple in ether, is at present one of the commonest methods for synthesising cyclopropane hydrocarbons:



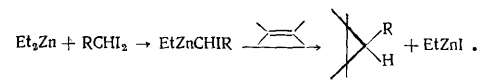
According to Blanchard and Simmons[104], the formation of cyclopropanes by the Simmons–Smith reaction is a stereoselective process in which the olefin is attacked by the electrophile, which corresponds to the possibility of the involvement of singlet methylene or its complex. The composition of the side products of the reaction, among which ethylene and a number of compounds usually formed on reaction of singlet methylene with the solvent have been detected, is also consistent with this hypothesis. On the other hand, the reaction is of second order overall (of first order with respect to the organozinc compound and the olefin), while the intermediate has more stringent steric requirements than the free methylene[104]. Accordingly, it has now been assumed that the Simmons–Smith reaction proceeds without the formation of kinetically independent methylene and the $CH_2$ fragment is transferred from the organozinc compound to the olefin via a five-centre transition state[6,8,104]. On the other hand, the dependence of the ease of decomposition of $ICH_2ZnI$ on the solvent is analogous to that observed for halogeno-derivatives of organolithium compounds: despite the much higher temperature, this compound is completely stable in boiling THF, but causes the introduction of the methylene group into olefins in ether. In conformity with the above ideas, this implies that the decomposition of the organozinc methylene precursor includes the interaction of the halogen electron pair with the free orbital of the metal, arising when the Zn ← O etherate linkage is ruptured. In this case, the second order of the reaction may be a consequence of the displacement of the ether by the olefin and the subsequent rapid decomposition of the resulting unstable complex:



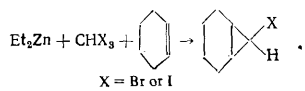
Under mild conditions, methylene halides do not react with ordinary zinc powder and the nature of the initial substances, the yields of the products of the Simmons–Smith reaction, and its duration depend to a large extent on the method used to activate the zinc. The galvanic zinc–copper couple with a low copper content, prepared by treating zinc powder with aqueous solutions of copper salts (sulphate[166–168] or acetate[169]), is usually employed for the reaction. A mixture of zinc powder with copper(I) chloride also exhibits a high activity in the reaction[170].

The zinc–copper couple, prepared using $CuSO_4$, reacts in ether only with $CH_2I_2$ and $CH_2ClI$.[167] On the other hand, when zinc is activated by copper acetate, it is possible to involve in the reaction also $CH_2Br_2$.[169] However, the most effective method of carrying out the Simmons–Smith reaction is associated with the use of the zinc–silver couple followed by the removal of the salts formed during the reaction as the pyridine complexes[171]. This mode of reaction makes it possible to introduce the methylene group (with a high yield of cyclopropanes) not only into olefins but also into many compounds with functional groups, for example unsaturated ketones, ethers, enol ethers, and enamines.

The conversion of olefins into cyclopropanes as a result of the joint treatment with diethylzinc and *gem*-di-iodoalkanes proceeds via a similar pathway—with the intermediate formation and decomposition of halogenomethyl derivatives of zinc[172]:

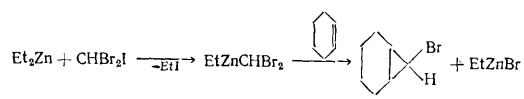


When this reaction is carried out with dihalogenoiodomethanes of the type CHIXY (X, Y = F, Cl, or Br), the corresponding monohalogenocyclopropanes are formed in yields up to 90%;[173] monoiodo- and monobromo-cyclopropanes are obtained in high yields by this reaction from $CHI_3$[174] and $CHBr_3$:[175]

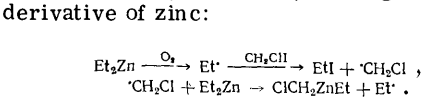


In the presence of benzene and its alkali derivatives, the corresponding cycloheptatrienes are obtained from $CHBr_3$ and $Et_2Zn$.[175] An attempt to involve chloroform in a reaction of this type has been described: 7,7-dichloronorcarane was synthesised in a low yield when cyclohexene was treated jointly with $CHCl_3$ and diphenylzinc[176].

When trihalogenomethanes containing different halogen atoms in the same molecule were used in the reaction with diethylzinc, the nature of the product was determined by the mobility of the halogen in the exchange reaction[120,121]. Thus 7-bromonorcarane can be obtained from $CHBr_2I$, diethylzinc, and cyclohexene, ethyl iodide being formed exclusively in the first stage of the reaction[172]:

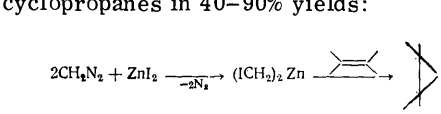


The interaction of organozinc compounds with methylene halides or haloforms is catalysed by oxygen[177]. Thus the reaction of $Et_2Zn$ with $CH_2ClI$ in nitrogen leads to norcarane in 61% yield after 6 h in the presence of cyclohexene; when dry air is passed through the reaction mixture, the same reaction proceeds to the extent of 99% in 30 min. This result undoubtedly indicates the involvement of free radicals in the exchange reaction, leading to a halogenomethyl derivative of zinc:



The involvement of free radicals in this reaction has also been demonstrated by the observation of the considerable polymerisation of styrene when an attempt was made to introduce the bromomethylene group into the latter by treatment with diethylzinc and bromoform in air[175].

Like the halogenomethyl derivatives of zinc described above, symmetrical compounds of the type $Zn(CHRX)_2$, which can be readily obtained by the thermolysis of the corresponding diazoalkanes in the presence of zinc salts, are also active agents for the introduction of the methylene group[178–180]. Thus, bis(iodomethylzinc), formed by the reaction of diazomethane with $ZnI_2$, reacts with olefins to form cyclopropanes in 40–90% yields:



$ZnCl_2$ reacts similarly with diazomethanes, forming the tetrameric etherate $[Zn(CH_2Cl)_2(OEt_2)_2]_4$,[179] the interaction of which with cyclohexene in ether gives rise to norcarane. The decomposition of bis(chloromethyl)zinc is appreciably catalysed by the addition of $ZnCl_2$ and proceeds at an appreciable rate in the presence of this salt even at 0°C, which indicates a weakening of the coordinate bond in the etherate of the $ClZnCH_2Cl$ formed.

An effective agent for the introduction of the methylene group is obtained on decomposition of diazomethane in the presence of zinc benzoate and $ZnI_2$:[181]

$$(PhCOO)_2Zn \xrightarrow{CH_2N_2} (PhCOOCH_2)_2Zn \xrightarrow{ZnI_2} \rightarrow PhCOOCH_2ZnI \longrightarrow \text{(yield 66\%)} .$$

Aryl- and diaryl-diazomethanes[182-184] are also readily decomposed by zinc salts, forming the corresponding arylhalogenomethyl derivatives of organozinc compounds, the decomposition of which in the presence of olefins leads to cyclopropanes. The stability of the zinc compounds formed in this reaction decreases as a function of the nature of the halogen in the sequence Cl > Br > I.[183]

Bis(dichloromethyl)zinc was obtained by treating $ZnCl_2$ with dichloromethyl-lithium[143]:

$$2LiCHCl_2 + ZnCl_2 \rightarrow (Cl_2CH)_2Zn + 2LiCl .$$

Like $ICH_2ZnI$, this compound is completely stable in boiling THF, but is converted into 7-chloronorcarane in a low yield on prolonged refluxing with cyclohexene in benzene.

Diethylcadmium reacts with *gem*-di-iodoalkanes similarly to diethylzinc, forming the corresponding cyclopropanes in the presence of olefins[185]:

$$Et_2Cd + RCHI_2 \longrightarrow \text{(R=H, Me, Ph)} .$$

The yields of the reaction products for zinc and cadmium compounds with analogous structures are similar.

Virtually identical mixtures, containing 30–40% of 1-chloropropane, were obtained also in the reactions of diethylzinc and diethylcadmium with $CHCl_3$ and $CCl_4$.[186] The formation of 1-chloropropene apparently indicates the intermediate generation and subsequent carbene decomposition of compounds of the type $RMCCl_2Et$:

$$RMCCl_2Et \xrightarrow{-RMCl} :CClEt \rightarrow ClCH{=}CHMe ;$$
$$R = Et, \text{ or } Cl;\ M{=}Zn,\ Cd .$$

Virtually exclusive formation of propene, which is apparently also a consequence of the carbene–olefin isomerisation, has been observed in the reaction of 1,1-di-iodopropane with the zinc–copper couple in the presence of cyclohexene[168].

Like zinc salts, $CdI_2$ reacts with diazomethane to form $ICdCH_2I$, which, however, is a much less active agent for the introduction of the methylene group than $IZnCH_2I$.[179]

## 4. Organomercury Compounds

The halogenocarbenes, formed when trihalogenomethyl compounds react with bases or on thermolysis of salts of trihalogenoacetic acids, are readily inserted into the Hg–X bonds of compounds of the type RHgX (R = aryl, alkyl, or halogen; X = halogen), giving rise to the corresponding $RHgCX_3$, for example:

$$PhHgCl + CHCl_3 + t\text{-}BuOK \rightarrow PhHgCCl_3 + t\text{-}BuOH + KCl ,$$
$$PhHgBr + Cl_3COONa \rightarrow PhHgCCl_2Br + CO_2 + NaCl .$$

These compounds decompose at moderate rates in the temperature range which is extremely convenient for carrying out chemical reactions (20–80°C) with formation of RHgX and the corresponding carbene:

$$PhHgCCl_3 \rightarrow PhHgCl + :CCl_2 .$$

The decomposition of such compounds, carried out in solvents (dimethoxyethane, benzene, THF, $CH_2Cl_2$, etc.) which are inert with respect to the carbenes generated, leads to the corresponding cyclopropane compounds in the presence of unsaturated compounds. Owing to the neutral medium and the absence of other reactive intermediates (for example $CX_3^-$ anions), the reaction proceeds exceptionally smoothly, giving high yields of cyclopropanes, not only with olefins but also with many of their derivatives having functional groups, being complicated only by the formation of $CX_2{=}CX_2$ dimers owing to the occurrence of reactions of the type

$$RHgCX_3 + :CX_2 \rightarrow RHgCX_2CX_3 \rightarrow RHgX + CX_2{=}CX_2$$

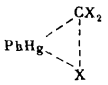
to a slight extent. Furthermore, since the carbene decomposition of trihalogenomethyl derivatives of mercury is reversible and the RHgX compounds formed on decomposition can be readily used virtually without loss for the regeneration of the initial reagent, compounds of this type are regarded nowadays as the most convenient agents for the transfer of carbenes to unsaturated compounds.

The study of the kinetics of the thermolysis of $PhHgCl_2Br$,[187] leading to PhHgBr and the corresponding *gem*-dichlorocyclopropanes with almost quantitative yields in the presence of olefins, showed that in the initial stage the reaction is of first order with respect to the organomercury compound and of zero order with respect to the olefin. On the other hand, the rate of reaction diminishes following the addition of PhHgBr and depends to some extent on the nature of the olefin, which can be readily interpreted by postulating a sequence of two stages, the slow stage involving the reversible formation of free dichlorocarbene:

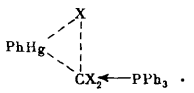
$$PhHgCCl_2Br \overset{slow}{\rightleftharpoons} PhHgBr + :CCl_2$$
$$:CCl_2 + \text{(olefin)} \xrightarrow{fast} \text{(dichlorocyclopropane)} .$$

The involvement in this reaction of the kinetically independent carbene was also confirmed by the virtual identity of the relative rates of introduction of the dichloromethylene group into various olefins (determined by the method of competition kinetics) in the generation of dichlorocarbene by the thermolysis of $PhHgCCl_3$, $LiCCl_3$, and $CCl_3COONa$, by treating $CHCl_3$ with t-BuOK,[150] and by the high-temperature pyrolysis of chloroform[148]. The intermediate formation of singlet $:Cl_2$ is also indicated by the explicit electrophilic mechanism of the conversion of olefins into dichlorocyclopropanes by treatment with $PhHgCCl_2Br$ [188] and $PhHgCCl_3$.[148,150,188] Since the rate of decomposition of compounds of the type $RC_6H_4HgCCl_2Br$ depends to only a slight extent on the nature of R (R = H, *p*-F, *p*-Cl, *p*-MeO, or *p*-Me), it is suggested that this reaction proceeds similarly to the decomposition of other organometallic compounds discussed above, in a single stage via a transition state produced as a result of the

coordination of the halogen electron pair to the free metal orbital[189]:



Since the bulky central mercury atom in the compounds $RHgCX_3$ is incapable of forming sufficiently stable complexes with weak Lewis bases, the rate of decomposition of these compounds is to a large extent independent of the nature of the solvent (benzene, dimethoxyethane, THF). Furthermore, in contrast to the analogous compounds of complex-forming metals, the decomposition of the mercury compounds is accelerated in the presence of strong Lewis bases (amines and phosphines), apparently owing to the formation of the complex involving the free orbital of the carbene[187]:



On the other hand, as for the $\alpha$-halogenomethyl derivatives of other metals, the stability of the mercury compounds under consideration is determined by the nature of the halogen: in conformity with the strength of the C–X bond and the radius of the X atom, the rate of decomposition of $PhHgCX_3$ increases in the sequence $F \ll Cl < Br < I$. The same relation determines also the mode of decomposition of mixed trihalogenomethyl compounds of the type $PhHgCXY_2$ and PhHgCXYZ (Table 5).

**Table 5.** Thermal stabilities of trihalogenomethyl derivatives of phenylmercury[9].

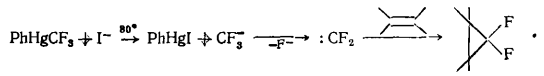
| Compound | Carbene | Total decomposition time in benzene | |
|---|---|---|---|
| | | at 80°C | at 20°C |
| $PhHgCCl_2I$ | $CCl_2$ | instantaneous | 24 h |
| PhHgCClBrI | CClBr | 3 min | 4 days |
| $PhHgCBr_3$ | $CBr_2$ | – | 15–16 days |
| $PhHgCClBr_2$ | CClBr | – | 15–16 days |
| $PhHgCFBr_2$ | CFBr | 20 min | 3 days |
| $PhHgCCl_2Br$ | $CCl_2$ | 2 h | 11 days |
| $PhHgCCl_3$ | $CCl_2$ | 48 h | — |
| $PhHgCCl_2F$ | CClF | 48 h | — |

According to the mechanism adopted for the decomposition reaction, a decrease in the electronegativity of the group R in $RHgCX_3$ should lead to the destabilisation of the molecule. Indeed alkyl and cycloalkyl derivatives of trihalogenomethylmercury are less stable than the corresponding aromatic compounds[190,191]. In particular, cyclo-$C_6H_{11}HgCX_3$, formed when the corresponding cyclo-$C_6H_{11}HgX$ reacts with $CHX_3$ (X = Cl or Br) and t-BuOK in THF at $-60°C$,[191] are so reactive that they are much less readily available than iodo-derivatives of the type $PhHgCX_2I$.

In contrast to the corresponding iodo-, bromo- and chloro-derivatives, trifluoromethylphenylmercury and other trifluoromethyl derivatives of mercury, which are readily obtained by the pyrolysis of the corresponding trifluoroacetates[102],

$$Hg(OCOCF_3)_2 \xrightarrow{200°} CF_3HgOCOCF_3$$

do not decompose with formation of $:CF_2$ even at relatively high temperatures. Thus $PhHgCF_3$ does not change on heating in solution for eleven days up to 140°C.[9,192] On the other hand, like other $RHgCX_3$ derivatives, these compounds readily form carbenes in the presence of NaI;[192–194] however, in this case the reaction proceeds with the intermediate formation of the $CX_3^-$ anions:



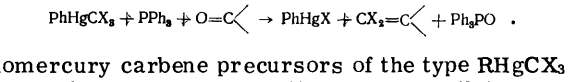
The formation of carbanions under these conditions was demonstrated by the formation of the corresponding trihalogenomethyldimethylmethanols on decomposition of $PhHgCCl_3$ and $PhHgCCl_2Br$ in the presence of NaI in acetone[195]. In contrast to $PhHgCF_3$, the compounds $ClHgCF_3$ and $BrHgCF_3$ do not decompose in the presence of NaI owing to the formation of stable complexes of the type $NaClIHgCF_3$ and $Na_2ClI_2HgCF_3$.[104]

**Table 6.** Carbenes obtained from halogenomethyl derivatives of mercury.

| Organomercury compound | Carbene formed | Refs. | Organomercury compound | Carbene formed | Refs. |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 1 | 2 | 3 |
| $Hg(CH_2Br)_2$ | $CH_2$ | 196 | cyclo-$C_6H_{11}HgCClBr_2$ | CClBr | 191 |
| $Hg(CH_2I)_2$ | $CH_2$ | 197 | $PhHgCCl_2F$ | CClF | 206 |
| $IHgCH_2I$ | $CH_2$ | 197 | $PhHgCBr_2F$ | CBrF | 207 |
| $PhCH_2HgCH_2I$ | $CH_2$ | 198 | $PhHgCCl_2CF_3$ | $CClCF_3$ | 208 |
| $PhHgCHCl_2$ | CHCl | 199 | $PhHgCClBrCF_3$ | $CClCF_3$ | 208 |
| PhHgCHClBr | CHCl | 200 | $PhHgCCl_2Ph$ | CClPh | 209 |
| $PhHgCHBr_2$ | CHBr | 200 | | | |
| $PhHgCHClCO_2Et$ | $CHCO_2Et$ | 201 | $PhHgCCl_2CON$ | CClCON | 210 |
| $Hg(CCl_3)_2$ | $CCl_2$ | 201 | | | |
| $ClHgCCl_3$ | $CCl_2$ | 202 | | | |
| $PhHgCCl_3$ | $CCl_2$ | 188 | $PhHgCBr_2CON$ | CBrCON | 211 |
| $PhHgCCl_2Br$ | $CCl_2$ | 188 | | | |
| $PhHgCCl_2I$ | $CCl_2$ | 203 | $PhHgCCl_2SO_2Ph$ | $CClSO_2Ph$ | 201 |
| $n\text{-}PrHgCCl_3$ | $CCl_2$ | 190 | $PhHgCBr_2SO_2Ph$ | $CBrSO_2Ph$ | 201 |
| $n\text{-}PrHgCCl_2Br$ | $CCl_2$ | 190 | $PhCH_2CH_2HgCCl_2CO_2Me$ | $CClCO_2Me$ | 201 |
| cyclo-$C_6H_{11}HgCCl_3$ | $CCl_2$ | 191 | $PhHgCCl_2CO_2Me$ | $CClCO_2Me$ | 201 |
| cyclo-$C_6H_{11}HgCCl_2Br$ | $CCl_2$ | 191 | $PhHgCClICO_2Me$ | $CClCO_2Me$ | 201 |
| $Hg(CBr_3)_2$ | $CBr_2$ | 204 | $PhHgCClBrCO_2Me$ | $CClCO_2Me$ | 212 |
| $PhHgCBr_3$ | $CBr_2$ | 188 | $PhHgCBr_2CO_2Me$ | $CBrCO_2Me$ | 212 |
| cyclo-$C_6H_{11}HgCBr_3$ | $CBr_2$ | 191 | $PhHgCClFCO_2R^*$ | $CFCO_2R^*$ | 213 |
| $PhHgCClBr_2$ | CClBr | 188 | $PhHgCBrFCO_2R^*$ | $CFCO_2R^*$ | 213 |
| PhHgCClBrI | CClBr | 205 | $Hg(CCl_2SiMe_3)_2$ | $CClSiMe_3$ | 214 |

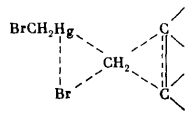
* R=Me, Et

The method of the liquid-phase thermolysis of halogenomethyl derivatives of mercury is widely used nowadays to synthesise various cyclopropane derivatives, many of which are formed in quantitative or nearly quantitative yields (Table 6), including the reaction involving weakly nucleophilic olefins. Among the applications of the carbene decomposition of organomercury compounds, mention should be made of the synthesis of numerous organic derivatives of other elements[9] and also the single-stage version of the Wittig reaction[215]:

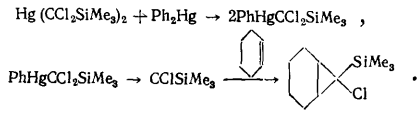


Organomercury carbene precursors of the type $RHgCX_3$, containing electronegative substituents R, exhibit a reduced reactivity and in some cases do not form free carbenes on liquid-phase thermolysis. Thus $Hg(CH_2Br)$ withstands prolonged boiling in benzene without appreciable decomposition, but readily introduces the methylene group

into olefins under the same conditions, evidently via the formation of an intermediate complex of the type[216]

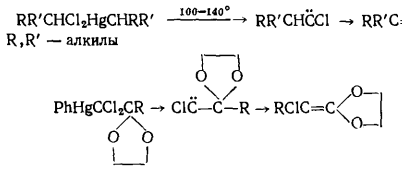


$BrHgCH_2Br$, which can introduce the methylene group into olefins only with low yields and under more severe conditions, is still more stable. However, it has been shown[196] that thermolysis of this and certain other stable halogenomethyl derivatives of mercury is greatly accelerated in the presence of $Ph_2Hg$ owing to a redistribution reaction with formation of the corresponding substituted derivatives of phenylmercury. Thus $Hg(CCl_2SiMe_3)_2$ reacts with cyclohexene at 120°C to form 7-chloro-7-trimethylsilylnorcarane in 24% yield, while in the presence of $Ph_2Hg$ the yield is 62%:[214]



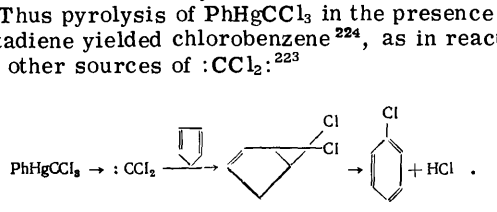
$:CBrSiMe$[217] and $:CHSiMe_3$[217,218] can be generated similarly from the corresponding symmetrical compounds.

More complex carbenes can also be generated from α-halogeno-derivatives of organomercury compounds by the method of liquid-phase thermolysis, but these species usually isomerise to the corresponding unsaturated compounds, for example[219-221]:



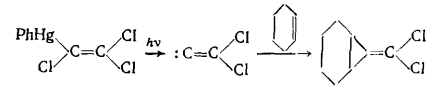
Instead of the carbene decomposition, 1,1-dichloroethylphenylmercury undergoes thermal dehydrochlorination with formation of chlorovinylmercury[222].

Trihalogenomethyl derivatives of mercury generate dihalogenocarbenes not only in the liquid but also in the gas phase. Thus pyrolysis of $PhHgCCl_3$ in the presence of cyclopentadiene yielded chlorobenzene[224], as in reactions involving other sources of $:CCl_2$:[223]



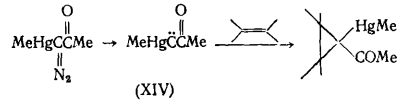
The intermediate formation of dihalogenocarbenes in the gas-phase pyrolysis (at 250–550°C) of $PhHgCClBr_2$, $PhHgCCl_2Br$, $PhHgCCl_3$, $Hg(CCl_3)_2$, and $ClHgCCl_3$ was demonstrated by their low-temperature stabilisation in an argon matrix with subsequent investigation using infrared spectroscopy[82,224-228]. The valence angle of this carbene (106° ± 4°) was found from the isotopic splitting of the $:CCl_2$ stretching vibration bands and the singlet state of this species was thereby demonstrated[82].

In contrast to the liquid-phase reactions, the gas-phase pyrolysis of trihalogenomethyl derivatives of mercury leads to the corresponding dihalogenomethyl radicals as well as carbene. The rate of formation of the radicals depends on the nature of the initial compound and generally increases with temperature[228], owing to the high degree of excitation of the vibrational-rotational levels of the molecule, which hinders the formation of the halogen–mercury bond in the transition state of the carbene decomposition reaction. Nevertheless the carbene pathway in the pyrolytic decomposition of these compounds predominates up to very high temperatures (about 500°C). In conformity with these ideas, the more vigorous excitation of molecules attainable following the ultraviolet irradiation of $PhHgCCl_3$ and $Hg(CCl_3)_2$ proceeds with the exclusive formation of trihalogenomethyl radicals[229,230]. On the other hand, in certain cases ultraviolet photolysis of α-halogeno-derivatives of organomercury compounds leads also to the formation of carbenes, for example[231]:



The above examples of the generation of carbenes from organomercury compounds are based on the use of α-halogeno-derivatives, a characteristic reaction pathway for which is α-decomposition. However, there are also examples in the literature of carbene-type photochemical decomposition of other organomercury compounds, particularly α-mercuri-derivatives of diazo-compounds.

Ultraviolet photolysis ($\lambda > 335$ nm) of methylmercuridiazoacetone ($MeHgCN_2OMe$) proceeds analogously to the photolysis of other diazo-compounds, leading to the metal-containing carbene $MeHgC\ddot{C}OMe$ (XIV), which interacts with olefins to form the corresponding cyclopropane derivatives in yields of 70–90%:[232]



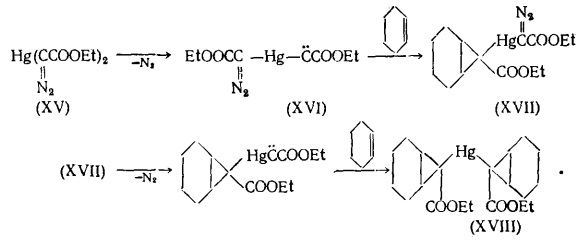
(XIV)

Like the other carbenes formed in the photolysis of diazo-compounds, compound (XIV) is probably generated in the triplet state, which rapidly relaxes to the singlet state (by virtue of the presence of the heavy metal atom next to the carbene centre), which can be inferred from the stereospecificity of the reaction with olefins and the absence from the reaction mixture of products of the Wolf rearrangement, which is characteristic of triplet ketocarbenes[233].

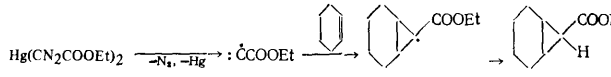
Analogous photochemical decomposition at $\lambda > 335$ nm, with formation of mercury-containing singlet carbenes, is also characteristic of many other compounds of the type $RHgC(N_2)X$ (where R = Me, Et, iso-Pr, t-Bu, Ph, or $PhCH_2$ and X = Me, Ph, CN, COMe, or COOMe), which are readily formed when RHgOEt reacts with diazo-compounds $XHCN_2$.[234] When the energy of the irradiation ($\lambda < 280$ nm) of a compound of this type increases, the mercury-containing fragment is split off together with a nitrogen molecule, forming intermediate compounds of formally univalent carbon—carbene-radicals or carbynes $:C\dot{X}$.

Similar relations are also observed in the ultraviolet photolysis of bis(diazoethoxycarbonylmethyl)mercury [$Hg(CN_2COOEt)_2$] (XV).[235-237] Thus compound (XV) initially splits off one nitrogen molecule on long-wavelength irradiation ($\lambda > 335$ nm) with formation of the singlet mercury-containing carbene (XVI), which reacts with cyclohexene to form the corresponding norcarane (XVII),

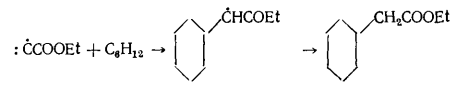
the subsequent decomposition of which, followed by the reaction with cyclohexene, leads to compound (**XVIII**):



The reaction involving the insertion of compound (**XVI**) in the allylic C–H bond of cyclohexene takes place simultaneously. More severe irradiation ($\lambda < 280$ nm) results in extensive decomposition of (**XV**), giving rise to the formation of ethoxycarbonylcarbyne (:CCOOEt) (in the doublet $^2\Pi$ ground state), which undergoes stereoselective addition to the C=C bonds of olefins like singlet carbenes. The ethoxycarbonylcyclopropyl radicals formed as a result of this reaction, subsequently deprotonate the initial olefin molecule, being converted into the corresponding ethoxycarbonylcyclopropane, for example:



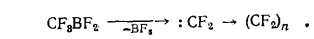
The same intermediate species is probably formed also in the thermolysis of $Hg(CN_2COOEt)_2$.[235] Photolysis of this compound in cyclohexane leads to products of the insertion of ĊCOOEt in the C–H bond:



## 5. Halogenomethyl Derivatives of Group III Elements

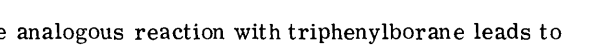
The halogenomethyl derivatives of Group III elements have been inadequately investigated as potential sources of carbenes, although the available literature data definitely indicate the validity also for this series of compounds of the fundamental relations determining the reactivity of organometallic carbene precursors.

Thus trifluoromethyldifluoroborane reacts with amines to form the extremely stable complexes $CF_3BF_2.NR_3$, but decomposes in a free state with formation of polymeric difluoromethylene[238]:

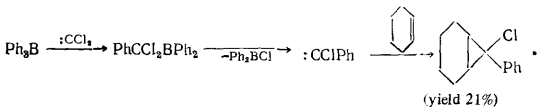


In contrast to the $\alpha$-decomposition reactions of halogenoderivatives of organometallic compounds discussed above, the latter reaction is catalytic and proceeds vigorously in the presence of traces of oxygen, moisture, and certain organic compounds. In the absence of these promoting agents, $CF_3BF_2$ is stable at room temperature[238]. $CF_3BBu_2$ exhibits a similar reactivity[238].

Compounds of the type $(RCH_2CH_2)_2BCCl_2CH_2CH_2R$ (R = Me or Et), formed in the thermolysis of $PhHgCCl_2Br$ in the presence of the corresponding trialkylboranes (80°C, benzene), are unstable under the conditions of their formation and decompose as a result of a series of transformations with elimination of the carbene $(RCH_2CH_2)_2C$:, which isomerises to an olefin. The reaction proceeds with a high degree of conversion and can serve as a preparative method for the synthesis of olefins with an inner double bond[239]:

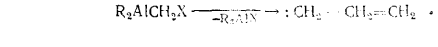


The analogous reaction with triphenylborane leads to $\alpha\alpha$-dichlorobenzyldiphenylborane, which decomposes slowly at 80°C with formation of chlorophenylcarbene:



Chlorophenylnorcarane is formed from $PhB(OMe)_2$ in a somewhat higher yield by an analogous reaction[239].

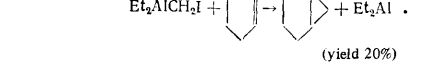
The method of synthesis of halogenophenyl derivatives of organoelement compounds by the decomposition of diazomethane in the presence of the corresponding halide salts, which was discussed above, is inapplicable to boron compounds, because they give rise to polymethylene exclusively. However, the analogous reaction with $AlCl_3$ in ether yields, together with polymethylene, a mixture of the etherates of chloromethyl derivatives of aluminium of the type $Al(CH_2Cl)_nCl_{3-n}OEt_2$ ($n = 0-3$) and the reaction of $CH_2N_2$ with $R_2AlX$ (R = alkyl; X = Cl, Br, or I) under the same conditions gives high yields of etherates of the type $R_2AlCH_2X.OEt_2$. These etherates are fairly stable and do not decompose up to 100°C. On the other hand, the free $R_2AlCH_2X$ formed when this reaction is carried out in a hydrocarbon medium are extremely labile and decompose at a high rate even at −10°C:



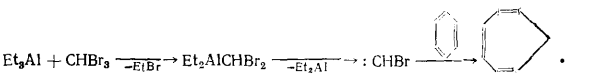
The free $RAl(CH_2X)_2$ species formed in the decomposition of $CH_2N_2$ in the presence of $RAlX_2$ [240,241] exhibit a similar reactivity.

A characteristic feature distinguishing $\alpha$-halogenomethyl derivatives of aluminium from similar compounds of other metals is the ease with which they add to the multiple bonds of olefins and acetylenes: $R_2AlCH_2X$ forms the corresponding $\gamma$-halogenopropyl compounds even at −50°C in the presence of unsaturated hydrocarbons; these products then decompose with formation of cyclopropane derivatives.

Like the "diethylzinc (or diethylcadmium) + $CH_2I_2$" systems[185], the "triethylaluminium + $CH_2I_2$" system introduces the methylene group into olefins, probably via the intermediate formation of $Et_2AlCH_2I$:[242]

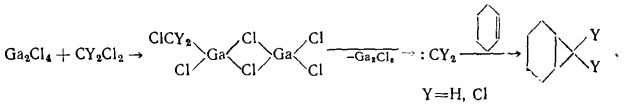


The ability of halogenomethyl derivatives of aluminium to decompose with formation of carbenes is indicated by the analogous reaction of $Et_3Al$ with bromoform in benzene, which leads to bromocycloheptatriene:

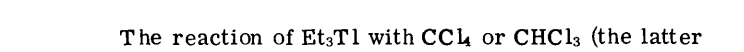


The reactions of $R_3Al$ (R = Et or iso-Bu) with $CHI_3$, $CHCl_3$, $CBr_4$,[242] and $CCl_4$ [242,243] also proceeds with the intermediate formation of carbenes.

Carbene decomposition is known to occur also for the analogous compounds of heavier Group III elements. Thus the formation of norcarane and 7,7-dichlorononorcarane was observed in the interaction of $Ga_2Cl_4$ with $CH_2Cl_2$ and $CCl_4$ in the presence of cyclohexene[244]:



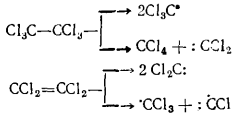
Like the boron and aluminium compounds, triethylthallium reacts with dichlorocarbene to form $\alpha\alpha$-dichloropropyldiethylgallium, which is unstable and decomposes via the carbene mechanism[190,245,246]:



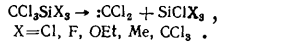
The reaction of $Et_3Tl$ with $CCl_4$ or $CHCl_3$ (the latter reaction takes place on heating) gives rise to $Et_2TlCCl_3$—an unstable compound which decomposes with formation of dichlorocarbene[190,245,246]. The same intermediates are readily formed when $CHCl_3$ interacts with $Et_2TlOCMe$ or $Et_2TlNMe_2$ at 0°C. The analogous reaction with $CH_2Cl_2$ leads to the unstable $Et_2TlCHCl_2$, which decomposes, probably with formation of CHCl. The indium compounds $Et_2InOCMe_3$ and $Et_2InNMe_2$ react with chloroform under much more severe conditions (100–150°C) also forming trichloromethyl compounds which decompose with formation of dichlorocarbene under the reaction conditions[246].

## 6. Compounds of Group IV Elements

It follows from the above data that the majority of $\alpha$-halogenomethyl derivatives of Group I–III metals are thermolabile compounds, which decompose via the coordination of the free electron pair of the halogen to a vacant $p$ orbital of the metal ($n$–$p$ coordination). Since the elements of Group IV and subsequent Groups do not have vacant $p$ orbitals in the ground state, the single-stage $\alpha$-decomposition of the halogenomethyl derivatives of these elements can take place only via the coordination of $p$ electrons of the halogen to higher sublevels of the metal, which entails an appreciable increase of the activation barrier. On the other hand, the single-stage carbene decomposition of compounds of the elements in the First Period is possible only via the coordination of the $n$-electron pair to the $d$ orbital of the next electronic level, which conflicts with the principle of the non-intersection of potential surfaces. As a consequence of this, the thermolysis of such compounds occurs only under very severe conditions, and proceeds exclusively via the homolytic dissociation mechanism, for example[223,249]:

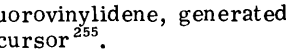


The $\alpha$-decomposition of compounds of the elements in the higher Fourth–Sixth Periods involves $n$–$d$ coordination, as a result of which $\alpha$-halogenomethyl derivatives of these elements are quite stable under the usual conditions, and decompose via the carbene mechanism only at relatively high temperatures (100–400°C). Thus the trichloromethyl derivatives of silicon [$Cl_3CSiCl_3$,[247,248] $CCl_3SiCl_2OEt$, $CCl_3SiCl(OEt)_2$, $CCl_3Si(OEt)_3$, $CCl_3SiMeCl_2$, $CCl_3SiCl_2CCl_3$, and $CCl_3SiF_3$ [248]] form the corresponding *gem*-dichlorocyclopropanes in yields of 30–80% on heating with olefins (100–250°C). A study of the kinetics of the reaction[248] showed that it is of first order and that its rate is independent of the nature of the olefin. Hence it follows that the initial reaction product is free dichlorocarbene:



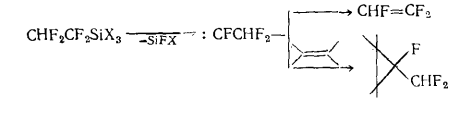
Furthermore, dichlorocarbene and $SiCl_4$ have been detected directly by infrared spectroscopy in an argon matrix as the primary products of the pyrolysis of $CCl_3SiCl_3$ (together with small amounts of the corresponding free radicals).[249]

In contrast to compounds of other elements, the fluoromethyl derivatives of silicon decompose at much lower temperatures than their chloro-analogues. Thus $CF_3SiF_3$ smoothly splits off $:CF_2$ even at 100°C:[250]



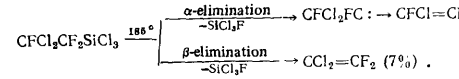
The cause of the reduced stability of fluoromethyl derivatives of silicon is undoubtedly associated with the considerable energy gain due to the unique stability of the Si–F bond formed (energy 170 kcal mole$^{-1}$ [251]). Possibly $H_3SiCH_2F$ is unstable for the same reason even at 20°C, although other compounds of the type $H_3SiCH_2X$ (X = Cl, Br, or I) are fully stable[252].

In conformity with the greater thermal stability of $\beta$-fluoroalkylsilanes, decomposing with formation of olefins only in the range 150–300°C,[253,254] compounds of the type $CHF_2CF_2SiX_3$ (X = F or Me) undergo mainly $\alpha$-decomposition on thermolysis, forming fluoro(difluoromethyl)carbene. In contrast to alkylcarbenes, the latter converts olefins into cyclopropane derivatives in quantitative yields and isomerises to $CHF{=}CF_2$ only in the absence of unsaturated acceptors[254]:



The difficulty of the carbene–olefin isomerisation was also noted for perfluorovinylidene, generated from an organomercury precursor[255].

When the alkyl chain of substituted silanes contains simultaneously F and Cl atoms, the thermolysis proceeds only with migration of the fluorine atom[247]:

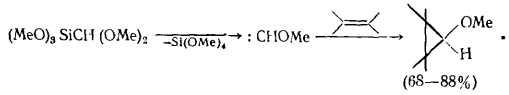


Certain compounds of this type have been found to undergo an exchange of Cl and F atoms prior to decomposition[256]. Such an exchange reaction, which is thermodynamically an extremely favourable process, occurs with $CH_3CF_2SiCl_3$ even at 100°C and is in no way complicated by the $\alpha$-decomposition[256]:



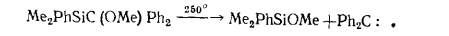
The acetals of silyl-substituted ketones[257] and aldehydes[258] apparently also have low thermal stabilities owing to thermodynamic causes[258]. Thus $(MeO)_3SiCH(OMe)_2$, readily obtained by the reaction of $Cl_3SiSiCl_3$ with $HC(OMe)_3$, decomposes under extremely mild conditions (125°C) with formation of an interesting carbene (methoxymethylene),

which converts olefins into the corresponding methoxycyclopropanes stereospecifically and with high yields[258]:

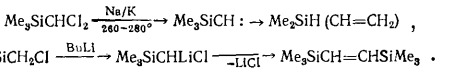


Kinetic data (overall first-order reaction) confirm the formation of free :CHOMe under these conditions.

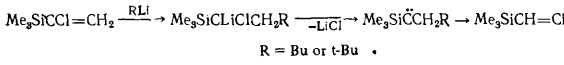
Monomethoxymethylsilanes have a higher thermal stability than the dimethoxy-derivatives but they too are capable of decomposing via the carbene mechanism[257]:



Certain organosilicon carbenes, whose reactivity and particularly their capacity for isomerisation are to a large extent determined by the lability of the C=Si bond, have been obtained from substituted silanes by the methods usually employed for the generation of carbenes. Thus, depending on the method and temperature of its generation, trimethylsilylcarbene isomerises to dimethylvinylsilane[259] or dimerises to 1,2-bis(trimethylsilyl)ethylene[260]:

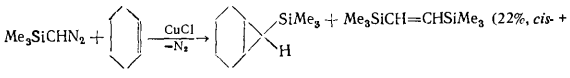


$\beta$-Alkylation of $\alpha$-chlorovinyldimethylsilane probably also proceeds with the intermediate formation of a carbene[261]:

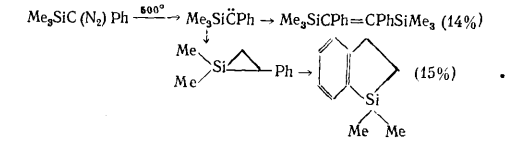


R = Bu or t-Bu .

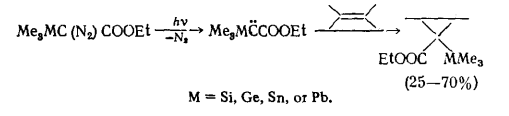
The thermocatalytic decomposition of trimethylsilyldiazomethane under the influence of CuCl in the presence of cyclohexene gives a high yield of trimethylsilylnorcarane, the dimers of the corresponding carbene being formed simultaneously[262]:



The thermolysis of phenyltrimethylsilyldiazomethane also leads to a carbene dimer together with 1,1-dimethyl-1-silaindan—the product of the isomerisation of the carbene, which probably proceeds via the corresponding silacyclopropane[263]:

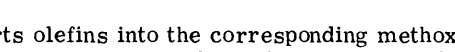


Photolysis of trimethylsilyldiazoacetate and of the analogous germanium, tin, and lead compounds leads, as in the case of the similar organomercury compounds, to substituted ethoxycarbonylcarbenes capable of introducing methylene groups into olefins with high yields[264,265]:



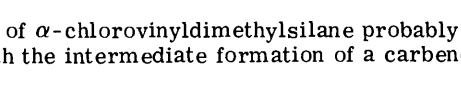
M = Si, Ge, Sn, or Pb.

Siloxycarbenes have been suggested as intermediates in the photolysis of acylsilanes[266]:



When this reaction is carried out in the presence of carbonyl compounds, the corresponding oxirans are formed, i.e. siloxycarbenes exhibit nucleophilic properties[267].

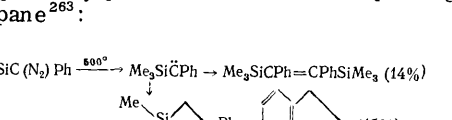
Owing to the considerable coordination unsaturation of the central atom, $\alpha$-halogenomethyl derivatives of heavy Group IV elements undergo carbene decomposition in general at somewhat lower temperatures than the corresponding silicon compounds (with the exception of the fluoro-derivatives). The thermolysis of $Ph_2CClGeCl_3$ at 150–220°C leads to $Ph_2C{=}CPh_2$, which is probably formed as a result of the dimerisation of the corresponding triplet carbene[268]. Dichlorocarbene, which gives rise to adducts with cyclohexene and cyclo-octene, is formed in the thermolysis of $CCl_3GeCl_3$ (200–400°C).[268,269] The formation of $:CCl_2$ in the pyrolysis of $Cl_3CGeCl_3$ has also been demonstrated by the matrix isolation method[270]. Possibly the thermolysis of $CHCl_2GeCl_3$, observed only under severe conditions (700°C) and leading to toluene in the presence of cyclohexene, may also proceed via the carbene pathway[268]. On heating, trifluoromethyltri-iodogermane forms difluorocarbene[271]:



Thermolysis of tri(fluoromethyl)trimethyltin (at 150°C) in the presence of $CF_2{=}CF_2$ leads to perfluorocyclopropane in a quantitative yield[272]. Like the decomposition of trifluoromethyl derivatives of mercury[192–194], this reaction is catalysed by NaI: difluorocarbene adducts are obtained in this way even at 80°C:[273,274]

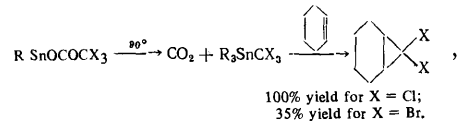


It is of interest that 2*H*-hexafluorocyclobutyltrimethylstannane is unstable and is converted into pentafluorocyclobutene even at 20°C, evidently via the corresponding carbenopentafluorocyclobutane[275]:



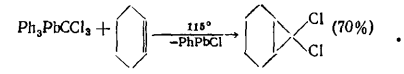
Like the mercury compounds, $Me_3SnCCl_2Br$ and $Me_2SnCCl_3$ are effective sources of dihalogenocarbenes[276,277]; however, their thermal stability is somewhat greater (the reaction is carried out at 140°C). In contrast to $PhHgCCl_2Br$,[187,188] $Me_3SnCCl_2Br$ gives on thermolysis a certain amount of :CClBr together with $:CCl_2$.[276] The carbene decomposition of dichlorobenzyltrimethylstannane also proceeds under the same conditions[277]:

Thermolysis of compounds of the type $R_3SnOCOCX_3$ (R = alkyl; X = Cl or Br) takes place in two stages[278,279]:

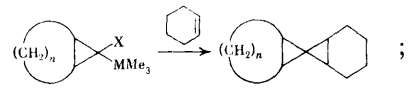


100% yield for X = Cl;
35% yield for X = Br.

Trichloromethyltriphenylplumbane undergoes the carbene decomposition under comparatively mild conditions[280]:



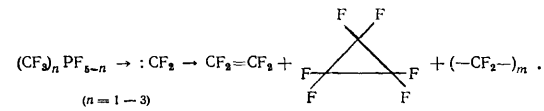
Substituted 1-bromo(iodo)-1-trimethylstannyl and 1-bromo-(iodo)-1-trimethylplumbylcyclopropanes decompose on thermolysis with formation of the corresponding cyclopropylidenes, which are capable of converting olefins into spiropentanes[281]:



X = Br, or I; M = Sn or Pb.

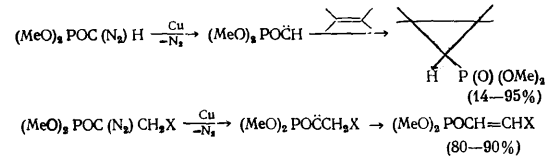
## 7. Compounds of Group V Elements

The numerous and widely used methods of synthesis of cyclopropane derivatives from compounds of Group V and VI elements belong to the ylid chemistry and are not the subject of the present review. Few examples of carbene reactions proper have been described for these compounds. Thus thermolysis of $(CF_3)_3Sb$ at 180–220°C and of $Ph_2SbCCl_3$ at 120°C as well as the decomposition of the unstable $(CCl_3)_3Sb$ proceed, judging from the reaction products, with the intermediate formation of the corresponding dihalogenocarbenes[282,283]. Free difluorocarbene is undoubtedly formed also in the thermolysis of perfluoromethylphosphoranes[284,285]:



$(n = 1-3)$

$\alpha$-Dimethylphosphonodiazoalkanes $RC(N_2)PO(OMe)_2$ are thermally extremely stable compounds which decompose under the influence of metallic copper with formation of the corresponding phosphonocarbenes, capable of converting olefins into cyclopropanes or (depending on R) of rearranging to the corresponding unsaturated compounds, for example[286-288]:



Diazo-compounds of the type $Ph_2POC(N_2)R$ (R = H, Ph, $CONH_2$, or COOEt) undergo ultraviolet photolysis to form the carbenes $Ph_2POCR$, which undergo the Wolff rearrangement, like carbonylcarbenes, leading to $O{=}P(Ph){=}CPhR$; the decomposition of these diazo-compounds under the influence of copper takes place without a rearrangement[289].

## 8. Carbenes Derived from Transition Metal Compounds

The most characteristic feature of transition metals is their exceptional tendency to fill their vacant atomic orbitals with the electron pairs of ligands; in particular, the occupied molecular orbitals of various organic compounds can play the role of electron pairs. For this reason, organic derivatives of transition metals in which all the coordination vacancies are occupied show the greatest stability. The above condition is satisfied by the carbene complexes of transition metals of the type $(CO)_5MCR(Y)$ (where M = Cr, Mo, or W; Y = OR or $NR_2$; R = alkyl or aryl), formed when the corresponding hexacarbonyls interact with RLi, this being followed by the methylation or aminomethylation of the adduct $(CO)_5MCR.(OLi)$.[290] Owing to the formation of the normal C–M$\sigma$ bonds and the coordinate bond involving nitrogen or oxygen $p$ electrons, compounds of this type are quite stable and can dissociate with formation of the nucleophilic carbenes :CYR only at elevated temperatures. Thus $(CO)_5CrCPh.(OMe)$ forms a mixture of stereoisomeric $\alpha\alpha'$-dimethoxystilbenes—dimers of the carbene :CPh(OMe)—only at 135°C.[291] However, the same compound is capable of converting crotonate esters into cyclopropane derivatives even at 80°C and $Ph_2SiH_2$ into $Ph_2SiHCH(OMe)Ph$ (albeit with a low yield) even at 55°C.[292,293] Under the influence of pyridine, the complex $(CO)_5CrC(OEt)Me$ decomposes at 60°C with the intermediate formation of the carbene :CMe(OEt), which does not, however, form the corresponding cyclopropane derivatives on reaction with olefins and isomerises wholly to methyl vinyl ether[294]. Complexes of the type $(CO)_5MCPh(OMe)$, where M = Cr, Mo, or W, convert the esters of $\alpha\beta$-unsaturated acids into cyclopropane derivatives at 90–140°C and alkyl vinyl ethers are converted into cyclopropanes even at 50°C in the presence of CO under pressure, the isomeric composition of the cyclopropane derivatives formed depending on the nature of the metal[295,296]. On being refluxed with $PhHgCX_3$ in benzene, the complex $(CO)_5Cr(OMe)Ph$ forms mixed dimers of electrophilic and nucleophilic carbenes of the type $Ph(MeO)C{=}CX_2$.[297] The compound $(CO)_5WCPh_2$ converts ethyl vinyl ether at 37°C and isobutene only at 100°C into cyclopropane derivatives[298].

The facts enumerated above undoubtedly show that in the vast majority of cases the transfer of the carbene from its transition metal complex takes place without the formation of the kinetically free carbene and is a consequence of the reaction of the complex with the substrate. This is confirmed by the fact that the chiral complex (–)-(*R*)-$MePrPhP(CO)_4CrPh(OMe)$ reacts with diethyl fumarate to form the optically active 2,3-diethoxycarbonyl-1-methoxy-1-phenylcyclopropane[299].

Several $\alpha$-chloromethyl compounds of transition metals, which behave as the precursors of the corresponding carbenes like the analogous compounds of other metals, are known. Thus, when $CrBPh_4$ or $(C_6H_6)_2CrBPh_4$ was heated with $CCl_4$ in the presence of cyclohexene, 7,7-dichloronorcarane was obtained in 50–54% yields. The reaction apparently proceeds with the intermediate formation of the trichloromethyl derivative of chromium $CCl_3CrClBPh_4$.[300] The chloromethyliridium compound $(Ph_3P)_2(CO)IrCH_2Cl$ interacts with styrene to form a mixture of phenylcyclopropane and 2-methylstyrene but is incapable of introducing the methylene group into cyclohexene[301]. In the presence of hydrochloric acid, the iron complex $(\pi\text{-}C_5H_5).(CO)_2FeCH_2OMe$ introduces the methylene group into cyclohexene at 50°C with a high yield; it has been suggested that $(\pi\text{-}C_5H_5)(CO)_2FeCH_2Cl$ is an intermediate in

this reaction. The same methoxymethyl derivative of iron as well as $(\pi\text{-}C_5H_5)(CO)_3MoCH_2OMe$ introduce the methylene group into cyclohexene on treatment with $HBF_4$ even at 0°C.[302]

Thermolysis of the iridium complexes $(Ph_3P)_2(CO)IrCl.(OCOCF_2Cl)X$, where X = H or $CHF_2$, proceeds with the elimination of $CO_2$ and difluorocarbene judging from the formation of compounds of the type $(Ph_3P)_2(CO)IrCl_2X$, but attempts to obtain by this reaction the adducts of difluorocarbene with olefins were unsuccessful[303]. On the other hand, the trifluoromethyl derivative of iron $CF_2Fe(CO)_4I$ decomposes at 100°C, forming difluoro- and perfluorocyclopropanes on reaction with ethylene and tetrafluoroethylene respectively[304].

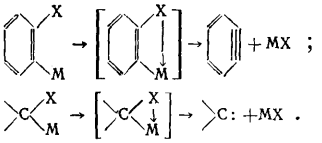
The complex $(CO)_5WCPh_2$, mentioned above, and the analogous chromium complex react with isobutene at 100°C to form not only the corresponding cyclopropane but also (mainly) 1,1-diphenylethylene. The analogous reaction with $\alpha$-methoxystyrene also gives $CH_2{=}CPh_2$ and the stable complexes $(CO)_5MC(OMe)Ph$. The reaction of the carbonyl complexes of diphenylcarbene with olefins thus proceeds via a redistribution of the fragments of the C=C bond, i.e. is an analogue of the metathesis of olefins[298]. The intermediate involvement of carbene complexes has been recently suggested in the discussion of the mechanism of the metathesis reaction proper[305].

The methylene complex of tantalum $(\pi\text{-}C_5H_5)_2Ta(CH_3).CH_2$, which was synthesised recently[306], disproportionates slowly at 25°C, forming the corresponding ethylene complex $(\pi\text{-}C_5H_5)_2Ta(CH_3)C_2H_4$, but the reaction apparently proceeds without the involvement of free $CH_2$. It is of interest that the methylene entering into the composition of this complex manifests nucleophilic and not electrophilic properties. According to NMR data, the barrier to the rotation of $CH_2$ about the Ta–C bond is approximately 20 kcal mole$^{-1}$.[307]

## VI. THE MECHANISM OF THE DECOMPOSITION OF HALOGENO-DERIVATIVES OF ORGANOMETALLIC COMPOUNDS‡

The data presented for the thermal stabilities of *o*-halogenoaryl and $\alpha$-halogenomethyl derivatives of organometallic compounds demonstrate convincingly that their decomposition with formation of arynes and carbenes proceeds with participation of a vacant orbital of the metal. Indeed, numerous lithium, magnesium, boron, aluminium, zinc, and transition metal compounds are much more stable in the form of their complexes with *n*-donor ligands, which is not observed for compounds of metals with a lone electron-accepting capacity (for example, mercury). The finding that halogeno-derivatives of organic Group I–III elements having vacant *p* orbitals are on the whole much less stable than their analogues formed from elements in Group IV and subsequent Groups is undoubtedly also associated with the involvement of a free metal orbital in the reaction.

On the other hand, analysis of the literature data shows that the reactions under consideration can be readily carried out as single-stage processes only when the second eliminated group contains a free electron pair. The generality of these conclusions suggests that the most probable pathway in the decomposition of organometallic precursors of arynes and carbenes is intramolecular coordination[308,309], being apparently the pathway involving least migration[310]:



This conclusion can evidently be justified theoretically on the basis of the simple theory of molecular orbitals and their interactions, the applicability of which (particularly of the principle of the conservation of the key properties of the molecular orbitals during the reaction[105]) to the related problems of the mechanisms of the reactions of organometallic compounds has been demonstrated recently[311].

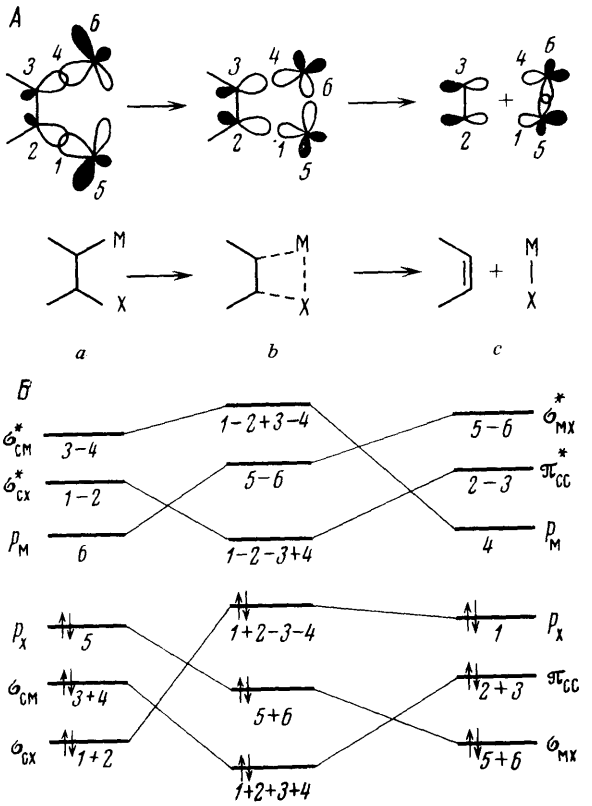



**Figure 2.** *A*) Changes in the molecular orbitals during the concerted decomposition of vicinal halogeno-derivatives of organometallic compounds [*a*) initial compound; *b*) transition state; *c*) reaction products]; *B*) correlation diagram (after Zimmerman[105]); the numerals on the diagram correspond to the numbering of the atomic orbitals.

It follows from the correlation diagram that the decomposition of vicinal (and similarly also geminal) halogeno-derivatives of organometallic compounds is symmetry-allowed when the coordinating orbitals are the boundary orbitals of the system (Fig. 2). In contrast to this, the

‡This section was written jointly with A.I. Ioffe.

synchronous decomposition of compounds of this type, which proceeds with participation of the molecular orbitals of the C–X and C–H bonds only, is symmetry-forbidden as a (2*s* + 2*s*) cyclodecomposition process[90]. It is quite evident that the characteristics of the reactions considered are consistent with the hypothesis that symmetry-allowed processes take place preferentially.

In considering the factors determining the stability of halogeno-derivatives of organometallic compounds, one must therefore take into account the fact that the activation energies for the decomposition reactions must depend not only on the heat of reaction (according to the Bell–Evans–Polanyi principle but also on a number of factors determining intramolecular coordination: on the energy gap between the molecular orbitals of the donor and acceptor (the *p* orbitals of the halogen and metal atoms respectively), on the distance between the M and X atoms in the molecule of the initial compound, and on the strength of the metal–ligand coordinate bond (when the reaction is carried out in the appropriate solvents). The first two factors determine the position of the transition state on the reaction coordinate, since it is formed sooner (and the activation energy is correspondingly smaller) the greater the sum of the valence radii of the M and X atoms and the smaller the difference between the corresponding orbital ionisation potentials. For this reason, the most important factors determining the stability of the compounds under consideration include their capacity for the formation of associated species, since an extremely effective decrease of the X–M distance is thereby achieved (for example the Li–F distance is 3.3 Å in the $C_6H_4LiF$ monomer, while the corresponding distance in the tetramer having a structure analogous to that of methyl-lithium[312] is only 2.0 Å). The analogous effect should also be observed for dimers and one may therefore expect that associated halogeno-derivatives of organometallic compounds should be less stable (in the presence of a free metal orbital) than the corresponding monomeric compounds.

Owing to the lack of thermochemical data, the correct calculation of the heats of the reactions considered ($Q = D_{MX} + D_{CC} - D_{CM} - D_{CX}$, where $D$ are the heats of dissociation of the corresponding bonds)—undoubtedly the most important factor determining the activation energy—is so far impossible. However, for compounds of a single metal decomposing in the same medium with formation of the same unstable species (for example, the process $o\text{-}XC_6H_4Li \rightarrow LiX + C_6H_4$), the relative heats of reaction (and hence the ratio of the activation energies) for reactions involving different X may be estimated from the differences $\Delta D$ between the heats of dissociation of the M–X and C–X bonds. Owing to the lack of the necessary data for the heats of dissociation of the C–M bonds, the effects of various metals in their compounds may be estimated qualitatively using the data for the corresponding M–H bonds, the heats of dissociation of which are usually close to those of the C–M bonds[251]. Only a qualitative allowance for the remaining factors influencing the stability of halogeno-derivatives of organometallic compounds is at present possible.

Since the C–X bond strength is only one of the factors determining the heat of reaction, the attempts to relate the stability of halogeno-derivatives of organometallic compounds to this quantity alone usually do not lead to correct predictions. Virtually the only examples of a satisfactory correlation between $D_{CX}$ and $T_d$ are provided by the compounds $o\text{-}XC_6H_4Li$, whose decomposition temperatures $T_d$ decrease in the following sequence of X: F > Cl > Br,[40] and by $LiCHX_2$ (Cl > Br > I).[133,144,145] However, in these cases too the values of $\Delta D$ represent more satisfactorily the sequence in which the temperatures $T_d$ diminish as a function of X (F > Cl > Br) than do the values of $D_{CX}$ (F ≫ Cl > Br). The correlation usually drawn between $T_d$ and the polarity of the C–M bond is inapplicable to thermolytic reactions and comparison of the values of $D_{CM}$ as criteria of the stability of compounds of different metals usually leads to incorrect estimates. Thus the values of $D_{CM}$ for the C–Li and C–Hg bonds are similar [62 kcal mole$^{-1}$ for $CH_3Li$ and 56 kcal mole$^{-1}$ for $(CH_3)_2Hg$ [251,313]], while the decomposition temperature $T_d$ of $LiCCl_3$ is lower than that of $C_6H_5HgCCl_3$ by approximately 300°C.[81,188] Much more reasonable correlations are obtained in the analysis of the heats of reaction. Thus the sharp increase of stability observed on passing from alkali metals and magnesium to heavy metal derivatives is associated with a decrease of $D_{MX}$, so that $\Delta D$ = 30 – 50 kcal mole$^{-1}$ (for virtually constant values of $D_{CM}$).

When the relative stabilities of compounds of more similar metals are considered, one must take into account also the differences between the values of $D_{CM}$. It follows from the known values of $D_{MH}$ that the differences between the $D_{CM}$ for alkali metal and magnesium compounds should not exceed 10 kcal mole$^{-1}$. Examination of the values of $\Delta D - D_{MH}$ makes it possible to estimate the heats of the decomposition reactions of the analogous lithium, sodium, potassium, and magnesium compounds, the results showing their extreme similarity; the highest heat and hence the smallest activation energy should be observed for lithium and magnesium compounds, which is usually the case. Thus the decomposition temperatures $T_d$ of the compounds $MCHBr_2$ lie in the sequence Na ≃ MgX > K ≃ Li and those of the compounds MCBr lie in the sequence Na ≃ MgBr > Li ≃ K.[144,161,164] The difference between the heats of reaction of magnesium and lithium compounds, having virtually the same values of $\Delta D$, is determined by the difference between the values of $D_{CM}$, which (together with the difference between the heats of dissociation of the M–O etherate linkages) probably also determines the relative stabilities of the corresponding trifluoromethyl compounds: $CF_3MgBr \ll CF_3Li$.[142,164,314] One should note that, when an ionic mechanism obtains, the stability should in all cases follow the sequence XMg > Li > Na > K.

The relative stabilities of compounds whose decomposition leads to different molecules are greatly influenced by $D_{CC}$—the energy of the C–C bond formed in an unstable molecule. In particular, owing to the much smaller energy of the triple bond in cyclopentyne than in cyclohexyne and cycloheptyne, 2-bromo-1-lithiocyclopentene is much more stable than the corresponding six- and seven-membered compounds[31–33,315]. For the same reason, compounds such as 1-lithioperfluoronorbornene[315], halogeno-1,2-dilithioferrocenes[317], and lithio-derivatives of halogenothiophens and furans[318,319] are also stable. $D_{CC}$ for carbenes is equivalent to $E_{ST}$; according to calculations[88,89], this quantity is a maximum for $CF_2$ and a minimum for $CH_2$, while its value for $CCl_2$ has been estimated as being intermediate[86]. This sequence of values of $D_{CC}$, which is the reverse of that of $\Delta D$, evidently equalises the decomposition temperatures $T_d$ for $LiCX_3$ (F ≃ Cl ≃ Br)[40,130,142,144] and is the reason why the relative stability of $LiCHCl_2$ is much greater than that of $LiCH_2Cl$.[101,133]

The influence of the distance between the eliminated groups undoubtedly causes the decomposition temperature of $KCBr_3$ to be smaller than that of $NaCBr_3$.[161] In contrast

to monohalogeno-compounds, pentachloro- and pentabromo-phenyl-lithium should be monomeric or should form less strongly bound associated species for steric reasons, as a result of which the halogen–metal distance in these compounds should be greater. In conformity with these considerations, pentachloro- and pentabromo-lithiobenzenes are much more stable than the monohalogeno-compounds.[42,52,53] Stabilisation of this kind is observed also for pentahalogenophenyl Grignard reagents[52,66-70,74,320,321] and for biphenyl[59,60,322], phenyl ether[61], and pyridine[65] derivatives. 2-Bromo-2-lithiobiphenyl, in the stable conformation of which the planes of the benzene rings are mutually perpendicular and the distance between the Li and Br atoms exceeds 4.3 Å, are stable even on boiling in ether[53].

It appears evident that the energetic and structural factors examined are the main ones among those which determine the resistance of halogeno-derivatives of organometallic compounds to carbene or aryne decomposition. At the same time, the correct treatment of this problem must take into account also many other factors, such as the change in bond energy under the influence of substituents, the stability of reaction products, their heats of solvation, etc., which does not appear possible at the present time.

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# The Electronic Structures and Properties of Polymeric Molecules with Conjugated Bonds

I.A.Misurkin and A.A.Ovchinnikov

Modern ideas about the electronic structure of the long molecules of polymers with conjugated bonds (CBP) are examined and their various physicochemical properties are discussed from the standpoint of these hypotheses.
The bibliography includes 162 references.

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## I. INTRODUCTION

The modern theory of the electronic structure of molecules with conjugated bonds has had significant achievements in the qualitative and quantitative explanation of the properties of such systems. The possibility of applying semiempirical methods in order to explain and predict the properties of small molecules has been examined in reviews [1,2]. For large molecules (polymers), the employment of the usual quantum-chemical methods becomes impossible mainly owing to the large amount of computational work involved. On the other hand, methods usually employed in statistical physics and in solid-state physics are effective in such systems.

Large molecules have properties which their individual units or components do not possess [3]. Some of these properties are associated with the mechano-statistical properties of the macromolecular units joined together in succession and others are due to the continuous conjugated system or the appearance of long-range order. Irregularity of structure, defects, and heteroatoms have a considerable influence on the observed properties of large molecules and hinder their explanation.

In the present review, we shall consider the achievements and difficulties encountered in semiempirical theories when an attempt is made to explain and predict special properties (optical, magnetic, etc.) of long molecules of polymers with conjugated bonds (CBP). As for small molecules with conjugated bonds, the theoretical analysis of the properties of CBP macromolecules is based on the $\pi$-electron approximation using the corresponding model Hamiltonians [1,2].

Interest in long molecules with conjugated bonds has recently increased sharply after the work carried out by Little [4], who put forward the idea of synthesising on the basis of CBP an organic superconductor having a high critical temperature. These hopes were not fulfilled because CBP possess properties quite different from those postulated by Little. However, the idea of using organic compounds, one-dimensional and quasi-one-dimensional systems, in order to obtain substances with unusual properties is extremely fruitful. This is confirmed by the detection of metallic conduction in complexes of tetracyanoquinodimethane (TCNQ) with tetrathiafulvalene (TTF), *N*-methylphenazine (NMP), and alkali metals, for example TCNQ-TTF, NMP-TCNQ, Rb-TCNQ, etc. where the conduction is strongly anisotropic and takes place along stacks of TCNQ and acceptor species [5,6]. Stacks of identical molecules are weakly bound to one another, which makes it possible to employ for the analysis of such systems the same models as for CBP macromolecules. However, we may note that charge transfer in these donor–acceptor crystals leads to the need to take into account the Coulombic interaction throughout the bulk of the crystal. It has been found that the Coulombic energy of the crystals or the Madelung energy influences significantly the nature and degree of charge transfer from the donor to the acceptor [7,8], complicating the overall physical picture. Nevertheless, one-dimensional systems manifest their characteristic properties in any situation.

The unusual properties of CBP or quasi-one-dimensional systems are the first consequence of the "unidimensionality" of these systems. Naturally all such systems consist of three-dimensional atoms or molecules, so that the macromolecules or molecular stacks possess not only length but also "width" and "thickness". However, electrons or excitations (electronic or vibrational) in such systems can migrate only along a chain of atoms or a stack of molecules. Thus the motion of electrons or excitations is one-dimensional and in this sense the corresponding systems—macromolecules, chains of atoms, and stacks of molecules—are one-dimensional or quasi-one-dimensional. The prefix "quasi" emphasises that the systems are in fact three-dimensional, although

their most significant physicochemical properties are associated with the one-dimensional motion of electrons and excitations.

The limitations imposed on the number of spatial dimensions in which electrons or excitations can migrate diminish the number of possible situations and, in terms of the language of statistical physics, alter the phase volume. For example, when one electron is scattered by another, the electron moments before and after the collision are located on the same straight line. This finding permits the exact solutions for certain models of one-dimensional systems, since it is possible to recalculate all possible situations arising in the interaction of electrons.

The unidimensionality of the system leads to the appearance of interesting properties, which are much more rarely encountered in three-dimensional systems. A comparatively small number of quasi-one-dimensional systems, which manifested their unusual properties, as it were, at random, have so far been investigated. Now that the relation between the quasi-unidimensionality of the systems and their unusual properties has been understood, the problem arises of a purposeful search for and synthesis of quasi-one-dimensional systems and of the investigation of their properties. In the solution of this problem, theoretical ideas formulated at the present time will prove useful. They are in fact the main subject of the present review in relation to CBP macromolecules.

One-dimensional models have been fairly widely investigated in the theory of the condensed state of matter to test various theoretical constructions and approximations. Starting with the work of Bethe[9], Hulten[10], Orbach[11], and others[12,13], the investigators of one-dimensional models have been attracted by the possibility of obtaining exact solutions, so that these studies were in the main of methodological interest. However, the number of real one-dimensioal systems started to increase recently. Numerous CBP have been synthesised[14-17] and organometallic compounds with chains of metal atoms[18,19] and charge-transfer complexes based on TCNQ[5-8,20] have become available. Intensive investigation of the properties of polymers has begun; in particular the $-(SN)_n-$ polymer has been found to exhibit superconduction, albeit with a fairly low critical temperature ($T = 0.3$ K).[21] However, we may note that it became clear very soon that the polymeric sulphur nitride is not a quasi-one-dimensional crystal owing to the significant contribution of interchain interactions[22].

In the study of the properties of real quasi-one-dimensional systems, both the most rigorous and approximate methods have been used. The old theoretical results, which were seemingly obtained in the course of purely academic research, unexpectedly provided a key to the explanation of the properties of macromolecules which had been previously rejected. The sudden success of the theory can be explained or, more correctly, is associated with fairly general features of the development of modern science. On the one hand, physical chemistry accumulated numerous interesting facts about the properties of one-dimensional systems, mainly CBP molecules. In order to explain these facts, all the known concepts of quantum-chemistry were used, but they proved to be inadequate and we now understand that the reason is that the correct allowance for the interaction of electrons (electronic correlations) is the key factor in these problems. The problem of the interaction of electrons has been usually solved in quantum chemistry for small molecules and the consequences of allowing for the interaction of electrons in macromolecules, for which semi-empirical versions of the self-consistent field (SCF) approximation were usually employed, were not evident. On the other hand, various models for one-dimensional systems have been discussed for a long time in theoretical physics in order to discover the qualitatively new features resulting from a more accurate allowance for the interaction of electrons. These models have names which are fairly unusual for chemists and even quantum chemists: the Ising model, the Heisenberg chain, the spin Hamiltonian... For a long time, the results of these two groups of investigations were published independently in the form of two separate streams of informations addressed to different scientific circles. In the middle 1960s, these two streams finally combined and, as a result, it was possible to achieve considerable progress both in the solution of exact problems and in the explanation and prediction of physicochemical properties. This process has continued, since it became possible to synthesise specific substances with unusual properties.

In order to create quasi-one-dimensional systems and new types of polymers, it is necessary to employ the rich experience gained in modern organic chemistry. For this purpose, one must begin at least with the formulation of a general scientific view concerning the problem as a whole. At the present time investigators prefer to work on "projects", whose likely outcome is known *a priori*. We believe that in such a situation the synthesis of a one-dimensional or quasi-one-dimensional compound is a still more favourable project, because one is very likely to obtain a substance with unusual properties.

An interesting example is the observation of the very high hyperpolarisability $\chi^{(3)}$ of single crystals of polydiacetylene (PDA), which makes the substance very promising for use in non-linear optics and laser engineering[23]. PDA single crystals are large, contain no amorphous phase, and are almost free from defects and impurities[24,25], which is to a large extent caused by the method of their synthesis by solid-phase polymerisation from the crystalline phase of the initial monomers at a moderate temperature[26].

Returning to the problem of the electronic structure of CBP, one should note that the description of this problem in Soviet and foreign literature lags far behind the actual present level of its understanding. This is due to a phenomenon, familiar in science, where whole blocks of references are transferred from one source to another when books, papers, and handbooks are written, which temporarily protects the given research field from being penetrated by new concepts and ideas. One of the aims of the present review is to shorten this period.

## II. THE EVOLUTION OF VIEWS ON THE STRUCTURE OF CBP MACROMOLECULES

The first quasi-one-dimensional object investigated was a polyene chain, to which the theoretical studies by Lennard-Jones[27] and Coulson[28] were devoted. At that time it was known that the bond lengths in short polyenes alternate in accordance with the familiar Kekulé structures. The problem of whether the alternation of bond lengths in the polyene persists with increase of its length or whether the bond lengths become equalised, formulated in the above investigations, was solved using the "bond length–bond order" formula obtained by Lennard-Jones[27] in terms of the Hückel molecular orbital approximation for $\pi$ electrons,

taking into account the elasticity of the $\sigma$ skeleton [the Hückel–Lennard-Jones (HLJ) approximation].

At the same time Broocker and coworkers[29-35] investigated the absorption spectra of compounds with polyene chains, which made it possible to establish[36] the following relations. In the spectra of symmetrical cyanine dyes with an odd number of carbon atoms in the polyene chain, the wavelength of the first electronic transition increases by $\lambda_C = 1000 \pm 50$ Å following the addition of each CH=CH group to the polyene chain. This "red" shift does not diminish with increase of the length of the polyene chain, so that the energy of the first optical excitation $\Delta E$ tends to zero with increase of the length of the polyene chain. On the other hand, in asymmetric dyes with an even number of carbon atoms in the main conjugation chain and in polyenes with an even number of atoms, the intense optical absorption band ceases to shift with increase of the conjugation length, so that $\Delta E$ tends to a finite limit. The limiting value for polyenes $\Delta E_\infty \simeq 2.25$ eV (Fig. 1) has been obtained by extrapolating data obtained in studies on linear polyenes and annulenes[37-40].

The behaviour of $\Delta E$ for symmetrical dyes appeared natural from the standpoint of the molecular orbital method[41,42] or the metallic model[43,44]. According to these ideas, the distance between the levels and hence $\Delta E$ is inversely proportional to the chain length and a satisfactory theoretical estimate of the "red" shift was obtained: $\lambda_C \simeq 900$ Å.[32,43,44] From this point of view, the finite value of $\Delta E_\infty$ for polyenes and asymmetric dyes was completely incomprehensible. This constituted a serious theoretical problem, since it did not concern a hypothetical infinite polyene, as in the earlier investigations[27,28], but real molecules with finite dimensions: a limiting value of $\Delta E(N)$ was approcched when the number of atoms was $N \simeq 10$–12 (Fig. 1).

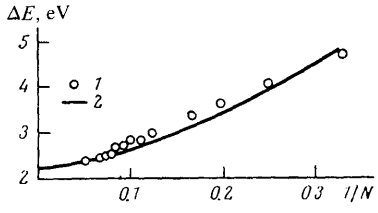



**Figure 1.** Dependence of the energy of the first electronic transition $\Delta E$ on $1/N$ in the polyene $(CH)_{2N}$: 1) experimental values[37]; 2) line drawn through points calculated by Eqn. (14).

The hypothesis of the alternation of bond lengths as the cause of the appearance of a $\Delta E_\infty$ gap in the spectra of excited polyenes was put forward for the first time by Kuhn[43,45,46], who proposed a model in which the non-interacting $\pi$ electrons migrate in a field with a sinusoidal potential, the minima of which correspond to the region of double bonds. By selecting a parameter $V_0$ associated with the amplitude of the potential, it was possible to make the $\Delta E$–$N$ relation consistent with experiment. However, it remained obscure which factors distinguish the double bonds in the chain. If we note that the early investigations[27,28] indicated that the bond lengths in an infinite polyene are equalised (a result which appeared erroneous in the light of the above ideas), then, apart from the intuitive feeling associated with Kekulé structures, there is no reason why the double bonds should be distinguishable. The problem of bond lengths in a polyene was soon solved in terms of the SCF approximation[47]. It was found that in the HLJ model[27,28] a long polyene with equal bond lengths passes to the energetically more favourable state with alternating bond lengths, provided that $N > N_{cr}$, where $N_{cr}$ depends on the model parameters.

In terms of the Hückel approximation, the energies of the molecular orbitals of $\pi$ electrons are given by

$$\varepsilon_n = \alpha_0 + 2\beta_0 \cos\frac{\pi n}{N}, \quad n = -N+1, \ldots, N, \qquad (1)$$

where $\alpha_0$ is the Coulomb integral and $\beta_0$ the resonance integral for the C–C bond. The total energy of the molecule is

$$E = E_\pi + E_\sigma,$$

where the energy of the $\sigma$ skeleton is additive with respect to the bonds:

$$E_\sigma = \sum_l E_{\sigma l}$$

and the energy of $\pi$ electrons is given by

$$E_\pi = 2\sum_{n=-\nu}^{\nu} \varepsilon_n, \quad \nu = \frac{N-1}{2}.$$

The number of levels (1) is equal to the number of $\pi$ electrons, so that in the ground state exactly half of the band defined by Eqn. (1) is occupied by two electrons in each molecular orbital. When the bond lengths alternate, the energies of the occupied molecular orbitals diminish and those of vacant orbitals increase, so that a gap $\Delta E_{alt}$ appears and $E_\pi$ decreases. However, under these conditions $E_\sigma$ increases because of the necessity to expend work against the elastic forces of the $\sigma$ skeleton during the extension and construction of bonds. As a result, the total energy minimum is reached for certain values of the alternating bond lengths. In the solid state theory, the alternation of bond lengths in a one-dimensional metal became known as the "Peierls theorem"[48]. In quantum chemistry, this result has been formulated in relation to polyenes[49-51].

In the light of the above ideas, it was natural to identify the optical gap with the gap obtained as a result of alternation:

$$\Delta E_\infty = \Delta E_{alt}. \qquad (2)$$

This view has been reflected in monographs[14-17,39] and became firmly established in the literature on CBP for a long time.

We may note that the alternation of bond lengths in the SCF or HLJ model is only fortuitously consistent with the ideas in theoretical chemistry on the alternation of double and single bonds. In fact, the bonds alternate (in the given models) because the number of $\pi$ electrons is equal to the number of atoms and the polyene $\pi$ band (1) with equal bond lengths is exactly half-filled; for this reason the gap $\Delta E_{alt}$ arises precisely above the filled band with a reduction of the energy of the latter, which is energetically favourable. If the polyene $\pi$ band (1) was one-third or two-thirds filled, then the state in which groups of three different bonds alternate forming three bands with a gap above the filled band, etc. would have become favourable for the same reasons. This problem has been investigated by the present authors[52].

In terms of the Hückel approximation, the spectrum of the molecular orbital energies of the polyene $(CH)_2N$ with alternating bond lengths (we shall consider a cyclic model to avoid the complication due to end effects) has the following form:

$$E_{\pm}(k) = \alpha_0 \pm [\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(\pi k/N)]^{1/2} \quad -\nu \leqslant k \leqslant \nu, \quad \nu = (N-1)/2, \tag{3}$$

where $\beta_1$ and $\beta_2$ are two resonance integrals corresponding to short and long bonds. In the ground state, the $E_-(k)$ levels are twice filled [with the minus sign before the root in Eqn. (3)], so that the gap is given by

$$\Delta E_{alt} = 2\,|\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(\pi\nu/N)]^{1/2} \simeq 2\,|\beta_1 - \beta_2|$$

for $N \to \infty$. Since the differences between the bond lengths are small ($R_2 - R_1 \simeq 0.04$ Å),[47,51] $\beta_1$ and $\beta_2$ can be expressed approximately in terms of the following expansions:

$$\beta_1 = \beta(R_1) = \beta_0 + \beta'\Delta R + \beta''\Delta R^2/2,$$
$$\beta_2 = \beta_0 - \beta'\Delta R + \beta''\Delta R^2/2,$$

where

$$\Delta R = R_2 - R_0 = R_0 - R_1, \quad \beta' = (\partial\beta/\partial R)_{R=R_0},$$
$$\beta'' = \left(\frac{\partial^2\beta}{\partial R^2}\right)_{R=R_0}$$

and $R_0$ is an average length equal to the C–C bond length in benzene. Then

$$\Delta E_{alt} = 2\,|\beta_1 - \beta_2| = 4\beta'\Delta R. \tag{4}$$

The main idea of the critical analysis of the scheme with alternation, carried out by the present authors[52-54], involved a test of the theory for the consistency of the semiempirical parameters. According to the alternation hypothesis (Eqns. (2) and (4)], $\Delta E_\infty$ is expressed in terms of $\beta'$, i.e. it depends on the form of the function $\beta(R)$. In vibrational excitations of molecules, the bond lengths also change, so that the vibration frequencies of molecules with conjugated bonds depend on the form of the same function $\beta(R)$. In order to secure information about the real parameters, expressions were obtained[53] for six frequencies of the in-plane vibrations of benzene in terms of three parameters of the HLJ model. Comparison with the experimental frequencies makes it possible to find these three parameters quite reliably: two elastic constants—for the extension of the bond ($k_1$) and the changes in the angle between adjoining bonds ($k_2$)—and (the third constant) the ratio

$$\beta'^2/\beta_0 = -1.23 \cdot 10^5 CGSE = -7.7 \text{ eV Å}^{-2}.$$

For the generally accepted value $\beta_0 = 2.4$ eV, we obtain $\beta' = 4.3$ eV Å$^{-1}$. This value of $\beta'$ agrees with X-ray diffraction data for bond lengths in conjugated molecules. Indeed, the following formula has been obtained[54] in terms of the same approximation for the C–C bond in a conjugated molecule:

$$R = R_0 - \frac{2\beta'}{k_0 + 2\beta''P} P, \tag{5}$$

where $P$ is the $\pi$-electron bond order, $R$ the bond length, $k_0$ the elastic constant of the $\sigma$ bond, and $R_0$ a constant. This formula is virtually identical with the familiar Coulson formula[55]

$$R = 1.517 - 0.18P, \tag{6}$$

which has been used effectively in calculations on conjugated systems. The coefficient 0.18 in Eqn. (6) is obtained from Eqn. (5) for $P \simeq 2/3$, $\beta' \simeq 4.3$ eV Å$^{-1}$, and $k_1 = k_0 + 2\beta''P \simeq 47.5$ eV Å$^{-2}$.

As a result, we obtain from Eqn. (4) $\Delta E_{alt} \simeq 0.3$ eV, which is smaller by a factor of ~10 than the experimental value of $\Delta E_\infty$ for polyene. This result can be understood on the basis of simple qualitative considerations: the energies associated with the distortion of bond lengths with alternation must be comparable in order of magnitude to the vibration energies, i.e. must amount to a fraction of an electron-volt. The above analysis shows that the considerable magnitude of the gap in the spectra of polyenes ($\Delta E_\infty \simeq 2.2$ eV) cannot be associated with the interactions of electrons with atomic vibrations and rearrangements of atomic configurations. At the same time, the necessity arises for the employment of a self-consistent set of semiempirical parameters. All these factors make it possible to interpret correctly the results obtained by methods more rigorous than the HLJ approximations. For example, in calculations of the first transition energies in a polyene[56], the Pariser–Parr–Pople (PPP) approximation was used, while another study[57] involved a method taking into account a limited number of excited configurations. A satisfactory agreement with experiment for the $\Delta E - N$ relation for polyenes with alternating bond lengths was achieved in this case using parameters which had not been adjusted for consistency with experiments on vibrations and with structural data. The same inconsistency between the parameters is characteristic of studies[16,58] where a semiempirical version of the SCF method was used to calculate the band structure of polyenes. Here too the agreement between the calculated energy gap and experiment did not demonstrate the validity of the alternation hypothesis.

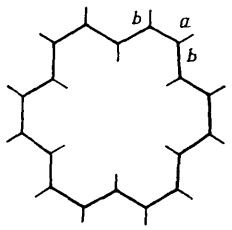



**Figure 2.** 18-Annulene. The group of three bonds *b*, *a*, *b* is repeated.

Analysis of experimental and calculated data for 18-annulene (Fig. 2) provided evidence against the alternation hypothesis. According to X-ray diffraction data[59], in this molecule 12 "inner" bonds have the length $b = 1.382 \pm 0.003$ Å and six outer bonds have the length $a = 1.419 \pm 0.004$ Å, i.e. a group of three bonds is repeated periodically and not a group of two, as in alternation. For such a structure, there is no gap in the spectrum, since among the three $\pi$-electron bands, the middle one is half-filled[52]. Nevertheless, the energy of the first transition in $C_{18}H_{18}$, which is $\Delta E = 2.77$ eV,[39,60] does not divide from the general relation (Fig. 1). Calculations by the PPP method, taking into account a large number of excited configurations, could not explain the observed absorption spectrum of 18-annulene; the energy of the first transition was much lower than the experimental value[60]. This did not naturally imply that the PPP method is inapplicable to many-electron molecules. Calculations on the spectra of coronene (24 $\pi$ electrons) and ovalene (32 $\pi$ electrons) by

the PPP method yielded excellent results[61]. It now became clear that the cause of the failure of the calculations on the spectrum of 18-annulene was that electron correlations are significant in one-dimensional chain molecules, and these are not taken into account in any way in the PPP method, where the ground state is described, as in the SCF or Hückel method, by a single configuration of $\pi$ electrons. The example of 18-annulene also showed that structural factors (bond lengths) do not have a significant influence on the energies of electronic optical excitations.

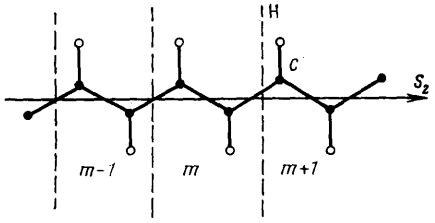



Figure 3. Schematic illustration of a polyene. The $(...m-1, m, m+1,...)$ cells into which the polyene was divided in the calculation in Ref. 62 and the mirror-rotational twofold symmetry axis $S_2$ are shown.

In conclusion of this section, we shall discuss the unexpected result obtained by Andre and Leroy[62], who investigated the electronic structure of a polyene by the SCF method taking into account all the valence electrons (the *ab initio* method in terms of the Hartree–Fock approximation). For a given polyene chain with equal C–C bond lengths, two $\pi$ electron bands were obtained (filled and vacant), separated by a gap of ~4 eV. This result, obtained *ab initio* from analytical basis functions in conjunction with computer calculations in accordance with a specified program, commanded respect and gave rise to the hope that latent causes exist for the appearance of $\Delta E_\infty$, which were overlooked in simpler semiempirical calculations. The authors[62] carried out calculations on a polyene with a structure close to the real structure taking into account hydrogen atoms (Fig. 3). The question arises if the cause involved the allowance for the interaction with the hydrogen atoms or the unusual structure of the real polyene. As frequently happens, numerical calculations did not provide an answer to such questions. The doubts were resolved in an elegant study by Ukrainskii [63], who analysed the method of calculation used by Andre and Leroy[62]. It was found that the latter workers artificially subdivided the polyene into CH–CH cells (Fig. 3) and, having specified the limiting distance for which the computer program no longer took into account the Coulombic interaction between the electrons, the computation was based on the number of neighbouring cells (in particular, it was restricted to three or five neighbouring cells). This condition artificially infringed the actual symmetry of the interaction and was equivalent to the superposition of an effective external field having a period with respect to the cells, which led to a pattern with two $\pi$-electron bands. The analysis showed[63] that the polyene illustrated in Fig. 3 possess a mirror-rotational twofold axis and that, in terms of the SCF approximation, the $\pi$ bands (filled and vacant) in a long polyene should adjoin in this case. In order to obtain this result, the authors[62] should have taken into account in their calculation a much larger number of neighbouring cells, since the Coulombic interaction weakens very slowly over large distances.

## III. THE INTERACTION BETWEEN ELECTRONS AND THE NATURE OF THE GROUND STATE OF CBP MACROMOLECULES

In a number of studies, an attempt was made to attribute the pronounced maximum in the absorption spectra of polyenes to the plasma vibrations of $\pi$ electrons. A large system with a regular structure can be excited to a state with regular changes in electron density at the atoms, which are characterised by a spatial period (wavelength) and frequency (energy) of the vibrations, referred to as the plasma vibrations. From the standpoint of the methods of quantum chemistry, plasma excitations are not fundamentally new types of excitations: their energies may be calculated in terms of the PPP approximation. Since the latter is fairly cumbersome when applied to large systems, other methods are effective in this instance: the random phase approximation (RPA), methods involving density matrices or Green functions, etc. The considerable similarity of the PPP and RPA approximations was discovered in calculations on small molecules where both approximations led to virtually identical energies and oscillator strengths for the excited states[64]. The relation between the PPP method and the plasma or RPA approximation has been analysed by Mestechkin[65].

It has been found[66,67] that, in one-dimensional systems of the type of polyene, the plasma vibration frequencies start from zero (in a polyene with equal bond lengths) or from the gap $\Delta E_{alt}$ (in a polyene with alternation). The specific features of one-dimensional systems were manifested by the absence of distinct plasma vibration frequencies, in contrast to a three-dimensional metal, where the plasma vibration frequencies have energies of the order of several eV and can be distinguished from other excitations. The calculations[66,67] were based on the SCF approximation for the ground state, which predetermined the resulting spectrum of plasma excitations.

The study of spin excitations in a polyene, where the spin density changes regularly at the atoms (the $\pi$-electron density remains unity) revealed the instability of the SCF state of the system in relation to the transition to an energetically more favourable state with alternating spin densities at the atoms[68]. In order to describe such a state, it was necessary to go outside the framework of the SCF approximation or the Hartree–Fock approximation in which two electrons with opposite spins occupy the same molecular orbital. Quantum chemistry already had at its disposal the corresponding approximate methods, but these were used mainly for the calculation of spin densities in radicals[2]. We have in mind primarily the method of alternant molecular orbitals (AMO) proposed by Löwdin[69,70] for the calculation of the electronic structures of molecules and crystals. The ideas concerning the distribution of electrons with different spins in different molecular orbitals used by Löwdin were applied for the first time by Hyleraas[71] in calculations on the helium atom and by Weinbaum[72] in calculations on the hydrogen molecule. The AMO method is also known as the method of different orbitals for different spins (DODS).[73] The DODS and AMO methods have been used in various calculations of the

electronic structures of solids [74-78] and conjugated systems [2,79]. The relation between the AMO method and the method of geminals was analysed by Kapuy [80]. Certain aspects of these methods have been discussed by Larson [81,82]. In all methods of the AMO type, allowance for the Coulombic repulsion of two electrons with different spins in the same atom is important. As a result, electrons with different spins "avoid" one another, which reduces the energy and favours the appearance of a spin structure of the antiferromagnetic type.

A generalised Hartree–Fock method (GHFM), which is a version of the AMO method adjusted for self-consistency, has been proposed [83,84] for the investigation of the electronic structures of long molecules with conjugated bonds. The Hamiltonian of the system of $\pi$ electrons for a cyclic polyene $(CH)_{2N}$ has the following form in terms of secondary quantisation†:

$$H_{\text{Hub}} = \alpha_0 \sum_{n\sigma} c^+_{n\sigma}c_{n\sigma} - \beta \sum_{n\sigma} (c^+_{n\sigma}c_{n+1,\sigma} + c^+_{n+1,\sigma}c_{n\sigma}) + \frac{\gamma}{2}\sum_{n\sigma} c^+_{n\sigma}c_{n\sigma}c^+_{n,-\sigma}c_{n,-\sigma}. \quad (7)$$

Here $\alpha_0$ is the Coulombic integral in the Hückel method, $-\beta$ the resonance integral of the C–C bond ($\beta > 0$), $\gamma < 0$ the parameter of the Coulombic repulsion of two $\pi$ electrons in a single carbon atom, and $c^+_{n\sigma}(c_{n\sigma})$ are the operators for the generation (annihilation) of an electron in the $n$th atom in the state with the $\varphi_n(r)$ basis function and the spin $\sigma = \pm 1/2$. The Hamiltonian defined by Eqn.(7) is called Hubbard's Hamiltonian [85] and differs from the PPP Hamiltonian defined by Eqn. (17) by the absence of terms with long-range Coulombic interaction. The use of Hubbard's Hamiltonian [Eqn. (7)] leads to a qualitatively correct description of the properties of polyene, although allowance for long-range Coulombic interaction may be important for other systems [86] (see Section VI below).

In terms of the GHFM approximation with the Hamiltonian defined by Eqn. (7), the variational wave function for the ground state of the polyene depends on the single variational parameter $\delta$ and has the following form:

$$|\Phi\rangle = \prod_{\sigma,|l|\leqslant\nu} f^+_{l\sigma}|0\rangle, \quad f^+_{l\sigma} = c^+_{l\sigma}\cos\theta_l + \lambda(\sigma)\, a^+_{l+N\sigma}\sin\theta_l, \quad (8)$$

where $\theta_l$ is defined by the formula

$$\sin 2\theta_l = \gamma\delta/[(\gamma\delta)^2 + 4\beta^2\cos^2(\pi l/N)]^{1/2}.$$

The operators $f^+_{l\sigma}$ correspond to the generation of an electron in the molecular orbital specified by the GHFM and are expressed in terms of the operators $a^+_{l\sigma}$ for the generation of an electron in the molecular orbital specified in the SCF approximation, the latter orbitals having the following form:

$$\psi^l_\sigma(r) = \frac{1}{\sqrt{2N}}\sum_n \exp(i\pi ln/N)\,\varphi_n(r)\sigma,$$

where $\delta$ is the spin function. The operators $a_{l\sigma}$, $c_{n\sigma}$, and $f_{l\sigma}$ are related by the following expressions:

$$c_{n\sigma} = \frac{1}{\sqrt{2N}}\sum_l \exp(i\pi ln/N)\, a_{l\sigma},$$
$$c_{n\sigma} = \sum_{l=-\nu}^{\nu} c^l_{n\sigma} f_{l\sigma} + \sum_{l=-\nu}^{\nu} c^{l+N}_{n\sigma} f_{l+N,\sigma}, \quad (9)$$
$$\nu = \frac{N-1}{2}.$$

†There are a few explanatory comments on secondary quantisation in quantum chemistry in the present authors' previous review [1].

Here the coefficients $c^l_{n\sigma}$ and $c^{l+N}_{n\sigma}$ are defined by the formulae

$$c^l_{n\sigma} = \frac{1}{\sqrt{2N}}[\cos\theta_l \exp(i\pi ln/N) + \lambda(\sigma)\sin\theta_l \exp(i\pi n(l+N)/N)],$$
$$c^{l+N}_{n\sigma} = \frac{1}{\sqrt{2N}}[-\lambda(\sigma)\sin\theta_l \exp(i\pi nl/N) + \cos\theta_l \exp(i\pi n(l+N)/N)], \quad (10)$$

where $\lambda(\sigma) = 2\sigma$ ($\sigma = \pm 1/2$), which corresponds to the ground state with alternation of spin densities at the atoms; the spin density at the $n$th atom is

$$\langle\Phi|(c^+_{n,1/2}c_{n,1/2} - c^+_{n,-1/2}c_{n,-1/2})|\Phi\rangle = -(-1)^n 2\delta. \quad (11)$$

This state will be conventionally referred to as the state with spin waves (SW). As will be shown below (Section III), in a long polyene this state has an antiferromagnetic spin structure, although the spin densities at the atoms disappear after the projection of the function (8) on the state with the total spin $S = 0$.

When $\lambda(\sigma) = 1$, Eqns. (8)–(10) define the state which we shall conventionally call the state with charge waves (CW). It may become the ground state for quasi-one-dimensional systems when account is taken in the Hamiltonian of terms with $\gamma_{mn}$, which will be described below (in Section VI).

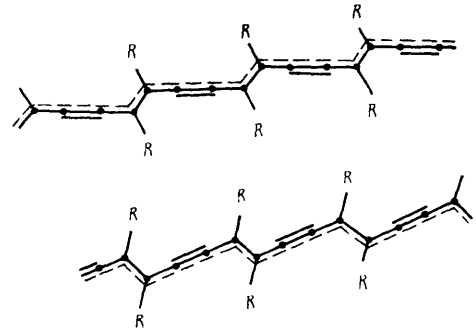



**Figure 4.** Schematic illustration of continuous conjugation (dashed lines) in the macromolecules of a polydiacetylene single crystal. The additional continuous lines indicate triple bonds.

The parameter $\delta$ for the polyene is determined from the equation

$$\frac{p}{2N}\sum_{l=-\nu}^{\nu}[(p\delta)^2 + \cos^2(\pi l/N)]^{-1/2} = 1, \quad p = \gamma/(2\beta), \quad (12)$$

which always has a solution $\delta \neq 0$. The molecular orbital energies are given by an expression of the type

$$E_{l\sigma} = \alpha_0 + \gamma/2 \pm [(\gamma\delta)^2 + 4\beta^2\cos^2(\pi l/N)]^{1/2}. \quad (13)$$

In the ground state, all the levels are filled, which corresponds to the minus sign before the root in Eqn. (13), so that the energy of the first electronic transition assumes the following form in terms of the GHFM approximation:

$$\Delta E(N) = 2[(\gamma\delta)^2 + 4\beta^2\cos^2(\pi\nu/N)]^{1/2}. \quad (14)$$

When $\beta = 2.4$ eV and $\gamma = 5.42$ eV, Eqn. (14) describes satisfactorily the energies of the first transitions in polyenes (Fig. 1). The value of $\gamma$ adopted is smaller by a factor of ~2 than that of $\gamma_{nn}$ in the PPP method, which is a consequence of the use of the approximation $\gamma_{mn} = 0$ (see Section VI). It follows from Eqn. (14) that $\Delta E_\infty = 2\gamma\delta$ when $N \to \infty$.

Recent experiments on the absorption of light by polydiacetylenes (PDA)[87] showed that $\Delta E_\infty \simeq 2$ eV for these polymers, which is in full agreement with the fact that the PDA macromolecule is in essence a polyene chain in which each fourth bond is somewhat shortened and close in properties to a triple bond (Fig. 4) owing to the presence in this bond of an additional pair of $\pi$ electrons in a molecular orbital at right angles to the polyene $\pi$-electron system corresponding to continuous conjugation in the polymer. The shortening of the individual bonds does not affect the nature of the ground state and the CBP absorption spectra, which is confirmed yet again by the example of PDA.

The optical gap $\Delta E_\infty$ in the absorption spectrum is virtually identical with the activation energy or the semiconductor gap of the CBP. For polymers of the type of a polyene[88] and crystalline PDA[89], it was found that the electrical conductivity $\Omega$ has a temperature dependence typical for an intrinsic semiconductor:

$$\Omega = \Omega_0 \exp(-E_{act}/(2kT)),$$

with an activation energy $E_{act} \simeq \Delta E_\infty \simeq 2$ eV. The activation energy for photoconduction in PDA[89] is also close to $\Delta E_\infty$.

## IV. THE SPIN STRUCTURE OF CBP MACROMOLECULES

In the discussion of the spin properties of CBP, we shall note in the first place that the function of the $\pi$ electrons of the polyene $|\Phi\rangle$ [see Eqns. (8)–(10)] with $\lambda(\sigma) = \sigma$ is an eigenfunction of the operator of the $z$-component of the total spin $\hat{S}_z$ with the eigenvalue $S_z = 0$, but is not an eigenfunction of the operator of the square of the total spin $\hat{S}^2$. This is a deficiency of the approximation, because the ground state should have a definite spin and, as a rule, this spin is zero (the singlet state). The average values of the components of the total spin in the $|\Phi\rangle$ state are zero:

$$\langle\Phi|\hat{S}_x|\Phi\rangle = \langle\Phi|\hat{S}_y|\Phi\rangle = \langle\Phi|\hat{S}_z|\Phi\rangle = 0,$$

but the average value of the square of the total spin is not zero[90]:

$$\langle\Phi|\hat{S}^2|\Phi\rangle \sim N.$$

One can say that in this sense $|\Phi\rangle$ is a state isotropic with respect to spin but not a singlet state. The variational solution for $|\Phi\rangle$ is close to the exact state with respect to energy (see Section VIII) and, in order to make it close to the exact state with respect to spin properties, it is necessary to project $|\Phi\rangle$ on to the state with the spin $S = 0$ or to isolate from $|\Phi\rangle$ the component with the total spin $S = 0$. This can be done in various ways[90–92]. The function $|\Phi_0\rangle$, which depends on a single parameter $\delta_0$ and has a more complex form than $|\Phi\rangle$, has been obtained[90,91]. It was found that in the $|\Phi_0\rangle$ singlet state the total energy, $\delta_0$ and the gap in the spectrum $\Delta E_\infty$ differ from the corresponding values for the $|\Phi\rangle$ state only by an amount $\sim 1/N$ for high values of $N$. It is important to know this in calculations, which can be carried out much more simply with a function of the $|\Phi\rangle$ type. However, the spin properties of the $|\Phi_0\rangle$ and $|\Phi\rangle$ states differ to a greater extent. The spin densities at the atoms in the $|\Phi_0\rangle$ state are zero, so that we have instead of Eqn. (11)

$$\langle\Phi_0|(c^+_{n,1/2}c_{n,1/2} - c^+_{n,-1/2}c_{n,-1/2})|\Phi_0\rangle = 0.$$

Nevertheless the $|\Phi_0\rangle$ singlet state will have an antiferromagnetic spin structure. This is because the average value of the spin correlation operator

$$\hat{K}(m) = \frac{1}{N}\sum_{n=1}^{2N}(\hat{S}_n\hat{S}_{n+m}),$$

where $\hat{S}_n$ is the spin operator at the $n^{th}$ atom, or the spin correlation function

$$K(m) = \langle\Phi_0|\hat{K}(m)|\Phi_0\rangle/\langle\Phi_0|\Phi_0\rangle$$

exhibit the following asymptotic behaviour when $m \to \infty$:

$$K(m) \simeq (-1)^m\delta^2.$$

This result indicates the presence of long-range antiferromagnetic spin order in a long polyene. We may note that the correlation function $K(m)$ has the same form for the $|\Phi\rangle$ and $|\Phi_0\rangle$ states[90,91].

A few other comments may be made concerning the unusual properties of antiferromagnetism in general and for organic molecules in particular. If we consider a small molecule ($H_2$, benzene, etc.), the corresponding correlation function $K(m)$ will be non-zero for any value of $m$ and in any approximation (ranging from the SCF approximation to the exact solution). This demonstrates simply the presence of spin correlation in the molecules, if only as a consequence of the Pauli principle. However, whatever the form of $K(m)$, it would be incorrect to speak of antiferromagnetism in such small molecules, because antiferromagnetism is in essence a property of a large and even infinite system with a regular steric structure when the spin structure is characterised by an antiferromagnetic long-range order. For example, when $K(m) \simeq (-1)^m \times$ const. for $m \to \infty$ in a system as large as in our case, we have an antiferromagnetic long-range spin order. For $K(m) \simeq$ const. and $m \to \infty$, we would have a ferromagnetic long-range spin order. The case where $K(m) = 0$ for $m \to \infty$ corresponds to the state without a spin structure and without a long-range spin order.

It would be incorrect to assume that the antiferromagnetic spin structure in long polyenes and other CBP macromolecules appears as a result of the application of the AMO method for which such a structure is typical. The AMO method is not optimal for the description of any alternant system with conjugated bonds. The method leads to a decrease of energy only for small molecules (where the concept of antiferromagnetism has no significance) or for large quasi-one-dimensional systems of the type of polyene, polyacene, etc. (see Section VII below). For the two-dimensional network of graphite the AMO state is unfavourable as regards energy[93]. For two- and three-dimensional systems, the parameters of the Hamiltonian defined by Eqn. (7) must satisfy very rigorous requirements to make a state of the AMO type favourable. These conclusions are in full agreement with the finding that in nature antiferromagnetism is an exception rather than the rule and at the same time leads to the conclusion that antiferromagnetism is a property characteristic of quasi-one-dimensional systems.

For small molecules, the state with a function of the AMO type is energetically favourable mainly as a consequence of the spin projection procedure. For example, the AMO state for $H_2$ or for the ethylene $\pi$ electrons is favourable only when special relations obtain between the parameters of the Hamiltonian, while the energy of the state with a singlet component of the AMO function for these molecules is always smaller than the energy of the state in the MO SCF approximation.

For large systems, the AMO energy also falls after spin projection. However, it has been shown[91] for a polyene that the energy of a large system decreases after spin projection by the constant $C_0 > 0$, which is independent of the number of electrons in the system $N$. As a result, it is found that, when the AMO method (without projection) is unfavourable compared with the MO SCF method, which is usually the case for two- and three-dimensional systems, then spin projection does not correct the situation. In fact, if we suppose that $E$(MO) and $E$(AMO) are the energies of a system of $N$ electrons in the MO and AMO methods without spin projection and that

$$E\,(\mathrm{MO}) \equiv \varepsilon\,(\mathrm{MO}) \cdot N < E\,(\mathrm{AMO}) \equiv \varepsilon\,(\mathrm{AMO}) \cdot N,$$

where $\epsilon$ is the energy per particle in both methods, spin projection diminishes the right-hand side of the inequality by the constant $C_0 > 0$, but does not infringe the inequality. We always have

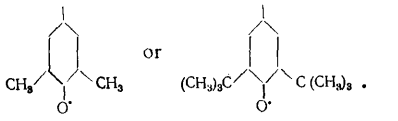
$$\varepsilon\,(\mathrm{MO}) \cdot N < \varepsilon\,(\mathrm{AMO}) \cdot N - C_0,$$

because

$$\varepsilon\,(\mathrm{MO}) < \varepsilon\,(\mathrm{AMO}) - C_0/N$$

for fairly large values of $N$.

The antiferromagnetic spin structure in CBP molecules is a consequence of the mutual repulsion of electrons with different spins in the same atom. If these two electrons did not repel one another (in conformity with the Coulomb law) and effectively attracted one another (which might be promoted by an electron–phonon interaction or some other interaction), we would obtain a superconductor and not an antiferromagnetic material. Since electron repulsion in the CBP marromolecules is considerable, the introduction of side groups with a high polarisability does not transform electron repulsion into attraction[94]. For this reason, the mechanism of superconduction proposed by Little[4] does not operate in CBP macromolecules. Antiferromagnetism in hydrocarbons is a fairly unexpected property, but unfortunately so far it has been found to be fairly useless. However, one cannot rule out the possibility that the spin structure may be "manifested" following the introduction of side groups into the polyene chain. These may be phenoxy-groups:



If, for example, phenyl substituents in polyphenylacetylene (PPA) are replaced, if only partially, by these groups so that the latter are linked to only even (or only odd) atoms of the polyene chain, then a macromolecule of this kind should become ferromagnetic, because all the unpaired spins of the phenoxy-groups are polarised in the same direction via the central chain. Organic ferromagnetic substances are discussed in greater detail in Section XII.

## V. COMPETITION BETWEEN TWO TYPES OF STATES—WITH ALTERNATING BOND LENGTHS AND WITH SPIN WAVES

We may note that the nature of the ground state of a polyene depends significantly on semiempirical parameters. For self-consistent values of the parameters of the polyene, it was actually found that $\Delta E_{\mathrm{alt}} \ll \Delta E_\infty(\mathrm{GHFM}) \simeq \Delta E_\infty$. The state with spin waves was then found to be energetically more favourable as a result of taking into account the significant contribution of the correlation energy. Bearing in mind other quasi-one-dimensional systems, it is natural to formulate problems concerning the possibility of a situation in which the alternation of bond lengths is favourable and concerning the coexistence of states of two types. For the $\pi$ electrons of a long polyene with Hubbard's Hamiltonian and an elastic $\sigma$-skeleton at the temperature $T = 0$, these problems have been solved by Popov[95] and Falikov and Harris[96] in terms of the GHFM approximation. It was found that the state with alternating bond lengths and a gap $\Delta E_{\mathrm{alt}}$ is more favourable energetically when interactions between electrons and atomic vibrations predominate in the chain or when the inequality

$$\gamma/(2\beta) < 4\beta'^2/(\beta k_1). \tag{15}$$

holds. If Coulombic repulsion between electrons is more significant in the chain or

$$\gamma/(2\beta) > 4\beta'^2/(\beta k_1), \tag{16}$$

an antiferromagnetic state obtains with identical bond lengths and the gap $\Delta E_\infty$(GHFM). In infinitely long chains, either type of state may obtain depending on the relative values of the parameters: there is no coexistence between the states of the two types. Since formula (16) holds for conjugated hydrocarbons with a large store of energy,, the nature of the ground state will be determined by the electron interaction and, despite the appreciable differences between bond lengths, which usually alternate by virtue of boundary effects, mainly the state with spin waves arises in not unduly long polyenes; this can also be concluded in view of the similarity of the energy of the first electronic transition $\Delta E(N)$ to $\Delta E_\infty$ for not very large values of $N$ (Fig. 1). These conclusions concerning the competition between the two types of states have been extended to non-zero temperatures[97].

## VI. THE INFLUENCE OF THE LONG-RANGE COULOMBIC INTERACTION ON THE PROPERTIES OF CBP MACROMOLECULES

Fukutome[98] showed that the long-range Coulombic interaction in long CBP molecules can lead to a ground state with spin waves (SW) or with charge waves (CW). However, the energies of these two types of ground states were not calculated, so that it remained unknown which type actually obtains.

In order to investigate this problem, the present authors[86] used the variational function of the GHFM approximation (Eqn. (8)] for a cyclic polyene with a PPP Hamiltonian:

$$H_{\mathrm{PPP}} = H_{\mathrm{Hub}} + \frac{1}{2}\sum_{\substack{mn\\(m\neq n)}}\sum_{\sigma\sigma_1}\gamma_{mn}c^+_{m\sigma}c_{m\sigma}c^+_{n\sigma_1}c_{n\sigma_1} - \sum_{mn}\sum_{\sigma}\tilde{\gamma}_{mn}c^+_{n\sigma}c_{n\sigma} + \frac{1}{2}\sum_{\substack{mn\\(m\neq n)}}\tilde{\tilde{\gamma}}_{mn}, \tag{17}$$

where $H_{\mathrm{Hub}}$ is Hubbard's Hamiltonian [Eqn. (7)], $\gamma_{mn}$ are the parameters of the Coulombic repulsion of the electrons in the $m$ and $n$ atoms, $\tilde{\gamma}_{mn}$ are the parameters of the attraction of an electron from the $n$ atom to a positive $m$ ion, and $\tilde{\tilde{\gamma}}_{mn}$ are the parameters of the repulsion of $m$ and $n$ ions. In terms of the PPP approximation, all the parameters with identical $m$ and $n$ are equal[99]:

$$\gamma_{mn} = \tilde{\gamma}_{mn} = \tilde{\tilde{\gamma}}_{mn}.$$

As noted above, function (8) depends only on the single parameter $\delta$ and describes a state of the SW type when $\lambda(\sigma) = 2\sigma$ and a state of the CW type when $\lambda(\sigma) = 1$. The total average energy of the ground state $E(\mathrm{PPP}, \delta)$ depends on $\delta$ and the parameters of the PPP Hamiltonian, only one term in the expression for the total energy depending on the choice of $\lambda(\sigma)$:

$$E(\mathrm{PPP}, \delta) = A_0 - WB_0^2. \qquad (18)$$

where $A_0$ and $B_0$ are known functions and $W = 1$ when $\lambda(\sigma) = 2\sigma$ (SW type) or $W = 4M - 1$ when $\lambda(\sigma) = 1$ (CW type), $M$ being the Madelung sum for the chain:

$$M = -\sum_{t=1,2,\ldots} (-1)^t \gamma_{m+t,m}/\gamma > 0.$$

Analysis of Eqn. (18) for the total energy yields the following criterion of the type of the ground state: the SW type obtains for $M < 0.5$ and the CW type obtains for $M > 0.5$. This criterion, which is independent of $\delta$, can be understood: when $M$ is fairly large ($M > 0.5$), it is favourable for the systems to pass to a state with charge waves, since the gain in the Coulombic energy from the alternating charges, which is proportional to $M$, will be fairly large.

For Hubbard's Hamiltonian [Eqn. (7)], $M = 0$ and the ground state is always of the SW type. For the PPP Hamiltonian [Eqn. (17)], which is closer to the real Hamiltonian, $M$ depends both on the geometrical configuration of the chain and on the type of the semiempirical relation for $\gamma_{mn}$. It was found that, for many real configurations of the polyene chain and when the generally accepted formulae are used for $\gamma_{mn}$,[100,101] $M < 0.5$ is always obtained. This implies that the ground state of a long polyene has a structure with spin waves. Furthermore, the size of the gap in the spectrum of one-particle excitations proved to be[86] $\Delta E_\infty \simeq 2$ eV [in good agreement with experiment and with the results based on Hubbard's model (Section III)] when the Nishimoto–Mataga formula[101] is used:

$$\gamma_{mn} = 1.2935\,\gamma/(1.2935 + R_{mn}), \quad \gamma = 11.13\ \mathrm{eV}.$$

Hence one may conclude that Hubbard's model with its parameters gives a correct qualitative description of the experimental situation in polyenes and apparently in other conjugated macromolecules.

We may also note that the dependence of the type of ground state on $M$ makes it possible to formulate a hypothetical situation where the nature of the ground state and of its characteristic properties may change in a macromolecule following an alternation in its geometrical configuration (under the influence of external forces).

## VII. THE ELECTRONIC STRUCTURES OF CERTAIN CBP

The electronic structures of a number of quasi-one-dimensional systems of hydrocarbons and of the planar two-dimensional network of graphite have been calculated in terms of the GHFM approximation with Hubbard's Hamiltonian[90,102].

### 1. Polyacenes

The first members of the series of polyacenes in which the number of rings is $N = 2$, 3, 4, 5, and 6 are respectively naphthalene, anthracene, tetracene, pentacene, and hexacene. The experimental spectra[103] appeared to indicate the existence of a finite limit to the first electronic transition energy. A group of four atoms $a$, $b$, $c$, and $d$ is repeated periodically in the polyacene molecule (Fig. 5), so that the system is quasi-one-dimensional in the direction of an increase in the number of rings. In terms of Hückel's approximation, among the four $\pi$-electron bands two are filled and the third (vacant) adjoins the second closely. The alternation of the lengths of the outer bonds does not reduce the energy and does not lead to the appearance of a gap between the second and third bands[104]. However, transition to the state with spin waves is energetically favourable and in the ground state two bands of levels are filled:

$$E_l^{1,2} = \gamma/2 - [(\gamma\delta)^2 + [\beta_2 \pm \sqrt{4FF^* + \beta_2^2}]^2/4]^{1/2},$$
$$F \equiv \beta_1 (1 + \exp(i2\pi l/N)), \quad l = 1, 2, \ldots N.$$

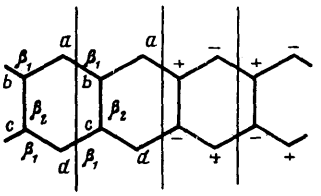



**Figure 5.** The polyacene cell with the designation of the opposite (+ and −) directions of the spin at carbon atoms and with an indication of the resonance integrals.

The third, vacant band is separated from the second (for $N \to \infty$) by a gap $\Delta E_\infty = 2\gamma\delta$ where $\delta$ is determined from the corresponding self-consistency equation. According to estimates, $\Delta E_\infty \simeq 1$–2 eV in polyacenes, which does not conflict with experimental data[103]. The antiferromagnetic spin structure in very long polyacenes (the opposite directions of the spins in the atoms are indicated by the plus and minus signs for atoms belonging to two of the periodically repeated polyacene cells in Fig. 5) must be understood in the same sense as for polyenes (see Section IV). Polyacenes are an example of quasi-one-dimensional systems differing from a linear chain of atoms.

### 2. Graphite

When aromatic rings are added in different directions and not in a single direction as in polyacenes, we obtain the planar hexagonal network of two-dimensional graphite. The properties of two- and three-dimensional graphite have been examined in detail in a review[105]. Here we shall consider the example of two-dimensional graphite in order to show how the "dimensionality" of the system is manifested in the calculation of its properties. It has been shown[90,102] that the two-dimensional network of graphite ($2N^2$ atoms) may exist in a state of the SW type if the GHFM self-consistency equation

$$\frac{\gamma}{2N^2}\sum_{j,k}[(\gamma\delta)^2 + |\varepsilon(jk)|^2]^{-1} = 1,$$
$$\varepsilon(jk) = \beta(1 + \exp(i2\pi k/N) + \exp(i2\pi j/N)),$$

has a solution $\delta \neq 0$. The function $|\epsilon(jk)|$ becomes zero in accordance with a linear law at two points in the region of variation of $(j, k)$, so that for double summation (a two-dimensional integral) these points are non-singular when $\delta \to 0$. The existence of a solution $\delta \neq 0$ therefore requires the fulfilment of the condition

$$\frac{\gamma}{2N^2}\sum_{j,k}|\varepsilon(j,k)|^{-1} \geqslant 1.$$

Hence we find that transition to a state with a spin structure is possible only for parameters satisfying the condition

$$\gamma/(2\beta) > (\gamma/2\beta)_{\text{crit}} \simeq 1.13, \qquad (19)$$

while in quasi-one-dimensional systems such a transition is possible for any parameters $\gamma/\beta \neq 0$. The "dimensionality" of the system is manifested in this sense.

The parameters of graphite are close to those of polyenes, for which the approximate equation

$$\gamma/(2\beta) \approx (\gamma/2\beta)_{\text{crit}}$$

holds. This leads to the following conclusions.

(1) The parameters of the electron interaction in graphite apparently do not satisfy inequality (19), so that the antiferromagnetic state does not occur (in agreement with experimental data).

(2) On the one hand, the closeness of the parameter $\gamma/(2\beta)$ to the critical value prevents conflict between the theory and experiment and, on the other, it indicates that graphite could make a transition to an antiferromagnetic state if it were possible, say, to extend somewhat all the bonds, to diminish $\beta$, and to satisfy inequality (19).

## 3. Cumulenes

Cumulenes are linear $=(C=C)_N=$ macromolecules consisting of carbon atoms and constituting in essence a third form of carbon (in addition to diamond and graphite [106-112]). In cumulene there are two mutually perpendicular subsystems of $\pi$ electrons (coupled systems of $2p_x$ and $2p_y$ functions; $z$ is the molecular axis). Each is analogous to the $\pi$-electron system of a polyene.

The electronic structure of cumulenes has been calculated [113] in terms of the SCF approximation on the hypothesis that the bond lengths alternate. However, as in polyenes, the effects of different bond lengths in cumulenes cannot play an appreciable role compared with the effects of electronic interactions. According to calculations in terms of the GHFM approximation [90,102], each of the $\pi$-electron subsystems of a long cumulene with identical bond lengths exists in a state with an antiferromagnetic spin structure and a gap in the spectrum of one-particle excitations, allowance for the Coulombic and exchange integrals $\gamma_{xy} = \langle xx|yy\rangle$ and $\tilde{\gamma}_{xy} = \langle xy|xy\rangle$ at each carbon atom leading to a correlation between the spin structures of these subsystems. As a result, the one-particle levels of each of the $\pi$-electron subsystems have the following form:

$$E_l = \gamma_{xy} \pm (\gamma - \tilde{\gamma}_{xy})/2 \pm [(\gamma \pm \tilde{\gamma}_{xy})^2\delta^2 + 4\beta^2\cos^2(\pi l/N)]^{1/2},$$

where the filled orbitals have the minus sign before the root and the vacant orbitals have the plus sign. The size of the gap in the spectrum of a long cumulene is

$$\Delta E_\infty = 2(\gamma \pm \tilde{\gamma}_{xy})\delta,$$

where $\delta$ is determined from the "polyene" Eqn. (12) but with another parameter: $p = (\gamma + \tilde{\gamma}_{xy})/(2\beta)$.

In order to estimate $\Delta E_\infty$, we shall assume that $\gamma = 5.42$ eV (as in polyenes), $\beta = k\beta_0$, where $k \simeq 1.5$, which corresponds, according to Streitwieser [114] to the C=C bond length in cumulene ($R = 1.28$ Å), [110,113] and $\beta_0 = 2.4$ eV. The value $\tilde{\gamma}_{xy} = 0.62$ eV was estimated from the formula $\tilde{\gamma}_{xy} = (\gamma_{xx} - \gamma_{xy})/2$, where the parameters $\gamma_{xx}$ and $\gamma_{xy}$ were found by analysing the spectra of atomic carbon and carbon ions [115,116]. We obtain as a result $\Delta E_\infty \simeq 1.2$ eV, in agreement with experiment [113] [$\Delta E_\infty$(exp) = 0.8–1.0 eV]. The state with spin waves ($\delta \neq 0$) is more favourable than the usual state ($\delta = 0$) for molecules with $N \geqslant 11$, i.e. for cumulene chains containing more than 22 carbon atoms.

In the crystalline phase, cumulene chains may contain several hundreds of atoms [110]. The results presented in Section V showed that the presence of an antiferromagnetic state in a long cumulene rules out the possibility of the alternation of bond lengths, since the bond lengths in long cumulenes are identical in the region remote from the ends of the chains.

It was convenient to use cumulenes for the investigation of the antiferromagnetic spin structure by the method of inelastic scattering of polarised neutrons, because they do not contain hydrogen atoms, whose nuclei interact strongly with neutrons. However, such studies are at present outside the scope of the available experimental technique.

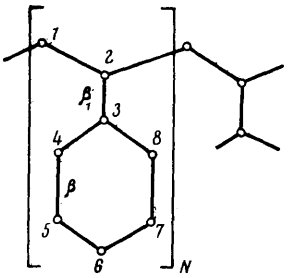



**Figure 6.** The elementary unit of polyphenylacetylene.

## 4. Polyphenylacetylene

The ground state of a long PPA molecule (Fig. 6) is characterised by an antiferromagnetic spin structure both in the central (polyene) conjugation chain of PPA, and in the benzene rings [117,118]. In conformity with the number of carbon atoms, there are in the elementary unit of PPA eight energy bands $E_{kl\sigma}$ ($k = 1,2,\ldots,8$), where $l = 1,2\ldots,N$ is the number of the level in the band and $N$ is the number of PPA units. For electrons with different spins and different values of $\sigma$, the molecular orbital energies are different (there is no such difference in polyenes, cumulenes, and polyacenes). The bands of cyclic PPA with $N = 17$ are illustrated schematically in Fig. 7. In the ground state, the levels of the bands with $k = 1$, 2, 3, and 4 are filled. Depending on the degree of conjugation of the benzene rings with the continuous conjugation chain (or on the resonance integral $\beta_1$; see Fig. 6), the limiting energy of the first one-particle excitation in the PPA

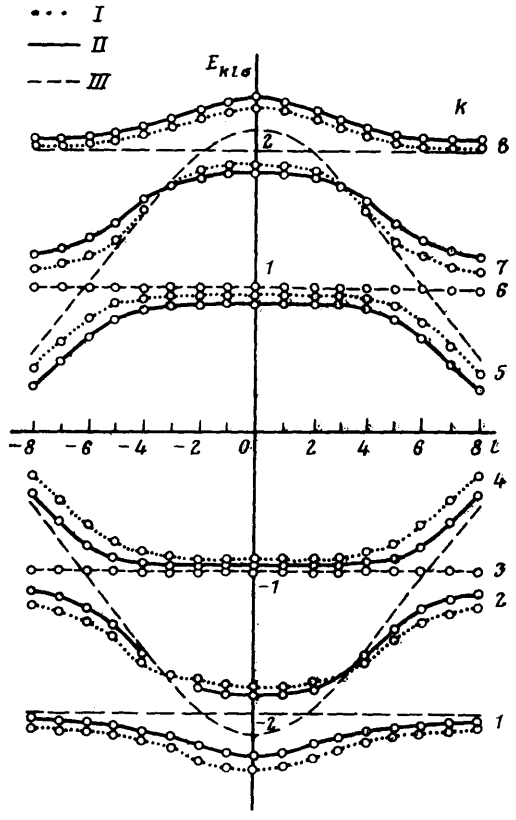



Figure 7. The one-electron energies (in units of $\beta$) $E_{kl\sigma}$ (circles) of cyclic PPA with $N = 17$ and $\beta_1/\beta = 0.875$ according to Refs. 117 and 118; $\sigma = -1/2$ (I) and $\sigma = 1/2$ (II); lines (III) correspond to $\beta_1 = 0$.

macromolecule changes from $\Delta E_{\infty}^{\min} = 1.6$ eV ($\beta_1 = \beta$, complete conjugation) to $\Delta E_{\infty}^{\max} = 2.2$ eV ($\beta_1 = 0$) when PPA is converted into a polyene with isolated benzene rings.

## VIII. EXACT METHODS FOR THE INVESTIGATION AND SYSTEMATIC TREATMENT OF EXCITED STATES

Despite the advances achieved in the application of GHFM approximation in order to explain the properties of long conjugated molecules, justified doubts remain about the adequacy of this approximation. In fact, it was known that a quasi-one-dimensional system described by Hubbard's Hamiltonian [Eqn. (7)] has excitations whose energies are not separated by a gap $\Delta E_{\infty}$ and approach the energy of the ground state for $\gamma/\beta \to \infty$, i.e. in the limiting case of isolated atoms. The energies of these states may be obtained by the diagonalisation of the effective Hamiltonian, which is called the Heisenberg spin Hamiltonian [119] and can be obtained from Hubbard's Hamiltonian [Eqn. (7)] for $\gamma/\beta \gg 1$, in the following form:

$$H_{\text{сп}} = \frac{4\beta^2}{\gamma} \sum_n \left( \hat{S}_n \hat{S}_{n+1} - \frac{1}{4} \right), \qquad (20)$$

where $\hat{S}_n$ is the spin operator at the $n$ atom. The eigenfunctions (states) for this Hamiltonian are called homeopolar (for $\gamma/\beta \gg 1$) or quasi-homeopolar (for the real values of the parameters). The spin Hamiltonian method for the description of the excigations of conjugated molecules was proposed by Bulaevskii [120,121]. Kohn [122] and Bulaevskii [120,121] found that the optical transitions from the ground to the quasi-homeopolar states are forbidden or their intensity is low. The GHFM approximation does not yield states of this type; however, it is shown below (Section IX) how triplet states of this type can be obtained in terms of the GHFM approximation.

The reliability of the GHFM approximation, the spin Hamiltonian methods, and other approximate methods was finally elucidated after obtaining the exact solutions for a one-dimensional system with Hubbard's Hamiltonian [Eqn. (7)]. The unidimensionality of the system is important for the exact solutions. Examination of a one-dimensional classical gas consisting of identical solid spheres which can move in only one direction before and after elastic collisions may help to understand the cause of this. By virtue of the energy and momentum conservation laws, when two spheres collide in a single dimension, they can only exchange velocities but cannot alter the values. Consequently in such a system the set of velocities of the spheres does not vary with time, i.e. the distribution function for the spheres with respect to momenta is an integral of motion. The appearance in a one-dimensional system of an additional conservation law analogous to that discussed above ensures the possibility of an exact solution of our quantum problem.

Only a few words need be said about the exact solution; it has been described in greater detail in the review of Ovchinnikov et al. [123]. Using the ideas put forward by Bethe [9], who obtained an exact solution for the ground state spin Hamiltonian [Eqn. (20)], Gaudin [124], Yang [125], and Lieb and Wu [126] obtained an exact expression for the eigenfunction of Hubbard's Hamiltonian [Eqn. (7)]. It has the following form:

$$\Psi(n_1, n_2, \ldots n_N) = \sum_P [Q, P] \exp\left( i \sum_j k_{P_j} n_{Q_j} \right);$$
$$n_{Q_1} \leqslant n_{Q_2} \leqslant \ldots \leqslant n_{Q_N},$$

where $n_Q$ are the coordinates of the electrons (the numbers of atoms in which the electrons are located), $k_{P_j} = k_1, k_2, \ldots, k_n$ is a set of quasi-momenta, which are the quantum numbers for the system, in conformity with the above comments on a one-dimensional gas, $Q = (Q_1, Q_2, \ldots, Q_n)$ and $P = (P_1, P_2, \ldots, P_n)$ are transpositions among the coordinates and quasi-momenta respectively. Furthermore, $[Q, P]$ are coefficients which depend on $Q$ and $P$; they are determined from the Schrödinger equation and the symmetry requirements. The total energy of the system is very simply expressd in terms of the quasi-momenta $k_j$:

$$E = -2\beta \sum_{j=1}^{N} \cos k_j. \qquad (21)$$

However, the quasi-momenta are determined from the solution of a system of transcendental equations and depend on certain quantum numbers. By an appropriate choice of these numbers, it is possible to find sets of quasi-momenta $k_j$ and to calculate the energies of the required states from Eqn. (21).

The exact energy of the ground state for an $N$-atom chain with Hubbard's Hamiltonian [Eqn. (7)] has been found by Lieb and Wu [126]:

$$E = -4N\beta \int_0^{\infty} \frac{\mathcal{J}_1(\omega) \cdot \mathcal{J}_0(\omega)\, d\omega}{\omega(1 + \exp(\omega p))}, \quad p = \frac{\gamma}{2\beta}, \quad N \gg 1.$$

where $\mathcal{J}_0(\omega)$ and $\mathcal{J}_1(\omega)$ are Bessel functions. The results of the exact calculation of the energy of the ground state are compared in Fig. 8 with the GHFM results for different ratios $\gamma/\beta$. We may note that, for real parameters $\gamma/\beta \simeq 2$, the energy gain (GHFM or exact) is small compared with the simple molecular orbital or Hartree–Fock approximation, but the rearrangement of the ground state is significant.

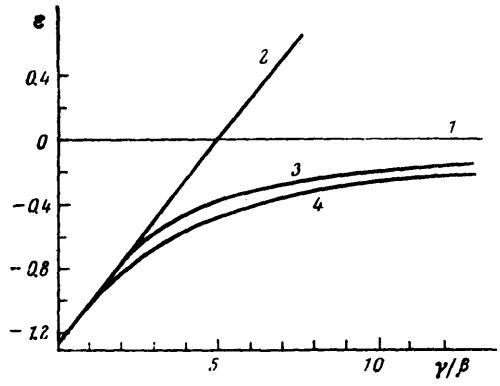



**Figure 8.** The energies of the ground state of the polyene $(CH)_{2N}$ $\pi$ electrons per electron $\epsilon = E/(2N\beta)$ in Hubbard's model as a function of the $\gamma/\beta$ ratio: 1) isolated atoms; 2) Hartree–Fock (MO SCF) method; 3) GHFM; 4) exact solution[127].

Hubbard's model, which is susceptible to an exact solution, makes it possible to carry out a complete qualitative investigation of the excitation spectrum of an $N$-atom model chain. All the states of the system with $\gamma/\beta \gg 1$, i.e. for large distances between the atoms, are subdivided into groups of states with similar energies. The first group consists of $2^N$ states of a quasi-homeopolar type, the energies of which, including the ground state, are also described by the spin Hamiltonian defined by Eqn. (20). For real parameters ($\gamma/\beta \simeq 2$), other approximations or exact methods are preferable. The exact spectrum of triplet excitations of the quasi-homeopolar type has been found by Ovchinnikov[128]. The first energy levels with the numbers $n = 1, 2, \ldots \ll N$ are equivalent:

$$\varepsilon_n^T = \frac{u}{N} n, \tag{22}$$

where

$$u = 4\pi\beta I_1(2\pi\beta/\gamma)/I_0(2\pi\beta/\gamma). \tag{23}$$

Here $I_0$ and $I_1$ are Bessel functions of an imaginary argument. The energy of each triplet excitation [Eqn. (22)] is inversely proportional to the number of atoms $N$ in a continuous conjugation chain and therefore may be smaller than $\Delta E_\infty$, approaching zero with increase of $N$. If $\beta = 2.4$ eV and $\gamma = 5.42$ eV,[84] then $u = 24.5$ Ev. For $\beta$-carotene (in this molecule the light absorption is determined by a linear polyene chain with $N = 22$), experiment gives[129] $\epsilon_1^T$(expt.) = 1.1 eV, while according to Eqns. (22) and (23) we have $\epsilon_1^T = 1.12$ eV. We shall describe below approximate methods for the calculation of $u$ in CBP (Section IX) and the influence of triplet states on the properties of CBP (Sections X and XI).

Apart from triplet states, the first group includes singlet quasi-homeopolar states, whose spectrum resembles that of triplet states (Fig. 9). The energies of the first singlet and triplet excitations are similar:

$$\varepsilon_1^S - \varepsilon_1^T \simeq N^{-3}; \quad N \to \infty.$$

A weak long-wavelength absorption of CBP is associated with the excitation of these singlet states[130]. In estimating the absorption coefficient $k(\omega)$, account was taken of the fact that polymers possess a broad molecular-weight distribution (MWD) in which it is important to know $p(N)$ (the density of macromolecules with a large number of atoms $N$ in a continuous conjugation chain) for the long-wavelength absorption:

$$p(N) = \frac{1}{\bar{N}} \exp(-N/\bar{N}), \tag{24}$$

where $\bar{N}$ is the MWD parameter. Assuming that only the first level $\epsilon_1^S = u/N$, to which corresponds an oscillator strength $f(N) \propto N$ and the line form parameter $\delta(\hbar\omega - \epsilon_1^S)$, is excited in each molecule and averaging with respect to MWD [Eqn. (24)], it is possible to derive the following formula for $k(\omega)$ [130]:

$$k(\omega) \propto \int \hbar\omega\, f(N) \cdot \exp(-N/\bar{N})\, \delta(\hbar\omega - u/N)\, dN. \tag{25}$$

The integration in Eqn. (25) is carried out with the aid of familiar rules for $\delta$-functions. As a result, we obtain the following relation between the absorption coefficient (proportional to the extinction coefficient) and the wavelength $\lambda$ of the absorbed radiation:

$$k(\lambda) = k_0 \lambda^2 \exp(-\lambda/\lambda_0), \qquad \frac{1}{\lambda_0} = \frac{u}{\bar{N}} \frac{1}{2\pi\hbar c}, \tag{26}$$

where $c$ is the velocity of light and $\hbar$ Planck's constant.

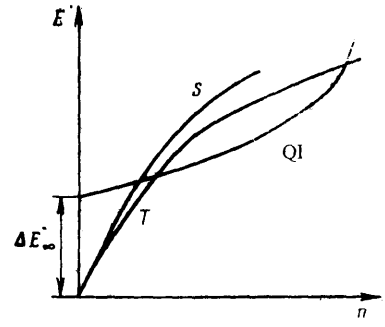



**Figure 9.** Schematic illustration of the energies $E$ of the excited states of a quasi-one-dimensional system; quasi-homeopolar singlet ($S$) and triplet ($T$) levels of the first group; quasi-ionic (QI) levels of the second group; $n$ is the number of the level.

The experimental absorption spectrum for PPA in the wavelength range from 700 to 1500 nm [131] is described with an adequate degree of approximation by Eqn. (26), whence it is possible to determine the ratio $u/\bar{N} \simeq 1.4$ eV. Thus the study of the long-wavelength absorption makes it possible to determine the MWD characteristics for CBP.[130] As will be seen below (Section X), the ratio $u/\bar{N}$ also

determines the paramagnetism of CBP at room temperature [130].

The second group of levels of the Hamiltonian defined by Eqn. (7), which becomes separated for $\gamma/\beta \gg 1$, consists of $N \times 2^N$ quasi-ionic states with excitation energies $\sim\gamma$. For the formation of such states, an electron of one atom must be transferred to another, where an electron is already present, which requires the expenditure of energy $\sim\gamma$ ($\gamma$ is exactly equal to the energy of repulsion of two electrons in the same atom). The resulting pair of charges (+ and −) on different atoms ensures the appearance of conduction, as a result of such excitations and justifies the term "quasi-ionic". This group of levels includes optically active excited states. Single-particle excitations, associated with electron transfer from a filled to a vacant GHFM band, describe very acuurately optically allowed excitations of states in the second group. The exact spectrum of quasi-ionic excitations has been found [132]. It was discovered that the latter have a gap in the spectrum (for $N \to \infty$):

$$\Delta E_\infty(\text{exact}) = \gamma - 4\beta + 8\beta \int_0^\infty \frac{\mathcal{J}_1(\omega)}{\omega} \frac{d\omega}{1+\exp(p\omega)}. \qquad (27)$$

This implies that the GHFM approximation reproduces correctly the situation with a gap in the spectrum of optically allowed excitations of long conjugated molecules. It has been found [128] that, for $\gamma/\beta \to 0$, we have

$$\Delta E_\infty(\text{exact}) \simeq \frac{8(\gamma\beta)^{1/2}}{\pi} \exp\left(-\frac{2\pi\beta}{\gamma}\right), \qquad (28)$$

whereas the GHFM approximation yields for the same limiting case

$$\Delta E_\infty(\text{GHFM}) \simeq 16\beta \exp\left(-\frac{2\pi\beta}{\gamma}\right).$$

The experimental value $\Delta E_\infty \simeq 2.2$ eV for polyenes is satisfactorily reproduced by Eqns. (27) and (28) with the parameters $\beta = 2.4$ eV and $\gamma = 8.5$ eV, which do not differ very greatly from the optimum GHFM parameters.

The third group of levels of the Hamiltonian defined by Eqn. (7), which becomes isolated for $\gamma/\beta \gg 1$, consists of $N(N-1) \times 2^{N-1}$ states with energies $\sim 2\gamma$ and a wave function having doubly ionic structures (with two pairs of + and − charges). The levels of this group (and all other groups) can occur in the visible and ultraviolet parts of the spectrum for real values of the parameters regardless of the number of the group.

We shall examine from the standpoint of this systematic treatment the excited states of the benzene molecule, paying attention to the covalent-ionic structure of the wave function, which were found by the exact numerical solution of the problem of benzene in the π-electron approximation (a six-atom chain) with the PPP Hamiltonian [68,133]. The ground state $^1A_{1g}$, the triplet state $^3B_{1u}$ (3.7 eV) and the singlet state $^1B_{2u}$ (4.8 eV) are quasi-homeopolar because the wave function of these states includes a contribution of covalent structures. The wave functions of the $^1B_{1u}$ (6.1 eV) and $^1E_{1u}$ (6.8 eV) states include no contributions of covalent structures and are therefore quasi-ionic [68,133]. The experimental excitation energies are indicated in brackets.

## IX. AN APPROXIMATE METHOD FOR THE CALCULATION OF THE SPECTRUM OF TRIPLET EXCITATIONS

The exact methods for the calculation of excitation energies are too complex to be applied to systems more complicated than polyene. Because of this, various approximations are as a rule used for real molecules. An approximate method, based on the calculation of the structure of CBP macromolecule in terms of the GHFM approximation and employing the technique of Green functions in a minimum volume, has been proposed [117,118,134] and applied to PPA and polyene chains (linear and closed). The fact that the Hartree–Fock equation for the Green function of a system of π electrons has solutions for both the ground and excited states is used in essence in this method. The proposed method of calculation is equivalent to the random phase approximation, which was shown by the identity of the secular equations for the excitation spectrum of a one-dimensional chain obtained by the two methods [74,75,117,134]. The study of the secular equations of the method of Misurkin and coworkers [117,134], which are not quoted here because of their cumbersome nature and the large number of new symbols, showed that they make it possible to find the energies of the singlet and triplet excitations of the system.

The energies of singlet excitation $\epsilon_i^S \geqslant E_\infty$. Transitions to these singlet states involve changes in electron density at the atoms and are responsible for the strong absorption in the optical region ($\hbar\omega \geqslant \Delta E_\infty$). The energies $\epsilon_i^S$ can be calculated with satisfactory accuracy in terms of the GHFM approximation as the difference between the energies of the corresponding molecular orbitals. However, the singlet excitations with energies $\epsilon_n^S < \Delta E_\infty$ are not described by this approximate method, so that in practice the only available information about these states has been obtained by exact methods for simple chains of the polyene type [128,132].

The spectrum of low-energy triplet excitations, obtained by the approximate method, is of the same form as that produced by the exact method [see Eqn. (22)]:

$$\epsilon_n^T = \frac{u}{N} n, \quad n = 1, 2, \ldots \ll N,$$

where $u$ is found by the numerical solution of the corresponding secular equations. These equations have been obtained and solved for cyclic and linear polyenes and for a cyclic model of the PPA macromolecule [117,118,134]. As an illustration, we quote below the secular equation for cyclic PPA with $N$ elementary units:

$$\sum_{m=1}^{8} A(mn \mid u) \cdot f(m) = f(n), \quad n = 1, 2, \ldots 8.$$

This system of linear equations has a non-trivial solution for $f(n)$, i.e. $f(n) \neq 0$, when one eigenvalue of the $A(mn|u)$ matrix is unity. From this condition, it is possible to find $u$ by means of a computer. The $A(mn|u)$ matrix has the following form:

$$A(mn \mid u) = A_1(mn \mid u) + \Delta(mn) \cdot A_2(mn \mid u),$$

$$A_1(mn \mid u) = -\frac{\gamma}{N} \sum_l \sum_{k=1}^{4} \sum_{p=5}^{8} \left[ \frac{c_{m\eta}^{k,l+1} c_{m\mu}^{pl} c_{n\eta}^{k,l+1} c_{n\mu}^{pl}}{E_{k,l+1,\eta} - E_{pl\mu} - u/2N} + \frac{c_{m\eta}^{p,l+1} c_{m\mu}^{kl} c_{n\eta}^{p,l+1} c_{n\mu}^{kl}}{E_{kl\mu} - E_{p,l+1,\eta} + u/2N} \right],$$

$$A_2(mn \mid u) = -\frac{\gamma}{N} \sum_{k=1}^{4} \sum_{p=5}^{8} \left[ \frac{c_{m\eta}^{k,-\nu} c_{m\mu}^{p\nu} c_{n\eta}^{k,-\nu} c_{n\mu}^{p\nu}}{E_{k,-\nu,\eta} - E_{p\nu\mu} - u/2N} + \frac{c_{m\eta}^{p,-\nu} c_{m\mu}^{k\nu} c_{n\eta}^{p,-\nu} c_{n\mu}^{k\nu}}{E_{k\nu\mu} - E_{p,-\nu,\eta} + u/2N} \right],$$

$$\eta = 1/2, \quad \mu = -1/2,$$

$$\Delta(mn) = 1 - 2(\delta_{n1} + \delta_{m1} - 2\delta_{m1}\delta_{n1}), \quad -\nu \leqslant l \leqslant \nu - 1, \quad \nu = (N-1)/2.$$

Here $m$ and $n$ are the numbers of atoms in the PPA unit ($m, n = 1, 2, \ldots, 8$), $k$ and $p$ are the numbers of filled and vacant MO bands, $l$ is the number of the molecular orbital in the band, and $c_{n\mu}^{pl}$ is the LCAO-MO coefficient for an electron with the spin $\mu = -1/2$ in a molecular orbital with the energy $E_{pl\mu}$. The remaining details and symbols are

described in the relevant papers [117,118]. Similar equations can be obtained and solved for any systems, both periodic and non-periodic: linear CBP, CBP with various defects, etc. The possibility of determining the energies of triplet excitations in long CBP molecules is particularly important, because properties of CBP such as paramagnetism at room temperature and catalytic properties are associated with these triplet states. Comparison of the results of the approximate and exact methods for a polyene with real values of the parameters [117,134] showed that they yield virtually the same values of $\epsilon_n^T$ (to within 6%).

## X. THE NATURE OF THE PARAMAGNETISM IN CBP

The presence of the electron spin (paramagnetic) resonance (ESR) signal is one of the characteristic properties of CBP. [135] The fairly complex dependence of the electronic structure of CBP on the conformation of macromolecules determines the complex nature of the dependence of the ESR signal on many external factors and makes it difficult to describe fully the paramagnetic properties of these polymers. A typical temperature dependence of the paramagnetic susceptibility $\chi$, measured by the ESR method for a PPA specimen, is illustrated in Fig. 10 (curve *1*) [136].

The paramagnetism of CBP is usually attributed to the presence of structural defects in the macromolecular chain [137-139], the presence of charge-transfer complexes (CTC), [140,141] and excitations to biradicals (triplet) states [142]. However, all these paramagnetic states have a formation energy which is too high (1–2 eV) and this precludes an explanation of the sharp increase of the ESR signal intensity on moderate heating in the region of room temperature. In fact, for the formation of biradical states the fragment of the macromolecule must be rotated about the conjugated bond by ~90°, which requires more than 1 eV [143] and leads to a triplet state with an odd number of $\pi$ electrons in each of the resulting fragments. In the condensed phase, this energy expenditure increases owing to steric hindrance. On formation of CTC, an electron is transferred from the highest occupied molecular orbital of one macromolecule to the lowest vacant molecular orbital of another, which requires the same energy expenditure as in the one-particle excitation, i.e. 1.5–2 eV (see Sections III and VII above). Nevertheless, stable paramagnetic defects of this type [137-142] can be formed in the synthesis of CBP and can contribute significantly to paramagnetism at low temperatures.

We may also note that, with increase of temperature, relaxation effects appear in the ESR signal of CBP, which cannot be explained, for example, by the recombination of paramagnetic centres. When the temperature is varied in the range 275–350 K, the ESR signal intensity varies in parallel with temperature, assuming initially an intermediate value, which continues to change slowly as the specimen is maintained at a given temperature. The ESR signal intensity or $\chi(T)$ reaches its limiting value (curve *1* in Fig. 10) after a time of the order of tens of minutes or hours, which depends strongly on temperature.

It has been suggested [144,145] that the thermal population of triplet states [with energies of the type defined by Eqn. (22)] in CBP macromolecules is responsible for a significant contribution to the paramagnetism of CBP at room temperature. A formula for the static paramagnetic susceptibility $\chi_N(T)$ per $\pi$ electron was obtained in the same investigations for a molecule with $N$ atoms in a continuous conjugation chain:

$$\chi_N(T) = \frac{2\mu_B^2 g^2}{kT} \exp\left(-\frac{u}{kTN}\right), \quad \frac{u}{kTN} \gg 1, \tag{29}$$

where $\mu_B = e\hbar/2mc$ is the Bohr magneton, $g = 2$, and $e$ and $m$ are the charge and mass of an electron. In the derivation of Eqn. (29), only the form of the triplet excitation spectrum [Eqn. (22)] was significant. The calculation of $u$ was described above (Section IX). For PPA, $u$ varies from 5.7 $\beta$ for $\beta_1 = \beta$ to 9.65 $\beta$ for $\beta_1 = 0$ (see Fig. 6 and Section VII above) [117,118]. CBP with a long continuous conjugation chain, for which triplet energies are smallest and their populations and contributions to paramagnetism are greatest, are important under the conditions of the thermal population of triplet states. Averaging of the quantity defined by Eqn. (29) with respect to the MWD [Eqn. (24)] for macromolecules with a large number of atoms leads to the following formula for the contribution of thermally excited triplet states to the static paramagnetic susceptibility [144,145]:

$$\chi(T) = \frac{2\mu_B^2 g^2}{kT} n_\pi \left(\pi^2 \frac{u}{\bar{N}kT}\right)^{1/4} \exp\left[-2\left(\frac{u}{\bar{N}kT}\right)^{1/2}\right], \tag{30}$$

where $n_\pi$ is the number of $\pi$ electrons in the CBP conjugation chain per gram.

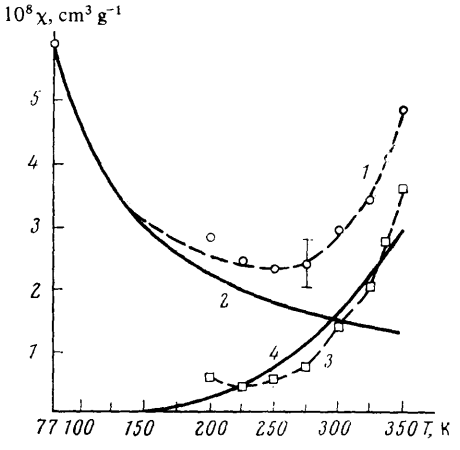



**Figure 10.** Dependence of the static paramagnetic susceptibility $\chi$ of PPA on the temperature T: 1) $\chi^{exp}(T)$ with an indication of the typical experimental error; 2) contribution of paramagnetic defects, $\chi_D = aT^{-1}$; 3) contribution of thermally excited triplet states, $\chi^{exp}(T) - aT^{-1}$; 4) theoretical dependence of the contribution of thermally excited triplet states according to Eqn. (30) with $n_\pi = 1.2 \times 10^{22}$ g$^{-1}$ and $u/\bar{N} = 0.76$ eV.

Since $\chi^{exp} \propto 1/T$ at low temperatures and $\chi^{exp}$ increases with increasing temperature when $T \geqslant 250$ K, $\chi^{exp}(T)$ has been represented [136] by the sum of two contributions with different temperature dependences:

$$\chi^{exp}(T) = aT^{-1} + bT^{-3/4} \exp(-cT^{-1/3}). \tag{31}$$

The first contribution, which obeys the Curie law, is due to different types of stable paramagnetic defects, CTC,

etc., which were discussed above. The contribution defined by the second term of Eqn. (31) is determined by the population of the triplet states and corresponds to Eqn. (30). The Curie constant $a$ was determined from the ESR signal intensity at 77 K where the contribution of the thermally excited paramagnetism is negligible: $a = 4.5 \times 10^{-6}$ cm$^3$ K g$^{-1}$. If the Langevin formula

$$a = n_D g^2 \mu_B^2 S(S+1)/3k$$

is used for $a$ and it is assumed that the paramagnetic defects have the spin $S = 1/2$, then the concentration of defects is $n_D = 6 \times 10^{18}$ g$^{-1}$. This implies that one defect corresponds to ~1000 PPA units.

Analysis showed that the experimental temperature dependence of the contribution of thermally excited triplets $\chi^{exp}(T) - aT^{-1}$ (Fig. 10, curve *3*) is described satisfactorily by the second term of Eqn. (31) (Fig. 10, curve *4*), provided that the theoretical expressions derived by identifying Eqn. (30) with the second term of Eqn. (31) are used to calculate the coefficients $b$ and $c$.[136] It has been found that $b = 1.03$ and $c = 187.7$ for the theoretical value $n = 1.2 \times 10^{22}$ g$^{-1}$ and the ratio $u/\bar{N} = 0.76$ eV, obtained for the values $u \simeq 14$ eV and $\bar{N} \simeq 18$, which are typical for PPA.[117,118,130]

Different types of paramagnetic centres should be reflected in the shape of the ESR signal. For PPA at room temperature, the signal consists of a superposition of at least two lines with $g = 2$ and having comparable intensities: one line has the width $\Delta H_1 = 5$–$8$ G and the other has $\Delta H_2 = 2$–$3$ G.[146] The hyperfine structure (HFS) of the first line resembles that of the PPA radical-anions arising following electron transfer from alkali metal atoms to PPA molecules[147]. The first line is apparently associated with stable paramagnetic defects or CTC and the second with thermally excited triplets, its small width being due to the considerable delocalisation of the triplet excitation over the macromolecule.

The problem of the relaxation of the ESR signal intensity in CBP is of interest and its investigation can yield useful information. The observed relaxation with characteristic times of the order of tens of minutes or hours is hardly associated with the intrinsic lifetimes of the excited triplet states, as has been suggested[144,145], because there are at present no adequate grounds for believing that these lifetimes are quite so long. The relaxation of the ESR signal can be explained more realistically by slow configurational distortions of the macromolecular skeleton, which partly alter the degree of bond conjugation.

In order to investigate this problem, a study was made[136] of a polyene chain with randomly distorted bonds, which have the resonance integrals

$$\beta_i = \beta_0 (1 - 0.1 q x_i), \quad i = 1, 2, \ldots 2N,$$

where $x_i$ are random numbers ($0 \leqslant x_i \leqslant 1$) and $q > 0$ is the disorder parameter. Calculations by the method described in Section IX showed that the parameter $u$, determining the extent of triplet excitation [Eqn. (22)], decreases almost linearly with increasing $q$ at a rate $\Delta u/\Delta q \simeq -\beta_0 < 0$. Using the dependence of $\beta_i$ on $\Delta R_i$ (increase in the length of the $i$th bond) or on $\Delta\varphi_i$ (the angle of rotation about the $i$th bond), estimates were made of the chain deformation energies using familiar semiempirical formulae[54,143]. It was found that the thermal energy at 300–350 K is in principle sufficient for deformations of macromolecules which lead to a change in the ESR signal intensity by 15–30%.

The deformation energy may be transmitted to the macromolecule from its environment and, according to the change in the ESR signal, only the deformations of very long molecules are appreciable, since only they contribute appreciably to the paramagnetism. The observed relaxation time is therefore the time during which very long molecules receive sufficient thermal energy and reach thermodynamic equilibrium with the molecules of the environment. The higher the temperature, the greater should be the number of small defects in the continuous conjugation chain. In other words, an increase of temperature entails an increase of the degree of disorder $q$ and hence a decrease of $u$, since the contribution of thermally excited triplet states to $\chi(T)$ should increase with $T$ faster than predicted by Eqn. (30) with a constant value of $u$. The systematic discrepancies between curves *3* and *4* in Fig. 10 for $T > 250$ K appear to confirm this view.

## XI. CATALYTIC ACTIVITY AND REACTIVITY OF CBP

The existence of triplet states with low excitation energies makes it possible to re-examine the known facts about the catalytic activity of CBP.[148–152] The catalytic activity of small amounts of added CBP in the *cis–trans* isomerisation of dimethyl maleate[149] has been examined theoretically[153]. During isomerisation, rotation about the central double bond results in an increase of the energy of the singlet state of the molecule and, in the vicinity of the angles of rotation $\varphi \simeq 70°$ and 110°, the singlet state intersects the triplet state, which has a significantly lower energy in the vicinity of $\varphi \simeq 90°$. A transition to the triplet state is therefore natural and this is interfered with only by the strong prohibition as regards multiplicity. When a long PCB molecule adjoins the molecule involved in the *cis–trans* transformation, the overall multiplicity of the complex may be conserved, provided that, simultaneously with the transition to the triplet state in the first molecule, there is also a transition to the triplet state in the CBP molecule[153]. As a result of the removal of prohibition of change in multiplicity, there is a significant increase (by a factor of $10^7$) in the pre-exponential factor in the expression for the rate of reaction, while the activation energy of the complex hardly changes and is given by

$$E_a = E_a^0 + \eta \frac{u}{N} - V_{13},$$

where $E_a^0$ is the activation energy for the non-catalytic reaction, $u/N$ the energy of the first triplet excitation [Eqn. (22)], $V_{13} = 0.1$–$0.3$ eV the exchange energy of the interaction of two molecules of the complex, and $\eta \simeq 0.5$ a coefficient which depends on the form of the intersection of the energy surfaces. The following expression has been obtained for the coefficient of the acceleration of the reaction $\kappa_N$ or the reaction rates in the presence of the catalyst ($W_{cat}$) and in its absence ($W_0$):

$$\kappa_N = W_{cat}/W_0 = 10^7 \exp(V_{13}/kT) \cdot \exp(-u/2NkT). \qquad (32)$$

At $T = 400$ K with the chosen values of the parameters $V_{13}$, $\eta$, and $u$ (Section X), we obtain $\kappa_N \simeq 10^{10} \times 10^{-160/N}$. Molecules with $N \geqslant 20$ can therefore catalyse the reaction at an appreciable rate. After averaging the quantity defined

by Eqn. (32) with respect to MWD [Eqn. (24)], we obtain the final expression for the acceleration coefficient [153]:

$$\varkappa = 10^7 \exp(V_{19}/kT) \cdot \left(\frac{u\pi^2}{2\bar{N}kT}\right)^{1/4} \cdot \exp\left[-2\left(\frac{u}{2kT\bar{N}}\right)^{1/2}\right]. \qquad (33)$$

For the chosen values of the parameters, $\kappa \simeq 10^5$.

CBP molecules with high values of $N$ catalyse the reaction either by the mechanism described above, without the involvement of a paramagnetic steady state, or as a result of the removal of prohibition of change in multiplicity in the presence of triplet species. The known examples of catalysis on graphite and with participation of CBP may be associated with both mechanisms. In terms of the ideas which have been developed, the correlation between the catalytic activity of CBP and their paramagnetic properties is understandable. One can also postulate that, in the presence of such correlation, the catalytic reaction requires the removal of prohibition of change in multiplicity. As an example, one may consider the reaction

$$CH_3CHOHCH_3 \rightarrow \begin{cases} CH_3{-}CH{=}CH_2 + H_2O \\ CH_3COCH_3 + H_2, \end{cases}$$

which is catalysed by CBP activated by charcoal and graphite [150]. The reaction apparently proceeds via a triplet state.

In conclusion, we shall consider the problem of the reactivity of CBP in addition reactions. According to a general postulate [154], the reactivity of $\pi$ systems in such reactions increases with increasing degree of conjugation. However, deviations from this rule are known, for example in reactions of the Diels–Alder type, where conjugation with the dienophile does not increase the reactivity [155]. It has also been suggested that the reactivity of polyenes longer than butadiene in addition reactions diminishes [156], despite the general postulate. Nevertheless, calculation on the model reaction involving the addition of the methyl radical to a polyene confirmed the validity of the general rule [157]. It was found that the stabilisation energy, which constitutes an effective reactivity index in this reaction decreases monotonically, tending to a definite limit as the length of the polyene increases. The activation energy $U$ also diminishes monotonically. According to the experimental data, $U_2 = 8$ kcal mole$^{-1}$ for the addition of the methyl radical to ethylene and $U_4 = 4.1$ kcal mole$^{-1}$ for its addition to butadiene. For a polyene with 20 carbon atoms, $U_{20} = 1.8$ kcal mole$^{-1}$, [157] which is virtually equal to the limiting value for the infinite polyene. One should note that the Hückel approximation was used in the calculation [157], because the activation energy is related to the differences between the total energies and the contribution of the correlation energy to this difference is insignificant.

## XII. THE MULTIPLICITY OF THE GROUND STATES OF LARGE ALTERNANT ORGANIC MOLECULES WITH CONJUGATED BONDS. ORGANIC FERROMAGNETIC SUBSTANCES [158]

In the first place, we shall specify more exactly what is understood by an alternant system. If the conjugated system is alternant, all its atoms can be divided into two groups, $A^0$ and $A^*$, in such a way that any $A^0$ atom has only $A^*$ atoms as neighbours and any $A^*$ atom has only $A^0$ neighbouring atoms. We assume that $A^0$ (or $A^*$) atoms may include chemically different atoms (C, N, O, etc.), so that our definition of alternant conjugated systems is wider than the generally accepted definition in which only conjugated hydrocarbons are considered.

When the problem of the multiplicity of the ground states of alternant conjugated systems is examined, a significant factor is, as shown by Bulaevskii [159], that the description of conjugated hydrocarbons by the spin Hamiltonian method is very exact when the ground state of the system and the quasi-homeopolar excited states with the lowest energies are considered. In order to determine the energies of all these states, it is necessary to find the spectrum of the Heisenberg Hamiltonian of the molecule:

$$H = \sum_{ll'} I_{ll'}\left(\hat{S}_l\hat{S}_{l'} - \frac{1}{4}\right), \qquad (34)$$

where $\hat{S}_l = (\hat{S}_l^x, \hat{S}_l^y, \hat{S}_l^z)$ is the spin operator ($S = 1/2$) of the carbon atom with the index $l$, the summation is carried out with respect to the neighbours $l$ and $l'$,

$$I_{12} = \frac{1}{2}\{((\gamma_{11} - \gamma_{12})^2 + 16\beta_{12}^2)^{1/2} - (\gamma_{11} - \gamma_{12})\};$$

and $\gamma_{11}$, $\gamma_{12}$, and $\beta_{12}$ are the usual parameters of the PPP Hamiltonian. We may note that, for large distances between atoms, we have $\gamma_{12} \ll \gamma_{11}$ and $\beta_{12} \ll \gamma_{11}$ and in this limiting state we obtain

$$I_{12} \simeq 4\beta_{12}^2/\gamma_{11},$$

so that the Hamiltonian defined by Eqn. (34) assumes the form defined by Eqn. (20). For the real parameters $\gamma ll'$, and $\beta_{ll'}$, the Hamiltonian defined by Eqn. (34) yields, for example, an energy of the first triplet excitation of benzene which differs by only 10% from the experimental value or the energy calculated in terms of the PPP approximation. This is in fact the accuracy of the spin Hamiltonian method which we postulated.

For an alternant conjugated system with the Hamiltonian defined by Eqn. (34), it is possible to prove the theorem that the ground state of such a system is non-degenerate [158]. In the derivation of this proof, which is not described here, the Hamiltonian defined by Eqn. (34) is expressed in the form

$$H = \frac{1}{2}\sum_{ll'} I_{ll'}^{(1)}(S_l^+S_{l'}^- + S_l^-S_{l'}^+) + \sum_{ll'} I_{ll'}^{(2)}\hat{S}_l^z\hat{S}_{l'}^z, \qquad (35)$$

$$S_l^{\pm} \equiv \hat{S}_l^x \pm i\hat{S}_l^y,$$

where

$$I_{ll'}^{(1)} = I_{ll'}^{(2)} = I_{ll'} > 0,$$

and use is made of the ideas put forward by Lieb et al. [160] and the fact that the system is alternant.

If $I_{ll'}^{(1)}$ and $I_{ll'}^{(2)}$ are now treated as independent parameters and it is assumed that $I_{ll'}^{(1)} = 0$, we obtain from Eqn. (35) the so called Ising Hamiltonian for which the ground state is one with spins directed upwards in $A^0$ atoms and downwards in $A^*$ atoms. If the number of $A^0$ atoms is not equal to the number of $A^*$ atoms, then $z$ — the projection of the total spin of the system in the Ising limit for the Hamiltonian defined by Eqn. (35) with $I_{ll'}^{(1)} = 0$ — will be non-zero and defined by the expression

$$S_z = \frac{|n_{A^0} - n_{A^*}|}{2},$$

so that the total spin is

$$S \geqslant \frac{|n_{A^0} - n_{A^*}|}{2},$$

where $n_A$ is the number of A atoms. Since according to the above theorem the ground state is non-degenerate, the

spin of the ground state will be the same whatever the value of $I_{ll'}^{(1)}$ and $I_{ll'}^{(2)}$. Hence it follows that, for the real spin Hamiltonian defined by Eqn. (35) or (34), the ground state will have the following total spin;

$$S \geqslant \frac{|n_{A^0} - n_{A^*}|}{2}. \qquad (36)$$

as for the Ising Hamiltonian. Examination of different examples showed that the following equality holds:

$$S = \frac{|n_{A^0} - n_{A^*}|}{2}. \qquad (37)$$

Thus, in order to determine the spin of the ground state of an alternant conjugated system, it is necessary to compute the numbers $n_{A^0}$ and $n_{A^*}$ and to use Eqn. (37).

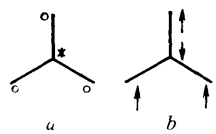


Figure 11. The trimethylmethylene molecule: *a*) atoms belonging to two groups, A* and A°; *b*) the arrangement of spins in the atoms in the ground state in the Ising limit.

We shall now analyse several examples. In the Ising limit, trimethylmethylene (Fig. 11*a*) has the configuration in the ground state with the arrangement of spins illustrated in Fig. 11*b*. Hence we have $S = 1$ for this molecule [in conformity with Eqn. (37)] and not $S = 2$, because the molecule can be obtained from an allyl radical ($S = 1/2$) and a carbon atom ($S = 1/2$) [carbyne radical (Ed. of Translation)] and, according to the moment addition rules, the combined spin can be either zero or one. The only possibility compatible with inequality (36) is $S = 1$.

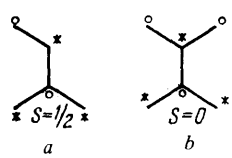



Figure 12. Hydrocarbon molecules having the total spins $S = 1/2$ (*a*) and $S = 0$ (*b*) in the ground state.

The molecules illustrated in Fig. 12 have the spins $S = 1/2$ and $S = 0$. The latter molecule is diamagnetic despite the fact that it has no Kekulé structure. Consequently an alternant molecule may not have a Kekulé structure and may be diamagnetic in the ground state.

Fig. 13 illustrates three isomeric hydrocarbons: (a) Chichibabin's hydrocarbon which Syrkin and Dyatkina[161] showed both experimentally and theoretically to be diamagnetic in the ground state but which has a small energy of excitation to the triplet state; (b) the Schlenk–Brauns hydrocarbon, which is firmly believed (according to the literature) to be a biradical, i.e. it has $S = 1$ in the ground state. This conflicts with our prediction, according to which this molecule should have $S = 0$ in the ground state. Hydrocarbons (a) and (b) have planes of symmetry with respect to the replacement of A* atoms by A° atoms, like the hydrocarbon illustrated in Fig. 12*b*. In the presence of such symmetry, the ground state always has $S = 0$. The third hydrocarbon (Fig. 13*c*), which does not have such symmetry, should have $S = 1$ in the ground state according to Eqn. (37).

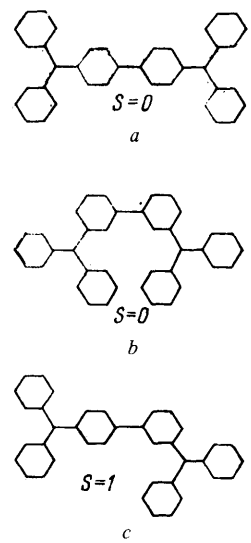



Figure 13. Large isomeric molecules: a) Chichibabin's hydrocarbon; b) Schlenk–Brauns hydrocarbon; c) hydrocarbon in which the number of atoms in one group is not equal to that in the other.

Next, Leo's triradical (Fig. 14) should have $S = 3/2$ in the ground state according to Eqn. (37). The condensed aromatic system illustrated in Fig. 15 has a total spin $S = (L - 1)/2$ which depends on the number of rows $L$ (with increasing number of rings in each succeeding row) (the fragment illustrated in Fig. 15 has $L = 5$ and $S = 2$). Other examples of polyradicals can be found in Buchachenko's book[162].

We shall now consider polymeric systems the total spin of which is proportional to their size. If these systems are synthesised, they will prove to be organic ferromagnetic substances. This can be seen from the preceding examples, one of which is discussed in Section IV; an unusual feature of these ferromagnetic substances is that the spins at neighbouring atoms are opposed, so that the spin order is the same as in an antiferromagnetic substance. However, the total number of atoms with the spins directed upwards is not equal to the number of atoms with the spins directed downwards and the difference between these numbers increases monotonically with increase in the size of the system; the total spin of the system is therefore proportional to its size. Fig. 16 illustrates several polymeric systems of

this kind. Either bivalent O, S, etc. atoms or some other stabilising groups can be selected as the substituent R. These systems are not hydrocarbons, but the above claims are valid also for alternant systems with heteroatoms.

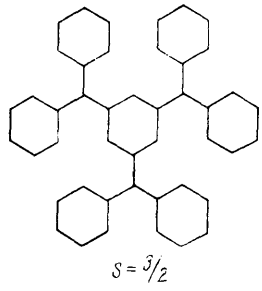



Figure 14. Leo's triradical.

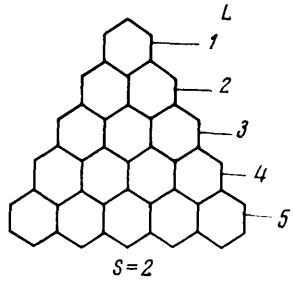



Figure 15. A triangular condensed aromatic system containing $L$ rows of rings ($L = 5$).

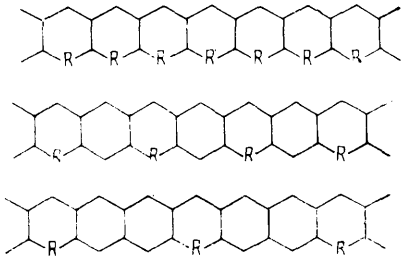



Figure 16. Macromolecules of hydrocarbons with periodically inserted heteroatoms (R = O or S).

Fig. 17 presents examples of two-dimensional infinite systems in which the total spin in the ground state is infinite: these are also ferromagnetic substances. The above systems can be constructed from the graphite network having replaced some of the carbon atoms by boron or nitrogen atoms. We may note that the graphite networks with boron atoms inserted at random have been known for a long time. The synthesis of all the structures of the above type will give rise to organic ferromagnetic substances.

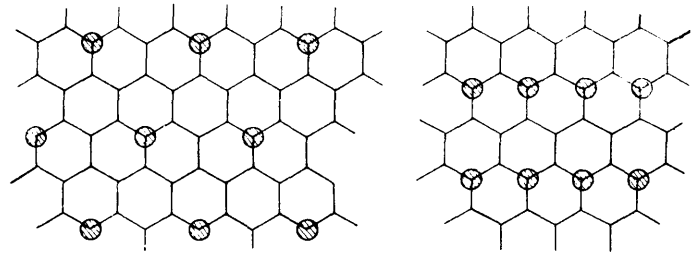


Figure 17. Two-dimensional structures obtained from the graphite structure by the replacement of the designated carbons atoms by boron or nitrogen atoms.

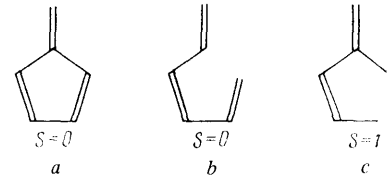



Figure 18. The fulvene molecule ($a$) and two alternant molecules obtained from the latter on dissociation of different bonds of the five-membered ring with $S = 0$ ($b$) and $S = 1$ ($c$).

The above theorems are invalid for non-alternant systems. However, some conclusions can be reached about them also. Consider, for example, the fulvene molecule (Fig. 18$a$). Its ground state has the spin $S = 0$, which has been demonstrated experimentally and by calculations. On opening the ring (Fig. 18$b$), the molecule is converted into a linear alternant system where the spin in the ground state is $S = 0$, while for another mode of ring opening (Fig. 18$c$) fulvene is converted into an alternant system with $S = 1$ in the ground state. Thus, using the ideas developed above, one may predict that the ring opening reaction in the $b$ molecule may occur under thermal conditions, while that in the $c$ molecule may occur with excitation to the triplet state, i.e. photochemically.

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# The Structure and Properties of Block Copolymers and Their Solutions

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The characteristics of the microphase structure of block copolymers and the decisive role of the incompatibility of the components of the block copolymer in this structure are examined and the factors influencing the type of structure and the size of the structural elements are discussed. A close relation is demonstrated between the segregation processes in dilute solutions and micelle formation on concentrating the solution, on the one hand, and the colloidal properties of solutions of copolymers determined by micelle formation and the structures of the solid polymers, on the other. The mechanical and physical properties of block copolymers are considered mainly in relation to thermo-elastomers.
The bibliography includes 254 references.

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## I. INTRODUCTION

Block copolymers constitute a specific class of polymers, the main chains of the macromolecules of which consist of two or more sections (blocks) each of which is in its turn made up of many identical units. The macromolecule is usually constructed of blocks of different types, so that it exhibits diphilic properties: This type of structure (in contrast to statistical copolymers characterised by a random alternation of units) leads to a combination of heterogeneous properties (for example the occurrence of two glass points) and even to the summation instead of the averaging out of the properties of the homopolymers. By varying the molecular weights of the blocks and their ratios within wide limits and hence the structure of the block polymers, which is determined by these parameters, it is possible to obtain polymers with specified properties.

The possibility of such modification of polymers together with the grafting of one polymer on another was suggested for the first time by Mark[1] at the beginning of the 1950s and since then research in this field has been developing vigorously[2-6]. Mechanochemical and other methods for the synthesis of block copolymers were used initially[7]. The discovery of anionic polymerisation and "live" polymers[8,9], whereby it is possible to obtain rigorously unimolecular block with any required molecular weight and to combine them with one another, was of fundamental importance for the successful development of this field. The method has been widely used to synthesise two-block (AB) and three-block (ABA) copolymers with a wide variety of compositions, the majority of which have been listed by Fetters[10]. A highly regular molecular structure is essential for the creation of long-range supermolecular order, which determines, as will be shown below, the most valuable properties of block copolymers. The polycondensation method was later used to obtain many-block polymers[11-14], whose molecular structure is not, however, quite so regular and this leads to certain characteristic features of these block copolymers, which will be considered below.

It is noteworthy that (despite the limited number of factual data available at the time) Soviet investigators Kargin, Plate, and coworkers were the first to conclude as early as 1960 that the occurrence of two glass points of a block copolymer, characteristic of its components, and in general the independent behaviour of these components can be accounted for solely by aggregation processes and the segregation of each component in the form of microphases or microregions[15,16]. Subsequently these ideas were extensively developed[17-19].

The formation of a two-phase structure and the degree of layer formation are determined by the degree of incompatability of the components constituting the blocks. The properties of block polymers are to a large extent determined by the size, form, and relative disposition of its structural elements. Microlayer formation processes and the formation of a structure occur as a rule in the solution from which the block copolymer is obtained and the properties of the solid block copolymer are therefore determined by those of the solution and the thermodynamic properties of the solvent. In connection with the foregoing, we shall consider the following problems in this review: (1) relation between the microlayer formation process in block copolymers and the incompatibility of its components and comparison of the relation with layer formation in mixtures of polymers; (2) dependence of the conformation of the macromolecules of block copolymers in dilute solutions on the segregation process and the relative conformational and thermodynamic properties of block copolymers and statistical copolymers; (3) transition from intramolecular to intermolecular aggregation as the solution becomes more concentrated, the formation of micelles, and the consequent manifestation of colloidal properties by block copolymers and their solutions; (4) dependence of the type of structure of the block copolymer on a number of factors; the possibility of predicting this dependence by means of models designed on the basis of statistical thermodynamic theories; the influence of the structure of the block copolymer on its mechanical and physical properties.

## II. CHARACTERISTICS OF THE MICROLAYER FORMATION PROCESS IN BLOCK COPOLYMERS

Having applied the Flory–Huggins theory of solutions [20], Scott obtained the following expression for the free energy of mixing of two polymers [21]:

$$\Delta G_{mix} = \frac{RTV}{V_r}\left(\frac{v_A}{x_A}\ln v_A + \frac{v_B}{x_B}\ln v_B + \chi_{AB} v_A v_B\right), \quad (1)$$

where $V$ is the total volume of the system, $V_r$ the volume per lattice site, $v_A$ and $v_B$ are the volume fractions of components A and B in the mixture, $x_A$ and $x_B$ the degrees of polymerisation of these components, and $\chi_{AB}$ is the interaction parameter, which is the fundamental characteristic of the miscibility of the components, i.e. their thermodynamic compatibility (or incompatibility).

The parameter $\chi_{AB}$ is frequently expressed in terms of Hildebrand's solubility parameters, which are listed in handbooks [22]:

$$\chi_{AB} = \frac{V_r}{RT}(\delta_A + \delta_B)^2, \quad (2)$$

where $\delta_A$ and $\delta_B$ are the solubility parameters of components A and B.

For critical conditions, corresponding to layer formation in the system, we have $\partial^2\Delta G_{mix}/\partial v_A^2 = \partial^3\Delta G_{mix}/\partial v_A^3 = 0$, and

$$(\chi_{AB})_{cr} = \frac{1}{2}\left[\frac{1}{x_A^{1/2}} + \frac{1}{x_B^{1/2}}\right]^2, \quad (3)$$

$$(v_A)_{cr} = \frac{x_B^{1/2}}{x_A^{1/2} + x_B^{1/2}}; \quad (v_B)_{cr} = \frac{x_A^{1/2}}{x_A^{1/2} + x_B^{1/2}}, \quad (4)$$

where $(v_A)_{cr}$ and $(v_B)_{cr}$ are critical layer-formation concentrations.

Eqn. (3) shows that $\chi_{AB}$ depends on the molecular weight of the polymer. A large value of the latter for polymers results in a corresponding value of $\chi_{AB}$, which is always small, so that the majority of polymers should be incompatible. This has been confirmed experimentally: of the enormous number of pairs of polymers investigated, the majority of which (102 pairs) have been listed in a review [23], only a few pairs proved to be compatible; all others formed layers starting from a definite critical concentration [defined in terms of Eqn. (4)] over a shorter or a longer period [24]. The application of Scott's theory to ternary polymer A–polymer B–solvent systems showed that the incompatibility in mixtures diminishes significantly with increasing molecular weights of both polymers and is independent of the solvent; however, this postulate is valid only in the sense that polymers which form layers in one solvent also form layers in another. The critical concentration proved to be different in different solvents and the difference is manifested to a greater extent the bigger the role played in the polymers by specific interactions with the solvent.

Similar relations have also been observed for block copolymers [25,26]. Krause [27] examined the case of phase layer formation in block copolymers when all the A–B contacts have been disrupted under the condition of an average ratio of components A and B and identical molecular weights of all the molecules. She obtained the following expression for $(\chi_{AB})_{cr}$:

$$(\chi_{AB})_{cr} = -\frac{V_r}{V_A n_A v_B}\ln[(v_A)^{v_A}(v_B)^{v_B}], \quad (5)$$

where $v_A$ and $v_B$ are the volume fractions of components A and B, $V_A$ is the molar volume of the A repeating unit, and $n_A$ is the number of these units. Calculation of the compatibility of polymers having the same molecular weight and taken in the same proportions in the mixture and in the block copolymer enabled the author [27] to conclude that the two components are more incompatible in a block copolymer than in a mixture of polymers. This conflicted with other theoretical studies [28], but subsequently, when account was taken of the surface free energy at the boundary between the microphase regions, Krause also concluded [29] that layer formation in the mixture proceeds more readily than in the block copolymer. Furthermore, it was shown [29] that, for the same molecular weight of the block copolymer, the formation of layers becomes increasingly more difficult with increase of the number of blocks, owing to the increase of the surface energy and of the number of segments at the boundary of the microphases, which leads to a decrease of the freedom of their movement and of the total entropy.

As in mixtures of polymers, a better compatibility of components A and B in block copolymers is achieved in solvents whose affinities for each component are most similar, i.e. the incompatibility of the pair of polymers is determined by the selectivity of the solvent in relation to them [30]. An unusual feature of the microlayer formation process in block copolymers and their solutions, compared with macrolayer formation in solutions of mixtures of polymers, is the retention of the integrity of the block copolymer specimen (i.e. the impossibility of the formation of two layers in its solution) owing to the combination of heterogeneous blocks in the block copolymer macromolecules via covalent bonds.

We may note that the blocks of A and B may be regarded as individual components only when their thermal motions are mutually independent. This requires a sufficient length and flexibility of at least one of the blocks and a decrease of flexibility requires an increase of length, i.e. of the degree of polymerisation of the block. With decrease of the size of the block, boundary conditions play an increasing role.

## III. CONFORMATIONS OF THE MACROMOLECULES OF BLOCK COPOLYMERS IN DILUTE SOLUTIONS

The fundamental conformational characteristics of the macromolecule in solution are the mean square distance between its ends and its unperturbed dimensions in a $\theta$-solvent, while one of the parameters used to estimate the degree of interaction between the polymer and the solvent in dilute solutions is the degree of swelling of the coil. According to the Fixman–Stockmayer equation [31], the unperturbed dimensions of the macromolecule are related to the intrinsic viscosity by the expression

$$[\eta]M^{-1/2} = K_\theta + 0.51\Phi_0 B \cdot M^{1/2}, \quad (6)$$

where $K_\theta = \Phi_0(\overline{R}_0^2/M)^{3/2}$, $\Phi_0 = 2.68 \times 10^{23}$ is Flory's constant, $\overline{R}_0^2$ the mean square distance between the ends of the chain, $B = 2(1/2 - \chi)/V_1\rho^2 N_a$ the long-range interaction parameter, $\chi$ Flory's interaction parameter, $M$ the molecular weight of the polymer, $V_1$ the molar volume of the solvent, $\rho$ the density of the solvent, and $N_a$ the Avogadro number.

For homopolymers, the slope of the plot of $[\eta]M^{1/2}$ against $M^{1/2}$ (i.e. the parameter $B$) is different in different solvents, but $K\theta$ (equal to the intercept which the plot makes on the ordinate axis), which characterises the $\theta$-conditions, is a constant and is independent of the nature of the solvent. In statistical copolymers, $K\theta$ is not constant and does depend on the solvent, so that the

conditions for the compatibility of such polymers also depend on the solvent. In this connection, Dondos and Benoit note [32], that $\theta$-conditions do not actually exist for statistical polymers. This is because of the hetero-contacts between groups A and B leading to a deviation from the Gaussian distribution and to a significant increase in the size of the chain compared with the corresponding homopolymers.

The situation in block copolymers is different. It is known [20] that the following relations hold under $\theta$-conditions with $\chi_{AB} = 0$ for a Gaussian conformation of a linear polymer chain consisting of two components:

$$\overline{R}^2_\theta = (\overline{R}^2_A)_\theta + (\overline{R}^2_B)_\theta \,, \quad (7)$$

$$[\eta]_\theta = [(x[\eta_A]_\theta)^{2/3} + \{(1-x)[\eta_B]_\theta\}^{2/3}]^{3/2} \,. \quad (8)$$

For $\chi_{AB} \neq 0$, these equations are valid when fairly long blocks A and B are completely separated in space, so that the Gaussian conformation holds for each [33]. This form of separation of heterogeneous blocks has been called segregation and the conformation itself, in which blocks A and B are separated in space and intramolecular heterocontact are reduced to a minimum, is called the segregated conformation.

Thus the more complete the segregation, the closer the chain size of the block copolymer to the sum of the sizes of the homopolymers making up these blocks. Under these conditions, the intrinsic viscosity of the block copolymer in effective solvents is intermediate between the intrinsic viscosities of the two homopolymers A and B, whose molecular weight is equal to that of the block copolymer; the $\theta$-temperature, the degree of swelling of the coil, the second virial coefficient, and the precipitation point obtained when a precipitant is added to a solution of the block copolymer are also usually intermediate between the corresponding values for the homopolymers [25,33-54]†. In the absence of segregation, these quantities exceed the corresponding values for the two homopolymers. Comparison of the intrinsic viscosities and chain sizes calculated by Eqns. (7) and (8) with the experimental quantities indicates the degree of segregation in solution.

The segregation of block copolymers in solution was first pointed out by Burnett et al. [55] They showed that the thermodynamic and hydrodynamic parameters of the block copolymer macromolecule also depend on the ratio of the overall masses of the blocks. Plots of the $\theta$-temperature, the entropic and energetic components of the free energy of solution, the intrinsic viscosity, and unperturbed size, and the swelling coefficient of the coil pass through a maximum as a function of the composition of the block copolymer, which corresponds to the component ratio A : B = 1 : 1. This behaviour was subsequently confirmed by other workers [56].

The majority of studies on the conformations of block copolymers were carried out using the same systems—two- and three-block copolymers of polystyrene and poly(methyl methacrylate) in different solvents without varying the component ratio, but the data obtained by different workers conflict; the intrinsic viscosity is consistent with Eqn. (8) in some cases, while in others it is greater or smaller than the calculated value. Thus, either owing to the different degrees of incompatibility of the blocks, manifested in the experiments of different workers, or owing to the quality of the given solvent (the incompatibility increases particularly when the solvent is selective with respect to one of the blocks [25,33,48]), or owing to the different molecular weights of the blocks or their ratio, the conformation of the molecule may be fully segregated, partly segregated, or pseudo-Gaussian, in which there is interpenetration of heterogeneous blocks [33, 45,52]. Froelich [38] showed that, under the conditions of complete separation, the chain length of the block copolymer is 15% greater than in the absence of segregation.

The fully segregated conformation of a two-block polymer can have the form of a "molecular micelle" [57], which comprises a nucleus, consisting of the coiled insoluble block surrounded by the soluble extensible block (Fig. 1*a*), or it has the shape of a loop [34], the size of which is smaller the longer the coiled block (Fig. 1*b*).

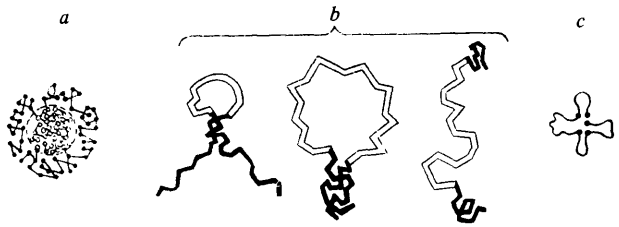



**Figure 1.** Various conformations of the aggregated macromolecule in solution: *a*) two-block copolymer—"molecular micelle" [77]; *b*) three-block copolymer with different block lengths—"loop" conformation (the insoluble block is indicated by the continuous line) [35]; *c*) a many-block copolymer—"bead" conformation (the circles indicate the insoluble blocks and the lines the soluble blocks) [58].

Bresler et al. [58] proposed a model for the segregation of many-block copolymers on the basis of the block copolymer of styrene and isoprene with a block ratio of 4 : 5 which they investigated. In an effective solvent, such a macromolecule obeys Gaussian statistics, while in a selective solvent the insoluble blocks are "precipitated" from solution, forming a rigid nucleus surrounded by the flexible "filaments" of the dissolved blocks. An example of such segregation is illustrated in Fig. 1*c*. Since, depending on the solvent employed, different blocks are "precipitated", the properties of the block copolymer obtained from solution depend significantly on the nature of the solvent. There has been yet another study on the properties of many-block polymers in dilute solutions [59]: the authors compared the block copolymers of styrene and isoprene with a rigorously constant molecular weight in which the number of blocks was varied from two to nine (with a corresponding change in the length of the blocks) in solution in toluene and its mixtures with methanol and iso-octane. It was found that the intrinsic viscosity increases with decrease of chain length and hence with increase of the number of blocks, since an increasing number of the latter "avoid" one another, which leads to an increase of the size of the macromolecule.

The same behaviour has been observed also when the properties of two- and three-block copolymers were

† It is noteworthy that the possibility of achieving $\theta$-conditions [38-40,49] for all block copolymers is not evident and requires further investigation.

compared. Overall, the properties of their dilute solutions differ little, but the intrinsic viscosity of a three-block copolymer is frequently greater than that of a two-block copolymer having the same molecular weight; this indicates a less complete segregation in a three-block copolymer and is consistent with the theoretical conclusion that layer formation in a block copolymer is hindered with increase of the number of blocks (see above).

Measurements of intrinsic viscosities in dilute solutions of block copolymers also make it possible to estimate qualitatively the degree of incompatibility of their components. The application of the equations of statistical thermodynamics to solutions of polymers is known to be capable of yielding a relation between the hydrodynamic parameters of the macromolecule (i.e. the ratio of the intrinsic viscosities in the given solvent and in a $\theta$-solvent), on the other hand, and quantities characterising the thermodynamic interaction of the polymer with the solvent, on the other[60]. Relations have been proposed for copolymer solutions which also include quantities characterising the interaction of the components with one another[61,62]. It was found that in many instances the theories developed for dilute solutions of homopolymers are also valid for solutions of block copolymers in a solvent which is effective in relation to both components. Deviations from these relations are associated with the action of selective solvents, which lead to a significant alteration of the conformations of the block copolymers.

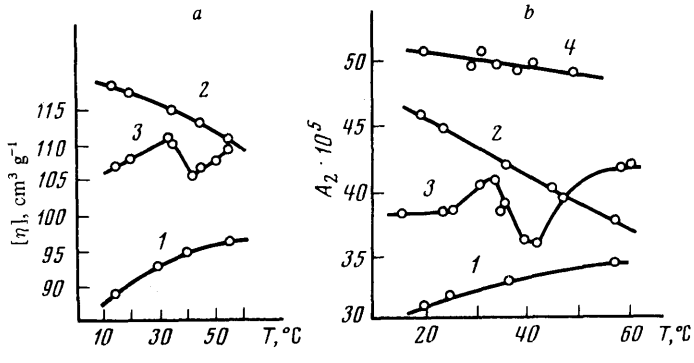



Figure 2. Dependence of the intrinsic viscosity (*a*) and the second virial coefficient (*b*) on temperature in homopolymers [poly(methyl methacrylate) (curves *1*) and polystyrene (curves *2*)], in a methyl methacrylate–styrene block copolymer (curves *3*), and in a statistical copolymer (curve *4*).[52,63]

The change in the conformation of the macromolecules of block copolymers with temperature, which is expressed in the temperature dependence of the intrinsic viscosity $[\eta]$ and of the second virial coefficient $A_2$ (determined by the light scattering method), characteristic of block copolymers alone, is of considerable interest. Fig. 2*a* shows that, with increase of temperature, the intrinsic viscosity of the copolymer increases initially to a maximum and then falls sharply, after which it again begins to increase. The nature of this variation is always the same, but the degree of the increase of the viscosity, the size of the peak, and the corresponding temperature depend significantly on the solvent and also on the ratio of the blocks and their molecular weights. All the observed transitions are fully reversible with respect to temperature. The peak is attributed to a conformational transition[45,52,63,64]. The segregated conformation exists below the transition temperature and the insignificant increase of viscosity is associated with the formation of a certain number of heterocontacts with increase of temperature, while the decrease of viscosity beyond the transition is due to the interpenetration of previously separated segments, which leads to a decrease of the volume of the macromolecule.

The validity of this treatment is confirmed, for example, by the fact that a film of a polystyrene–polyisoprene block copolymer, prepared below the transition temperature (i.e. when the segregated conformation of the copolymer obtains), has two glass points corresponding to the two separate blocks, while in a film prepared above the transition temperature, where the separation of the blocks is less pronounced, the glass point of polystyrene is appreciably displaced towards lower temperatures (the shift depends on the component ratio)[64]. The temperature of this conformational transition should be close to the glass point of the block copolymer, which is closely related to the degree of incompatibility of its components in the given solvent (i.e. the greater the incompatibility, the higher the glass point[33]). For example, it has been shown[32] that $\chi_{AB} = 0.031$ in benzene, 0.046 in tetrahydrofuran, and 0.053 in *p*-xylene for styrene–methyl methacrylate copolymers. The transition temperature of this block copolymer is smallest in benzene, where the incompatibility is a minimum. Urwin and Giralomo[64] believe that the transition temperature is near the $\theta$-temperature of the copolymer and may be the most important characteristic of the block copolymer.

The temperature dependence of the second virial coefficient $A_2$ is analogous to that of the intrinsic viscosity, as can be seen from Fig. 2*b*, where data for a statistical copolymer and a block copolymer are also compared.

When a precipitant is added to the solvent, i.e. when the quality of the latter is impaired, the transition temperature increases, in conformity with the ideas described above[52]. On the other hand, at a constant temperature, the addition of a precipitant (particularly one selective for one of the blocks) to a dilute solution of the block copolymer leads to a sharp decrease of the intrinsic viscosity[12,65–67], which is associated with the coiling of the insoluble blocks and their displacement to the interior of the macromolecule. It is of interest that, in solutions of polystyrene–poly(methyl methacrylate) block copolymers treated with a precipitant specific to poly(methyl methacrylate)[67], the same content of precipitant gives a lower intrinsic viscosity of the block copolymer regardless of its composition than the solution of poly(methyl methacrylate) alone. This demonstrates the decisive role of the blocks insoluble in the given system, which become coiled, and the independence of their behaviour of the presence of polystyrene blocks; they apparently form microgel particles in the soluble polystyrene. On the other hand, owing to the stronger interaction between the components as the concentration of the component which becomes insoluble following the addition of the precipitant is reduced, in a statistical copolymer the viscosity

increases with increase of the concentration of the precipitant—this is yet another manifestation of the difference between the conformations of block copolymers and statistical copolymers.

However, a decrease of the viscosities of both homopolymers and block copolymers is not observed in all solvent–precipitant mixtures. It has been shown [63] that this effect depends on the parameter $\chi_{12}$ of the interaction between the solvent and the precipitant: when $\chi_{12} > 0$, the addition of the precipitant causes a fall of the viscosity, while under conditions where $\chi_{12} < 0$, the addition of the precipitant results in an increase of the viscosity.

We shall consider yet another approach to mixtures of polymers and block copolymers. The solvent in which component B is dissolved behaves as a less effective solvent in relation to component A than the pure solvent itself owing to the incompatibility of these components. From this it follows that the intrinsic viscosity and the size of the macromolecule of A will decrease in the presence of component B. This has been confirmed by systematic studies on mixtures of polymers by viscometric and light scattering methods [68–73]. Such joint study of the solvent and component B as a single solvent for component A made it possible to apply the so called method of invisible species in order to determine the molecular weight of one of the components in the presence of the other: if the solvent and component B have the same refractive indices, the solution of component A in this mixture is optically a two-component system and light is scattered solely by component A, whose molecular size and weight can thus be determined by measuring the light scattering parameters. The aggregation of the system can be followed by the same procedure—from the change in the molecular weight of component A in the presence of component B. This method can also be used to determine the molecular weights of block copolymers.

In connection with the possibility of determining the molecular weight of a block copolymer by the light scattering method, we shall mention briefly the general approach to the estimation of the molecular weights and the microheterogeneity of copolymers proposed for the first time by Benoit and coworkers [74,75] and widely used by many investigators [76]. Since the increments in the refractive indices of the copolymer components are different, for a correct measurement of the molecular weight of the block copolymer it is necessary to know the increment of the refractive index in the given solvent for each component. The relation between the measured apparent molecular weight $M_{app}$, the true molecular weight of the block polymer $M_W^{AB}$, and the molecular weights of the individual blocks $M_W^A$ and $M_W^B$ is expressed by the following equation:

$$M_{app} = (\nu_A^2/\nu^2) M_w^A x + (\nu_B^2/\nu^2) M_w^B (1-x) + 2(\nu_A \nu_B/\nu^2) M_w^{AB}, \quad (9)$$

or the equivalent equation

$$M_{app} = M_w^{AB} + 2[(\nu_A - \nu_B)/\nu] P + [(\nu_A - \nu_B)/\nu]^2 Q, \quad (10)$$

where $\nu_A$, $\nu_B$, and $\nu$ are the increments in the refractive indices of the homopolymers A and B and of the block copolymer AB respectively, $x$ is the weight fraction of component A, and $P$ and $Q$ are parameters characterising the inhomogeneity of the composition of the copolymer. By determining the molecular weight of the block copolymer in three different solvents, we obtain a system of three equations from which the values of $M_W^{AB}$, $M_W^A$, and $M_W^B$ can be determined.

## IV. COLLOIDAL PROPERTIES OF BLOCK COPOLYMERS AND THEIR SOLUTIONS

Gallot et al. [77] noted that the following cases of the dissolution of block copolymers in selective solvents are possible. If the soluble block is short or if its content in the copolymer is unduly low and its affinity for the solvent is insufficient, the block copolymer does not dissolve at all. If the degree of solvation of the soluble blocks and their number are sufficient for the dissolution of the polymer, the latter results either in a molecular dispersion (the solution is then completely transparent), or a polymolecular dispersion, or a micellar solution. The molecular dispersion corresponds to solution of the "macromolecular micelles" mentioned above; a coiled insoluble block in such a solution is fully surrounded by a shell of the uncoiled soluble block, which prevents it from coming into contact with other insoluble blocks. With increase of the concentration of the polymer, intermolecular contacts arise between the insoluble blocks and, when combined, the latter give rise to a lyophobic nucleus surrounded by fairly flexible lyophilic blocks (Fig. 3*a*), i.e. micelles analogous to soap micelles in aqueous solutions are formed. Thus, at moderate concentrations, solutions of block copolymers are typically colloidal.

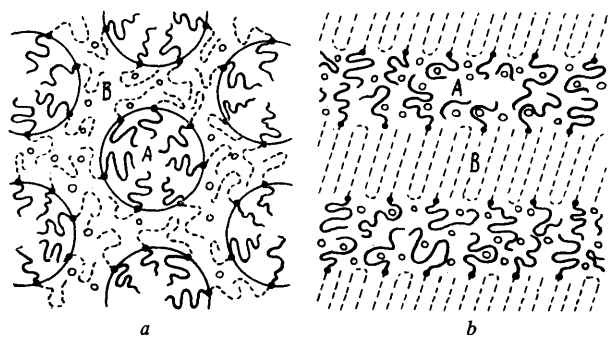



Figure 3. Types of colloidal micelles of block copolymers. The influence of the solvent on the type of micelles of a styrene (A)–ethylene oxide (B) block copolymer; solvent: *a*) nitromethane; *b*) dibutyl phthalate (the solvent molecules are shown as circles) [98].

A very important consequence of the micellar nature of solutions of block copolymers is the possibility of varying the type of micelles, i.e. the composition of the nucleus and the shell, by selecting various precipitants. Thus Merrett showed for the first time [78,79], in relation to a graft copolymer of natural rubber and poly(methyl methacrylate), that it is possible to obtain a "hard" or "soft" form of the polymer by inducing the formation of micelles and the subsequent precipitation of either poly(methyl methacrylate) or the rubber. Virtually at the same time, Korotkov [9] and Bresler [58] obtained analogous results for a styrene–isoprene block copolymer. Such studies were frequently carried out subsequently [80–82] and established the possibility of varying within wide limits the properties of objects obtained from solutions, by altering the nature of the binary solvent.

The critical concentration for micelle formation (CCM) depends on the chemical structure and the number of blocks in the polymer, the phase state, the molecular weight, and the quantitative ratio of the blocks as well as the thermodynamic properties of the solvent in relation to the polymer [77,83-86].

The selectivity of the solvent is usually achieved by adding a $\theta$-solvent which is effective for both components or a substance which does not dissolve one of the blocks [83]. For example CCM for styrene–butadiene block polymers in toluene amounts to 9%, [84] while after the addition of ethanol to dioxan in the same block copolymer micelles are formed starting from a concentration of 1%. [83] CCM and its dependence on the nature of the solvent are closely related to the degree of segregation of the macromolecules of block copolymers in dilute solutions in various solvents: the more pronounced the segregation in the given solvent, the lower the value of CCM in the latter.

In order to assess micelle formation, light scattering measurements are used in the first place [87-91] as well as viscosity and diffusion measurements, the determination on their bases of the ratio of the hydrodynamic particle radii [83,87] and the study of sedimentation in an ultracentrifuge [89]. The characteristic variation of the intensity of the scattered light during micelle formation as the temperature is altered is seen in Fig. 4. A molecular solution is formed at 65°C in a block copolymer of polystyrene and polyisoprene with a block ratio of 1 : 3 in n-decane, which is a selective solvent for polyisoprene; when it is cooled to 55–40°C, the intensity of the scattered light increases sharply, indicating the appearance of large scattering particles and a further increase of their dimensions, while below 25°C the scattering intensity is again constant and corresponds to the establishment of a stable micellar solution [88].

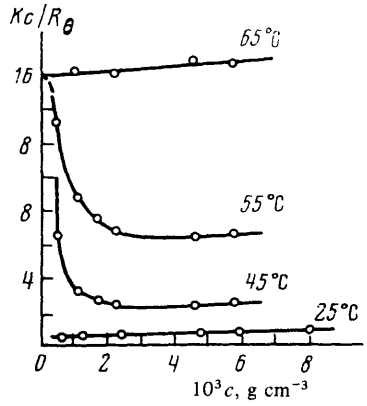



**Figure 4.** Dependence of the light scattering intensity $R\theta$ in a solution of a polystyrene–polyisoprene block copolymer on temperature and concentration [87].

The molecular weight of the micelles is usually greater by two orders of magnitude than that of the individual macromolecules ($10^6$ in the example under consideration compared with $10^4$), but their radius of inertia is extremely small (~200 Å) which demonstrates their compact nature. This is also indicated by the intrinsic viscosity and the Huggins constant [83]. The weight fraction of the micelles in solution increases with increase of the polymer concentration and impairment of the quality of the solvent, but their molecular weight remains constant under these conditions [83].

A characteristic property of micellar solutions of block copolymers is their similarity to lyotropic liquid crystals. The manifestation of this phenomenon involves the double refraction [84,91,92], optical anisotropy [91], and rainbow colours [84,93] of such solutions. Vanzo showed that below CCM (to which a light transmittance maximum corresponds), the solution is colourless, while above CCM it acquires various colours, which depend on the concentration (ranging from pale blue to green and pink) [84]. In 1% solutions of the polystyrene–poly(ethylene oxide) block copolymer in solvents selective with respect to both blocks, the Kerr effect is observed [75]. All these characteristics indicate the formation in moderately concentrated solutions of block copolymers having specific ordered structures which do not exist in solutions of homopolymers.

These microheterogeneous highly ordered structures were investigated in particular detail by Skoulious and coworkers for polystyrene–polyvinylpyrrolidinone (both components are amorphous) [92,94-97] and polystyrene–poly(ethylene oxide) or polystyrene–poly(propylene oxide) (one of the components crystallises) [97-107] block copolymers. At certain concentrations in selective solvents, these systems form gels, which the authors referred to as mesomorphic phases characterised by a high degree of order. The structure of these gels depends on the nature of the solvent and the concentration of the block copolymer. For example, in nitromethane, which is a solvent for poly(ethylene oxide) but does not dissolve polystyrene, the insoluble phase forms discrete structural elements in the form of cylinders in a continuous dispersion medium consisting of a solution of poly(ethylene oxide) blocks in nitromethane (Fig. 3*a*). In dibutyl phthalate, which dissolves polystyrene but not poly(ethylene oxide), the crystallising poly(ethylene oxide) forms structural elements in the form of plates in a solution of polystyrene in dibutyl phthalate (Fig. 3*b*). We shall consider the structures of these gels in greater detail below in connection with the general characteristics of structure formation in block copolymers. On solidifying the block copolymer, by evaporating the solvent, the structural elements or micelles involved in an ordered arrangement remain dispersed in the dispersion medium or matrix consisting of soluble blocks. These micelles have the same compositions, constituting regions of a microheterogeneous system with interfaces, which are, however, linked by chemical bonds with the continuous dispersion medium. In order to indicate their difference from the usual phase particles and the usual micelles, these "micelles" can be called microphase regions. In the non-Soviet literature, the term "domain" is used for this purpose.

The wide variety of the colloidal properties of solutions of block copolymers is also manifested by their emulsifying action in oil–water systems, by the increase of the mutual compatibility of the homopolymers, by the stabilisation of organic latexes, etc. [108-118] The compatibility of block copolymers with homopolymers having the same structures as the blocks constituting the block copolymer and the acquisition of some compatibility in the presence of block copolymers by polymers which are usually incompatible are due to a kind of solubilisation, i.e. the dissolution of the homopolymer in the corresponding "micelle" of the block copolymer. Riess et al. [108] and

subsequently other workers[109,110] suggested that the transparency of the resulting films be used as a criterion of the compatibility of the systems obtained. These data can be conveniently represented graphically on triangular diagrams in which the transparency of the film is plotted against the composition of the ternary systems block copolymer (with a specific block ratio)–homopolymer A–homopolymer B. It was found that, for a ratio of blocks A and B in the block copolymer of 80:20 or 20:80, there is no solubilisation at all; it occurs when the amounts of the blocks are more similar and is a maximum for the 50:50 ratio[108].

This procedure can be used to increase the compatibility of only those homopolymers whose molecular weight is lower than that of the corresponding blocks, which is important for solubilisation. Furthermore, solubilisation is more pronounced, the most distinct the segregation of the micelles in the solution of the block copolymer[111]. For example, polyisoprene is solubilised in polyisoprene micelles and its solubilisation therefore occurs for the compositions of the block copolymer in the solvents or their mixtures which promote the segregation of the polyisoprene micelles in the block copolymer. Polystyrene is solubilised most effectively under conditions where polystyrene blocks are segregated as a discrete phase; it has been shown that up to 30% of polystyrene may be solubilised[111]. Despite the turbidity of the solubilised solutions, they are extremely stable[111].

If the molecular weight of the homopolymer exceeds that of the corresponding block, it is not solubilised and may be dispersed in the continuous phase, but after a time it is separated in the form of a gel[112]. The size of the spherical regions of the block copolymer where solubilisation takes place increases and they are frequently converted into an elliptical form[111]. It has been shown by the light scattering method that, although the molecular weight of the mixed micelles of the styrene–isoprene block copolymer and a styrene homopolymer increases from $10^6$ for the block copolymer to $10^{10}$, their size increases comparatively little and does not exceed 300 Å.[111]

The same solubilisation phenomenon has been observed by the low-angle X-ray scattering method[113]. It has been shown that it is common for structures of any type—not only spherical but also cylindrical and lamellar (see below), and in all cases the size of the structural elements of the block copolymer increases on solubilisation and in many instances there is a change in the conformation of the block copolymer macromolecule. Homopolymer molecules become ordered under these conditions, like the blocks of the block copolymer, and a case has been described[113] where homopolystyrene with a molecular weight of 60 000 is solubilised, apparently as a result of a change in the conformation of the homopolymer molecules on solubilisation in a polystyrene block with a molecular weight of 40 000.

It is noteworthy that the increase of the compatibility of the polymers is observed only in the presence of block copolymers; neither statistical nor graft copolymers give rise to this effect. According to Molau and Wittbroadt[86], this effect cannot be regarded as a true increase of compatibility; it is purely colloidal in nature and is associated with the formation of a finer dispersion of one phase in the other.

A thermodynamic study by Unoue and coworkers[109,110] showed that, when CCM is found outside the binodal curve separating the region of the homogeneous solution from the region corresponding to its separation into layers comprising solutions of the block copolymer and the homopolymer, solubilisation occurs and the resulting solution is homogeneous; on the other hand, when CCM is found within the binodal curve, layer formation occurs even before a film is produced from the solution and there is no solubilisation.

Block copolymers are used as emulsifying agents both in order to obtain emulsions of high-molecular-weight substances in organic solvents and to prepare emulsions of low-molecular-weight substances. The first case includes emulsions obtained on polymerisation of a monomer in which a polymer of another type is soluble[114-117]. This entails the formation of a homopolymer and a graft or block copolymer, which prevents the separation of the two polymers into layers and promotes the formation initially of an emulsion of the polymer in the monomer (for example, of natural rubber in styrene), which then becomes fixed after the polymerisation of styrene. One such example is impact-resistant polystyrene, obtained by this procedure, in which natural rubber particles are dispersed in solid polystyrene.

The emulsifying effect of the polystyrene–poly(ethylene oxide) block copolymer on the water–toluene system has been investigated[118] and it has been shown that 1% of the block copolymer is sufficient for the formation of the emulsion, that the most stable emulsions are obtained in the region of phase reversal, and that a three-block copolymer makes it possible to emulsify a larger amount of toluene in water than does a two-block copolymer.

Thus it follows from the foregoing that the colloidal properties of solutions of block copolymers are manifested starting from extremely low concentrations of the latter. Such colloidal nature of the block copolymer solutions make it possible, on the one hand, to employ them in many specific applications and, on the other, it constitutes the basis for the formation of the structures of solid block copolymers obtained from these solutions.

## V. THE TYPES OF STRUCTURES OF BLOCK COPOLYMERS AND THE FACTORS INFLUENCING THEM

The structure of solid block copolymers, which can be of three main types (spherical, cylindrical, or lamellar phase formations), constitutes an extremely unusual manifestation of the supermolecular organisation, which is characteristic of polymers in general—not only in the crystalline but also in the amorphous state. As a result of the fairly considerable length of the block, whose macromolecules are homogeneous, the structural elements with interfaces formed under conditions where the blocks are incompatible are not only homogeneous with respect to size but are also arranged in a very regular manner. Despite the amorphous nature of the components constituting the block copolymer, its structure is therefore in most cases characterised by long-range order and the presence of a lattice with long periods, which is usually characteristic of single crystals only; spherical structural elements are packed in a cubic lattice, cylindrical elements are in a hexagonal lattice, and plates are arranged parallel to one another in the plane of the film[119-123]. Similar instances of the presence of long-range order in non-crystalline materials are also known for certain non-polymeric systems: soaps, minerals[124], latexes[125], silica gel[126], etc. The detection of such order in block copolymers, where the microheterogeneity of the system leads to a distinct two-phase state, and the study of the characteristics of such structure formation are therefore of great interest.

The principal methods for the investigation of the structures of block copolymers are electron microscopy [127-132] and low-angle scattering of X-rays [133-139]. A distinct representation of the structure of electron microscope photographs is achieved by shading thin films of block copolymers containing double bonds with the aid of $OsO_4$ vapour in order to increase the difference between the electron densities of the microphases [140]. If the experimental conditions are such that the electron photomicrographs of thin films show structural elements in only one plane, then the volume fraction of these aggregates can be calculated from their shape and distribution. On the basis of the conditions governing the packing of the aggregates, the volume fractions of different types of structures are defined by the following relations [121]:

$$\varphi_{sph} = 0.74\left(\frac{D_{sph}}{A_{sph}}\right)^3, \quad (11)$$

$$\varphi_{cyl} = 0.91\left(\frac{D_{cyl}}{A_{cyl}}\right)^2, \quad (12)$$

$$\varphi_{lam} = \frac{D_{lam}}{A_{lam}}, \quad (13)$$

where $D$ is the size and $A$ the distance between the aggregates. The volume fractions calculated in this way agree well with the results of the chemical analysis of the block copolymer.

The method of low-angle X-ray scattering makes it possible to determine the average dimensions and the distribution of the numerous aggregates. Its advantage is that it permits the study of the structure of films in the presence of a solvent and when the temperature is varied. The quantitative assessment of the structure and of the type of packing by this method is based on a comparison of experimental scattering diffractometer traces with scattering by various model structures for which formulae have been proposed [134,137,139]. Each type of structure is characterised by a definite number of reflections and a definite distance between them. Thus diffractometer traces with five or seven reflections, the reciprocals of the Bragg radii of which are in the ratios $1:2:3:4:5:6:7$, correspond to lamellar structures; the ratios of the reciprocal radii $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ correspond to hexagonal packing of cylinders and the ratios $1:\sqrt{2}:\sqrt{3}:\sqrt{4}$ correspond to cubic packing of spheres. In order to reveal these structures more effectively, Keller extruded specimens of the block copolymers. Extrusion leads to the formation in amorphous block copolymers of structures with a particularly high degree of order, usually encountered only in single crystals and therefore referred to as supercrystals [141,142]. The results of both methods discussed above are usually in good agreement [130,132,138]. The size of the structural elements may be determined also from the scattering of polarised light [143]. The dimensions of the structural elements vary from 60 to 1000 Å as a function of the structure of the block copolymer and the conditions under which it is obtained, but usually they are in the range 200–300 Å. [119,120,130,137]

The type of structure of the block copolymer depends on many factors: on the ratio of the blocks in the copolymer, on the molecular weight of the blocks, on the concentration of the copolymer in solution, on the nature of the solvent, and on the temperature conditions under which the specimen is obtained. The dependence of the structure on the component ratio is clearly illustrated in the styrene–butadiene block copolymers obtained from an effective solvent (toluene) [119]. With increase of the weight fraction of butadiene from 20 to 80%, five types of structures, illustrated in Fig. 5, are observed: spherical polybutadiene domains dispersed in the polystyrene matrix; hexagonally distributed cylindrical polybutadiene domains in the polystyrene matrix; layer structures consisting of alternating polystyrene and polybutadiene plates (or lamellae) in the region where the concentrations of both types of block are similar and where phase reversal takes place; on further increase of the concentration of polybutadiene, the latter forms a continuous phase in which cylindrical polystyrene domains are dispersed and, when the concentration of polystyrene is lowered further, its domains become spherical. Similar structures have been detected also in other systems [138,144,146].

The change in the length and number of blocks (from two to four) for the same component ratio does not lead to a significant change in the structure [119]. As a rule, in

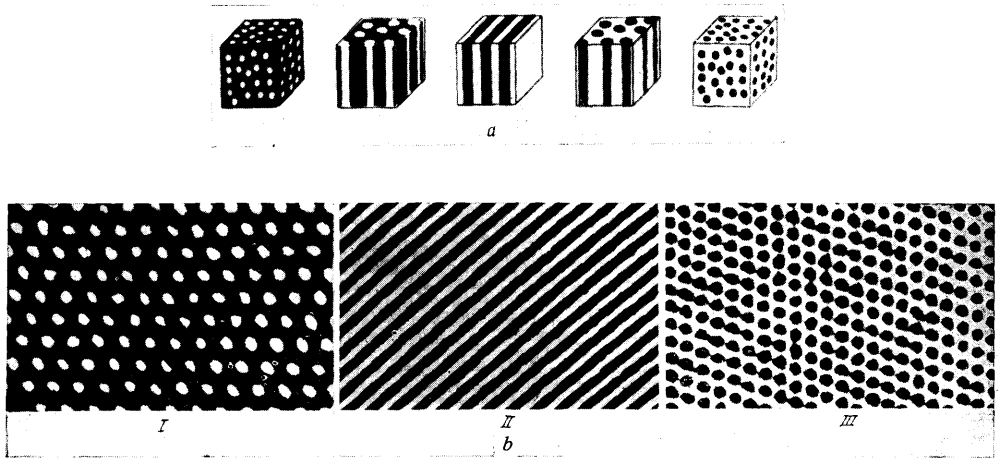



**Figure 5.** Types of structures of block copolymers as a function of the ratio of the blocks: *a*) schematic representation; *b*) electron microscope photographs of styrene–butadiene block copolymers containing different percentages of polystyrene [145]: I) 28.3; II) 61; III) 69.5.

the middle range of compositions of block copolymers obtained from solution in toluene (which is an effective solvent for polystyrene and polydienes), these block copolymers form alternating lamellar structures; from other solvents, less distinct structures of the "islands in a matrix" type are obtained[92]. The resulting structure is insensitive to temperature changes in the range 20° to 60°C.[105]

A specific feature of block copolymers is that the type of solvent plays just as important a role in the formation of their structure as the composition of the polymer. By a suitable choice of selective solvents, it is possible to achieve phase reversal for the same composition of the block copolymer, i.e. as already stated above, blocks which are insoluble in the given solvent are "precipitated" as a discrete phase[78-82], which has a sharp effect on the properties of the block copolymer.

A large series of studies designed to determine the structures of block copolymers in solution has been carried out by Skoulious, Gallot, and coworkers, mainly by the low-angle X-ray scattering method[147-152]. One structural dimension—the distance between the structural elements—can be determined directly from X-ray diffractometer traces; the size of the structural elements (the diameter of the sphere or cylinder and the thickness of the layer in the plate occupied by each block) can be calculated from the measured distance, the polymer concentration in the solution, the ratio of the blocks in the polymer, and the densities of the blocks and the solvent. For the hexagonal packing of cylinders, two versions of such structure are possible: either the cylinders are formed by the block insoluble in the given solvent and the continuous medium consists of the soluble block together with the solvent or the cylinders are filled by the solvent together with the soluble block and the continuous medium consists of the insoluble block.

The study of the dependence of the size of the cylinders (and other structural elements) on solvent concentration and on the molecular weights of the blocks helps to establish which specific type of structure obtains. As the solvent is varied, the structure is reversed. The concentration of the solvent has different effects on the structure for different block copolymers. The formation of a distinct ordered liquid-crystal structure, i.e. the mesomorphic gel already mentioned, proceeds from a polymer concentration of 40–60%, while at a lower concentration there is no structure at all. On further alteration of solvent concentration, either only the dimensions of the structural elements and of the distances between them change (in different directions determined by the solvent selectivity) or the very type of structure is altered. Thus cylindrical structures have been detected in polystyrene–polyvinylpyrrolidinone block copolymers with a polymer concentration of 70%, while at a higher concentration lamellar structures were found. When the monomer is used as the solvent and is subsequently polymerised, it is possible to obtain solid polymeric systems with a fixed highly ordered structure of the gel or the solution at any stage during its concentration. In such systems, it is more convenient to investigate by electron microscopy the block copolymer structure obtained on passing from a solution to the solid state than in films obtained from solutions at different concentrations by evaporating the solvent. It has been shown by this method that, regardless of the polymer concentration in the initial solution (between 0.8 and 10%), the same structure is observed in films of the styrene–isoprene block copolymer obtained from toluene[153], which enabled the authors to regard it as the equilibrium structure produced at the critical concentration for micelle formation.

Kinetic phenomena play a major role in the formation of the structure of block copolymers[121,154]. Thus an increase of the molecular weight of the block copolymer leads to a decreased regularity of its structure and to an increase of the distances between the structural elements as a consequence of the increased viscosity of the solution, which hinders the attainment of a state of equilibrium[122]. The temperature and the rate of removal of the solvent on formation of the film are just as important. When the solvent is removed rapidly, the size and distribution of the microphase regions in the film are insufficiently homogeneous and are far from equilibrium. The films formed from solution are therefore annealed at temperatures above the glass points of both blocks, the structure being rearranged during the annealing process[122,154,156]. Under these conditions, the distance between the domains decreases and the plates frequently become thicker. On the other hand, annealing at a temperature somewhat below the glass point frequently leads to some breakdown of order in the structure and the appearance of an intermediate phase[153,155]. Extremely interesting data concerning the dependence of the time required for the attainment of the equilibrium degree of order in an SBS (styrene–butadiene–styrene) block copolymer on the annealing temperature have been published[122]:

| Annealing temp., °C | Time, min |
|---|---|
| 120 | 5 |
| 110 | 25 |
| 90 | 180 |
| 80 | 1800 |
| 70 | 3600 |

It is significant that this temperature dependence of the rate of rearrangement of the structural elements of polystyrene is similar to the temperature dependence of the viscosity of polystyrene near the glass point.

In certain cases, particularly when one of the components of the block copolymer is crystallisable, the nature of the structure formed depends also on the temperature at which the film is formed from solution. For example, films of the polythiacyclobutane–polyisoprene–polythiacyclobutane block copolymer[157] obtained at room temperature are isotropic, while a highly regular hexagonal packing of cylinders at right angles to the plane of the film is observed in the films obtained at 60°C, which is clearly manifested in their mechanical properties. This is associated with the kinetics of the crystallisation of polythiocyclobutane and the superposition of two processes: liquid microlayer formation, which is usual for block copolymers, and the formation of a crystalline phase.

Owing to the complexity of the structure of the block copolymers, there is a possibility of different types of phase equilibria in polymer–solvent systems.

Phase diagrams of two types have been described in the literature: (1) those characterising the transition from the liquid-crystal (highly ordered) state to an isotropic (structureless) solution and (2) those characterising the compatibility of the components and the liquid layer formation in the system polymer–selective solvent for the first block–selective solvent for the second block or in the system first block–second block–solvent. When a crystallisable block is present in the block copolymer, the regions corresponding to the appearance (disappearance) of the crystalline phase are indicated on phase diagrams of both types. Diagrams of the first type have been obtained by French investigators (Gallot, Douy, and

Gervais)[158-162] by plotting the temperature of the disappearance of the liquid-crystal (and crystalline) phase (determined by scanning calorimetry) against solvent concentration. Fig. 6*a* illustrates an example of this type of diagram for the polystyrene–poly(ethylene oxide) block copolymer, which is characterised by the presence of regions corresponding to the existence of a crystalline lamellar poly(ethylene oxide) phase [the form of the chains in the latter is analogous to pure crystalline poly(ethylene oxide)], an amorphous lamellar phase, and isotropic solution. Investigations showed that the nature of the blocks in the polymer determines the number of mesophases and the nature of the solvent determines the region where they are stable (i.e. the greater the affinity of the solvent for the polymer, the greater the reduction of the transition temperature caused by it).

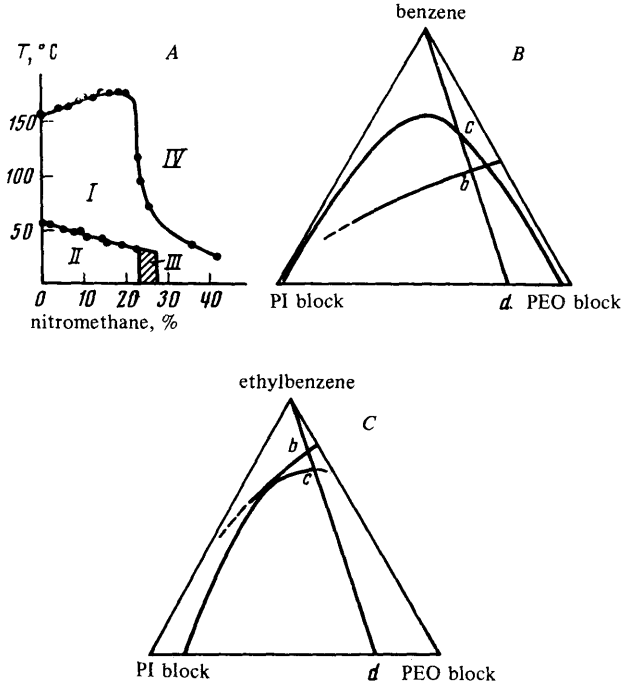



Figure 6. Phase diagram for polystyrene–poly(ethylene oxide) block copolymers (A)[162] [I) lamellar amorphous structure; II) lamellar crystalline structure; III) transitional region between them; IV) isotropic solution] and a polyisoprene (PI) and poly(ethylene oxide) (PEO) block copolymer in benzene (B) and ethylbenzene (C); curve *c* represents CCM for the block copolymer with the composition *d* and curve *b* represents the critical concentration for the crystallisation of the block copolymer having the same composition[144].

The ternary diagrams illustrated in Figs. 6*b* and 6*c* for the poly(ethylene oxide) (PEO)–polyisoprene (PI) block copolymers in two selective solvents are an example of diagrams of the second type[144]. Fig. 6 shows that in benzene, an effective solvent for PEO, the critical concentration of the latter at which it crystallises (point *c*) is much higher than the critical concentration for micelle formation at which the phases are separated into layers (point *b*), while in ethylbenzene, a poor solvent, the opposite situation obtains. Accordingly, crystallisation in the effective solvent for PEO takes place after microlayer formation and therefore has little effect on the structure of the block copolymer, while in the poor solvent crystallisation precedes microlayer formation and determines the structure of the block copolymer. For example, fibrils of almost the same shape and thickness as in the crystallisation of pure polytetrahydrofuran are observed in the block copolymer of styrene and crystallisable polytetrahydrofuran[163]. The nature of the kinetic curves for the crystallisation of polytetrahydrofuran in the block copolymers remains the same, but, with increase of the content of the amorphous component, the crystallisation of the crystallisable component is retarded; the degree of crystallinity and the melting point decrease monotonically with decrease of the fraction of the crystallisable component in the block copolymer.

The study of the kinetics of the crystallisation of polystyrene–poly(ethylene oxide) block copolymers from dilute solutions, carried out by both structural methods and by dilatometric and calorimetric methods[164-169], showed that both the nature of the crystallisation and the morphology of the crystalline formations in the block copolymers correspond to those of pure PEO. The same behaviour was confirmed for block copolymers containing crystallisable polyphenylenesiloxanes[170,171] and polyurethanes[172]. However, a decrease of the size of the block below a definite limit and an increase of the content of the solvent lead to the disappearance of the ability of the block to crystallise[168]. For example, poly(ethylene oxide) with a molecular weight in the range 1000–20 000 does not crystallise in the block copolymer of poly(ethylene oxide) and polycarbonate[11].

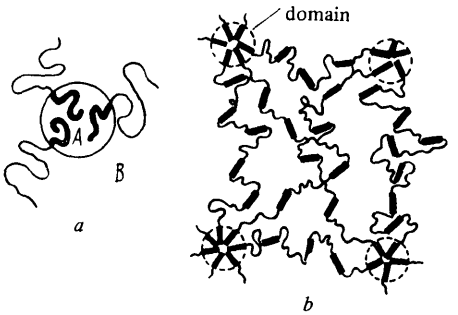



Figure 7. Models of the structure of block copolymers: *a*) Meier's model[28]; *b*) LeGrand's model for a polycarbonate–polydimethylsiloxane many-block copolymer[223].

The influence of the above factors on the type of structures formed can be treated theoretically by applying statistical thermodynamics to various selected models. This approach makes it possible to predict the type of structures arising under different conditions. Thus, in Meier's theory[28,173,174], attention is concentrated on the uniform filling of space by blocks in order to achieve a uniform density within the domains. In his model, which is illustrated in Fig. 7*a*, all the units A are distributed within the domain, while all the units B are outside it. Since contacts between heterogeneous units occur only at

the boundaries of the domains, the author estimated exactly the limits to the configurational entropy corresponding to the domain morphology. Using the general diffusion equation of statistical thermodynamics, he calculated the probability of the distribution of chains within the domain as function of their size and hence obtained the stable size of the domain corresponding to a conventionally uniform density. This stable size depends on the shape of the domain and amounted to $1.33\alpha\ KM^{1/2}$ for spheres, $1.00\alpha\ KM^{1/2}$ for cylinders, and $1.40\alpha\ KM^{1/2}$ for plates (where $M$ is the molecular weight of the polymer forming the domain, $K$ a constant relating the unperturbed dimensions of the polymer to the molecular weight, and $\alpha$ a parameter characterising the degree of perturbation of the chains). Thus, in order to maintain the conditions for a uniform density, the distance between the ends of the chains must differ from that for a Gaussian coil. The observed relation between the size of the domain and the size of the macromolecule was confirmed experimentally by low-angle X-ray scattering in polystyrene–polybutadiene–polystyrene block copolymers [130,175,176].

Subsequently Meier expressed the free energy of the above system as the sum of three components: the surface energy, the enthalpy of formation of the domains, and the change in entropy owing to volume restrictions and elastic deformations of the A and B blocks. By minimising the free energy, taking into account the shape of the domains, he obtained the conditions for microlayer formation and morphological transitions from one shape of the domain to another, expressed in terms of the dimensions of the blocks and their ratio.

The critical size of the polystyrene block thus obtained for the polystyrene–polybutadiene block copolymer proved to be greater by a factor of 2–2.25 than the critical molecular weight determined experimentally for macrolayer formation in mixtures of the same polymers. After introducing simplifying assumptions, Fedors [176] found that the minimum molecular weights of the blocks for which incompatibility is manifested amount to 2500 for polystyrene and 6000 for polybutadiene. The estimation of these quantities plays a major role in block copolymers of the ABA type, since the stabilising effect of the rigid component is shown only as a consequence of microlayer formation, i.e. when the dimensions of the blocks exceed the critical values indicated.

The critical dimensions of the blocks depend significantly on the nature of the polymer and on the affinity of the polymers for one another. Thus in polydimethylsiloxane–polysulphone block copolymers, incompatibility begins to be manifested starting from a molecular weight of polydimethylsiloxane of 2000, [80,178] while in polycarbonate–polydimethylsiloxane block copolymers it appears starting from a molecular weight of 875. [179] Furthermore, the size of the block should exceed the size of the segment for each polymer, determined by the condition that the glass point ceases to depend on the molecular weight. According to Kanig [177], this value is 12 000 for polystyrene. The greater of the two quantities—the size of the segment and the critical molecular weight for microlayer formation—determines the minimum size of the block which can be usefully employed in a block copolymer. For a given component ratio in the block copolymer, determined by the volume fraction $\Phi_A$ of one of the components, which is related to the molecular weights $M_A$ and $M_B$ and the densities $\rho_A$ and $\rho_B$ of the blocks by the expression

$$\Phi_A = \frac{2M_A\rho_B}{2M_A\rho_B + M_B\rho_A}, \qquad (14)$$

the selected molecular weight of one of the blocks determines the molecular weight of the second block.

Inoue and coworkers [153,180] expressed the surface free energy of formation of microphase regions in terms of their geometrical dimensions, their volume fraction (for different shapes of these regions—spherical, cylindrical, and lamellar), and the parameters of the interaction of the blocks with the solvent. The total free energy consists of the surface free energy and a term related to the entropy change:

$$G_{sph} = 6V_A^{2/3}(1/D_{sph})\ \Delta W + {}^3/_2 kTN\left\{\frac{D_{sph}^2}{4}\left[\frac{(1-V_A^{1/3})^2}{\sigma_B^2 n_B a_B^2} + \frac{V_A^{2/3}}{\sigma_A^2 n_A a_A^2}\right] - 2\right\} \qquad (15)$$

$$G_{cyl} = 4V_A^{1/2}(1/D_{cyl})\ \Delta W + {}^3/_2 kTN\left\{\frac{D_{cyl}^2}{4}\left[\frac{(1-V_A^{1/2})^2}{\sigma_B^2 n_B a_B^2} + \frac{V_A^{2/3}}{\sigma_A^2 n_A a_A^2}\right] - 2\right\} \qquad (16)$$

$$G_{lam} = 2(1/L)\ \Delta W + ({}^3/_2) kTN\left\{\frac{L^2}{4}\left[\frac{(1-V_A)^2}{\sigma_B^2 n_B a_B^2} + \frac{V_A^2}{\sigma_A^2 n_A a_A^2}\right] - 2\right\} \qquad (17)$$

where $L_{sph}$ and $D_{cyl}$ are the diameters of the sphere and the cylinder, $L$ is the length of the plate, $\Delta W$ the energy of the surface contact per unit surface, $V_A$ the volume fraction of the domain occupied by block A, $\sigma_A$ and $\sigma_B$ are the swelling parameters of the blocks characterising the ratio of their mean square distances in solution and in the free state (i.e. the interaction of the polymer with the solvent), $n_A$ and $n_B$ the degrees of polymerisation of the blocks, and $a_A$ and $a_B$ the sizes of the blocks.

Since the first terms on the right-hand sides of Eqns. (15)–(17) lead to a decrease of free energy and the second terms lead to its increase with increased geometrical size of the microphase region, the dependence of the free energy on the size of the microphase region is characterised by a minimum corresponding to a specific size of the region. The presence of this minimum shows that the microphase separation is thermodynamically the most stable process, in contrast to macroscopic phase separation in mixtures characterised by zero free energy of mixing. Since microphase regions having mainly the shape corresponding to the smallest relative free energy minimum are formed for the given weight fraction of block A, it follows (as can be seen in Fig. 8) that, with increase of the weight fraction of block A, there should be a transition from spherical to cylindrical and then to lamellar forms, which, as stated above, has been confirmed by numerous experimental data. The weight fraction of block A, corresponding to the transition from one type of structure to another, is found to depend on $\sigma_A/\sigma_B$, i.e. on the relative solvating capacity of the solvent in relation to each type of block, or on the selectivity of the solvent.

The size of the microphase region corresponding to the free energy minimum is expressed by the product of the surface tension and a function of three quantities: the degree of polymerisation of block A, its weight fraction, and the parameter $\sigma_A$. The concentration of the block copolymer in solution is not included among these parameters and therefore has little influence on the size of the microphase region. Two- and three-block polymers are characterised by identical thermodynamic features; the only difference is that in three-block polymers account must be taken of the possibility of a different disposition of the ends of the chain on the surfaces of the microphase regions (the two ends of the middle block may be located at the boundaries of the same or different regions). The size of the structural elements in three-block copolymers should be greater, other conditions being equal, than in two-block copolymers.

As the block structure becomes more pronounced, the conditions for the free energy minimum are significantly complicated, because microlayer formation does not go to completion (see Section II) which entails a less ordered form and distribution of the aggregates and in general a less distinct heterogeneous structure [176,181]. A similar theoretical examination of the transition temperatures in a three-block styrene–butadiene copolymer has been carried out [170,171] on the basis of approximately the same model for different types of structure and under different structure formation conditions. These temperatures proved to be in good agreement with the transition temperatures determined experimentally under the same conditions by scanning calorimetry, by turbidity measurements, and by electron microscopy.

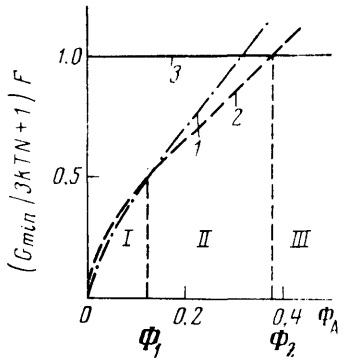



Figure 8. Dependence of the minimum in the free energy for layer formation on the composition of the block copolymer for spherical (line *1*), cylindrical (line *2*), and lamellar (line *3*) structures [153]; $F = (8/3)^{1/3}[(na^2\sigma_A^2)^{1/3}/\gamma^2]$, where $a$ is the size of block A, $n$ the degree of polymerisation of block A, $\sigma_A$ the swelling parameter of block A, and $\gamma$ the surface tension. The Roman numerals denote the regions corresponding to the existence of the lamellar (I), cylindrical (II), and spherical (III) formations.

Thus it follows from the above that a theoretical treatment involving statistical thermodynamics makes it possible to predict all the main properties of block copolymers (see also Refs. 153, 184, 185).

## VI. RELATION BETWEEN THE STRUCTURE OF BLOCK POLYMERS AND THEIR MECHANICAL AND PHYSICAL PROPERTIES

The vast majority of the published studies on the mechanical and other physical properties of block copolymers refer to two- and three-block copolymers of polystyrene with elastomers because, as already mentioned above, three-block copolymers of this class, in which the elastomeric (polybutadiene, polyisoprene) block is located between two blocks of the thermoplastic polymer, for example polystyrene, have found important practical applications as thermoelastoplastic materials [143,186–189]. The mechanical and physical properties of the block copolymer are determined by those of the continuous phase. The microphase regions in polystyrene, which consist of particles of the filler dispersed in the continuous elastomer matrix whatever the disposition of the blocks, tend to increase the strength of the elastomer [177]. However, only in polystyrene–elastomer–polystyrene block copolymers do the polystyrene domains serve simultaneously as nodes of a three-dimensional network between which the elastomeric blocks making up the matrix are deformed. Such polymers are therefore much stronger and less brittle than polymers of the elastomer–polystyrene–elastomer type having the same composition [17,123,143]. This makes it possible to obtain non-vulcanised rubbers with a fairly considerable strength, whose mechanical properties and the temperature range where they can be usefully employed are determined by the degree of microlayer formation, the perfection of the microphase structure of the block copolymer, and the glass points of the corresponding homopolymers. Above a definite polystyrene content, phase reversal takes place, which leads to a transition from thermoelastoplastic to thermoplastic polymers accompanied by a sharp increase of strength and the loss of viscoelasticity. Thermoelastoplastic properties have also been observed in other three-block copolymers, for example poly(ethylene sulphide)–polyisoprene [190] and polyster–poly(methyl methacrylate) [191] copolymers.

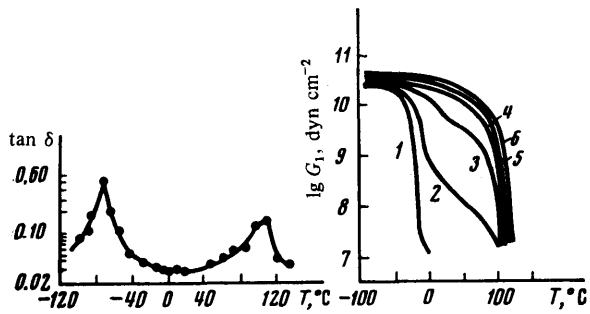



Figure 9. Temperature variation of tan δ (*a*) [195] and the dynamic modulus of elasticity (*b*) [198] for a polystyrene–polybutadiene block copolymer; percentage of polystyrene by volume: 1) 0; 2) 20; 3) 42; 4) 60; 5) 80; 6) 100.

The most characteristic property of block copolymers, which follows from their separation into individual microphases, is the presence of two glass points, reflecting the individual properties of each block. These two glass points are usually revealed by two maxima on plots of the temperature dependence of the mechanical [192–197] losses and two corresponding transitions on plots of the dynamic modulus against temperature [198–205]. The transition temperatures in block copolymers are also determined by differential thermal analysis and by scanning calorimetry [183]. There are block copolymers in which the glass points correspond fairly exactly to those of each component. Thus two loss peaks, at −80° and +100°C, are observed in the polybutadiene–polystyrene block copolymer (Fig. 9*a*), the polybutadiene glass point being independent of the composition and arrangement of the blocks [195]. Similar properties have been observed also for the polydimethylsiloxane and polyarylate block copolymers [14]. At the

same time the loss and dynamic modulus peaks depend on the composition of the block copolymer, starting from a definite fraction of polystyrene [192]. Fig. 9*b* illustrates the temperature dependence of the modulus of elasticity for styrene–butadiene block copolymers of different compositions. Evidently, at a fixed temperature the modulus varies sharply in the range of compositions corresponding to phase reversal.

However, complete microphase layer formation is by no means always observed and in many-block polycondensation copolymers is normally absent. Owing to the interpenetration of the blocks at the microphase interfaces, the glass points in the block copolymer are in most cases somewhat displaced: the glass point of the low-temperature block is higher and that of the high-temperature block is lower than for the pure components, the shift depending on the composition of the block copolymer. Whereas the glass point of the low-temperature, usually viscoelastic block, which in many cases constitutes a continuous matrix, usually changes by only several degrees (for example, the glass point of polydimethylsiloxane in the block copolymers of the latter with polysulphone [178], polycarbonate [179], and poly-$\alpha$-methylstyrene [206]), that of the high-temperature rigid block frequently decreases sharply (by many tens of degrees) with increase in the concentration of the second component (for example, the glass point of polysulphone in its block copolymers with polydimethylsiloxane [178]). In this respect, the polyblock polydimethylsiloxane–polyarylate copolymer is an exception, probably as a consequence of the marked incompatibility of the components. Only one glass point is frequently observed in the block copolymer, diminishing significantly with increase of the content of the low-temperature block [207-209]. This usually occurs in block copolymers where there is no microlayer formation owing to the mobility of both blocks (at a temperature below the glass points of both homopolymers) and the system consists of a single phase [210,211]. In those cases where the degree of interpenetration of the blocks is fairly considerable in systems with layer formation, a third, intermediate phase is produced, as in mixtures of polymers, this being indicated by the appearance of an intermediate maximum on the plot of the temperature variation of the tangent of the loss angle [212]. The existence of an intermediate phase in the majority of block copolymers is indicated by an increasing amount of data [213-217]; according to various estimates, its thickness is 13–15 Å and the ratio of the difference between the radii of the sphere surrounding this domain and of the domain itself, i.e. the thickness of the intermediate layer, to the radius of the domain is 0.1–0.2. [212]

In certain block copolymers, mainly polycondensation copolymers, the properties of the individual components are not manifested at all and, when the composition is altered, there is a gradual transition from the properties of one component to that of the other. Thus, whereas the double refraction arising on deformation of a thermoelastoplastic specimen, for example in a styrene–butadiene block copolymer, is determined by the elastic polybutadiene matrix and increases with increasing polystyrene content (as a result of the formation and orientation of an elastic network of polystyrene domains [217-222]), in the polydimethylsiloxane–polycarbonate block copolymer the optical stress coefficient is intermediate between the corresponding values for the pure components [223]. A model has been proposed for this block copolymer, according to which the intermediate phase is not concentrated around discrete microphase regions and its presence is manifested by the fact that some of the polycarbonate blocks are segregated into individual microregions, while others form part of the continuous matrix, alternating with dimethylsiloxane blocks (Fig. 7*b*). Models and equations (proposed for the theory of two-phase systems consisting of spheres immersed in a continuous matrix), whereby the fraction of each component in the continuous and discrete phases of homopolymers and block copolymers can be determined from the moduli of elasticity or stress corresponding to the transformation of the material into an elongated shape with a constriction (neck) (or some other parameter), have been used by Robeson et al. [80] Faucher [224] calculated the moduli of elasticity of block copolymers from the volume fractions of the components alone without taking into account the presence of microphases and the calculated data agreed fairly satisfactorily with experiment.

The presence of an intermediate phase is also revealed by relaxation phenomena in block copolymers. The experimental dependence of the relaxation of stress has been described satisfactorily [225-229] from the standpoint of the superposition of several relaxation mechanisms—mechanisms characteristic of homopolymers as well as additional mechanisms. One of the latter is associated with the simultaneous movement of the elastic and plastic segments at the grain boundaries, i.e. the boundaries of the microphase regions. The segments of the soft component become less mobile in this intermediate region, while those of the rigid component become more mobile, the molecular order in the segment being the same as in statistical copolymers. Another, additional relaxation mechanism is associated with the flow of the entire block copolymer after the fusion of the domains. The constants for these relaxation mechanisms depend on the component ratio in the block copolymer.

The microheterogeneity and the operation of several relaxation mechanisms lead to numerous transitions in block copolymers and cause the principle of the temperature–time superposition to be inapplicable [230]. It has been shown for a three-block thermoelastoplastic styrene–butadiene copolymer [231] that, below a specific temperature, where the polystyrene microregions play the role of an inert filler in the elastomer, both relaxation and creep obey a reduction formula with constants close to those of polybutadiene; above the polystyrene glass point, a reduction formula is again valid, but this time with constants close to those of polystyrene; between these temperatures, the temperature dependence of the relaxation times and hence of the reduction factor is quite different, which indicates the operation of a new relaxation mechanism. Creep in block copolymers is manifested to a greater extent the lower the degree of order in the microregions [232].

Despite the distinct microheterogeneity of block copolymers, one of their specific properties is a high degree of transparency, which distinguishes them from mixtures of polymers and which is caused by the limited size of the microregions (as pointed out above, their diameter does not exceed the length of the polystyrene block and reaches 200–300 Å) and by their regular arrangement [188,221,222].

One of the most characteristic mechanical properties of polymers is the relation between stress and elongation, characterising the modulus of elasticity, the characteristics of the deformation of the system, and its strength. A specific feature of block copolymers is that the nature of the plots of stress against elongation depends mainly on the ratio of the blocks. The size of the individual blocks and the molecular weight of the block copolymer have

comparatively little influence on its mechanical properties. With increased content of polystyrene, there is a transition from the properties of the pure elastomer to those of pure polystyrene, which is clearly shown in Fig. 10*a*.

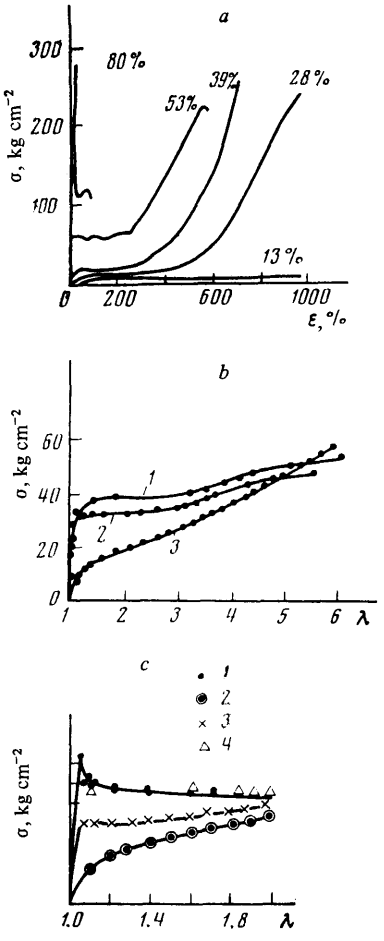



**Figure 10.** Dependence of the stress on deformation in films of SBS block copolymers having different compositions (*a*) [188], cast from different solvents (*b*) [236], and subjected to re-extension and annealing (*c*) [196];
*a*) for different polystyrene contents shown by the numerals against the curves;
*b*) [1) from ethyl methyl ketone; 2) from toluene; 3) from heptane];
*c*) [1) first extension; 2) repeated extension; 3) annealing for 8 min; 4) annealing for 41 days; λ is the relative elongation equal to the ratio of the final and initial lengths of the specimen].

This transition and the increased modulus of elasticity of the block copolymer are particularly marked when the content and the molecular weight of polystyrene are such that it is segregated as a separate phase [188], which depends to a considerable degree, as mentioned above, on the quality of the solvent, determining the conditions governing the incompatibility of the components. It follows from the results of Hendus et al. [130] that this happens in the presence of 50% of polystyrene in the polystyrene–polybutadiene system obtained from a solvent which is effective for both components. In films obtained from selective solvents, this phenomenon occurs in the presence of a much lower content of polystyrene.

The mechanical properties of block copolymers depend very significantly on the solvent from which the film has been cast [196,235–240]. The general rule is that the properties of the block copolymer approach those of the block in relation to which the given solvent is selective [80]. For example, Fig. 10*b* shows [241] that the properties of the film obtained from heptane, which is a selective solvent for isoprene, are typical for an elastomer, whereas the film obtained from ethyl methyl ketone, which is a selective solvent for polystyrene, has properties characteristic of polystyrene. In this case, this is manifested by the modulus of elasticity and the nature of the deformation, while the tensile stresses and deformations of the polymer are similar. In polysulphone–polydimethylsiloxane block copolymers obtained from various solvents, the strength varies from 130 to 220 kgf cm$^{-2}$ and the deformation is in the range from 310 to 517%. [80,165] The solvent has a particularly marked influence on polydimethylsiloxane–polyarylate block copolymers, while the deformation with rupture on passing from chloroform to a chloroform–hexane or chloroform–toluene mixture increases by a factor >3 (from 120 to 400%) with a comparatively small decrease of strength [242].

Thus, owing to the change in the conformation of the macromolecule and in the structure of the block copolymer when the quality of the solvent in relation to each block is altered, one can achieve in the general case, without altering the composition of the block copolymer, a transition from "rigid" systems to "soft" systems and conversely. In connection with the discussion of the influence of the solvent, it is interesting to note that, when the film is placed in a selective solvent where the entire block copolymer does not dissolve but merely swells vigorously, there is a significant increase in the elasticity of the film after subsequent drying and a simultaneous decrease in its strength (for example, the deformation of the polymethylsiloxane–polysulphone block copolymer increases from 410 to 970% after swelling in carbon tetrachloride, while its strength diminishes from 220 to 150 kgf cm$^{-2}$). [178]

The presence of a quasi-network in thermoelastoplastic materials leads to additional characteristics of their mechanical properties. One of their manifestations is different forms of the plots of the stress against elongation for primary and secondary deformation [196]. Primary deformation is characterised by the development of a neck, of the type characteristic of the plastic component of the block copolymer; on repeated deformation, when the rigid structure formed by the network of polystyrene microregions has been disrupted, the extension curve is typical of an elastomer. After a long time, particularly when the specimen is annealed at an elevated temperature, the plot recovers its initial form (Fig. 10*c*), which indicates the restoration of the network structure. Annealing also leads to the disappearance of the apparent residual deformations from the block copolymer [176].

Another characteristic feature of the mechanical properties of thermoelastoplastic materials consists in the dependence of the nature of the deformation on its extent. For small deformations, the system behaves as a "soft" system, i.e. only the elastic block is deformed, while the

rigid domains are either not deformed at all or undergo an extremely insignificant extension; for large deformations, the system becomes "rigid", i.e. the rigid blocks undergo plastic deformation, which leads to the disruption of the network nodes. As a result, the system again becomes "soft" for still larger deformations, i.e. is purely viscoelastic [188].

The rate of relaxation processes in block copolymers is lower than in statistical copolymers [243,244]. It is independent of temperature and deformation up to certain values of the latter, but, on further increase of these parameters and of the stress, the rate increases owing to the disruption and plastic flow of the polystyrene domains. The gradual disruption of the network nodes with increase in the degree of deformation also affects the linear increase of the optical stress coefficient with increase of deformation [208]. This effect is very small for homopolymers (non-cross-linked polybutadiene and polystyrene) and reaches its maximum value in the presence of a polystyrene content such that its domains create most effectively a network ensuring a rubber-like state of the system [209]. The size of the elastic block $M_c$ between the nodes of the quasi-network under consideration can be calculated using the statistical theory of viscoelasticity [20], applying this theory [245] with allowance for the dependence of the stress on the volume fraction of the filler, or using the Flory–Rehner theory [20], from the swelling of the block copolymer in the solvent interacting solely with the elastic matrix. However, one should note that the value of $M_c$ determined in this way is significantly smaller than the actual length of the elastic block. The possibility of applying the Flory–Rehner equation on swelling of block copolymers has not been demonstrated unambiguously [157,196,235], in particular it has been questioned in a theoretical study [247] where a significant dependence not only of the magnitude but also of the nature of the swelling on the shape of the structural elements in the block copolymer was demonstrated. The final solution of this problem requires further study.

The two-phase structure of the block copolymer is retained up to temperatures much above the glass point of polystyrene. This results in a maximum on the curve relating the viscosity of the melt to the composition of the block copolymer in the presence of the polystyrene content for which the network structure is most marked below the glass point [244]. However, this structure is shown much more clearly above the glass point; this is readily seen from the fact that at 100°C the moduli of elasticity of the block copolymer and the statistical copolymer having the same composition are identical, but on cooling the modulus of elasticity of the block copolymer increases sharply. The presence of a two-phase structure in the block copolymer melt is manifested by the existence of two different states of the melt, distinguished by the activation energy for viscous flow, which at 100°C is closer to the activation energy for polystyrene and at 200°C is closer to that for polybutadiene, this being associated with the onset of the flow of polystyrene domains above 120°C. [188,244] Hence it follows that the viscosity of the melts of block copolymers is extremely sensitive to a change of temperature: when the latter is raised from 80° to 180°C, the viscosity falls from $10^{10}$ to $10^5$ P. In contrast to the deformation properties of solid block copolymers, the viscosity of the melt depends very strongly on the molecular weights of the blocks and the entire block copolymer and to a lesser extent on its composition [244]. The viscosities of block copolymers can be measured not only above but also below the glass point; their finite values at 25°C indicate a fairly high degree of instability of the polystyrene domains.

The flow of block copolymers is non-Newtonian [248]. It has been shown [244] that the flow curves depend on the number and arrangement of the blocks for the same molecular weight of the polystyrene–polybutadiene block copolymer, namely the viscosity corresponding to the same stress decreases in the sequence SBS > SB > BSB, the differences being greater the lower the temperature. The dependence of the viscosity on stress in SBS is weaker than for other block copolymers, since the elastomeric blocks in this substance are clamped between the network nodes, but, for stresses exceeding $10^6$ dyn $cm^{-2}$, the temperature dependence of the viscosity is manifested to the greatest extent in this polymer. The influence of stress on the viscosity and rate of relaxation is of the same type and is related to the disruption of the polystyrene microregions.

Specific rheological characteristics are also shown in concentrated solutions [249–251] and gels of block copolymers. The gels are formed either on swelling of the block copolymers in selective solvents or following the addition of a selective precipitant to a solution of the block copolymer in an effective solvent. Apart from the polystyrene–poly(ethylene oxide) gels already described (see Section V), the following systems have been obtained: poly(methyl methacrylate)–polyacrylonitrile–chloroform; starch–polystyrene–water; poly(methyl methacrylate)–poly(vinylidene chloride)–benzene; polytetrafluoroethylene–poly(methyl methacrylate)–chloroform [81]. In the second method, the addition of the precipitant causes increased aggregation of the insoluble blocks, which leads to the formation of a continuous network in solution in the case of three- and many-block copolymers. In this type of structure formation process, there is a sharp increase of viscosity, in contrast to solutions of homopolymers and statistical copolymers, where the viscosity diminishes after the addition of the precipitant [252]. Solutions of polystyrene–polybutadiene block copolymers in n-decane exhibit a Newtonian viscosity up to a concentration of 30%. When they are treated with decalin, the non-Newtonian viscosity is shown at decreasing concentrations, a maximum appears on the curves relating the stress to time for a constant rate of shear, characteristic of the gel-like state, a limiting shear stress appears, the elasticity increases, and the system becomes thixotropic [253]. Analogous changes have been observed also in a many block polydimethylsiloxane–polyarylate copolymer.

One of the important physical properties of block copolymers is their permeability to gases, which depends, like mechanical properties, on the composition of the block copolymer and changes sharply in the region of phase reversal [254]. This makes it possible to combine the effective permeability of one homopolymer and the mechanical properties of another for a definite composition of the block copolymer. Such materials are extremely promising for use as gas-separating membranes.

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The above data demonstrate the exceptionally unusual structures and properties of the polymeric materials formed by macromolecules consisting of two or more blocks. The properties of solutions and gels of block copolymers are no less interesting.

These unusual combinations of properties are already used in engineering and give rise to the prospect of an extremely wide variety of applications of polymers of this

class. The most interesting and important practical application of block copolymers involves their use as thermoelastoplastic materials, whereby one may obtain cast articles with adequate strength from non-vulcanised rubbers. The wide-scale employment of thermoelastoplastic materials is delayed by their low thermal stability, determined by the glass point of polystyrene, which gives rise to the problem of finding the optimum chemical structure of the block copolymer. Other technical applications of block copolymers include their use as the so called pluronics—(rubbers based on polyethylene–polypropylene block copolymers having the properties of surfactants), as well as the use of block copolymers to increase the miscibility of homopolymers, to increase the stability of emulsions of both low- and high-molecular-weight compounds, as gas-separating membranes, and for many other purposes.

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# Recent Equilibrium and Kinetic Studies of the Adsorption of Gases and Vapours by Microporous Adsorbents

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Thermodynamic theories of adsorption equilibrium in micropores are discussed with special reference to the osmotic theory of adsorption, based on the vacancy solution model, and to the analogy between adsorption and osmotic equilibria. A thermal adsorption equation is derived, and its special cases are discussed, thus giving a quantitative description of adsorption on microporous adsorbents over a wide range of pressure and temperature. New methods of investigating the kinetics of vapour adsorption on microporous adsorbents and of describing the process theoretically by the bipore model are reviewed. Good agreement between experiment and theory is obtained. 40 references.

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## I. INTRODUCTION

This review describes the most important results obtained in recent years in the Sorption Processes Section of the Institute of Physical Chemistry of the USSR Academy of Sciences. We shall discuss the theoretical and experimental studies of equilibrium physisorption carried out by Bering and Serpinskii with the cooperation of Yakubov and Fomkin, and the studies of the kinetics of physisorption on adsorbents with a bipore structure by Zolotarev and Voloshchuk with Erashko, Gorlov, Shen, and Ulin.

## II. ADSORPTION EQUILIBRIA ON MICROPOROUS ADSORBENTS

Zeolites are typical microporous adsorbents. The similarity in size between the micropores and the adsorbed molecules produces a marked increase in the adsorption potential associated with dispersion forces. The presence of cations in the zeolite holes causes a large increase (by electrostatic interactions) in the energy non-uniformity of the adsorption sites of the micropores as compared with similar but chemically different adsorbents (e.g. carbons).

Our experimental and theoretical studies of the equilibrium adsorption of various vapours on micropores, started in 1946, have gradually led to the concept of a qualitative difference between adsorption in micropores and adsorption on non-porous or coarsely porous surfaces of a similar chemical nature. The theory of volume filling of micropores was proposed as a reasonable approximation to the description of adsorption in micropores [1-4]. We shall outline below only those aspects of this theory which are needed for the later discussion.

The most important function used in this theory is the differential molar heat of adsorption $A$,

$$A = -\Delta G = RT \ln (p_s/p), \quad (1)$$

which expresses the negative change in the Gibbs free energy $G$ when the standard state is defined as the normal liquid at temperature $T$ in equilibrium with its saturated vapour. In general the equilibrium vapour pressure and the saturation vapour pressure are replaced by the corresponding fugacities in order to correct for the non-ideality of the vapour.

The limiting adsorption $a_0$ corresponds to filling of the micropore volume, which can be treated as constant to a good approximation. Hence the temperature dependence of $a_0$ can be expressed as

$$a_0 = a_0^0 \exp [-\alpha (T - T_0)], \quad (2)$$

where $\alpha$ is the volume expansion coefficient of the adsorbate, which can be calculated approximately from the physical properties of the substance to be adsorbed (adsorband) [4]. If the adsorption at the equilibrium pressure $p$ and temperature $T$ is $a$, the coverage $\theta$ is defined as $a/a_0$.

The fundamental theoretical postulate of temperature invariance

$$(\partial A/\partial T)_\theta = 0 \quad (3)$$

was taken as an experimental fact from the work of Polanyi [5,6]. However the interpretation of the function $A$ [Eqn. (1)] as an adsorption potential and the attempt to justify the postulate (3) in terms of adsorption layers in micropores with equipotential surfaces are not entirely convincing. It should be noted that the experimental evidence for Eqn. (3) was obtained [4] not with relatively coarsely porous (e.g. mesoporous) adsorbents as expected but with typically microporous adsorbents such as active carbons.

By treating the temperature-independent characteristic adsorption equation $\theta = f(A)$ as a distribution of coverages with respect to differential molar free energy of adsorption, expressed in the form of the statistical Weibull equation, we arrive at the thermal adsorption equation

$$a = a_0 \exp[-(A/E)^n], \quad (4)$$

where $E$ is the characteristic adsorption energy ($E = A$ for $\theta = 1/e$) and $n$ is a small integer having a value between 2 and 6 in the main variant of the theory [2]. The temperature independent parameters of the distribution function of $E$ and $n$ are also parameters of Eqn.(4). This equation, combined with Eqns.(1) and (2), gives the thermal adsorption equation

$$a = a_0 \varphi(p/p_s, T). \quad (5)$$

We have shown [3,4] that both the adsorption equilibria and the corresponding differential heats of adsorption $Q(\theta)$ are satisfactorily described by Eqn.(4) in many adsorption systems involving microporous adsorbents, and in particular in zeolites. However the assumed temperature invariance of $A$ is only a rational approximation, which can be applied with acceptable precision only in the most favourable cases and in the temperature range 100° to 150°C. Furthermore it can predict only a decrease in differential heat of adsorption with increasing coverage. Heats of adsorption increasing with coverage lie outside the scope of the theory.

These considerations point to the need for a more perfect model of the equilibrium adsorption of vapours in micropores and for theoretical and computational approaches free from the above shortcomings. Bering and Serpinskii have developed and experimentally validated a more general theory of the thermodynamics of adsorption equilibria which has been termed the osmotic theory of adsorption [7]. We shall discuss the main variant of the theory with reference to microporous adsorbents.

## III. FUNDAMENTALS OF THE OSMOTIC THEORY OF ADSORPTION IN MICROPORES

Hill has shown [8] that physisorption equilibria between an adsorbent and a gas phase can be described either by adsorption thermodynamics or by solution thermodynamics. The adsorbent is usually assumed to be thermodynamically inert towards adsorption, and the methods of adsorption thermodynamics are used. However in microporous adsorbents like zeolites the linear dimensions of the crystallites vary during adsorption [9]. In this case the chemical potential of the adsorbent also varies, and it becomes more convenient to use the methods of solution thermodynamics.

This approach to the description of adsorption equilibria is particularly successful when used in conjunction with the solution model which has been termed the "vacancy solution". In this model the so-called adsorption vacancies are treated as one of the components of the solution in place of the solid adsorbent [10]. The term adsorption vacancy denotes the free elementary volume of the adsorption space of the micropores which is filled by one molecule of adsorbate during adsorption. Since the adsorption space of the micropores is limited by the micropore volume, we can define a maximum number of vacancies (equal to the limiting number of adsorbed molecules) per unit mass of the adsorbent. The adsorption tends asymptotically towards this number as the pressure of adsorband in the gas phase rises towards infinity. At any finite equilibrium pressure of the adsorband the adsorption space of the micropores contains adsorbed molecules and adsorption vacancies, which constitute the binary vacancy solution. At constant temperature the relationship between the equilibrium pressure in the gas phase and the mole fraction of solute (adsorbate), i.e. the extent of adsorption, is equivalent to a partial pressure curve for the vacancy solution or to an adsorption isotherm. Thus adsorption equilibrium between the adsorbent and the gas phase is equivalent to equilibrium between the vacancy solution and the same gas phase. In this model all the properties of the adsorbent are treated as properties of the vacancies, i.e. of the solvent. An adsorption equilibrium of this type is most conveniently analysed by solution thermodynamics.

These ideas have proved to be very fruitful because a physical as well as a formal thermodynamic analogy exists between adsorption equilibrium and osmotic equilibrium. This analogy was first recognised, for the simplest case of adsorption at a liquid surface, by Frumkin [11] in 1925, and it was subsequently formulated in detail by Adam [12]. Unfortunately it was not developed further.

Let us consider the physical basis of this analogy. We shall denote the number of moles of adsorbate and the number of vacancies per unit mass of the adsorbent by $a$ and $a^*$ respectively. For any equilibrium situation we have

$$a + a^* = a_m, \quad (6)$$

where $a_m$ is the limiting adsorption, assumed to be independent of temperature. We now define the mole fractions of adsorbate ($x$) and of vacancies ($x^*$) in the vacancy solution as

$$x = a/a_m, \quad x^* = a^*/a_m. \quad (7)$$

We shall treat the equilibrium between a microporous adsorbent and a gas phase as an equilibrium between two vacancy solutions at different concentration. One of these is the vacancy solution in the micropores, the other is a solution of adsorband molecules in a vacuum. In the latter solution the role of "solvent" is played by vacancies in the gas phase. Two solutions of the same components at different concentration can be in equilibrium only if one of them is exposed to an external potential field. It can easily be shown that the effect of this field is formally equivalent to a difference in hydrostatic pressure between the solutions. This difference is termed the osmotic pressure in solution theory.

We shall write expressions for the chemical potentials of the vacancies in these two solutions, using the subscript $\alpha$ to denote the quantities relating to the gas phase. The vacancy solution corresponding to the gas phase is always very dilute, and can be treated as an ideal solution:

$$\mu_\alpha^* = \mu_{\alpha 0}^* + RT \ln x_\alpha^* + p_\alpha V^*, \quad (8)$$

$$\mu^* = \mu_0^* + gRT \ln x^* + pV^*, \quad (9)$$

where $V^*$ is the molecular volume of the vacancies and $g$ is the osmotic coefficient which characterises (like an activity coefficient) the non-ideality of the vacancy solution in the micropores [13].

At equilibrium $\mu_\alpha^* = \mu^*$, and from Eqns.(8) and (9) we have

$$\mu_{\alpha 0}^* + RT \ln x_\alpha^* + p_\alpha V^* = \mu_0^* + gRT \ln x^* + pV^*. \quad (10)$$

When $x_\alpha^* = 1$, i.e. at zero concentration of the adsorband in the gas phase, we can write $x^* = 1$, $g = 1$, and $p_\alpha = p$.

Hence $\mu^*_{\alpha 0} = \mu^*_0$ in Eqn.(10). Defining the osmotic pressure as

$$\Pi = p - p_a, \tag{11}$$

we obtain

$$\Pi V^* = -gRT \ln x^* + RT \ln x^*_a. \tag{12}$$

As was pointed out above, the vacancy solution in the gas phase is very dilute, and $x^*_\alpha \simeq 1$: therefore the second term in Eqn.(12) can be ignored. If $W$ is the volume of micropores per unit mass of adsorbent the ratio $W/V^*$ is the limiting adsorption $a_m$:

$$W/V^* = a_m. \tag{13}$$

From Eqns.(12), (13), and (7) we obtain

$$W\Pi = -a_m gRT \ln (1 - a/a_m). \tag{14}$$

We now write the Gibbs–Duhem equation for the vacancy solution in the micropores, taking unit mass of the adsorbent at $T$ = const:

$$a\,d\mu + a^*\,d\mu^* = W\,d\Pi, \tag{15}$$

where $\mu$ is the chemical potential of the adsorbate. Since this solution is in osmotic equilibrium $d\mu^* = 0$, and therefore

$$a\,d\mu = W\,d\Pi. \tag{16}$$

Hence $\Pi = (1/W)\int_0^a a\,d\mu = \Phi/W$, where $\Phi$ is the integral of the Gibbs adsorption equation calculated from the adsorption isotherm. Obviously the value of $\Phi$ is proportional to the osmotic pressure of the vacancy solution in the micropores.

Introducing the only non-thermodynamic assumption of our argument—constancy of the osmotic coefficient $g$ at $T$ = const—we obtain the adsorption isotherm equation from Eqns.(14) and (16). Eqn.(14) is differentiated to give $d\Pi$ which is inserted into (16), from which we obtain an expression for $d\mu$:

$$d\mu = \frac{a_m gRT}{a(a_m - a)}\,da. \tag{17}$$

Integration of Eqn.(17) gives

$$\mu = \mu^0 + RT \ln p = gRT \ln \frac{a}{a_m - a} + K, \tag{18}$$

leading to the adsorption isotherm

$$p^{1/g} = \frac{a/\beta}{a_m - a}, \tag{19}$$

where $K$ is an integration constant and $\beta$ is a constant, or

$$a = a_m \beta p^{1/g}/(1 + \beta p^{1/g}). \tag{20}$$

Eqn.(20) has been used for a long time as an empirical adsorption isotherm with three parameters $a_m$, $\beta$, and $g$ (see, for example, Ref.14). The successful use of this equation over a wide range of coverages $a/a_m$ confirms the validity of our assumption of a constant osmotic coefficient $g$ at constant temperature.

The only temperature-dependent parameters of the adsorption isotherm equation (20) are $g$ and $\beta$. Expressions for their temperature dependence can be obtained from two almost self-evident non-thermodynamic assumptions. By analogy with the osmotic equilibrium we assume that the osmotic coefficient $g$ is a linear function of reciprocal temperature[15]:

$$g = C\left(1 - \frac{b}{T}\right), \tag{21}$$

and we further assume that this expression is a good approximation over a wide range of coverage. To express the temperature dependence of the parameter $\beta$ we assume that the adsorption isostere is linear at half-coverage (i.e. for $a = 0.5a_0$):

$$\ln p_{0.5} = C_{0.5} - \frac{L_{0.5}}{T}. \tag{22}$$

Introducing the symbol

$$\varphi(a) = \ln \frac{a}{a_m - a}, \tag{23}$$

and taking logarithms of Eqn.(19) we find

$$\ln p = g\varphi(a) - g \ln \beta. \tag{24}$$

Since $\varphi(a) = 0$ at $a = 0.5a_m$ we can write in this case

$$\ln p_{0.5} = -g \ln \beta. \tag{25}$$

Equation (26) for the temperature dependence is obtained in the form $f(a, p, T) = 0$ of the osmotic theory of adsorption by inserting $g$ from (21) and $\ln p_{0.5}$ from (25) into Eqn.(24), with allowance for Eqn.(22):

$$\ln p = C_{0.5} - L_{0.5}/T + C(1 - b/T) \ln \frac{a}{a_m - a}. \tag{26}$$

This equation can be written

$$\ln p = C_a - L/T, \tag{27}$$

where

$$C_a = C_{0.5} + C\varphi(a) \tag{28}$$

and

$$L = L_{0.5} + Cb\varphi(a) \tag{29}$$

are temperature-independent parameters. However their relationship to the amount of adsorption can be shown explicitly by using Eqn.(23).

Thus the thermal adsorption equation (26) has been obtained from the known adsorption isotherm (19), the thermodynamic variation of the osmotic coefficient with temperature (21), and the empirically justified assumption (22). The equation corresponds to linear isosteres over a wide range of adsorption values: linearity of the adsorption isosteres is known to be a universal property of adsorption equilibria, and is usually observed experimentally.

We note that in the initial portion of the adsorption isotherm, when the adsorption is very small and the vacancy solution approaches ideal behaviour at infinite dilution, the osmotic coefficient $g$ tends towards unity and the parameter $b$ tends towards zero. Thus it can be assumed that $g = 1$ in the initial portion of any adsorption isotherm, but as $a$ increases this coefficient rapidly changes to some other value which remains constant over a wide range of adsorptions.

## IV. EXPERIMENTAL FOUNDATIONS OF THE THERMAL EQUATION OF THE OSMOTIC THEORY OF ADSORPTION

The thermal adsorption equation (26) contains five parameters: $a_m$, $L_{0.5}$, $C_{0.5}$, $C$, and $b$, and in order to determine their values we need at least two experimental adsorption isotherms for temperatures $T_1$ and $T_2$, which must not be too close. The parameter $a_m$ can be evaluated from one of the isotherms (see below), and corresponding values of $\ln p_1$ and $\ln p_2$ are then found from the isotherms, by interpolation, for two or three suitable

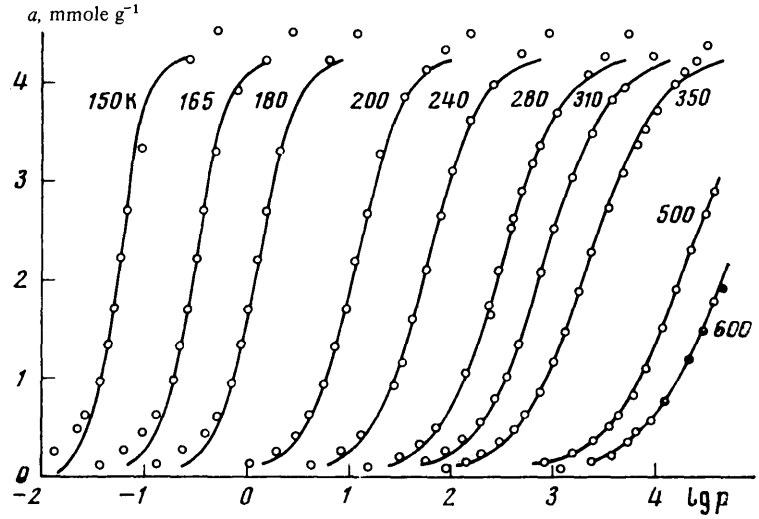



**Figure 1.** Adsorption isotherms of Xe on NaX zeolite. Full lines are calculated by Eqn. (26), circles are experimental.

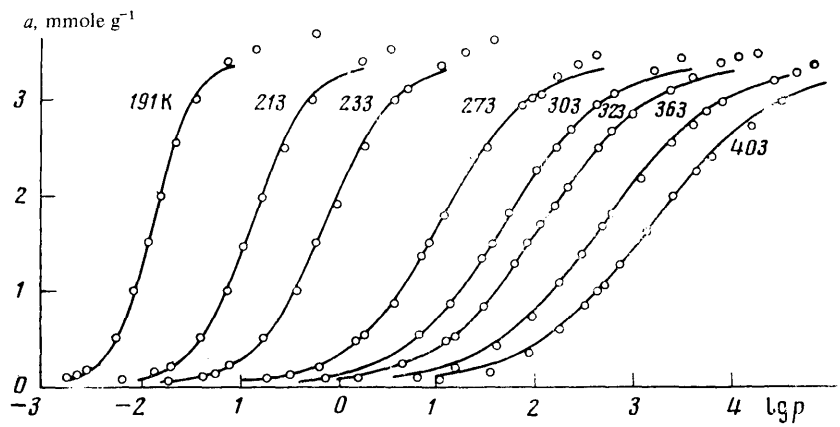



**Figure 2.** Adsorption isotherms of $CF_3Cl$ on NaX zeolite. Full lines are calculated by Eqn. (26), circles are experimental.

values of the adsorption. The parameters $C_a$ and $L$ are calculated by Eqn. (27) for the chosen values of $a$ = const, and $C_{0.5}$ and $C$ are determined by Eqn. (28). $L_{0.5}$ and $b$ are determined similarly by Eqn. (29).

The thermal equation (26) of the osmotic theory of adsorption gives a very accurate description of adsorption equilibria of gases and vapours on different microporous adsorbents such as zeolites and active carbons over a wide range of temperature and pressure. We shall illustrate the agreement between theory and experiment by considering two of the systems which have been studied in the writer's laboratory[16,17]: Xe on NaX zeolite and $CF_3Cl$ on NaX zeolite. This work is experimentally interesting because the apparatus developed for it has proved suitable for precise measurements of adsorption equilibria over very wide ranges of pressure (from $\sim 10^{-2}$ mmHg to 100 atm) and of temperature (from 150 to 600 K).

Plots of $a$ against lg$p$ in Fig. 1 show as full lines the adsorption isotherms of Xe on crystals of NaX zeolite calculated for different temperatures by Eqn. (2) with the following values of the parameters: $a_m$ = 4.30 mmole g$^{-1}$, $L_{0.5}$ = 1225 K, $C_{0.5}$ = 6.76, $C$ = 1.14, and $b$ = 109 K. The agreement between theory and experiment is good in the range of coverage ($a/a_m$) from 0.09 to 0.93 for a wide range of temperature (150–600 K) including the critical temperature of the adsorband ($T_c$ = 290 K). An analogous family of isotherms for the adsorption of $CF_3Cl$ on the same sample of NaX zeolite is shown in Fig. 2. The parameters $a_m$ = 3.40 mmole g$^{-1}$, $L_{0.5}$ = 1850 K, $C_{0.5}$ = 7.80, $C$ = 2.38, and $b$ = 154 K were used for calculations by Eqn. (26). The experimental temperature range again

includes the critical temperature ($T_c$ = 302 K), and the agreement between theory and experiment is again good for coverages between 0.09 and 0.97.

It is important to note that the adsorption isosteres are linear in both systems for this range of coverage. The thermal adsorption equation (26) applies at temperatures both above and below the critical temperature with the same set of parameters. The excellent agreement between the calculated and the experimental adsorption isotherms and the linearity of the isosteres (e.g. for $a = 0.5a_m$) are direct experimental confirmation of the validity of the basic assumptions of the osmotic theory of adsorption: constancy of the osmotic coefficient $g$ at $T$ = const and linearity of the standard adsorption isostere.

## V. THERMODYNAMIC ADSORPTION EQUILIBRIUM FUNCTIONS

Expressions for the main thermodynamic functions of the adsorption equilibrium in the range of $p$ and $T$ values for which the gas phase can be treated as almost ideal are easily obtained from Eqns.(22) and (29). According to Eqns.(24) and (25) the differential Gibbs free energy $G$ is given by the expression

$$G = RT \ln p = G_{0,s} + gRT\varphi(a). \quad (30)$$

Differentiating this expression with respect to $T$ with $a$ = const, and allowing for the temperature dependence of $g$ [Eqn.(21)], gives an expression for the differential entropy of adsorption $S$:

$$S = -(\partial G/\partial T)_a = S_{0,s} - CR\varphi(a). \quad (31)$$

If the equilibrium gas phase is ideal we have $RL = Q$, where $Q$ is the differential heat of adsorption. Hence, from Eqn.(29),

$$Q = Q_{0,s} + CbR\varphi(a). \quad (32)$$

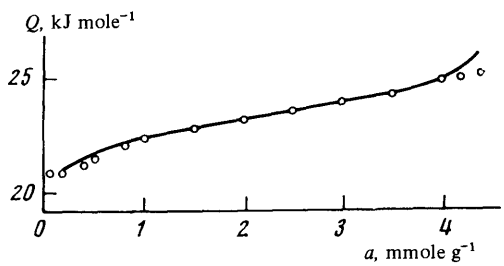



Figure 3. Differential heat of adsorption of Xe on NaX zeolite against $a$. The full line is calculated by Eqn.(32), the circles are experimental values of $Q$.

It can be shown by thermodynamic arguments that the parameter $C$ in formula (21) cannot be negative. Hence it follows from Eqn.(32) that for $T$ = const the dependence of the heat of adsorption $Q$ on $a$ is determined by the sign of the parameter $b$. For $b > 0$, $Q$ increases with adsorption (and coverage), whereas for $b < 0$ $Q$ decreases as $a$ increases.

The variation with adsorption of the differential heat calculated by Eqn.(32) (full line) is compared in Fig. 3 with experimental results for the Xe–NaX system at $T$ = 165 K in the region of $p$ values for which the gas phase can be treated as ideal. The agreement between calculation and experiment is satisfactory.

Thus the osmotic theory of adsorption equilibria leads to a thermal adsorption equation which allows us to express the isotherms, isosteres, and thermodynamic equilibrium functions in terms of a single set of parameters.

## VI. COMPARISON OF CALCULATIONS USING VARIOUS EQUATIONS OF ADSORPTION IN MICROPORES

A computer study has shown[18] that the parameters of the adsorption equations given by the micropore volume filling theory and the osmotic theory of adsorption can be optimised to enable Eqns.(4) and (20) to describe accurately the same experimental results over a wide range of coverage:

$$a_m = \varkappa a_0 \quad (33)$$

$$g = \frac{E}{RT}F \quad (34)$$

$$\ln\beta = \left[\frac{\ln(2/\varkappa)}{F}\right]^{1/n} - \frac{1}{g}\ln p_s. \quad (35)$$

Table 1. Conversion coefficients.

| $n$ | $\varkappa$ | $F$ | | $\theta_{min}$ | $\theta_{max}$ |
|---|---|---|---|---|---|
| 2 | 1.182 | 0.3440 | 2.109 | 0.21 | 0.91 |
| 3 | 1.054 | 0.2228 | 3.869 | 0.35 | 0.96 |
| 4 | 1.025 | 0.1696 | 5.330 | 0.46 | 0.98 |

Table 2. Adsorption isotherms of methane on zeolite L.

| $T$=156 K * | | | $T$=156 K * | | | $T$=243 K ** | | | $T$=243 K ** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $p$, mmHg | $a$, mmole g⁻¹*** TVF | OTA | $p$, mmHg | $a$, mmole g⁻¹*** TVF | OTA | $p$, mmHg | $a$, mmole g⁻¹*** TVF | OTA | $p$, mmHg | $a$, mmole g⁻¹*** TVF | OTA |
| 3 | 0.709 | 0.714 | 100 | 1.814 | 1.813 | 500 | 2.099 | 2.098 | 1 500 | 1.236 | 1.239 |
| 5 | 0.871 | 0.872 | 120 | 1.857 | 1.855 | 400 | 0.635 | 0.640 | 2 000 | 1.361 | 1.364 |
| 10 | 1.105 | 1.104 | 140 | 1.891 | 1.888 | 450 | 0.685 | 0.689 | 3 000 | 1.519 | 1.521 |
| 20 | 1.339 | 1.341 | 160 | 1.919 | 1.916 | 500 | 0.731 | 0.734 | 4 000 | 1.617 | 1.617 |
| 40 | 1.562 | 1.564 | 200 | 1.963 | 1.958 | 750 | 0.916 | 0.917 | 6 000 | 1.731 | 1.728 |
| 60 | 1.681 | 1.682 | 250 | 2.002 | 1.998 | 1000 | 1.050 | 1.052 | 10 000 | 1.835 | 1.833 |
| 80 | 1.758 | 1.758 | | | | | | | | | |

*Assuming $a_0$ = 2.207 mmole g$^{-1}$, $n$ = 3, $E$ = 2.350 kcal mole$^{-1}$, $a_m$ = 2.213 mmole g$^{-1}$, $g$ = 1.539, $\beta$ = 0.2281, $f_S$ = 8200 mmHg.

**Assuming $a_0$ = 1.934 mmole g$^{-1}$, $n$ = 3, $E$ = 2.350 kcal mole$^{-1}$, $a_m$ = 2.213 mmole g$^{-1}$, $g$ = 1.237, $\beta$ = 0.003315, $f_S$ = 62 000 mmHg.

***TVF denotes calculation by the equation of the theory of volume filling, OTA denotes calculation by the equation of the osmotic theory of adsorption.

The conversion coefficients $\kappa$, $F$, and $y$ for the adsorption systems to which Eqn.(4) is applicable are listed in Table 1, together with the ranges of coverage $\theta = a/a_m$ within which formulae (33)–(35) can be used with adequate

precision at temperatures between 100 and 150 K. As an example, points on the isotherm for the adsorption of methane on zeolite L calculated by Eqns. (4) and (20) for 156 K are compared in Table 2. The range of coverages $\theta$ lies within the limits given in Table 1 for $n = 3$. The results of the calculations are almost indistinguishable. However the osmotic theory of adsorption allows us to describe adsorption equilibria in microporous adsorbents over wider ranges of pressure and temperature, and in particular above the critical point.

## VII. THE BIPORE MODEL OF MICROPOROUS ADSORBENTS IN THE KINETICS OF PHYSICAL ADSORPTION

Pores in adsorbents can be classified[4,19] according to the mechanism of the adsorption and of the capillary phenomena in the adsorbent grains into micropores ($r < 6-7$ Å), supermicropores ($6-7 < r < 15-16$ Å), mesopores ($15-16 < r < 1000-2000$ Å), and macropores ($r > 1000-2000$ Å). The symbol $r$ denotes the equivalent pore radius, equal to twice the ratio of the normal cross-sectional area to the perimeter of the pore.

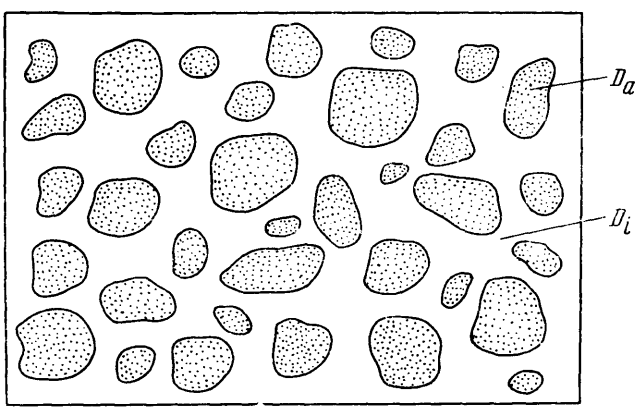



Figure 4. Model of the biporous adsorbent.

In many practical cases we can simplify the structure of the adsorbent and consider only two types of pore with very different properties: adsorption pores (micro- and supermicropores) and transport pores (meso- and macropores). This bipore model of the adsorbent, which can be applied successfully to zeolites, is illustrated in Fig. 4. The grey areas represent microporous regions of the adsorbent, consisting exclusively of adsorption pores. The transport pores are located in the region between the microporous regions.

The adsorption kinetics of biporous adsorbents have been studied by other workers[20-24] as well as in our laboratories[25-39]. The equations of inner diffusion in biporous adsorbents have been investigated for the general case of non-linear adsorption isotherms, and generalised for microporous regions (crystals) of difference size with a finite diffusional resistance to the entry of molecules into the crystal[26,28,31,32]. The latter resistance arises from the potential barrier at the boundary of the microporous region which the molecules must overcome. By using the statistical moment method fairly simple analytic expression can be obtained relating the characteristic times of diffusion in adsorption pores ($\tau_a$) and in transport pores ($\tau_i$) to the moments of the kinetic curves[28-33]. For inner-diffusion kinetics in microporous regions of equal size the first- and second-order moments are

$$M_1 = g_{v1}\tau_i + g_{\mu 1}\tau_a,$$
$$M_2 = g_{v2}\tau_i^2 + 4g_{v1}g_{\mu 1}B\tau_i\tau_a + g_{\mu 2}B\tau_a^2. \qquad (36)$$

In these equations $\tau_i = L^2(1+\Gamma)/D_i$, $\tau_a = r_0^2/D_a$, $\Gamma = a_0/c_0$, $L$ and $r_0$ define the size of the granule and of the microporous regions, $D_i$ and $D_a$ are the diffusion coefficients for the transport pores and for the microporous regions respectively, $a_0$ is the equilibrium value of the adsorption, $c_0$ is the concentration of adsorband at the surface of the granule. For industrial adsorbents we can take $B = 1$. The coefficients $g_{v1}$, $g_{\mu 1}$, $g_{v2}$, $g_{\mu 2}$ are determined by the geometric shape of the granule and of the microporous regions: their values for various assumed geometries are tabulated, for example, in Ref. 33. We have discussed and generalised Eqns. (36) by allowing for a distribution of crystal sizes and for the finite diffusional resistance to the entry of adsorbate molecules into zeolite crystals[31,32]. We have also developed a method of determining the coefficients in biporous adsorbents by monitoring the diffusion of the adsorband between two vessels through a granule of the adsorbent[34]. The diffusion coefficients for the adsorption pores and the transport pores have been determined separately by using the above expressions, and the transport mechanism in real microporous adsorbents such as zeolites and active carbons has been analysed[33,34]. The analysis has confirmed the validity of the bipore model of real microporous adsorbents.

A comparison[35] of calculated and experimental results has shown that the equations of the bipore model can be used to describe the sorption kinetics of low-molecular compounds (benzene, hexane) on two-phase polymer systems such as block copolymers and mixed polymers for the case of a linear adsorption isotherm. Furthermore these polymer systems can be treated as real models of a biporous medium, since their diffusional, structural, and sorption characteristics can be quantitatively determined by independent methods.

Considerable interest has been shown in the direct calculation of $\gamma(t)$ kinetic curves (where $\gamma$ is the relative adsorption averaged over a grain) for a biporous adsorbent with different ratios of the $\tau_i$ and $\tau_a$ relaxation times. Computer calculations for linear adsorption isotherms and spherical, cylindrical, or flat adsorbent grains have been reported[36,37].

## VIII. KINETICS OF PHYSISORPTION ON BIPOROUS ADSORBENTS FOR SHARPLY CONVEX ADSORPTION ISOTHERMS

The inner diffusion equations for biporous adsorbents have been studied in our laboratory for the case of linear adsorption isotherms[25,26,28-33] and also for sharply convex isotherms quickly approaching saturation ("rectangular" isotherms)[39,40]. We examined the case of cylindrical (or prismatic) adsorbent grains with an impermeable side surface, and we studied changes in the local concentration of adsorbate in the grain as a function of time [$a(x)$, where

$x$ is the distance from the end-face of the grain] as well as changes in the relative adsorption averaged over the grain [$\gamma(t)$, the kinetic curve]. The result is strongly dependent on the ratio of the characteristic times for the establishment of adsorption equilibrium in the transport pores and in the microporous regions ($\tau_i$ and $\tau_a$ respectively).

With sharply convex isotherms we can obtain a clear picture, which confirms the validity of the bipore model of zeolites and microporous active carbons, by studying the adsorption kinetics of vapours which give X-ray contrast under irradiation with X-rays [25,27,33]. The main advantage of this method is the possibility of visual observation of the formation and propagation of an adsorption front in the adsorbent grain. Consider a cylindrical grain of zeolite in which the side surface and one of the end faces are impermeable, and adsorption of an X-ray contrasting vapour is proceeding from the other end-face (Fig. 5). If the rate of adsorption is determined by diffusion in the zeolite crystals ($\tau_a \gg \tau_i$) the X-ray pictures show a gradual darkening of the entire adsorbent granule (Fig. 5*a*). On the other hand if the process is limited by diffusion in the transport pores ($\tau_i \gg \tau_a$) we expect a sharp adsorption front to be created in the case of a sharply convex adsorption isotherm, i.e. the zeolite granule should be filled "layer by layer" (Fig. 5*c*). In this case the adsorption wave $a(x)$ is almost rectangular in shape, and the kinetic curve is $\gamma(t) \propto \sqrt{t}$.

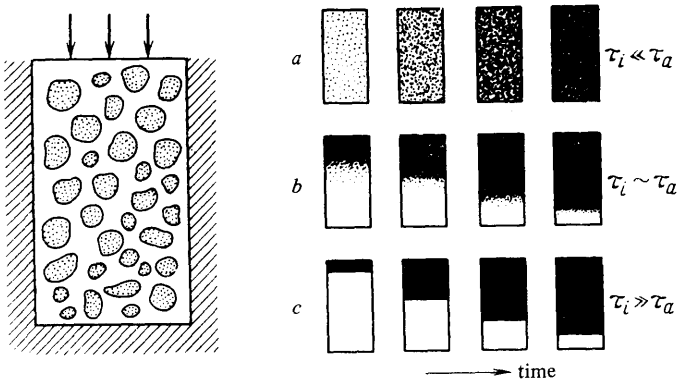



Figure 5. Granule of formed zeolite with an impermeable side surface (adsorption flow is indicated by arrows) and distribution of adsorbate in the adsorbent granule for different relative values of $\tau_a$ and $\tau_i$.

In the intermediate case (when $\tau_i$ and $\tau_a$ are comparable) we observe the formation and propagation through the grain of an adsorption wave [$a(x)$] with a diffuse front (Fig. 5*b*). In this case theory predicts [38,39] a $\gamma(t)$ variation more complex than a simple $\sqrt{t}$ law. The exact form of the $\gamma(t)$ relationship is determined by the form of the kinetic function describing the filling of the microporous regions such as the zeolitic crystallites within the grain [$\varphi(t)$, where $0 \leqslant \varphi(t) \leqslant 1$]. We have obtained, for this case, an approximate integral equation for the law of motion of the leading front of the adsorption wave $l(t)$ (Fig. 6):

$$\hat{l}^2(s) = \frac{2D_i}{s^2[(a_0/c_0)\, s\hat{\varphi}(s) + 1/6]}, \qquad (37)$$

where

$$\hat{l}^2(s) = \int_0^\infty e^{-st} l^2(t)\, dt \text{ and } \hat{\varphi}(s) = \int_0^\infty e^{-st}\varphi(t)\, dt \qquad (38)$$

are the transforms of the functions $l^2(t)$ and $\varphi(t)$. In particular, an analytic solution was obtained for the kinetic functions $\varphi(t) = 1 - \exp(-t/\tau_a)$ and $\varphi(t) = 6\sqrt{t/\pi\tau_a}$, where $\tau_a = r_0^2/D_a$ is the characteristic time for diffusion in the micropores, which provide a model of the diffusional mechanisms operating in the initial and the final stages of adsorption in the microporous regions. If the function $\varphi(t)$ is more complex, $l(t)$ can be obtained from Eqn. (37) by numerical inversion of the Laplace transform. The deviation from the true solution introduced by the use of Eqn. (37) is less than 5% in the limiting case ($\tau_a = 0$). In principle Eqn. (37) allows us to determine the kinetics of adsorption in the microporous regions [$\varphi(t)$] from the known equation of motion of the leading front of the adsorption wave [$l(t)$], and vice versa. The equation can also be used to calculate the diffusion coefficients.

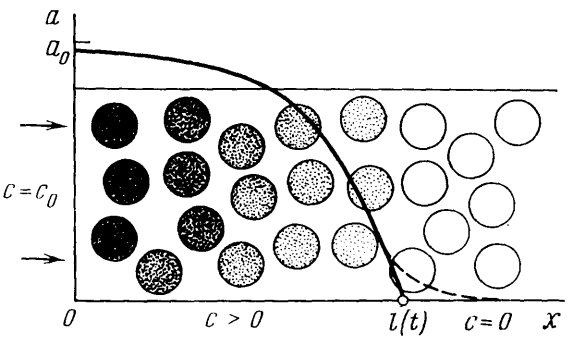



Figure 6. Adsorption front in a granule of biporous adsorbent. The filling of the crystals is indicated qualitatively by the darkening of the circles.

We have also studied theoretically the time dependence of the width of the front of the adsorption wave in the intermediate case ($\tau_i = \tau_a$). [39] For a rectangular adsorption isotherm we found that this quantity ($\Delta t$) decreases with time. The exact form of the falling function $\Delta(t)$ depends on the form of the kinetic function which describes the filling of the micropores [$\varphi(t)$]. In particular, if $\varphi(t) = 1 - \exp(-t/\tau_a)$, we have

$$\Delta(t) = \sqrt{\frac{2D_i\tau_a c_0}{a_0}}\left[\sqrt{\frac{t}{\tau_a} + \ln(1-\varepsilon_1) + 1} - \sqrt{\frac{t}{\tau_a} + \ln\varepsilon_1 + 1}\right]. \qquad (39)$$

In this expression $\epsilon_1 > 0$ is a small quantity used in the definition of the width of the adsorption wave front $a(x)$:

$$\Delta(t) = x_2(t) - x_1(t)$$
$$a(x_1)/a_0 = 1 - \varepsilon_1, \quad a(x_2)/a_0 = \varepsilon_1. \qquad (40)$$

The theoretical prediction of a changing width of the adsorption wave front can be tested experimentally by studying the adsorption kinetics of substances opaque to X-rays. We have used this method to study the adsorption kinetics of ethyl iodide, ethyl bromide, and bromobenzene from a stream of nitrogen on CaA, CaX, and NaX zeolites, and on active carbons. Adsorption on the type-X zeolites and on active carbons from a stream of carrier

gas gave a clear indication of "layer by layer" filling of the granules (Fig. 5*c*). With CaA zeolites containing different binders and with granules formed in different ways all three cases were observed (Fig. 5). The intermediate situation ($\tau_i \simeq \tau_a$, Fig. 5*b*) is most easily observed in the adsorption of bromobenzene and xenon from a one-component gas phase on microporous active carbons with molecular-sieve properties [33,40]. The results of these experiments are shown in Fig. 7. Initially the adsorption front is quite diffuse in all the series of photographs, but it becomes sharper with time and at long enough times we observe "layer by layer" filling of the granules.

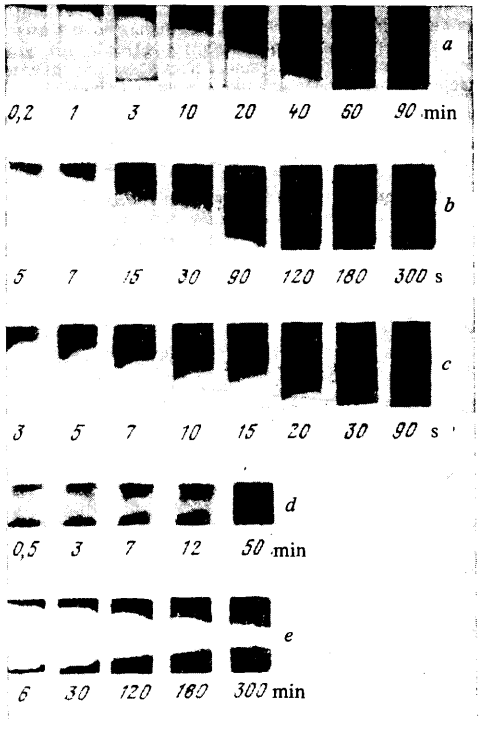



Figure 7. Distribution of xenon (*a*, *b*, *c*) and bromobenzene (*d*, *e*) in a granule of active carbon at successive times. The temperature is $T$ = 195 K (*a*, *b*, *c*) or $T$ = 303 K (*d*, *e*); pressure of adsorband $p$ = 0.9 kPa (*a*), 13.3 kPa (*b*), 26.6 kPa (*c*), 27 Pa (*d*), concentration of adsorband $c$ = 10 mg litre$^{-1}$ (*e*).

## IX. THE STATISTICAL MOMENT METHOD AND ANALYSIS OF EXPERIMENTAL DATA ON ADSORPTION KINETICS

The statistical moment method has been widely used in recent years for analysing quantitatively experimental data on the kinetics of adsorption on biporous adsorbents with linear adsorption isotherms. It can be shown that in the case of rectangular adsorption isotherms the statistical moments of the kinetic curve $M_k$ can also be related to the law of motion of the boundary $t_*(x)$ and to the moments of the kinetic filling function of the microporous regions $M_{\varphi k}$ by analogous expressions, which in this case take the form

$$M_1 = M_{\varphi_1} + \frac{1}{R}\int_0^R t_*(x)\,dx, \qquad (41)$$

$$M_2 = M_{\varphi_2} + 2M_{\varphi_1}\frac{1}{R}\int_0^R t_*(x)\,dx + \frac{1}{R}\int_0^R t_*^2(x)\,dx \qquad (42)$$

where $R$ is the characteristic dimension of the adsorbent grains.

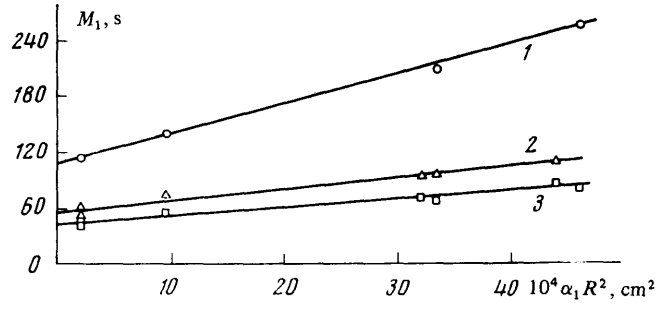



Figure 8. Moments of the kinetic curves ($M_1$) against $\alpha_1 R^2$; xenon on MSC-5A; 195 K; $p$ = 0.8 kPa (*1*), 13.3 kPa (*2*), 26.6 kPa (*3*).

These expressions can be combined with the law of motion of the boundary to analyse experimental data on the adsorption kinetics of biporous adsorbents. In particular, it follows from Eqn. (41) that if the adsorption kinetics in the microporous regions are exponential and the characteristic time $\tau_a$ is not too great (more strictly, $\tau_a < R^2 a_0/2D_i c_0$) we can write

$$M_1 = \frac{\tau_i}{6} + \frac{2}{3}\tau_a\sqrt{\frac{2\tau_a}{\tau_i}}, \quad \tau_i = \frac{a_0}{c_0}\frac{R^2}{D_i}. \qquad (43)$$

The result of a gravimetric study of the adsorption kinetics of xenon by granules of active carbon of different size are illustrated in Fig. 8, where the first moments of the kinetic curves ($M_1$) are plotted against $\alpha_1 R^2$. $\alpha_1$ is the shape factor of the granules. The moment of the kinetic function for the microporous regions $M_{\varphi 1}$ can be determined by extrapolation as the intercept on the vertical axis. We stress that Fig. 8 relates to the analytically more demanding situation of intermediate adsorption kinetics, when the characteristic diffusion times in the adsorption pores ($\tau_a$) and in the transport pores ($\tau_i$) are comparable. The integral of Eqn. (41) can be calculated from plots of $l(t)$ or $t_*(x)$ (Fig. 9), constructed from the radiographs of Fig. 7. The total moments $M_1$ calculated from Eqn. (41) agree with the experimental values.

The law of motion of the adsorption front $l(t)$, which can be determined for example by X-radiography, allows us to evaluate not only the integral characteristics of the kinetic function ($M_{\varphi k}$) but also the function $\varphi(t)$ itself. This involves solving the integral equation (37) with respect to $\varphi(t)$. The solution of this problem (inversion of the integral Laplace transform) is unstable towards small changes in the initial function $l(t)$, and therefore the experimental determination of $l(t)$ must be made with great care. This requirement is typical of the present

state of adsorption studies, with measurements of the microscopic properties of the adsorbent aimed not only at the integral properties of the adsorption process but also at its local characteristics (for example, as in this case, the distribution of adsorbate within the grain of adsorbent).

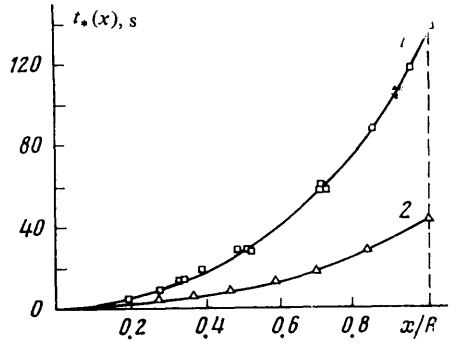



Figure 9. Plots of $t_*(x)$: $p$ = 13.3 kPa (*1*) 26.6 kPa (*2*).

Work in our laboratory [25-40] and elsewhere [20-24] has shown that the bipore kinetic model offers some important advantages in the study of adsorption kinetics on real adsorbents, and in particular on formed zeolites. It gives a correct interpretation of the experimental results, free from the limitations of the classical quasi-diffusional model. However our model needs further experimental confirmation, particularly as regards the mechanism of mass transport in the microporous regions. The bipore model should ultimately lead to a rational choice of real adsorbents with the most favourable pore structure.

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# Present State of the Chemistry of Technetium

V.I.Spitsyn, A.F.Kuzina, and A.A.Oblova

We review recent work in the Soviet Union and abroad on the chemistry and technology of technetium which allows the properties of this element to be discussed in the light of Mendeleev's Periodic Law. A section outlining the history of the discovery of technetium is included because of the many inaccuracies in the published accounts of the search for this element. 129 references.

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## I. INTRODUCTION

The rapid development of nuclear energy has highlighted the problems associated with the treatment of nuclear fuels, including the regeneration of uranium and plutonium and the extraction from the waste products of the nuclear industry of valuable isotopes for use in various technological processes.

Among the most interesting fission products of uranium is the isotope technetium-99, the first artificially radioactive element, found in nature in insignificant amounts. It can be prepared from waste products of the atomic energy industry[1,2]. Technetium has some unique superconducting[3], anti-corrosion[4,5], and catalytic properties[6,7], as well as a high melting point (2200°C)[8] and boiling point (4700°C),[9] and therefore it offers a number of possibilities as a new technological material for refractory, corrosion-resistant, and superconducting structures.

Table 1. Unit cell parameters of technetium and rhenium compounds.

| Compound | Cell parameter, A | Reference |
|---|---|---|
| $K_2[TcCl_6]$ | $a=9.89$ | 12 |
| $K_2[ReCl_6]$ | $a=9.84$ | 12 |
| $[TcO_2Py_4]Cl\cdot 2H_2O$ | $a=14.40$; $b=12.34$; $c=15.06$ | 13 |
| $[ReO_2Py_4]Cl\cdot 2H_2O$ | $a=13.95$; $b=12.04$; $c=15.04$ | 13 |
| $[ReO_2Py_4]Cl\cdot 2H_2O$ | $a=13.592$; $b=11.973$; $c=15.55$ | 14 |
| $K_3[Tc(CN)_6]$ | $a=12.106$ | 15 |
| $K_3[Re(CN)_6]$ | $a=12.033$ | 15 |
| $K_2TcH_9$ | $a=9.64$; $c=5.56$ | 16–18 |
| $K_2ReH_9$ | $a=9.607$; $c=5.508$ | 16–18 |

The study of the properties of technetium—a transition element with an unfilled outer electronic *d*-shell—should help to clarify the nature of its chemical bonding. Technetium, like its subgroup and period analogues, forms a multiplicity of structurally unusual complexes which are difficult to synthesise because of their low stability and also because of the radioactivity of the element. In addition to the classical tetrahedral and octahedral structures we find technetium compounds obeying new structural rules, such as the cluster compounds (binuclear complexes)[10,11].

Structural studies of technetium and rhenium compounds have shown that the unit cell of technetium compounds is larger than that of the isostructural rhenium compounds, although the technetium atom is smaller than the rhenium atom (Table 1). This effect can be ascribed to the higher ionicity of the technetium–ligand bond as compared to the rhenium–ligand bond in which the covalent contribution is predominant.

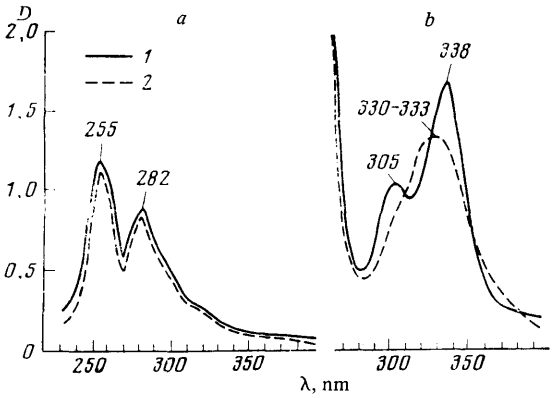



Figure 1. Time changes of absorption spectra: *a*) $(PyH)_2[ReCl_6]$, *b*) $(PyH)_2[TcCl_6]$; *1*) freshly made compound, *2*) after 1 day.

The rhenium compounds are more stable in solution, as shown by a spectrophotometric study[19] of the complexes $(PyH)_2[ReCl_6]$ and $(PyH)_2[TcCl_6]$ (Fig. 1).

Technetium belongs to a group of elements showing strongly developed complex-formation properties[20]. Its ability to form coloured complexes with high molar extinction coefficients has been exploited in the analytical chemistry of the element (Fig. 2).[2] Methods of extracting technetium from industrial solutions, of purifying it from radioactive and stable elements, and of preparing it in a

metallic form have all been based on complex formation. Thus the chemistry of technetium is essentially the chemistry of its complexes, but unlike the "typical" complex-forming elements of the platinum group, technetium forms relatively unstable compounds, resembling rhenium in this respect. Nevertheless it has been shown experimentally that technetium compounds can exist (under certain conditions) both in solution and in the solid state.

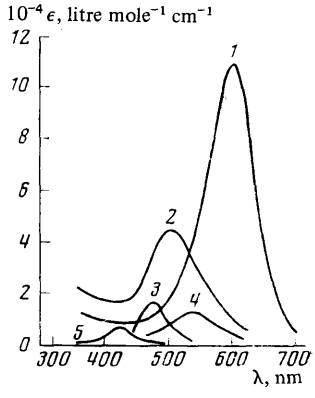



Figure 2. U. v. spectra of technetium complexes with: *1*) Methyl Violet, *2*) thiocyanate, *3*) α-benzildioxime, *4*) α-furyldioxime, *5*) 1,2-dioxime.

This review aims to discuss the properties of technetium in relation to those of its nearest period and group analogues: no attempt is made to describe in detail all the published work on the chemistry of technetium, which includes over 1000 publications.

## II. HISTORY OF THE DISCOVERY OF TECHNETIUM

The existence of element "43" was predicted by Mendeleev on the basis of his Periodic Law[21]. Several workers claimed to have discovered an analogue of manganese, and even proposed new names for it: ilmenium (Hermann, 1846),[22] devium (Kern, 1877),[23] lucium (Barriere, 1896),[24] and nipponium (Ogawa, 1908).[25]

In 1925 Noddack, Tacke, and Berg[26] described the physical properties of eka-manganese by interpreting the properties of its neighbouring elements in the Periodic Table. They made a comprehensive study of the X-ray spectra of various ore concentrates including those of the platinum minerals (columbite etc.). They claimed to have obtained a preparation containing 0.5% of eka-manganese, for which they proposed the name masurium. Their claim was soon refuted by Prandtl[27]: however, the element rhenium was discovered during the search for element "43"[26]. In 1927 Zvyagintsev and coworkers re-examined a range of platinum minerals and concluded that element "43" was absent[28].

Work on the structure and properties of the atomic nucleus led to the suggestion that elements which had not yet been discovered in Nature were unstable and could be obtained only by synthesis. By using the arguments of the Periodic Law, and by applying recent developments in atomic physics (atomic reactors and accelerators), Perrier and Segre[29,30] were able to prepare technetium after 70 years' unsuccessful attempts to discover the element in Nature. These workers demonstrated the possibility of preparing elements artificially by transmutation.

The first minute quantities of the element ($\sim 10^{-10}$ g) were prepared in the Berkeley cyclotron by the reactions

$$^{92}_{42}\mathrm{Mo}\,(d,\ n)^{93}_{43}\mathrm{Tc};\quad ^{92}_{42}\mathrm{Mo}\,(d,\ 2n)^{92}_{43}\mathrm{Tc}$$

In 1938 Seaborg discovered the long-lived isotope $^{99}$Tc, which was later isolated from uranium fission products by Segre and coworkers[30].

16 technetium isotopes are now known, with masses ranging from 92 to 107, and 6 isomers[31]. All the technetium isotopes are radioactive, as expected from the Shchukarev–Mattauch rule.

The possibility of finding primary technetium in the earth's crust is excluded by the half-lives of the technetium isotopes. The small trace of technetium ($10^{-9}$ g per kilogramme) detected[32] in pitchblende is the result of spontaneous fission of uranium; traces of technetium may be present in other minerals through the interaction of cosmic neutrons with molybdenum, ruthenium, or niobium.

Thus the primary technetium which existed in Nature several billion years ago when the Earth was formed has now disappeared by radioactive decay. If any technetium exists at present it has been formed by secondary nuclear reactions on the Earth. However, weak lines of ionised technetium have been detected in the Sun's spectrum[33] and in that of some of the younger stars[34,35]. The presence of technetium in some stars in amounts comparable with that of its analogues suggests that technetium is being formed in stars at the present time. This observation is of the utmost importance to the cosmological theory of the development of the chemical elements, which denies the hypothesis of pre-stellar formation of the elements and states that stars are continuously active "factories" of chemical elements.

## III. SOURCES AND METHODS OF PREPARATION

The knowledge that technetium is a transition element able to form a variety of complexes enables us to develop methods of preparing the element.

Technetium-99 at present is obtained from the fission products of uranium-235, among which it was first detected by Hahn and Strassmann[36] in 1939. It can also be produced by the action on slow neutrons on molybdenum:

$$^{98}_{42}\mathrm{Mo}\,(n,\gamma) \rightarrow {}^{99}_{42}\mathrm{Mo} \xrightarrow[T_{1/2}=6.7\ \mathrm{h}]{\beta,\gamma} {}^{99}_{43}\mathrm{Tc} \xrightarrow[T_{1/2}=6.1\ \mathrm{h}]{\text{i.p., }\bar{e},\gamma} {}^{99}_{43}\mathrm{Tc} \xrightarrow[T_{1/2}=2.12\cdot10^{5}\ \mathrm{years}]{\beta} {}^{99}_{44}\mathrm{Ru}_{\text{stable}}$$

It is very difficult to obtain a high yield of technetium-99 from this source. Thus, irradiation of 1 kg of molybdenum for 1 year in a flux of $\sim 8\times10^{13}$ neutrons cm$^{-2}$ s$^{-1}$ yields approximately 60 mg of Tc.[37]

The technetium can be isolated from this source by various methods, which can be classified in the following order of effectiveness: extraction, ion exchange, precipitation, distillation, electrodeposition. Under industrial conditions combined methods are often used: for example, precipitation and extraction, ion exchange and extraction, etc.

Technological methods of preparing technetium from solutions used in the atomic energy industry have been developed over a number of years both in the Soviet Union and abroad. We shall mention only those which have

yielded appreciable amounts of technetium[38-42]. Among the foreign developments the most interesting is the American technology for the isolation of technetium during the treatment of uranium hexafluoride in a gaseous diffusion plant[39,40]. The method depends on the similarity in physicochemical properties of the two volatile compounds (uranium and technetium hexafluorides) formed during the fluorination of uranium being regenerated. The two fluorides are separated by a sorption method and the technetium is finally purified by extraction.

The isolation of technetium from industrial atomic energy solutions is a complex technological problem, with special emphasis on the problem of waste solutions. Any increase in the volume of these solutions as a result of additional treatments aimed at concentrating the technetium must be avoided. Only the sorption technology in conjunction with ion exchange can satisfy this requirement.

Ion-exchange methods of concentrating technetium by the use of highly basic resins have been patented[41,42]; the eluent is nitric acid, and the product is purified by extraction with ethyl methyl ketone. The ion-exchange method has been developed and applied also in the Soviet Union, in conjunction with acetone extraction and precipitation as technetium heptasulphide[2,38]. An important advantage of ion exchange over all other methods of separating technetium is its ability to separate technetium from ruthenium. Both high-basicity and low-basicity organic resins have been shown[38-44] to be usable, in a variety of chemical compositions and structures.

Treating the ion-exchange properties of technetium in the light of the periodic classification of the elements we note that the perrhenate ion and the pertechnetate ion are both readily adsorbed by anion exchange resins over a wide range of solution pH. The permanganate ion is reduced by these resins, and therefore ion exchange is not applicable in the presence of manganese(VII). Manganese(II) is adsorbed to a moderate extent by cation exchange resins.

The selectivity of the resins towards the $[TcO_4]^-$ ion arises partly from the properties of the resins themselves and partly from the special structure of the ion, its tendency towards complex formation, and its low degree of hydration.

## IV. CHEMICAL PROPERTIES

The structure of the outer electron shells of the technetium atom, whose configuration is given as $4d^65s^1$ ($S$ 9/2)[45,46] or $4d^55s^2$ ($S$ 5/2)[47,48], is responsible for the properties of the element as a transition metal of the second series of the $d$ group (Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag).[49] This electronic structure makes possible several oxidation states, from +7 to −1, and it explains the tendency towards disproportionation, hydrolysis, hydride formation, formation of compounds with metal–metal bonds, and complex formation, all of which play an important part in the chemistry of the element.

The chemical properties of technetium are similar to those of rhenium, but they are quite different from those of manganese in spite of some analogy in the stereochemistry of several of their compounds: the oxo-anions $[MO_4]^-$, $[MO_4]^{2-}$, the oxides $M_2O_7$, $MO_2$, the hexa-halogen complexes $[MX_6]^{2-}$, and the $\pi$-complexes $[M(CN)_6]^{5-}$, $M_2[CO]_{10}$, $M[CO]_5Cl$. However manganese tends to favour the lower oxidation state+2, which is more stable than manganese(VII), $d^0$, as a result of the configuration involving unpaired spins with a $d^5$ electronic shell. Manganese(II), $d^5$, occurs mainly in a series of high-spin complexes and in simple cationic compounds, usually with an ionic bond. In the heptavalent state manganese is unstable, and behaves as a strong oxidising agent. On the other hand technetium and rhenium typically adopt the heptavalent $d^0$ state with a weak tendency towards reduction, as shown by their standard redox and ionisation potentials:

| Redox potentials, V | | Ionisation potentials, eV (Ref.5) | |
|---|---|---|---|
| $[MnO_4]^-/MnO_2$ | −1.695(Ref.50) | Mn | 122 |
| $[TcO_4]^-/TcO_2$ | −0.738(Ref.51) | Tc | 95 |
| $[ReO_4]^-/ReO_2$ | −0.510(Ref.52) | Re | 79 |

This difference between the properties of technetium and rhenium is explained by the difference between the electronic shells of these elements. The main feature of the $4d$ shell of the technetium atom, and also of the $5d$ shell of its nearest analogue, rhenium, is that the electrons in these shells are much further from the nucleus than the electrons in the $3d$ shell of manganese. As a result the interaction between the positive nucleus and the outer electrons is much weaker, the pairing of the electrons is enhanced, and the splitting of the levels by the ligand field is increased, leading to the formation of the characteristic low-spin complexes of technetium and rhenium. Manganese forms high-spin complexes as a rule. Typical of these are the halogen $o$-phenylene-*bis*-dimethyldiarsine complexes of Tc(II), $[TcDiars_2Hal]^0$,[54] with the $d^5$ configuration, spin paired with $\mu_{eff} = 1.9–2.1\ \mu_B$, corresponding to the presence of one unpaired electron. The analogous complex of manganese(II) is a spin-free complex. The low-spin complexes of Mn(II) with one unpaired electron, of composition $[Mn(CN)_6]^{4-}$ and $[Mn(CN)_5NO]^{3-}$, are exceptional in the chemistry of manganese; the Mn(III) complex $[Mn(CN)_6]^{3-}$ with two unpaired electrons is also known[49]. In all these complexes the pairing of the electrons is governed by a strong ligand field.

The partly filled $d$-shell and the presence of "spare" electrons (not involved in bond formation with the ligand) in increasing numbers as the oxidation state of technetium and rhenium decreases tend to favour the interaction between electrons of the metal atoms and the formation of metal–metal bonds. Rhenium and technetium begin to display a tendency to form compounds of this type when in the oxidation state +4 (as $ReO_2$ and $TcO_2$).[55]

It has been reported that aquo-ions do not play a significant part in the chemistry of technetium and rhenium[49], although they are characteristic of manganese and of the whole of the first group of transition elements. However more recent work[56,57] has shown that aquo-complexes are formed by rhenium and technetium in the oxidation states +2, +3, and +4. In the highest oxidation state Tc(VII), having the $d^0$ configuration, forms complexes with a coordination number of 4 as the $[TcO_4]^-$ ion, analogous not only to manganese(VII), $[MnO_4]^-$, and rhenium(VII), $[ReO_4]^-$, but also to chlorine(VII), $[ClO_4]^-$, iodine(VII), $[IO_4]^-$, bromine(VII), $[BrO_4]^-$, ruthenium(VII), $[RuO_4]^-$, and neptunium(VII), $[NpO_4]^-$.[49,58,59]

Studies by vibrational spectroscopy have shown that a tetrahedral ion such as $[TcO_4]^-$ with a $T_d$ point symmetry is stable in aqueous solution[63], but undergoes changes in crystalline compounds[62,64,65]. The nature of the cation has a strong influence on the structure of the anion, as shown by an analysis[62] of the vibrational spectra of pertechnetates, according to which the crystal field decreases as the ionic radius of the cation increases.

Pertechnetic acid forms dark red, hygroscopic crystals of composition $H[TcO_4]$.[68] The structure of this compound has not yet been established, and it is not known whether the anhydrous acid corresponds to the stereochemical composition $Tc_2O_7.H_2O$ or $HTcO_4$: it would be

interesting to resolve this question. The acid strength of Group VII elements falls on going from the main subgroup to the secondary subgroup. It is known that $H[ClO_4]$ is a very strong acid in aqueous solutions, and that the oxidising power of perchlorates is higher than that of permanganates; $H[MnO_4]$ has an acid strength comparable to that of HCl, and $H[TcO_4]$ is weaker than these acids but stronger than $H[ReO_4]$.

All three acids $H[ReO_4]$, $H[TcO_4]$, and $H[MnO_4]$, like their isostructural acid $H[ClO_4]$, form sparingly soluble salts with the cations $Tl^{3+}$, $Cs^+$, nitronium, tetraphenylarsonium $[(C_6H_5)_4As]^+$, and tetraphenylphosphonium $[(C_6H_5)_4P]^+$. The salts of all four acids are isomorphous.

Alkali metal and ammonium pertechnetates crystallise in the scheelite structure (tetragonal system), but $Cs[TcO_4]$ is rhombic, like $Tl[TcO_4]$ ($D_{2h}^{16}$–$Pnma$, $z = 4$, the so-called pseudo-scheelite type)[60,61].

Pertechnetates (like perrhenates) are colourless in solution, unlike the salts of permanganic acid which have a violet–red colour: the chromophoric power decreases steeply from Mn to Tc and Re. The colour of the pertechnetates of some organic cations (berberinium, Methyl Violet) is due to the chromophoric properties of the cations themselves.

An interesting property of pertechnetates is the formation of crystal hydrates as the cation changes from the Group I metals to metals of Groups II and III. The solubility along the subgroups decreases as the ionic radius of the cation increases ($K[TcO_4]$ 2.130 g/100 g, $Cs[TcO_4]$ 0.412 g/100 g of solution).[47]

The following compounds of technetium(VII) have been synthesised in recent years: $Pr[TcO_4]_3$, $Pr[TcO_4]_3.4H_2O$, $Pr[TcO_4]_3.3H_2O$, $Nd[TcO_4]_3.4H_2O$;[66] $Ba_3[TcO_5]_2$, $Sr_3[TcO_5]_2$, $Ca_3[TcO_5]_2$, $Ba[TcO_4]_2$, $Sr[TcO_4]_2$, $Ca[TcO_4]_2$, $Ba_5[TcO_6]_2$, $Sr_5[TcO_6]_2$, $Ca_5[TcO_6]_2$, $Ba[Na_{0.5}Tc_{0.5}]O_3$, $Sr[Na_{0.5}Tc_{0.5}]O_3$, $Ba[TcO_4]_2.2H_2O$, $Sr[TcO_4]_2.2H_2O$, $Ca[TcO_4]_2.2H_2O$, $Ca[TcO_4]_2.H_2O$, $Sr[TcO_4]_2.H_2O$.[67]

The Group VII elements of the main subgroup behave as non-metals in both the higher and the lower oxidation states, whereas the elements of the secondary subgroup (Mn, Tc, Re) show definite metallic properties in the lower valence states but retain their non-metal character in the heptavalent state. The elements of this subgroup, unlike those of the main subgroup, show a great deal of similarity with elements in the same period.

The oxide $Mn_2O_7$ is a dark green oily liquid; $Tc_2O_7$ and $Re_2O_7$ are orange–yellow crystalline compounds. Their relative stabilities are indicated in Table 2. $Tc_2O_7$ crystallises in the orthorhombic system with lattice parameters $a = 13.756$, $b = 7.439$, and $c = 5.617$ ($z = 4$). A full X-ray diffraction analysis of this oxide[69] has shown that the centro-symmetrical $Tc_2O_7$ molecule has a tetrahedrally coordinated metal atom and a linear Tc–O–Tc bond. The structure of technetium heptoxide is more similar to the layer structure of $CrO_3$, $RuO_4$, and $OsO_4$ than to the polymeric layer structure of $Re_2O_7$. The $Tc_2O_7$ lattice is not isostructural with the $Re_2O_7$ lattice. The compound $Tc_2O_7$ is weakly paramagnetic. It is readily soluble in dioxan, and it forms $H[TcO_4]$ when dissolved in water[68].

The oxyhalides of technetium(VII), $TcO_3F$[72] and $TcO_3Cl$,[73] have both practical and scientific interest. The latter has not been isolated in a pure form.

An important role in the technological separation of technetium is played by the heptasulphide $Tc_2S_7$, a dark brown sparingly soluble compound precipitated from 2–4 *N* solution of HCl or $H_2SO_4$,[2,74] unlike rhenium sulphide, which is obtained from more concentrated acid solutions. This property of technetium is related to its reduction to lower oxidation states, whose sulphides are soluble in mineral acids. In this respect technetium is similar to manganese.

Technetium(VI) exists in both cationic and anionic forms. The most stable are the fluorine and chlorine compounds $TcCl_6$,[75] $TcF_6$,[76] $TcOF_4$,[77] and $TcOCl_4$.[73,78]

Table 2. Physicochemical properties of oxides[53].

| Oxide | Heat of formation from the elements, kcal mole$^{-1}$ | Melting point, °C | Thermal behaviour |
|---|---|---|---|
| $Mn_2O_7$ | 177 | 6 | Decomposes explosively at 90°C |
| $Tc_2O_7$ | 266 | 120 | Decomposes at 260°C and sublimes |
| $Re_2O_7$ | 296 | 296 | Boils without decomposition at 362°C |

Astheimer and Schwochau[79] have reported a coulometric synthesis of oxygen-containing complexes of technetium(VI), rhenium(VI), and manganese(VI) with an organic cation, using the controlled potentials $E_{\frac{1}{2}} = 1.74$, 2.3, and 0.6 V respectively. They obtained complexes of composition $[(CH_3)_4N]_2MO_4$, crystallising in the cubic system with lattice parameters $a = 11.20$ Å (Tc), 11.35 Å (Re), and 11.09 Å (Mn).

The formation of Tc(VI) had been observed previously[2] during coulometric treatment of a weakly acid solution of Tc(VII) (1 *M* KCl + $4 \times 10^{-4}$ *M* HCl + $0.9 \times 10^{-5}$ *M* $NH_4TcO_4$). The u.v. absorption spectrum of the solution was shown to have a maximum at 231 nm.

By comparing the properties of the technetates, manganates, and rhenates we conclude that the six-valent state of all three analogues (Tc, Mn, and Re) is unstable and undergoes disproportionation by the reaction

$$3M\,(VI) \rightarrow 2M\,(VII) + M\,(IV).$$

The electronic structure of the manganate and rhenate is still unknown, and therefore we cannot predict their properties from the ligand field theory because of the excessive overlap of the metal and oxygen orbitals[49]. No attempt has been made to describe the properties of the technetate ion in terms of its electronic structure.

Derivatives of pentavalent technetium, like those of technetium(VI), are known in the form of cationic and anionic complexes. The most stable are the halogen compounds[77] $TcF_5$, $NaTcF_6$, and $KTcF_6$, isostructural with the corresponding ruthenium salts but different from the rhenium salts.

Compounds of the anion $[TcO_4]^{3-}$ have not been prepared, though the manganese analogues are known (prepared by thermal decomposition of the permanganate). Rhenium(V) forms both tetrahedral ions with a coordination number of 4, $[ReO_4]^{3-}$, and ions of composition $[Re_2O_7]^{4-}$ and $[ReO_3]^-$.[80]

The synthesis of the following complexes has been reported: technetium oxide tribromide $TcOBr_3$,[75] technetium oxide trichloride $TcOCl_3$,[78,81] and tetrachlorodi-*o*-phenylene-bis-dimethylarsinetechnetium chloride $[TcDiars_2Cl_4]Cl$.[82] Technetium is eight-coordinated in the latter complex.

The reaction between the $[TcO_4]^-$ ion and concentrated hydrochloric acid is very interesting. This reaction clearly illustrates the position of technetium in the

Periodic Table. Thus, Mn(VII) in the form of the $[MnO_4]^-$ ion is reduced to Mn(II), $[ReO_4]^-$ does not react with HCl, and the $[TcO_4]^-$ ion reacts with HCl to give the complex ion $[TcCl_6]^{2-}$ as the final product[2,83-85]. This anion can be obtained at room temperature[19].

The reduction of the $[TcO_4]^-$ ion by hydrochloric acid has been studied in detail, and shown to involve an intermediate step: the formation of Tc(V). The compounds $(NH_4)_2[TcOCl_5]$,[83] $K_2[TcOCl_5]$, and $K_2[TcO(OH)Cl_4]$ [84] have been isolated in a solid crystalline form. The absorption band of the $[TcO(OH)Cl_4]^{2-}$ anion in the u.v. spectrum is shifted towards longer wavelengths, showing that the hydrolysed compound is less stable than the $[TcOCl_5]^{2-}$ complex anion (Fig. 3).

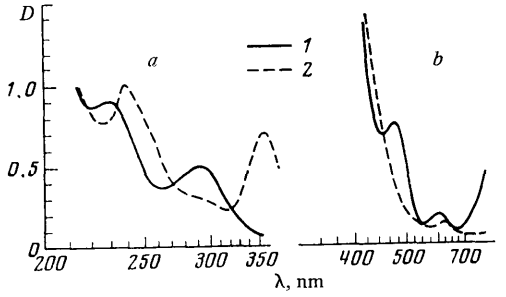
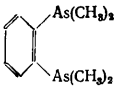



Figure 3. Adsorption spectra in (*a*) the u.v. and (*b*) the visible region of: *1*) $K_2[TcOCl_5]$, *2*) $K_2[TcO(OH)Cl_4$.

The effect of an organic ligand on the stability of technetium(V) compounds has been demonstrated by the synthesis of dioxotetrapyridinetechnetium chloride $TcO_2Py_4Cl$ [19] and tetrachlorodi-*o*-phenylene-bis-dimethylarsinetechnetium perchlorate $[TcDiars_2Cl_4]ClO_4$.[54] The latter contains no unpaired electrons ($\mu_{eff} = 0.7\ \mu_B$), as expected from its formula with a coordination number of eight. This coordination allows the use of the chelating arsine group of *o*-phenylene-bis-dimethylarsine




which is widely used as a ligand in transition metal complexes (including technetium compounds).

The compounds $[TcO_2Py_4]Cl$ and $[TcO_2Py_4]Cl.2H_2O$,[19] which are isostructural with the analogous rhenium compounds $[ReO_2Py_4]Cl$ and $ReO_2Py_4Cl.2H_2O$,[86] are formed in neutral solution. The powerful stabilising effect of the water of crystallisation in these compounds has been demonstrated by i.r. spectral studies[19].

The compounds of technetium(IV) have been investigated most fully because in this valence state the *d*-shell is half full and as a result the complexes are structurally stable[87]. A series of stable technetium compounds with the formula $[TcHal_6]^{2-}$, analogous to the manganese, rhenium, platinum, molybdenum, and tungsten compounds, is known. The anion of the salts of hexachlorotechnetic acid, $[TcCl_6]^{2-}$, is a regular octahedron with a halogen atom at each apex and a technetium atom at the centre. The octahedra of the crystalline salt are located at the corners and at the face centres of an elementary cubic cell, with cations at the centres of eight octants[88-92].

These compounds are spin-free, and are strongly paramagnetic. In the presence of an inorganic cation their magnetic moment is strongly temperature dependent[12,93] (Table 3).

Table 3. Magnetic properties of technetium(IV) compounds.

| Compound | *T*, K | $\mu_{eff}$, $\mu_B$ |
|---|---|---|
| $K_2[TcCl_6]$ | 78—398 | 2.93—3.88 |
| $(PyH)_2[TcCl_6]$ | 84.7—289 | 3.97—3.97 |
| $(ChH)_2[TcCl_6]$ | 78—291 | 3.78—3.78 |

Hexachlorotechnetic acid, which was recently synthesised by the present writers, is a typical member of the class of technetium complexes containing the $[TcHal_6]^{2-}$ anion. A structural study of this compound[94] has shown that the phase $H_2[TcCl_6].9H_2O$ crystallises in the triclinic system. This low symmetry is due to the hydrogen bonds of the water molecules, which distort the $[TcCl_6]^{2-}$ octahedron (Fig. 4), whereas the ionic forces acting on the structural units in the alkali metal salts tend to preserve the octahedral structure of the anion[92].

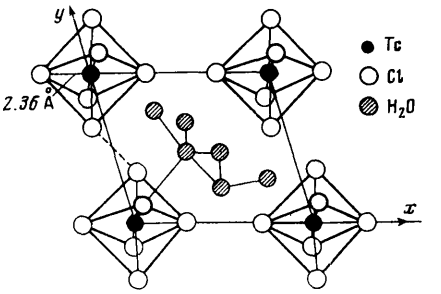



Figure 4. Projection of the $H_2[TcCl_6].9H_2O$ structure on the *xy* plane.

A comparative study of the salts of hexachlorotechnetic acid with inorganic cations ($K_2[TcCl_6]$, $Na_2[TcCl_6]$, $(NH_4)_2[TcCl_6]$) and with organic cations ($(PyH)_2[TcCl_6]$, $(ChH)_2[TcCl_6]$, $(DpH)_2[TcCl_6]$) has shown that the latter crystallise in a low-symmetry system, whereas the former have a cubic structure[88,90-92]. The magnetic moments of $(PyH)_2[TcCl_6]$ and $(ChH)_2[TcCl_6]$ are independent of temperature (Table 3). It is thought[93] that the decreased exchange interaction in the complexes with organic cations gives rise to some measure of diamagnetism.

The thermal stability of the $[TcCl_6]^{2-}$ anion is not very high: the compound $(NH_4)_2[TcCl_6]$ begins to decompose at 350°C; the decomposition is rapid at 420°C, and is complete at 535°C, with formation of the metal without intermediate steps (Fig. 5).

In dilute acid solutions the $[TcHal_6]^{2-}$ anion is readily hydrolysed. Formation of the monaquo- and diaquochloro-complexes $[TcCl_5(H_2O)]^-$ and $[TcCl_4(H_2O)_2]^0$ has been confirmed by paper chromatography[57]. A binuclear complex of composition $K_4[Tc_2OCl_{10}]$ has been synthesised[47]; the alternative formula $K_2[Tc(OH)Cl_5]$ has been suggested for this compound[97].

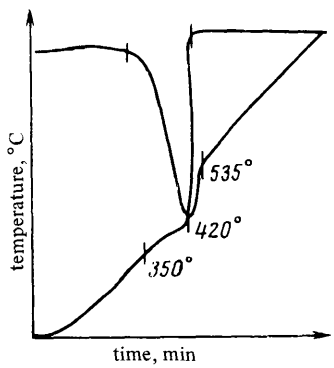



Figure 5. Thermogram of $(NH_4)_2[TcCl_6]$.

The compound $TcO_2$ is fairly stable and can exist in a hydrated and a non-hydrated form. Technetium dioxide $TcO_2$, like the analogous rhenium compound, crystallises in the monoclinic system with a metal–metal bond length of 2.5 Å. The technetium (or rhenium) atoms lie at the centres of oxygen octahedra[55]. These compounds are weakly paramagnetic. Unlike the rhenium and manganese dioxides, technetium dioxide can be sublimed in a vacuum without decomposition at 900–1100°C,[12] but it decomposes to the metal at 600°C in a stream of CO (0.75% CO).[71]

Compounds of tervalent technetium were known only in solution for a long time. They were detected during polarographic reduction of the $[TcO_4]^-$ ion at a dropping mercury cathode[2,119], and in micro-cocrystallisation experiments[95], but the pure compounds were not isolated.

Technetium(III) compounds have been obtained more recently. Like rhenium(III) and manganese(III), technetium(III) forms complexes, but only manganese(III) has yielded a large number of simple compounds. Simple compounds of rhenium(III) and manganese(III) are not known. Among the known compounds of technetium(III) are the complexes with *o*-phenylene-bis-dimethyldiarsine of composition $[TcDiars_2Hal_2]Cl$,[54] which were successfully obtained on the theory that spin-paired technetium complexes in low states of oxidation are favoured by the use of ligands having a strong field, such as *o*-phenylene-bis-diarsine.

However it was shown more recently that compounds of technetium in a low oxidation state can be obtained with a ligand as simple as the $Cl^-$ ion. The very interesting compounds of the octachloroditechnetate ion $[Tc_2Cl_8]^{3-}$, with a metal–metal bond and an oxidation number of 2.5, have been synthesised by two methods. In the first method[10] zinc was used to reduce the pertechnetate ion in concentrated HCl solution, whereas the second method uses molecular hydrogen under pressure[11]. Both methods yield binuclear complexes consisting of a slightly distorted tetragonal prism with chlorine atoms at the corners and two technetium atoms within the prism (Fig. 6). The anions are held by a weak Tc–Cl bond 3.54 Å long. Water molecules are not accommodated in the inner sphere of the $K_3[Tc_2Cl_8].2H_2O$ complex. The Tc–Tc distance is 2.14 Å, as compared to 2.73 Å in metallic technetium[96]. The octachloroditechnetate ion $[Tc_2^{2.5+}Cl_8]^{3-}$ and the octachlorodirhenate ion $[Re_2^{3+}Cl_8]^{2-}$ belong to the same structure type of binuclear complexes, with $D_{4h}$ symmetry, but they have different states of oxidation. The analogous technetium(III) binuclear complex, with the anion $[Tc_2Cl_8]^{2-}$, has recently been prepared[128].

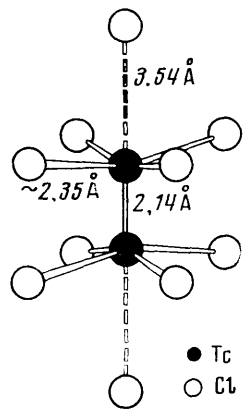



Figure 6. Structure of $[Tc_2Cl_8]^{3-}$ complex (cluster) anion.

Tc(II) is known to form a halogen-diarsine complex of octahedral structure, analogous to the rhenium and manganese complexes of composition $[MDiars_2Hal_2]^0$.[54] The $d^5$ electronic configuration, corresponding to a valence state of two, is theoretically a stable configuration. However only the Mn(II) compounds are spin-free, whereas the Tc(II) and Re(II) complexes have a spin-paired configuration with one unpaired electron.

Eakins and coworkers[10] have isolated a complex of composition $[Tc^{2+}(NH_2OH)_2(NH_3)_3]Cl_2$, dihydroxylaminetriamminetechnetium dichloride, which has no analogues among the manganese and rhenium compounds and has not yet been characterised physicochemically. This compound can form stable aqueous solutions.

Using the $CN^-$ ion as a strong-field ligand, Herr and Schwochau[98] obtained the diamagnetic cyano-complex of univalent technetium $K_5[Tc(CN)_6]$, isomorphous with the known rhenium and manganese analogues.

The binuclear carbonyl $Tc_2(CO)_{10}$ has been synthesised[99] and shown to have a distorted octahedral structure[100]. In carbon tetrachloride solution this compound reacts with halogens to give pentacarbonyls and tetracarbonyls by the reaction

$$Tc_2(CO)_{10} + Hal_2 \rightarrow 2Tc(CO)_5Hal \xrightarrow[100°C,\ 1000\ atm]{} [Tc(CO)_4Hal]_2 + 2CO$$

The dibenzenetechnetium complex cation $[(C_6H_6)_2Tc]^+$,[101] formed by the $\beta$-decomposition of $^{99}Mo(C_6H_6)_2$, and the diamagnetic bis-dicyclopentadienyltechnetium $[Tc(C_5H_5)_2]_2$, consisting of golden yellow crystals unstable in air[102], have been reported. The latter is an analogue of the complex $ReH(C_5H_5)_2$,[103,104] which has a Re–H bond: although

this bond is absent in the technetium compound, the bond between the ring and the metal is similar in the compounds $[Tc(C_5H_5)_2]_2$ and $ReH(C_5H_5)_2$, and it differs from the metal–ring bond in the paramagnetic $MnH(C_5H_5)_2$ complex[105].

Metallic technetium is a dark grey powder which acquires a silvery sheen when heated to 1000°C. It is similar to rhenium, molybdenum, and platinum in external appearance, unlike manganese, which is similar to iron. The physical and mechanical properties of metallic technetium have been studied in our laboratory[106]: the metal can be formed into rods, tape, foil, and wire by cold working, with recrystallising anneals. Its cold working properties are better than those of many familiar metals. The highest strength is obtained by cold working, the highest ductility by annealing at 1000°C. The thermal expansion coefficient at right angles to the rolling direction is 8.9 (sic.).

Metallic technetium crystallises in the hexagonal system and is close-packed. Each atom is surrounded by twelve nearest neighbours at a distance of 2.73 Å. Important new information on the structure of technetium was obtained[107] in a study of sputtered thin films of the metal. Technetium films less than 150 Å thick consist of a new modification, stable at room temperature, with a face-centred cubic structure (lattice parameter $a_0 = 3.68 \pm 0.05$ Å).

Studies of the physical properties of metallic technetium[3,108] showed that this metal is superconducting, like rhenium but unlike manganese. For technetium $T_{cr} = 8.2$ K[108]. The neighbours of technetium and rhenium in the Periodic Table (ruthenium and osmium respectively) also show superconducting properties. Technetium is one of the refractory metals (m.p. = 2200°C).[8]

The chemical activity of metallic technetium is lower than that of manganese but somewhat higher than that of rhenium. In the electromotive force series technetium lies to the right of hydrogen and copper, and (like rhenium) it is not attacked by HCl, whereas manganese lies to the left of hydrogen—between magnesium and zinc—and reacts readily with water and acids. At elevated temperatures technetium reacts with chlorine, fluorine, and carbon. The metal burns in oxygen, forming $Tc_2O_7$. It is easily oxidised by aqua regia and by nitric acid (with formation of $H[TcO_4]$), and it is also oxidised by solutions of hydrogen peroxide, bromine water, and sulphuric acid.

Technetium(VII) exists as the $[TcO_4]^-$ ions in aqueous solutions over a wide range of solution acidity or alkalinity. The $[TcO_4]^-$ ion, like its analogues, has the stable tetrahedral configuration. In aqueous solution the $[TcO_4]^-$ ion is strongly absorbing in the u.v. region; its spectrum is similar to those of the isoelectronic forms $[ReO_4]^-$, $[RuO_4]^-$, and $[MnO_4]^-$.

There are many published reports of the tendency of technetium(VII) to be reduced to lower valence states by various reducing agents: hydrazine, hydroxylamine, and ascorbic acid. These reactions have been studied by spectrophotometric, paper chromatography, and polarographic methods[129]. Technetium(VII) is reduced by hydrochloric acid solutions. In concentrated hydrochloric acid the first step of the reduction is instantaneous, with formation of technetium(V) oxide chloride $[TcOCl_5]^{2-}$, which is slowly converted into $[TcCl_6]^{2-}$. An additional reducing agent—hydrogen—is needed for more complete reduction, which can be achieved by electrochemical reduction methods or by autoclave techniques.

The $[TcO_4]^-$ ion can be extracted[95,109–117] by various organic solvents from acid, neutral, or alkaline solutions. Alcohols, ethers, ketones, and nitrogen- and phosphorus-containing organic compounds have been used successfully. Technetium(VII) is extracted as solvated pertechnetic acid in the form of complex salts. The $[TcO_4]^-$ ion can form ionic associations containing large organic cations such as tri- and diphenylguanidinium, tetraphenylarsonium, and tetraphenylphosphonium, which are easily extracted by non-polar solvents (chloroform, Chlorex, etc.). The mechanism of extraction in this case depends on the high solubility of the association in the non-polar solvent. Cyclohexanol, cyclohexane, tributyl phosphate, trioctylphosphine oxide, and trioctylamine can extract the $[TcO_4]^-$ ion from acid solution[109]. The following reactions occur during extraction with amines and tributyl phosphate:

$$[R_4NNO_3]_{org} + [TcO_4]^- \rightleftarrows [R_4NTcO_4]_{org} + NO_3^- ,$$

$$H^+ + NO_3^- + n(H_2O) + n[TBP] + TcO_4^- \rightleftarrows HTcO_4(H_2O)_n \cdot (TBP)_n + NO_3^- .$$

An interesting extraction scheme involves trimethyloctylammonium chloride[117] and pyridine[114]. A detailed study[116] of the extraction of technetium(VII) from alkaline solutions by quinoline and by pyridine derivatives (2-methylpyridine, 2,4-dimethylpyridine, 2-methyl-5-ethylpyridine) has shown that the distribution coefficient of technetium in these solvents is much higher than in pyridine. However the use of 2-methylpyridine as an extractant for technetium is limited in practice by the high solubility of this compound. Extraction methods continue to be the most widely used in the technology of technetium separation at the refining stage.

Polarographic studies of the oxidation–reduction reactions of oxygen-containing anions of the Group VII elements yield a great deal of information on the reactivity of these species and on their oxidation state in solution. Many papers have already been published on this topic. The earliest work[118] gave contradictory results, but a later paper[119] showed that the $[TcO_4]^-$ ion is reduced to Tc(IV) at a dropping mercury electrode in neutral solution. Sharp reduction waves are not obtained in strongly acid solutions, and in alkaline solutions a two-electron reduction process is observed, with formation of Tc(V). Similar results were obtained by other workers[120–123].

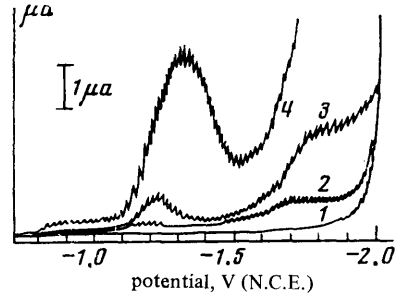



Figure 7. Catalytic waves on the polarograms of the $[TcO_4]^-$ ion in neutral $NH_4TcO_4$ solution; base electrolyte 1 *M* KCl + 0.01% gelatine, technetium concentration: *1*) 0, *2*) $4.3 \times 10^{-6}$, *3*) $8.6 \times 10^{-6}$, *4*) $2.5 \times 10^{-5}$ *M* $NH_4TcO_4$.

The electrochemical reduction of the $[TcO_4]^-$ ion at a dropping mercury electrode was studied[119–123] over a wide range of acidity and alkalinity, and the following general features were noted. Reduction of the $[TcO_4]^-$ ion is by

the diffusion and catalytic mechanism, irrespective of the nature of the base electrolyte and of different media. The polarograms show maxima due to the fast evolution of hydrogen on metallic technetium. The height of the waves showing these maxima is greater than the current corresponding to the maximum possible (eight-electron) reduction (Fig. 7). These waves are similar to the catalytic waves in the polarograms given by rhenium [124,125]. The hydrogen maxima have been ascribed [124] to a lowering of the hydrogen overvoltage upon the formation of the rhenide ($Re^-$) ion. According to Zhdanov and coworkers [123] metallic technetium is formed by the reduction of $[TcO_4]^-$.

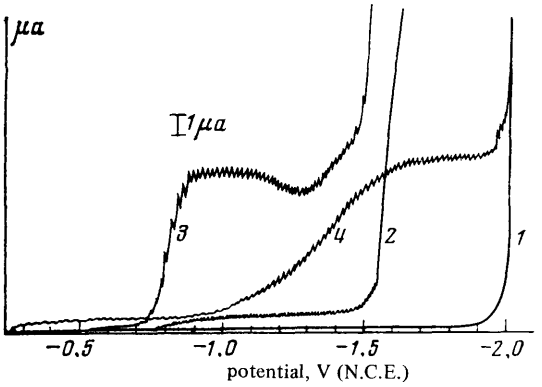



Figure 8. Effect of hydrogen peroxide on the polarogram of the $[TcO_4]^-$ ion in alkaline solution. Composition of solutions: *1*) base electrolyte 0.58 *M* HCl + 0.3 M KOH + 0.01% gelatine, *2*) base electrolyte + $8.0 \times 10^{-5}$ *M* $NH_4TcO_4$, *3*) base electrolyte + $8.0 \times 10^{-5}$ *M* $NH_4TcO_4$ + $8.1 \times 10^{-4}$ *M* $H_2O_2$, *4*) base electrolyte + $8.1 \times 10^{-4}$ *M* $H_2O_2$.

Catalytic waves occur in all media, and are independent of the nature of the base electrolyte with the exception of ammoniacal solutions in which the waves disappear [122]. Catalytic currents are produced also by the interaction of an oxidising agent with the products of electrochemical reduction of technetium. This type of wave is observed only in alkaline peroxide solutions (curve *3* of Fig. 8). A comparative study of the polarograms of $[MO_4]^-$ ions of the three analogues rhenium, technetium, and manganese has shown [118,126,127] that the electrochemical behaviour of the three elements is quite different during reduction at a dropping mercury electrode.

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In conclusion we note that technetium is among the most interesting of all the elements from the standpoint of its chemical properties. It exhibits many valence states, it is readily converted from one state into another, and it can exist in solution in different valence states at the same time. The other important properties of this element are its tendency towards disproportionation, complex formation, and hydrolysis.

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# Advances in the Chemistry of Ambident Enolate and Phenoxide Ions

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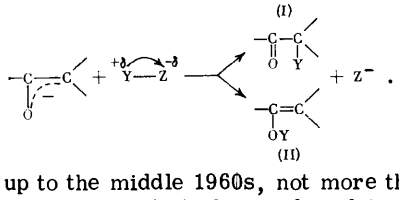
The reactivities of ambident enolate and phenoxide ions in alkylation reactions are examined. It is shown that the mode of *C*- and *O*-alkylation of an ambident anion is determined by the structures of the alkyl group and the group eliminated from the alkylating agent, the nature of the solvent, and the type of counter ion. The influence of each of these factors on the dual reactivity of the enolates of carbonyl and β-dicarbonyl compounds and esters as well as phenoxides and naphthoxides is analysed in detail.
The bibliography includes 160 references.

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## I. INTRODUCTION

Enolate ions are the most important type of ambident anions. Without exaggeration, one may claim that enolate ions are the key reagents in organic synthesis. When faced with the problem of forming a new carbon–carbon bond, the organic chemist usually turns to the large group of reactions (alkylation, acylation, aldol and ester condensations, and Dieckmann and Michael condensations) of alkali metal enolates. On the other hand, enolate ions, being typical representatives of the class of ambident anions, should manifest a dual reactivity in reactions with electrophiles, forming not only *C*-substitution products (I) but also *O*-substitution products (II).




Nevertheless up to the middle 1960s, not more than 3–4 examples of *O*-alkylation of alkali metal enolates of carbonyl and β-dicarbonyl compounds and esters were known. Systematic studies on the factors determining the mode of reaction of enolate ions were begun only in the last decade. This became possible, firstly, owing to the discovery of exact methods for the analysis of the composition of the reaction mixture (gas–liquid chromatography and $^1$H NMR) and, secondly, following the introduction into practical organic synthesis of dipolar aprotic solvents. Bimolecular nucleophilic substitution reactions between anions and neutral molecules (the alkylation of enolate ions) are much faster in dipolar aprotic solvents than in a proton-donating medium. This difference is determined primarily by the weak solvation of the anions in dipolar aprotic solvents. For many enolate ions in solvents such as monoglyme, dimethylformamide (DMF), and dimethyl sulphoxide (DMSO), *O*-alkylation reactions were carried out for the first time. In the general case, the mode of reaction of the enolate ion is determined by the following main factors: (1) the nature of the counter ion; (2) the nature of the solvent; (3) the nature of the electrophile; (4) the structure of the ambident anion.

The influence of each of the above factors on the ratio of the products of the *C*- and *O*-alkylation of metal derivatives of carbonyl and β-dicarbonyl compounds and esters will be examined in succession. The reaction products have been analysed quantitatively during the last 10–15 years and attention will be concentrated on this research. Ambident phenoxide ions are in all respects very close analogues of enolate ions. In order to emphasise the close relation between these two classes of ambident anions, data on the *C*- and *O*-alkylation of phenoxide ions have been included.

## II. DEPENDENCE OF THE MODE OF THE ALKYLATION REACTION ON THE NATURE OF THE CATION

An important factor influencing the ratio of the alkylation products of metal enolates and phenoxides is the nature of the cation. The influence of the nature of the alkali metal cation on the ratio of the *C*- and *O*-isomers has been investigated in greatest detail. In this case, the problem reduces in essence to the solution of the problem of the state of these salts in solution. Alkali metal enolates can exist in solution in the form of associated species comprising ion pairs with different degrees of aggregation, and, in a fairly basic and polar solvent, in the form of monomeric ion pairs of different types and as free ions. Naturally, the nature of the solvent has a decisive influence on the position of equilibrium between the different forms of ionic species. The degree of association of ion pairs depends also on the size, charge density, and hardness of the cation and anion. Sodium and potassium alkoxides form, for example, associated species of the type $(ROM)_3$ even in a basic and polar solvent such as DMSO.[1,2] The degree of association in a less polar medium and also for small cations with a high charge density ($Li^+$, $Mg^{2+}$, etc.) is even greater[2-5]. As regards the tendency towards self-association, alkali metal enolates occupy an intermediate position between alkoxides and alkali metal salts of carbanions, which are monomeric in solvents, coordinating effectively alkali metal cations[6]. The molecular weight of the sodium salt of n-butyl malonate (in 0.1 *N* solution in benzene) exceeds 11 000 which corresponds to the formation of a monodisperse

micelle comprising 40–50 monomeric ion pairs of this salt, i.e. almost a colloidal particle [7,8]. However, in a more polar and, what is more important, a more basic medium, the degree of association decreases sharply. Thus the sodium salt of butyrophenone in ether exists in the form of a three-dimensional association of ion pairs [9], while in dimethoxyethane (DME) [10] the degree of association is lower still. The addition of small amounts of dipolar aprotic solvents such as DMF [8,11], DMSO [12], and hexamethylphosphoramide (HMP) [13] to solutions of alkali metal enolates in media of low polarity breaks up the ionic association complexes until the formation of monomeric ion pairs. The same effect is achieved by the introduction of strong complex-forming agents: polyglymes and macrocyclic polyesters [14]. In dipolar aprotic solvents at concentrations below 0.2 M, alkali metal enolates (with the exception of lithium salts) are hardly associated. In the ion pair of an alkali metal enolate, the cation is coordinated to the hard oxygen centre of the enolate ion and the electrostatic interaction between the two oppositely charged ions is intensified with decrease of the radius and with increase of charge density in the sequence $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ i.e. with increase of the hardness of the cation. Ion association has a marked influence on the reactivity of the anion. The electrostatic interaction between the ions in the ion pair in media of moderate polarity is very considerable; the free ion is as a rule the most reactive species and ion association therefore causes an appreciable decrease of nucelophilic reactivity. For ambident anions, association of the cations with one of the reaction centres causes a disproportionate diminution of the nucleophilic properties of both reaction centres. In an ion pair with an enolate ion, the alkali metal cation is associated with a hard oxygen centre, which leads to an increase of the fraction of the product of *C*-alkylation of the ion pair relative to the free anion.

The ratio of the *C*- and *O*-isomers increases particularly markedly on association of ions pairs into dimers, trimers, and larger aggregates. The agglomeration of ion pairs is undoubtedly the main cause responsible for the exclusive formation of the products of *C*-alkylation and *C*-acylation of alkali metal enolates of carbonyl and β-dicarbonyl compounds in benzene, dioxan, petroleum ether, and other non-polar and weakly basic solvents. In the general case the ratio of the *C*- and *O*-isomers in the alkylation of alkali metal enolates in an aprotic medium should decrease in the sequence $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > NR_4^+$, but the effect should be smoothed out on passing to more basic and polar solvents.

Curtin et al. [15] showed that, in the alkylation of sodium and potassium 2,6-dimethylphenoxides with allyl bromide in ether, the dienone/ether ratio diminishes from 1 to 0.5 when $Na^+$ is replaced by $K^+$. A detailed study of the influence of the nature of the cation in the alkylation of phenoxides has been carried out using β-naphthol salts as an example [16] (Table 1).

The yield of the *O*-isomer increases in the sequence $MgBr^+ \ll Na^+ < K^+ < N(CH_3)_4^+$; the exclusive formation of the *C*-alkylation product from magnesium β-naphthoxide is striking. An increase of the fraction of the *O*-alkylation product for tetraalkylammonium enolates was noted by Nesmeyanov and Sazonova in the methoxymethylation of alkali metal derivatives of ββ-diphenylpropiomesitylene. [17] In the alkylation of ammonia-saturated acetoacetic ester (AAE) with chloroacetone in ether, Hurd and Wilkinson detected only the *O*-isomer; when the same alkylating agent reacts with the sodium salt of AAE in alcohol, only the *C*-alkylation product is formed [18]. An appreciable increase of the ratio of the *C*- and *O*-isomers, from 3.4 to 7.7, was observed also in the alkylation of alkali metal salts of the benzophenone dianion with methyl iodide in liquid ammonia when the potassium counter ion was replaced by sodium [19]. The influence of the alkali metal cation has also been studied for the alkylation of the enolates of cyclic β-ketoesters with ethyl α-bromopropionate in a 2 : 5 DMF–benzene binary mixture [20]. The results show that, regardless of the size of the ring, the yield of the *O*-alkylation product increases for all the β-ketoesters in the series of cations $Li^+ < Na^+ < K^+$. The ratio of the *O*- and *C*-isomers increases most sharply on passing from the sodium enolate of 2-ethoxycarbonyl-1-indanone to the potassium enolate.

Table 1. The alkylation of β-naphthol salts with benzyl bromide.

| Cation | Solvent | Total yield, % | Relative yield, % | |
|---|---|---|---|---|
| | | | *O*-isomer | *C*-isomer |
| $K^+$ | Dioxan; 100° | 46 | 58 | 42 |
| $Na^+$ | Dioxan; 100° | 49 | 48 | 52 |
| $Li^+$ | Dioxan; 100° | 47 | 47 | 53 |
| $MgBr^+$ | Dioxan; 100° | 64 | — | 100 |
| $K^+$ | Alcohol–benzene (1 : 1) | 47 | 84 | 16 |
| $NMe_4^+$ | Alcohol–benzene (1 : 1) | 50 | 91 | 9 |

In dipolar aprotic solvents, where alkali metal enolates are partly dissociated, the influence of the alkali metal cation is extremely weak [21–24]. For example, the ratio of the *C*- and *O*-isomers of the products of the alkylation of alkali metal enolates of acetylacetone (AcAc) with ethyl toluene-*p*-sulphonate in HMP at 20°C is almost independent (with the exception of the lithium salt) of the nature of the counter ion [24]. The above ratio also does not change with decrease of the concentration of the enolate and when HMP is replaced by another solvent containing the phosphine oxide group (diaphos, mediphos). When ethyl toluene-*p*-sulphonate is replaced by ethyl bromide and particularly ethyl iodide, the yield of 2-ethoxypent-2-en-4-one decreases sharply, but remains constant for sodium, potassium, and tetrabutylammonium enolates. This means that the reactive species is the "free" AcAc anion. In a more differentiating solvent (DMF), the relative yield of the *O*-alkylation product increases in the series of cations $Li^+ < Na^+ < K^+ \sim Cs^+$, i.e. not only the ions but also the ion pairs of acetylacetonates participate in the reaction.

The fraction of the *O*-alkylation products of enolates increases particularly markedly on passing to quaternary ammonium enolates. The formation of the products of the *O*-alkylation of tetrabutylammonium enolates of AAE, AcAc, and benzoylmalonic ester has been noted even in a weakly basic medium such as chloroform and methylene chloride [25–27].

The counter ion has been found to have an unusual influence in the alkylation of alkali metal enolates of 2-ethoxycarbonylcyclopentanone in DMSO. [28] On alkylation with isopropyl iodide or butyl bromide, the sodium enolate unexpectedly gives rise to a greater amount of the *O*-isomer than does the potassium enolate. These data are in sharp conflict with those of other studies concerning the influence of the cation on the ratio of the *C*- and

*O*-isomers in an aprotic medium. If it is supposed that the main reactive species is in this case the ion pair of the alkali metal enolate, the different types of behaviour of the sodium and potassium enolates must be associated with the different degrees of solvation of the cation in ion pairs. The ion pair of sodium enolate may prove to be more reactive, since DMSO is coordinated more effectively to the sodium cation than to the potassium cation[29].

Strictly speaking, all the above data yield only a quantitative and extremely superficial picture of the influence of the alkali metal cation on the ratio of the *C*- and *O*-isomers in the reaction products. This ratio is determined by at least two processes involving the free enolate ion and ion pairs (and in some cases there is also a possibility of their agglomeration), and by the relative contribution of each process. In order to characterise quantitatively the influence of the cation, it is necessary to determine $(C/O)_p$—the ratio of the isomers in the alkylation of the ion pair of the alkali metal enolate. $(C/O)_{obs}$ and $(C/O)_p$ can, in principle, differ fairly markedly. Table 2 presents the ratios $(C/O)_{obs}$, $(C/O)_p$, and $(C/O)_{ion}$ for the alkylation of alkali metal salts of methyl 3-hydroxybenzofuran-2-carboxylate with methyl iodide in methanol[30]. The data presented in Table 2 clearly demonstrate significant differences between these quantities as a function of the nature of the cation; at the same time, it is easily seen that the general sequence in the variation of the quantities $(C/O)_p$ and $(C/O)_{obs}$ as function of the nature of the counter ion does not change. This factor is very significant, since it justifies the hypothesis that $(C/O)_{obs}$ can serve as a criterion in the estimation of the influence of the nature of the cation on the dual reactivity of alkali metal enolates. The data in Table 2 also reveal a considerable difference in the influence of the nature of the counter ion in aprotic and protic media. The ratio of the *C*- and *O*-isomers in the methylation of salts of the β-hydroxycoumarate ester in methanol decreases on passing from $Li^+$ to $Na^+$, but increases again for potassium and bispiperidinium salts.

Table 2.

| Cation | $(C/O)_{obs}$ | $(C/O)_p$ | $(C/O)_{ion}$ | Cation | $(C/O)_{obs}$ | $(C/O)_p$ | $(C/O)_{ion}$ |
|---|---|---|---|---|---|---|---|
| $Li^+$ | 5.9 | 5.0 | 6.0 | $K^+$ | 4.4 | 2.63 | 6.0 |
| $Na^+$ | 3.5 | 2.1 | 6.0 | Bipy* | 5.0 | 4.1 | 6.0 |

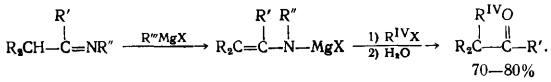
*Bipy = bispiperidinium cation.

The data obtained by Stetter and Dierichs[31] for the alkylation of the lithium, sodium, and potassium salts of dihydroresorcinol with butyl bromide in methanol serve as a very clear example of this difference. The ratio of the *C*- and *O*-isomers decreased in the sequence $K^+ > Na^+ > Li^+$, which is the opposite to that corresponding to the influence of the cation in an aprotic medium. The interpretation of data for the influence of the nature of the counter ion in protic solvents is very difficult. As will be shown below, proton-donating solvents solvate selectively and effectively the oxygen centre of the enolate ion, which promotes the reaction at the second centre of the ambident anion. Thus the selective solvation of the enolate ion via hydrogen bonding as well as the shielding of the oxygen centre in the ion pair owing to the electrostatic interaction with the alkali metal cation lead to an increase of the ratio of the *C*- and *O*-isomers in the alkylation products. In principle, a situation may arise in which the shielding of the oxygen atom of the enolate ion by solvent molecules owing to hydrogen bonding is stronger than the electrostatic interaction with the cation in the ion pair, which is particularly likely for large cations with a low charge density ($Cs^+$, $NR_4^+$, $AsPh_4^+$, etc.), i.e., in contrast to an aprotic medium, in a protic medium the case where $(C/O)_{ion} > (C/O)_p$ is quite real[30] (Table 2).

Many examples of the alkylation of covalent metal derivatives of carbonyl and β-dicarbonyl compounds are known. A change in the amount of ionic character of the bond has a very strong influence on the ratio of the *C*- and *O*-alkylation products. In addition, one must also take into account the structure of metallic derivatives of keto-enols. Whereas the enolate structure has been generally acknowledged for alkali metal, alkaline earth metal, and thallium derivatives[32], there is convincing evidence that the mercurated carbonyl and β-dicarbonyl compounds exist in the keto-form[33-37]. Derivatives of tin and germanium, where a metallotropic equilibrium between the *O*- and *C*-forms has been demonstrated, constitute an intermediate group[38-41]. It has been suggested, although without adequate arguments, that the magnesium derivatives of certain ketoenols also exist in the form of a mixture of two metallotropic forms[42-45].

In the solution of the problem of the structure of metal derivatives of carbonyl compounds, the application of Pearson's principle of hard and soft acids and bases (HSAB)[46] has been extremely fruitful. Alkali metal cations and the $Mg^{2+}$, $Tl^+$, and $R_3Si^+$ cations, which belong to the group of hard acids, should be coordinated to the hard oxygen centre of the enolate ion, while soft Lewis acids, for example the mercury cation, should be coordinated to the soft carbon centre. For an intermediate group ($R_3Ge^+$ and $R_3Sn^+$), there is a possibility of the existence of both forms with different equilibrium positions between them.

Magnesium enolates and magnesium salts of aldehyde and ketone derivatives are alkylated solely at the carbon atom. Stork and Dowd[47] found that the alkylation of the magnesium derivative of an imine is one of the best methods for the selective mono-*C*-alkylation of carbonyl compounds. Asymmetric ketones are alkylated at an unsubstituted carbon atom:

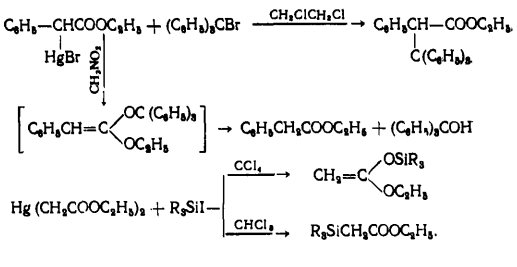



The alkylation of the magnesium salts of various ketoenols in HMP has been investigated in greatest detail. It has been shown[48] that, on treatment with a wide variety of alkylating agents, products of *C*- and di-*CC*-alkylation only are formed with high yields. The alkylation of thallium enolates by alkyl halides without a solvent[49] or in benzene[50] also gives rise to high yields of *C*-isomers. Taylor et al.[50] suggested that this reaction be used as a preparative method for the mono-*C*-alkylation of ketoenol systems. Their data permit the conclusion that the alkylation of thallium(I) enolates is the best method for the synthesis of *C*-isomers in a chromatographically pure form. However, it has been recently reported[51] that the alkylation of the thallium(I) salt of dihydroresorcinol gives rise to the *O*-alkylation products regardless of the nature of the solvent. Evidently, depending on the $pK_a$ of the β-dicarbonyl compound, a change in the mode of reaction

in the alkylation of thallium(I) enolate is to be expected, in which the compound with the lower $pK_a$ undergoes preferential *O*-alkylation. Hooz and Smith[52] reinvestigated the alkylation of the thallium enolates of AAE and AcAc by methyl, ethyl, and isopropyl iodides. Their data are in striking conflict with those of Taylor et al. Firstly, the selective mono-*C*-alkylation of the enolate was not observed in any instance and the reaction mixture always contained mono- and di-alkylation products. Secondly, *C*-ethylation and *C*-isopropylation is accompanied by the competing *O*-alkylation reaction. The latter factor is particularly surprising bearing in mind that magnesium enolates are alkylated at the carbon atom. Thus thallium(I) used as a counter ion in the alkylation reaction resembles the lithium cation more closely than an alkaline earth metal cation.

Silver enolates are known to exhibit an enhanced tendency towards the formation of *O*-alkyl derivatives. For example, when alkyl halides interacted with the silver derivatives of dihydroresorcinol[53], AcAc [54], AAE [55], and certain bicyclic triketones[56], *O*-alkylation products were isolated. At the same time the alkylation of the silver and mercury salts of the diazoacetic ester by benzyl and allyl bromides in ether leads to the formation of *C*-alkylation products with retention of the diazo-group[57]. The alkylation of tin derivatives of ketoenols has been studied in relation to an extremely limited number of examples and only *C*-alkylation products could be detected (with a low yield) in the reaction mixture[58-62].

Numerous studies have been made on the alkylation of $\alpha$-mercurated derivatives of carbonyl compounds. It has been established that these compounds do not react with the majority of alkylating agents, positive results being obtained solely when mild alkylating agents were used: allyl, benzyl, and trityl halides. $\gamma$-Mercuribis-AAE gives rise to a low yield of a mixture of $\alpha$-allyl- and $\alpha\alpha$-diallyl(benzyl)-AAE on alkylation with allyl and benzyl iodides[63]. A high yield of the products of the alkylation of mercury derivatives of oxo-compounds has been observed only when trityl halides were used as the alkylating agents[64-67]. An important condition for the occurrence of this reaction is nucleophilic cooperation by the leaving group of the alkylating agent. Thus ethyl $\alpha$-bromo-mercuriphenylacetate does not react with trityl perchlorate, but is alkylated under the influence of bromotriphenylmethane, which involves the nucleophilic cooperation of bromine[66]; the mode of the alkylation reaction depends very strongly on the nature of the solvent:



The reaction is very sensitive to a change in the structure of the alkylating agent. Thus mercuribisacetylaldehyde interacts with chlorotriphenylmethane to form $\beta\beta\beta$-triphenylpropionaldehyde, while the analogous reaction with chlorotri-(*p*-nitrophenyl)methane gives rise to the enol ether as the only product[35]. The above examples illustrate the extremely high sensitivity of the mode of reaction to factors whose influence cannot be predicted beforehand.

## III. THE INFLUENCE OF THE SOLVENT ON THE RATIO OF THE *C*- AND *O*-ALKYLATION PRODUCTS

The solvent has an extremely marked influence on the rate and mode of alkylation of phenoxides and enolates. In the early stages of the study of the problem of the dual reactivity of ambident systems, it was already noted that a change of solvent can alter completely the mode of reaction. Thus Claisen et al.[68] showed that the alkylation of sodium phenoxide by allyl bromide in alcohol or acetone leads to the formation of allyl phenyl ether, while in benzene and ether the product is *o*-allylphenol.

In the assessment of the influence of solvents on the dual reactivity of the salts of ambident anions, one must distinguish two types of interaction of the solute with the solvent: the specific solvation of the cation and the interaction of the solvent with the ambident anion proper. Alkali metal enolates are to some extent associated to ion pairs and more complex aggregates of ion pairs in the majority of organic solvents. The degree of association of alkaline earth metal enolates and phenoxides is undoubtedly even greater. The derivatives of other metals must be evidently regarded as covalent compounds with different amounts of ionic character. As noted above, the position of equilibrium between different forms of ionic species depends to a large extent on the nature of the solvent. In weakly polar and weakly basic solvents (hydrocarbons, ether, dioxan, etc.), the ion pairs of alkali metal enolates are highly associated, which is the reason for the formation of *C*-alkylation products in these media. The introduction of dipolar aprotic solvents and linear polyethers (glymes) into the medium where alkali metal enolates exist as associated species causes the disruption of the latter to ion pairs. The disruption of ionic association complexes is accompanied by an appreciable acceleration of the alkylation of alkali metal enolates. Zaugg and coworkers[7,69] showed that the addition of even small amounts ($<5\%$) of certain dipolar aprotic solvents to a benzene solution of the sodium enolate derived from the n-butylmalonic ester causes a sharp acceleration of *C*-alkylation under the influence of butyl bromide. The acceleration of the reaction is caused by the specific solvation of the cation by molecules of the dipolar aprotic solvent; in the presence of the polar component, the reaction rate constant varies in parallel with the basicity of this solvent. The continuous increase of the rate of reaction with increase of the DMF and DMSO concentrations in binary mixtures with benzene[69] is evidently due to the gradual disruption of the associated species following the introduction of the polar component[8]. The ratios of the rates of reaction in benzene, tetrahydrofuran (THF), DME, DMF, and DMSO are 1 : 14 : 80 : 970 : 1420 respectively[69]. In dipolar aprotic solvents, alkali metal enolates apparently exist as ion pairs and free ions. A study of the alkylation of alkali metal enolates in an aprotic medium revealed a general feature: an increase of the basicity of the aprotic solvent promotes *O*-alkylation; the ratio of *C*- and *O*-alkylation products is not correlated with the dielectric constant of the aprotic solvent and is determined mainly by the capacity of the solvent for the specific solvation of the cation, which depends in its turn on the basicity of the solvent. The quantity $\Delta\delta_\infty$—the change in the chemical shift of the chloroform proton at an infinitely low concentration of chloroform in the given solvent—may serve as a measure of the basicity of the aprotic solvent[70]; the quantity $\Delta H_{solv}$—the enthalpy of solvation of the sodium cation—may serve as a more reliable characteristic of the basicity of the solvent[71] (Table 3)

The fraction of the product of the *O*-alkylation of the sodium salt of 2,6-dimethylphenol increases in the sequence benzene < toluene < $O(C_3H_7)_2$ < $O(C_2H_5)_2$.[15] The influence of the solvent is more clear-cut in the reaction of sodium β-naphthoxide with benzyl bromide and methyl iodide[79] (Table 4).

Table 3. The values of $\Delta\delta_\infty$ and $\Delta H_{solv}$ for certain aprotic solvents[70,71].

| Solvent | $\Delta\delta_\infty$, p.p.m. | $\Delta H_{solv}$, kcal mole$^{-1}$ | Solvent | $\Delta\delta_\infty$, p.p.m. | $\Delta H_{solv}$, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| HMP | —2.03 | —0.58 | Acetonitrile | —0.63 | 0 06 |
| N-Methylpyrrolidinone | —2.03 | — | DME | —0.84 | —0.45 |
| Tetramethylurea | —1.37 | — | Tetraglyme | — | —4.82 |
| DMSO | —1.34 | —0.34 | Sulpholane | —0.68 | — |
| DMF | —1.30 | —0.23 | THF | —0.80 | —0.08 |
| Acetone | —0.94 | 0.00 | Dioxan | —0.64 | —0.06 |

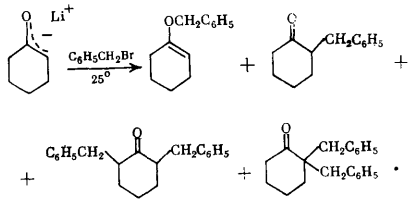
The increase of the yield of the *O*-isomer on passing to dipolar aprotic solvents has also been observed in the alkylation of the sodium salt of dimethyloctalone by benzyloxymethyl chloride[74].

Table 4. The *C*- and *O*-alkylation of sodium β-naphthoxide.

| Solvent | Yield of isomers*, % | | | |
|---|---|---|---|---|
| | *O*-isomer | *C*-isomer | *O*-isomer | *C*-isomer |
| | Benzyl bromide | | Methyl iodide | |
| DMF | 97 | — | 91 | 4 |
| DMSO | 95 | — | 90 | 3 |
| DME | 70 | 22 | 86 | 10 |
| THF | 60 | 36 | 80 | 13 |

*The absolute yields are quoted.

A similar effect has been observed[75] in the methylation and ethylation of the potassium enolates derived from acetophenone, cyclohexanone, cyclopentanone, and other ketones by dimethyl and diethyl sulphates. A very small amount of the enol ether (~3%) is formed even in the benzylation of the lithium enolate derived from cyclohexanone in HMP, while in ether and DME a complex mixture of products of *C*- and *CC*-alkylation is formed[76].




| | | | | |
|---|---|---|---|---|
| Ether | — | 45% | 5% | 5% |
| Dimethoxyethane | — | 51% | 4% | 9% |
| Hexamethylphosphoramide | 3% | 27% | 5% | 20% |

The ratio of the *C*- and *O*-products obtained from alkali metal enolates derived from β-dicarbonyl compounds also diminishes when weakly polar aprotic solvents are replaced by dipolar aprotic solvents. It has been shown[77] that the yield of the *O*-isomer in the alkylation of the potassium salt of AAE by butyl chloride at 100°C increases on passing from acetone to dipolar aprotic solvents (Table 5).

Table 5. The alkylation of the potassium salt of AAE with butyl chloride.

| Solvent | Yield of *O*-isomer, % | Solvent | Yield of *O*-isomer, % |
|---|---|---|---|
| N-Methylpyrrolidinone | 51 | DMSO | 47 |
| NN-Dimethylacetamide | 49 | Acetonitrile | 19 |
| DMF | 46 | Acetone | 10 |

The influence of the solvent on the ratio of the products of the *C*- and *O*-alkylation of the tetrabutylammonium salt of AcAc by isopropyl iodide is less pronounced (Table 6)[78]. The low ratios of the *C*- and *O*-products in weakly polar and weakly basic media are probably associated with the large interionic distance in the ion pair of the tetrabutylammonium salt (the Stokes radius of the $NBu_4^+$ cation is independent of the nature of the solvent and amounts to 3.85 Å).[79]

Table 6. The *C*- and *O*-alkylation of the tetrabutylammonium enolate of acetylacetone with isopropyl iodide.

| Solvent | Yield of isomer, % | | Ratio of *C*- and *O*-isomers | Solvent | Yield of isomer, % | | Ratio of *C*- and *O*-isomers |
|---|---|---|---|---|---|---|---|
| | *C*-isomer | *O*-isomer | | | *C*-isomer | *O*-isomer | |
| DMSO | 42 | 58 | 0.72 | Chloroform | 51 | 49 | 1.04 |
| Acetone | 42 | 58 | 0.72 | Dioxan | 63 | 37 | 1.91 |
| Acetonitrile | 48 | 52 | 0.92 | Toluene* | 69 | 5 | 13.8 |

*26% of the enolate was recovered unchanged.

The influence of the nature of the solvent on the mode of alkylation of alkali metal enolates has been investigated in greatest detail for the AAE and AcAc enolates[80]; the experimental data are presented in Tables 7 and 8. These show in the first place that the influence of aprotic solvents is determined mainly by the values of $\Delta\delta_\infty$ and $\Delta H_{solv}$ for the sodium cation in the given medium and not by the dielectric constant. The ratio of the *C*- and *O*-ethylation products is correlated quite satisfactorily with the above parameters of the solvent basicity. The comparatively low yield of β-ethoxyethyl crotonate in tetraglyme and the higher yield of the *O*-isomer in acetonitrile then in monoglyme show that the basicity of the solvent is not the only factor determining the ratio of the isomers. The polarity of the medium also plays a definite role. The solvent basicity is of decisive importance in the disruption of ionic association complexes into monomeric ion pairs, while the medium polarity influences mainly the position of the equilibrium between ions and ion pairs. Aprotic solvents can be approximately divided into four groups in terms of their influence on the process: 1. highly basic dipolar aprotic solvents (HMP, diaphos, mediphos), in which the reacting species is the enolate ion and the isomer ratio is determined by its mesomerism. 2. Dialkylamides, DMSO, and pyridine, in which the reactive species

are not only ions but also K–AAE and Na–AcAc ion pairs. 3. Moderately polar and weakly basic solvents (acetonitrile, acetone, and sulpholane). The coordinating capacity of these solvents in relation to alkali medium cations is low, so that the contribution of ion pairs and possibly also of higher association complexes increases sharply, which leads to an increase of the ratio of the *C*- and *O*-products by a factor greater than 2. 4. Weakly polar solvents (ether, dioxan, THF, methylene chloride) in which *C*-alkylation takes place exclusively. The reacting species is apparently an association complex comprising several ion pairs. In DME and tetraglyme, which effectively solvate alkali metal cations but are at the same time insufficiently polar, a certain amount of the *O*-isomer is formed. It has been found that the addition of even small amounts of complex-forming agents such as glymes and particularly of macrocyclic crown polyethers alters significantly the ratio of the *C*- and *O*-alkylation products[81,82]. Thus the fraction of the *O*-alkylation product obtained in the alkylation of the potassium salt of AAE with ethyl toluene-*p*-sulphonate in benzene, ether, and dioxan increases approximately by a factor of 100 after the introduction of an equimolar amount of dicyclohexyl-18-crown-6 ether[81].

Table 7. The ethylation of the potassium enolate of acetoacetic ester with diethyl sulphate ($c_0$ = 0.33 M, $t$ = 20°C).

| Solvent | Yield, % | | | | ε | $\Delta\delta_{\infty}$, p.p.m. (Ref.70) |
|---|---|---|---|---|---|---|
| | total yield | *O*-isomer* | *C*-isomer* | dialkylation products* | | |
| HMP | 93 | 83 | 15 | 2 | 30 | —2.03 |
| Diaphos | 91 | 83 | 16 | 1 | 31.6 | — |
| *N*-Methylpyrrolidinone | 90 | 80 | 18 | 2 | 32 | — |
| Tetramethylurea | 95 | 78 | 20 | 2 | 23 | —1.37 |
| DMF | 93 | 71 | 26 | 3 | 36.7 | —1.30 |
| DMSO | 92 | 70 | 27 | 3 | 49 | —1.34 |
| Pyridine | — | 63 | 35 | 2 | 12.3 | — |
| Propylene carbonate | 78 | 51 | 46 | 3 | 65 | — |
| *N*-Methylformamide | 75 | 40 | 58 | 2 | 170 | — |
| Acetone | 67 | 38 | 51 | 11 | 20.5 | —0.94 |
| Acetonitrile | — | 32 | 61 | 7 | 37.5 | —0.63 |
| Tetraglyme | 95 | 26 | 68 | 6 | 7.7 | — |
| Monoglyme | 88 | 18 | 74 | 8 | 7.3 | —0.84 |
| Sulpholane | 80 | 15 | 76 | 9 | 44 | —0.68 |
| Ethanol | 84 | 8 | 87 | 5 | 24.3 | — |
| THF | 78 | <1 | 94 | 6 | 7.6 | —0.80 |
| Ethyl ether | — | <1 | 95 | 5 | 4.3 | — |
| Dioxan | 85 | <1 | 96 | 4 | 2.2 | |
| Methylene chloride | — | <1 | 97 | 3 | 8.9 | — |
| t-Butyl alcohol | — | <1 | 94 | 6 | 10 | — |

*The relative yields are quoted.

Hitherto we have considered the influence of the solvent on the ratio of the *C*- and *O*-isomers in the alkylation of enolates and phenoxides taking into account only the specific solvation of the cation. Another and more interesting possibility in the influence of the solvent on the dual reactivity of ambident anions is associated with the specific solvation of the ambident anion itself. The two reaction centres of enolate and phenoxide ions differ sharply in their electronegativity and the distribution of electron density. The hard oxygen atom serves simultaneously as the centre of the highest electron density. The hardness and electronegativity differences are responsible for the more extensive solvation of the oxygen centre of the enolate ion. Selective solvation of the oxygen atom causes a disproportionate diminution of the nucleophilic properties of the two centres of the ambident anion, which entails an increase of the fraction of the *C*-alkylation products. Thus, like the counter ions in ion pairs formed from enolate and phenoxide ions, solvation effects lead to the shielding of the atom with the higher electron density. "Shielding" plays a major role primarily in a protic medium as a result of the formation of a strong hydrogen bond with the oxygen centre of the ambident anion. Kornblum called this phenomenon "selective solvation"[72,83].

Table 8. The ethylation of the sodium salt of acetylacetone with ethyl toluene-*p*-sulphonate ($c_0$ = 0.3 M; $t$ = 20°C).

| Solvent | Yield, % | | | | ε | $\Delta\delta_{\infty}$, p.p.m. | $\Delta H_{solv}$ (Ref.71) |
|---|---|---|---|---|---|---|---|
| | absolute yield | *C*-isomer | *O*-isomer | dialkylation product* | | | |
| Diaphos | 93 | 10 | 90 | <1 | 31.6 | — | — |
| Mediphos | 90 | 10 | 90 | <1 | 24.6 | — | — |
| HMP | 90 | 10 | 90 | <1 | 30 | —2.03 | —0.58 |
| *N*-Methylacetamide | 75 | 20 | 80 | <1 | 179 | — | — |
| *N*-Methylpyrrolidinone | 75 | 22 | 78 | <1 | 32 | —2.05 | — |
| α-Pyrrolidinone | 36 | 22 | 78 | <1 | — | — | — |
| Tetramethylurea | 92 | 19 | 77 | 4 | 23 | —1.37 | — |
| DMSO | 77 | 25 | 75 | <1 | 49 | —1.34 | —0 34 |
| DMF | 74 | 26 | 74 | <1 | 36.7 | —1.30 | —0.23 |
| Propylene carbonate*** | 58 | 47 | 51 | 2 | 65 | — | — |
| Acetone*** | 37 | 64 | 36 | <1 | 20.5 | —0.94 | 0.00 |
| Acetonitrile*** | 45 | 65 | 35 | <1 | 37.5 | —0.63 | +0.06 |
| Dimethoxyethane | 32 | 77 | 13 | 10 | 7.3 | —0.84 | —0.45 |
| Sulpholan | 28 | 77 | 11 | 12 | 44 | —0.68 | — |

*The relative yields are quoted.
**The yields of dialkylation products (mixture of the *CC*-isomers with a small amount of the *CO*-isomers) [?not shown (Ed. of Translation)].
***The reaction proceeds heterogeneously at 50°C.

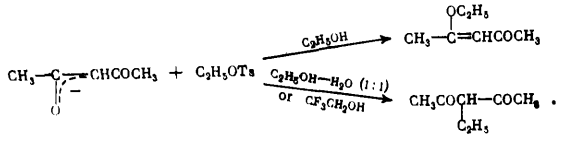
Table 9. The influence of specific solvation on the mode of reaction of the ambident anion.

| Solvent | Yield, % | | | |
|---|---|---|---|---|
| | *C*-isomer | *O*-isomer | *C*-isomer | *O*-isomer |
| | Sodium phenoxide + allyl chloride | | Sodium β-naphthoxide + benzyl bromide | |
| Ethanol | — | 100 | 28 | 52 |
| Methanol | — | 100 | 34 | 57 |
| Water | 41 | 49 | 84 | 10 |
| 2,2,3,3-Tetrafluoropropanol | 37 | 58 | — | — |
| 2,2-Trifluoroethanol | 42 | 37 | 85 | 7 |
| Phenol | 78 | 22 | — | — |

In the classical studies by Claisen at the beginning of the XXth century, it was shown that phenoxides are alkylated in alcoholic media exclusively at the oxygen atom. When solvents capable of forming stronger hydrogen bonds were used, it was possible to alter the mode of reaction. Thus the addition of water lowers the yield of the *O*-isomer in the reaction of sodium phenoxide with allyl bromide in an alcoholic medium[84]. This effect becomes enhanced when the reaction is carried out in water or phenol. A sharp increase of the ratio of the *C*- and *O*-isomers is observed when fluorinated alcohols are used as solvents[72,83] (Table 9). The increase of the fraction of the *C*-alkylation product takes place in parallel with the increase of the tendency of the solvent towards the formation of strong hydrogen bonds with the oxygen atom of the phenoxide ion. Experimental evidence for the

selective solvation of the heteroatom of the ambident anion in protic media was obtained in a study[85] where a strong hypsochromic shift of the absorption maximum was observed in the ultraviolet spectrum of the anion of 1-nitroindene on passing from dipolar aprotic solvents to water and trifluoroethanol, which is the strongest donor species in the formation of a hydrogen bond.

An analogous effect was noted in the NMR and ultraviolet spectra of alkali metal phenoxides in solvents of different classes[86]. It is striking that the absorption bands of the 1-nitroindene anion in trifluoroethanol and of the *aci*-form of a nitro-compound in water are very similar. This shows that the reactivity of solvated anions of this kind approaches that of the protonated form, as a result of which the activation energy for the substitution reaction involving the other, unshielded centre is also much higher than in any aprotic medium. Indeed, the rate of alkylation of sodium phenoxide in water and trifluoroethanol is extremely low[83]. Selective solvation of the oxygen centre of the anion has been observed also for the enolate ions of β-dicarbonyl compounds. The low yield of the product of the *O*-alkylation of the potassium salt of AAE by diethyl sulphate in ethanol and particularly in *N*-methylacetamide and *N*-methylformamide (Table 7)[80], despite the exceptionally high value of ε and the high solvating capacity of these solvents in relation to alkali metal cations, is undoubtedly due to the selective solvation of the oxygen atom in the AAE anion via hydrogen bonding. A stronger hydrogen bond donor is necessary if selective solvation of the AcAc anion is to be possible. Such an effect is manifested in water and in trifluoroethanol[87]. The ratio of the *C*- and *O*-isomers is almost fully inverted in trifluoroethanol relative to alkylation in ethanol, where the *O*-isomer is virtually the only reaction product. The addition of water to the alcohol also alters the mode of reaction, and in 50% alcohol the only product of the alkylation reaction is 3-ethylacetylacetone. Thus, by altering slightly the reaction conditions, it is possible to change completely the mode of alkylation:



In another study[88], it was shown that the rate constant for the *O*-alkylation of the potassium salt of AAE by ethyl toluene-*p*-sulphonate increases by a factor of 400 on passing from ethanol to HMP, while the rate of *C*-alkylation increases only by a factor of 25. The decrease of the ratio of the *C*- and *O*-isomers by a factor of 16 when alcohol is replaced by HMP as the reaction medium reflects the influence of selective solvation on the mode of alkylation of the ambident AAE anion.

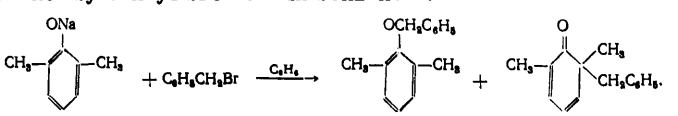
It is of interest to compare data for the selective solvation of various phenoxide and enolate ions. In conformity with the HSAB principle, protic solvents solvate, like hard Lewis acids, the harder oxygen centre of the ambident anion. The harder the oxygen centre of the anion, the harder the acid and the stronger the donor component of the hydrogen bond needed to shield the centre. The AAE anion is solvated selectively by ethanol. In relation to the AcAc ion, ethanol is an insufficiently hard Lewis acid; in this case methanol, trifluoroethanol, and water are effective. When the phenoxide ion is alkylated, the formation of the *C*-isomer is observed only in water, trifluoroethanol, and phenol (Table 9).

## IV. DEPENDENCE OF THE REACTION PATHWAY ON THE STRUCTURE OF THE ELECTROPHILE

The most important factor determining the mode of alkylation of enolates and phenoxides is the nature of the electrophile. Here account must be taken simultaneously of the electronic and steric effects of the alkyl group and of the nature of the leaving group of the alkylating agent. Different ambident anions manifest different sensitivities in relation to the nature of the electrophile; phenoxides and naphthoxides are least sensitive. The alkylation of these salts by alkyl toluene-*p*-sulphonates, dialkyl sulphates, and alkyl halides usually leads to the formation of the corresponding ethers.

### 1. The Structure of the Alkyl Group

Claisen and Eisleb[89] showed that the products of the *C*-alkylation of alkali metal phenoxides can be obtained only when allyl and benzyl halides are used as alkylating agents. However, using the results of the gas–liquid chromatographic (GLC) analysis of reaction mixture, Kornblum and coworkers showed that, when sodium β-naphthoxide is acted upon by methyl iodide in ethanol, 12% of the *C*-isomer is formed and, following the replacement of methyl iodide by propyl bromide, only traces of the *C*-isomer are detected[72]. The use of allyl and benzyl halides as alkylating agents leads to a significant increase of the yield of *o*-substituted phenols. Thus Gomberg and Buchler[90] observed for the first time the formation of 50% of *o*-benzylphenol in the alkylation of sodium phenoxide by benzyl chloride in water. Somewhat later Claisen at al. isolated *o*-benzylphenol as the sole product of the reaction of sodium phenoxide with benzyl bromide in toluene or ether (in 80–90% yield)[91]. The composition of the mixture of benzylation products depends on the nature of the substituent in the benzene ring of benzyl bromide. It has been shown that, in the alkylation of sodium β-naphthoxide in acetone by benzyl bromide and *p*-nitrobenzyl bromide, only benzyl ethers are formed, while alkylation with *p*-methoxybenzyl bromide gives rise to a mixture of 47% of the *O*-isomer and 24% of 1-(*p*-methoxybenzyl)-2-naphthol.[92] The formation of *o*-allylphenol when allyl bromide in ether is used as the alkylating agent was observed by Claisen et al.[91] The yield of the *C*-isomer increases in alkylation by γ-substituted allyl bromides. The alkylation of sodium phenoxide by γ-phenylallyl bromide in benzene leads to the formation of *o*-(γ-phenylallyl)phenol only[93]. A significant increase of the yield of the *C*-isomer (a mixture of *o*- and *p*-alkylphenols) is observed in the alkylation of 2,6-disubstituted phenoxides, although the formation of the *o*-isomer requires in this case the breakdown of the aromaticity of the system. The formation of a considerable amount of dienone was observed in a study of the alkylation of the sodium salt of 2,6-dimethylphenol by benzyl bromide in benzene[94]:



A high yield of the dienone was obtained in the reaction of sodium 2,6-di-(t-butyl)-4-methylphenoxide with methyl iodide[95]. However, the alkylation of alkali metal phenoxides and naphthoxides leads to the formation of *O*-alkylation products except in the case of sterically hindered phenols.

The opposite behaviour is observed in the alkylation with alkyl halides of alkali metal and other metal enolates derived from ketones, esters, and β-dicarbonyl compounds. In this case, *C*-alkylation products are formed preferentially. The influence of the nature of the alkylating agent on the ratio of the *O*- and *C*-isomers has been studied in detail[12] in the alkylation of the sodium enolates of certain alkyl aryl ketones in ethyl ether and glymes (Table 10):

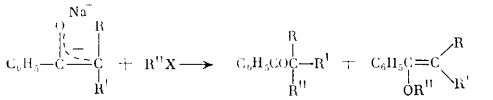


Table 10. The ratio of the products of the *O*- and *C*-alkylation of the sodium enolates of alkyl aryl ketones.

| R | R′ | Solvent | Alkylating agents | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | MeI | AllBr | EtBr | n-PrBr | Iso-PeBr | EtOTs |
| H | $C_6H_5$ | DMF | 0.0 | 0.0 | 0.0 | — | 0.0 | — |
| $CH_3$ | $CH_3$ | Ether | 0.0 | — | — | 0.0 | — | 0.63 |
| $CH_3$ | $CH_3$ | DME | — | — | 0.19 | 0.25 | 0.36 | — |
| $CH_3$ | $CH_3$ | Diglyme | 0.0 | 0.05 | 0.16 | 0.27 | — | 1.2 |
| $C_6H_5$ | $CH_3$ | Diglyme | — | 0.2 | 0.61 | — | — | 2.4 |
| $C_6H_5$ | $C_6H_5$ | Diglyme | — | — | 0.76 | — | — | 3.0 |
| $C_6H_5$ | $C_6H_5$ | Diglyme | 0.09 | — | 18 | 100 | — | — |
| $C_6H_5$ | $C_6H_5$ | t-Butyl alcohol | 0.04 | — | 1.4 | 2.5 | — | — |
| $C_6H_5$ | mesityl | t-Butyl alcohol | — | — | 100 | — | — | — |

The data presented in Table 10 show that the ratio of the *O*- and *C*-isomers increases with increase of the length of the alkyl group in the alkylating agent and is very sensitive to the influence of the steric effect in the alkylating agent and the substrate. The fraction of the *O*-alkylation product increases with increase of the bulk of the substituent at the α-carbon atom of alkyl phenyl ketone, which is particularly notable for diphenylacetophenone and mesitylphenylacetophenone, which undergo mainly the *O*-alkylation reaction. *C*-Alkylation is more sensitive to the steric effect, since in this case the carbon atom in the product has the tetrahedral $sp^3$ configuration, in contrast to the planar $sp^2$ configuration arising in the *O*-alkylation of the enolate. Thus steric hindrance favours the *O*-alkylation of alkali metal enolates. The ratio of the *O*- and *C*-isomers increases on moving along Table 10 from left to right and from above downwards, which reflects the influence of the steric effect in the alkylating agent and the substrate on the mode of the alkylation reaction. The sharp increase of the products of the *O*- and *C*-propylation of the sodium enolate of diphenylacetophenone on passing from diglyme to t-butyl alcohol is caused, according to the authors, by the selective solvation of the enolate ion via hydrogen bonding. The influence of the structure of the substituent of the alkylating agent on the mode of the competing *C*- and *O*-alkylation reactions has also been studied for alkali metal salts of β-dicarbonyl compounds. The relative yield of the *O*-isomer in the alkylation of the sodium salt of 1-cyanocyclohexanone increases on passing from methyl iodide to ethyl, n-propyl, and isopropyl iodides (18, 35, 41, and 79% respectively), but falls sharply when allyl and benzyl bromides are used, for which the yields of the *O*-isomers are only 4 and 12%.[96] Bearing in mind that the reaction mixtures were analysed by the preparative separation of the components, presumably some of the data do not reflect the true ratio of the *C*- and *O*-isomers. The yield of the *C*-alkylation products is particularly high for allyl and benzyl halides, which we already noted previously for alkali metal phenoxides and isobutyrophenone enolates. A similar sequence has also been observed in the alkylation of the sodium salt of ethyl β-hydroxycoumarate in alcohol[97], where the ratio of the *C*- and *O*-isomers decreased in the sequence allyl ≫ benzyl > $CH_3$ > $C_2H_5$ > n-$C_3H_7$. When sodium enolate was allowed to react with dimethyl sulphate, only the *O*-alkylation product was isolated. A sharp increase of the yield of the *O*-isomer on passing from methyl iodide to ethyl iodide was also noted in a study of the *C*- and *O*-alkylation of the sodium salts of dihydroresorcinol in alcohols[31]; a further increase of the length of the carbon–carbon chain in the alkyl substituent has only a slight influence on the ratio of the products of *C*- and *O*-alkylation.

An important stage in the study of the dual reactivity of ambident enolate ions was reached with the report[98] that, under the classical conditions of the *C*-alkylation of the sodium salt of AAE by alkyl halides in alcohol (the Conrad method), 6–8% of the *O*-alkylation product is obtained when s-butyl iodide is used. This report stimulated systematic study of the dual reactivity of the enolates of β-dicarbonyl compounds using the most modern methods for the analysis of the reaction mixture. Before the appearance of this report, *O*-alkylation of alkali metal enolates of β-ketoesters and β-diketones was regarded as an unusual and to some extent an exceptional phenomenon. Only isolated examples were known in which *O*-alkylation was the main or at least the competing reaction pathway. In particular, it was known that, in the interaction of the sodium salt of AAE with chloromethyl ether in ethyl ether, ethyl β-alkoxycrotonate is formed[99], the enol ether being the main product of the methylation of AAE and AcAc with diazomethane.[100] Kabachnik and coworkers showed with the aid of GLC analysis[101] that a small amount of the *O*-alkyl derivative is formed even in the alkylation of the sodium salt of AAE by alkyl bromides in alcohol and also in the reaction of the dry sodium salt of AcAc with an alkyl iodide in the absence of solvent. The increase of the content of *O*-alkylation products on passing to reagents with s-alkyl substituents is noteworthy, this being associated with the steric hindrance to the competing *C*-alkylation reaction. The influence of the nature of the alkyl group on the ratio of the *C*- and *O*-isomers was investigated also in the alkylation of the tetrabutylammonium salts of AAE,[25] AcAc,[27] and benzoylmalonic ester[28] by alkyl iodides in chloroform (Table 11). A sharp increase of the yield of the *O*-isomer was also observed on passing to isopropyl iodide. The fraction of the *O*-alkylation product increases significantly when methyl iodide is replaced by ethyl iodide.

A thorough investigation of the influence of the structure of the alkyl group and of the leaving group of the alkylating agent on the mode of the *C*- and *O*-alkylation of the potassium salt of AAE in DMSO and HMP was carried out by Le Noble and Morris[23] (Table 12).

The relative yield of the *O*-isomer for any alkylating agent is significantly higher in HMP than in DMSO. The products of *CO*-dialkylation were detected in the above study with the aid of GLC. As noted previously, steric hindrance is very strongly reflected in the mode of the alkylation reaction. This effect is particularly notable relative to data for alkylation with propyl and isopropyl chlorides and s-butyl chloride, where the ratio of the

*C*- and *O*-isomers varies by a factor >4; neopentyl chloride alkylates the AAE enolate ion only at the oxygen atom. A similar sharp difference is observed on passing from benzyl chloride to diphenylmethyl chloride, whereupon the ratio of the *C*- and *O*-isomers decreases from 6.7 to 1.6. The data presented in Table 12 also indicate the necessity for taking into account the electronic effects in the alkyl group of the alkylating agent. The steric hindrance due to the allyl and propyl groups is approximately the same, but the ratios of the products of the *C*- and *O*-alkylation of potassium enolate under the influence of allyl and s-propyl chlorides nevertheless differ very markedly. It is quite evident that the difference is due to electronic effects. The high polarisability of the allyl group promotes substitution at the carbon atom of the enolate ion—the most polarised centre in the given ambident system.

Table 11. The alkylation of the tetrabutylammonium enolates of β-dicarbonyl compounds in chloroform.

| RI | Yield*, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *C*-isomer | *O*-isomer | *CC*-isomer | *C*-isomer | *O*-isomer | *CC*-isomer | *C*-isomer | *O*-isomer |
| | acetoacetic ester | | | acetylacetone | | | benzoyl-malonic ester | |
| $CH_3I$ | 80 | — | 10 | 98.5 | — | — | 100 | — |
| $C_2H_5I$ | 83.5 | — | 9 | 72 | 12 | 16 | 54 | 46 |
| $n\text{-}C_4H_9I$ | 90 | — | 5 | 87 | 13 | — | 47 | 53 |
| $iso\text{-}C_3H_7I$ | 70 | 23.5 | — | 50.5 | 49.5 | — | 14 | 86 |

*The absolute yields of reaction products are quoted.

Extensive experimental data concerning the influence of the nature of the alkyl group on the mode of reaction of phenoxide and enolate ions are inconsistent with Kornblum's rule [102], which predicts the mode of alkylation of the ambident anion. The ratio of the *C*- and *O*-alkylation products should be determined by the competing interaction of the alkylating agent with two nucleophilic centres, as postulated in the classical theory of nucleophilic substitution. The significant difference is that in ambident nucleophiles both centres are linked via the mesomeric effect. According to Kornblum's rule, the fact that the transition state in the reaction between an ambident anion and the alkylating agent is identical with or similar to the $S_N2$ type promotes the formation of products corresponding to substitution at the most polarised reaction centre of the ambident anion; when a mechanism of the $S_N1$ type operates, attack is directed to the most electronegative centre, which behaves simultaneously as the centre of the highest electron density and the lowest polarisability. The formation of a mixture of products implies that the reaction proceeds in the intermediate $S_N1$–$S_N2$ region. The oxygen atom in enolate and phenoxide ions is the centre of maximum electron density and the carbon atom is the most polarised centre. According to Kornblum's rule, a higher ratio of the *C*- and *O*-isomers of the alkylation products was to be expected for allyl and benzyl halides than for other alkyl halides. The transition state in the reaction involving allyl, benzyl, and diphenylmethyl halides occurs as a rule in the boundary region with a much greater contribution of the $S_N1$ mechanism than for methyl, ethyl, and other alkyl halides with an n-alkyl group. [103] In all the examples quoted above, the ratio of the *C*- and *O*-isomers for benzyl and allyl halides is in fact much higher than for n-alkyl halides. Alkylation of alkali metal enolates by n-alkyl chlorides [23,104] is a bimolecular nucleophilic substitution process. However, the main products of this reaction are enol ethers, which is completely contrary to Kornblum's rule in its initial form. Finally, it is known that silylation of alkali metal enolates of carbonyl and β-dicarbonyl compounds [105,106] and certain esters [107] leads to the formation of silyl-substituted enols, despite the fact that this reaction proceeds via an $S_N2$ mechanism.

Table 12. The *C*- and *O*-alkylation of the potassium salts of acetoacetic ester.

| Alkylating agent | Absolute yield, % | | Relative yield, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *O*-isomer | | *C*-isomer | | *CC*-isomer | | *CO*-isomer | |
| | HMP | DMSO | HMP | DMSO | HMP | DMSO | HMP | DMSO | HMP | DMSO |
| n-Propyl chloride | 89 | 73 | 61 | 47 | 23 | 25 | 8 | 28 | 8 | — |
| Isopropyl chloride | 78 | 52 | 81 | 62 | 19 | 38 | — | — | — | — |
| n-Propyl bromide | — | 66 | — | 31 | — | 40 | — | 23 | — | — |
| n-Propyl iodide | — | 74 | — | 14 | — | 50 | — | 36 | — | — |
| Allyl chloride | 88 | 80 | 17 | 0 | 45 | 100 | 38 | — | — | — |
| Benzyl chloride | 93 | 60 | 13 | 5 | 51 | 45 | 36 | 50 | — | — |
| Methyl β-chloro-crotonate | — | 60 | — | 10 | — | 90 | — | — | — | — |
| s-Butyl chloride | 75 | — | 86 | — | 14 | — | — | — | — | — |
| Neopentyl chloride | 13 | — | 100 | — | — | — | — | — | — | — |
| Diphenylmethyl chloride | 93 | — | 39 | — | 61 | — | — | — | — | — |
| 2,6-Dimethylbenzyl chloride | 93 | — | 19 | — | 81 | — | — | — | — | — |
| 4-Methoxybenzyl chloride | 88 | — | 11 | — | 57 | — | 32 | — | — | — |
| 4-Methylbenzyl chloride | 97 | — | 13 | — | 54 | — | 33 | — | — | — |
| 4-Chlorobenzyl chloride | 95 | — | 11 | — | 48 | — | 41 | — | — | — |
| 4-Trifluoromethyl-benzyl chloride | 97 | — | 9 | — | 50 | — | 41 | — | — | — |

In a short review devoted to the theoretical principles of the problem of the dual reactivity of ambident anions, Gompper [108] treats Kornblum's rule somewhat differently. As a consequence of Coulombic attraction, a polar electrophile attacks primarily the atom of the ambident system which has the highest electron density. If the electrophile has a slight positive charge on the carbon atom linked directly to the leaving group, there is an enhancement of the role of the London intermolecular interaction dispersion forces, which stabilise the transition state involving the most polarised centre of the ambident anion. It is easily seen that this general formulation is in no way related to the classification according to which there exist two types of mechanisms of substitution at a saturated carbon atom; these mechanisms determine, according to Kornblum's view, the mode of reaction.

In conformity with Gompper's view, many reactions of enolates and phenoxides proceeding via the $S_N2$ mechanism lead to the formation of *O*-alkylation and *O*-acylation products. Gompper's view is close to Pearson's HSAB concept [46,109,110]. In conformity with the main postulate of this principle, an increase of the hardness of the alkyl group should promote *O*-alkylation. The sharp increase of the fraction of the *O*-isomer in the alkylation of alkali metal enolates [99] and enols [100] by chloromethyl ether and diazomethane must be attributed to the introduction into the alkyl group of hard methoxy- and diazo-groups. On the other hand, the tendency of allyl and benzyl halides to form products corresponding to substitution at the carbon atom of the enolate ion can be explained by the presence of the soft allyl or benzyl

group. Thus, knowing the relative hardness of the alkyl group linked to the same leaving group of the alkylating agent, it is possible, in principle, to predict the direction of attack on the ambident anion.

According to a current view, the alkyl group attached to an $sp^3$-hybridised carbon atom exhibits a small $-I$ effect. Certain thermodynamic and kinetic data [111-115] as well as dipole moment data [116] are consistent with this hypothesis. In a paper devoted to the application of the HSAB principle in organic chemistry, Pearson [109] quoted the following series based on the hardness of alkyl groups: t-$C_4H_9$ > iso-$C_3H_7$ > $C_2H_5$ > $CH_3$. However, there are few experimental data showing that the alkyl group attached to a saturated carbon atom has electron-accepting properties; furthermore, they are mainly concerned with the gas phase and it is not clear what situation obtains in the liquid phase. According to earlier and more common idea, based on kinetic data for $S_N2$ reactions in solution, the alkyl group at an $sp^3$-hybridised carbon atom exhibits a small $+I$ effect.

Table 13. The alkylation of the potassium enolate of acetoacetic ester with various alkylating agents in HMP ($c_0$ = 0.25 M).

| R | X | Yield of isomer, % | | | | | t, °C |
|---|---|---|---|---|---|---|---|
| | | total yield, | *O*-isomer | *C*-isomer | dialkylation products* | ratio of *O*- and *C*-isomers | |
| $CH_3$ | OTs | 96 | 89 | 7 | 4 | 8.1 | 20 |
| | Br | 87 | 14 | 42 | 44 | 0.16 | 20 |
| | I | 93 | 5 | 31 | 64 | 0.05 | 20 |
| $C_2H_5$ | OTs | 90 | 88 | 11 | 2 | 7.5 | 20 |
| | Cl | 65 | 60 | 32 | 8 | 1.5 | 20 |
| | Br | 92 | 39 | 38 | 23 | 0.64 | 20 |
| | I | 95 | 13 | 71 | 16 | 0.15 | 20 |
| n-$C_4H_9$ | OTs | 84 | 90 | 10 | <1 | 9 | 20 |
| | Cl | 75 | 68 | 27 | 5 | 2.1 | 20 |
| | Br | 88 | 40 | 47 | 13 | 0.67 | 20 |
| iso-$C_3H_7$ | OTs | 78 | 84 | 16 | — | 5.3 | 20 |
| | Cl | 70 | 81 | 19 | — | 4.3 | 20 |
| | Br | 90 | 69 | 31 | — | 2.2 | 20 |
| | I | 77 | 40 | 60 | — | 0.66 | 20 |
| s-$C_4H_9$ | OTs | 78 | 86 | 14 | — | 6.2 | 40 |
| | Cl | 75 | 86 | 14 | — | 6.2 | 40 |
| | Br | 70 | 78 | 22 | — | 3.6 | 20 |
| | I | 60 | 56 | 44 | — | 1.3 | 20 |
| Allyl | OTs | 88 | 22 | 43 | 35 | 0.28 | 20 |
| | Cl | 88 | 17 | 45 | 38 | 0.21 | 20 |
| | Br | 92 | — | 48 | 52 | 0 | 20 |
| | I | 90 | — | 50 | 50 | 0 | 20 |
| Neopentyl | OTs | 40 | 100 | — | — | — | 80 |
| $CH_3OCH_2$ | Cl | 75 | 100 | — | — | | 45 |

*When RI and RBr are used, only $\alpha\alpha$-dialkyl-AAE derivatives are formed. When the alkylating agents are RCl and ROTs, a mixture of *CC*- and *CO*-dialkylation products is formed.

The ratio of the *C*- and *O*-isomers in the alkylation of enolate ions is determined by both electronic and steric factors, the latter always increasing the fraction of the *O*-isomer. Since it is not possible to estimate separately the contribution of each effect for the same leaving group, it remains obscure whether the increase of the ratio of the *C*- and *O*-isomers in the series s-$C_4H_9$ < iso-$C_3H_7$ < $C_2H_5$ < $CH_3$ [23,27,101] is caused by the simultaneous operation of both factors, which is consistent with the concept of the electron-accepting nature of the alkyl group attached to a saturated carbon atom, or whether the hardness of

Table 14. The alkylation of sodium acetylacetonate with various alkylating agents in HMP ($c_0$ = 0.5 M).

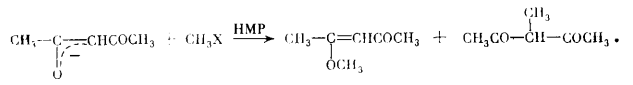
| R | X | Yield of isomer, % | | | | | t, °C |
|---|---|---|---|---|---|---|---|
| | | total yield, % | *O*-isomer | *C*-isomer | dialkylation products | ratio of *O*- and *C*-isomers | |
| $CH_3$ | OTs | 77 | 97 | 3 | — | 32 | 20 |
| | Br | 59 | 12 | 88 | <1 | 0.14 | 20 |
| | I | 54 | 3 | 96 | 1 | 0.03 | 20 |
| $C_2H_5$ | OTs | 90 | 90 | 10 | — | 9 | 20 |
| | Cl | — | 62 | 33 | 5 | 1.73 | 20 |
| | I | 84 | 17 | 60 | 23 | 0.20 | 20 |
| | Br | 73 | 42 | 41 | 17 | 0.72 | 20 |
| n-$C_3H_7$ | OTs | 85 | 92 | 8 | — | 11 | 20 |
| | Br | 85 | 48 | 38 | 14 | 0.9 | 20 |
| n-$C_4H_9$ | OTs | 81 | 96 | 4 | — | 24 | 20 |
| | Cl | 65 | 87 | 12 | 1 | 7.1 | 20 |
| | Br | — | 62 | 23 | 15 | 1.6 | 20 |
| | I | — | 24 | 39 | 37 | 0.32 | 20 |
| n-$C_6H_{11}$ | OTs | 66 | 99 | 1 | — | 99 | 60 |
| | Cl | 65 | 95 | 4 | 1 | 19 | 50 |
| | Br | 84 | 68 | 12 | 20 | 2.1 | 65 |
| | I | 87 | 46 | 16 | 38 | 0.85 | 60 |
| iso-$C_3H_7$ | OTs | 80 | 86 | 14 | — | 6.1 | 50 |
| | Cl | — | 79 | 21 | — | 3.5 | 50 |
| | Br | 79 | 70 | 30 | — | 2.3 | 50 |
| | I | 82 | 52 | 48 | — | 1.1 | 50 |
| s-$C_4H_9$ | OTs | 53 | 85 | 15 | — | 5.7 | 50 |
| | Cl | — | 83 | 17 | — | 4.9 | 50 |
| | Br | 43 | 81 | 19 | — | 4.3 | 50 |
| | I | 62 | 62 | 38 | — | 1.6 | 50 |
| Allyl | OTs | 79 | 37 | 9 | 54 | 0.60 | 20 |
| | Br | — | 7 | 18 | 75 | 0.08 | 20 |
| | I | 85 | — | 22 | 78 | — | 20 |
| Neopentyl | OTs | 65 | 100 | — | — | — | 70 |
| $CH_3OCH_2$ | Cl | 32 | 100 | — | — | — | 55 |
| | I | — | 82 | 18 | — | 4.5 | 20 |

*When RI, RBr, and Allyl OTs are used, only the *CC*-dialkylation product is formed. With RCl as the alkylating agent, there is a small admixture (~1%) of the *CO*-dialkylation products.

alkyl groups varies in a sequence which is the inverse of that proposed by Pearson and the electronic and steric effects therefore act in opposition and the ratio of the *C*- and *O*-isomers is determined by the dominant contribution of the steric effect when the leaving group consists of iodide, bromide, or chloride ions. In order to determine the relative hardness of alkyl groups, a study was made of the influence of the alkyl substituent at a saturated carbon atom of the alkylating agent on the ratio of the products of the *C*- and *O*-alkylation of alkali metal enolates of AAE and AcAc by alkyl toluene-*p*-sulphonates in HMP [117,118] (Tables 13 and 14). In this case, the sequence based on the influence of the alkyl group on the ratio of the *C*- and *O*-isomers, namely s-$C_4H_9$ ≥ iso-$C_3H_7$ > $C_2H_5$ > $CH_3$, is exactly the opposite of the sequence observed for halides. This implies that the two effects are opposed and that the polar effect plays a dominant role for alkyl toluene-*p*-sulphonates. The increase of the ratio of the *C*- and *O*-isomers in the sequence s-$C_4H_9$ > iso-$C_3H_7$ > $C_2H_5$ > $CH_3$ shows that the alkyl substituent at the reaction centre of the alkylating agent is electron-donating. Thus the hardness of alkyl groups in the alkylation of enolate ions varies contrary to the Pearson's hardness sequence derived from thermodynamic data. The qualitative identity of the sequence characterising the influence of alkyl groups in the alkylation of alkali metal enolates by alkyl halides and Pearson's hardness sequence implies that the steric effects of alkyl groups play the dominant role for these softer alkylating agents.

2. Effect of the Leaving Group

The nature of the leaving group of the alkylating agent is one of the factors controlling the mode of alkylation of alkali metal enolates. The fraction of the product of the *O*-alkylation of enolate ions increases in the sequence $I^- < Br^- < Cl^- < F^- < SO_4^{2-} < OTs^- < CF_3SO_3^-$. The data presented in Tables 13 and 14 show that the ratio of the *O*- and *C*-isomers in the methylation of the potassium salt of AAE and the sodium salt of AcAc decreases by a factor of $10^2$–$10^3$ when methyl toluene-*p*-sulphonate is replaced by methyl iodide as the alkylating agent[117,118]:



| | | |
|---|---|---|
| X=OTs | 97% | 3% |
| X=I | 3% | 97% |

The effect of the leaving group is distinct although less pronounced also in the ethylation of the two enolate ions. However, for the even softer iso-$C_3H_7$ and s-$C_4H_9$ groups, the nature of the leaving group has only a very weak influence on the mode of reaction. Thus the replacement of toluene-*p*-sulphonate by chloride or bromide in s-$C_4H_9X$ is hardly reflected in the composition of the mixture of the alkylation products and for s-$C_4H_9I$ the ratio of the *O*- and *C*-isomers is actually greater than unity. Thus the effect of the leaving group depends in its turn on the hardness of the alkyl group of the alkylating agent.

The influence of the leaving group on the ratio of the *C*- and *O*-alkylation products has also been investigated in the alkylation of the benzophenone dianion[19]. The fraction of the *O*-isomer increases sharply on passing from methyl iodide to methyl toluene-*p*-sulphonate, for which *O*-alkylation becomes the sole reaction pathway. Although the benzophenone dianion is an extremely unusual ambident system, the overall dependence of the ratio of the *C*- and *O*-isomers on the nature of the leaving group remains the same as for the usual ambident enolate ions: $OTs^- < SO_4^{2-} < Br^- < I^-$. In the alkylation of the lithium salt of buryrophenone by pentyl halides in DMSO, the ratio of the *C*- and *O*-isomers diminishes from 5.0 for $C_5H_{11}I$ to 2.0 for $C_5H_{11}Br$ and to 0.77 for $C_5H_{11}Cl$.[119] In the study by von Auwers[96] quoted previously, it was also shown that, when the sodium salt of 1-cyanocyclohexanone is alkylated by alkyl halides in alcohol, bromides give rise to a higher yield of *O*-alkylation products than iodides. In the alkylation of the enolates of β-dicarbonyl compounds, the same effect of the leaving group is observed as for the enolates of monocarbonyl compounds. Kornblum et al.[120], who investigated the influence of the leaving group in the benzylation of the sodium salt of ethyl β-hydroxycoumarate in DMF, noted that the relative yields of the *O*-alkylation product are 18, 29, and 50% for the iodide, bromide, and chloride respectively. The same sequence has been observed in the alkylation of the potassium salt of AAE by alkyl halides in DMF [77] and in DMSO [22] and also in the alkylation of the sodium salt of a derivative of octalone by benzyloxymethyl halides in dioxan[121]. In all these instances, the fraction of the *O*-alkylation product increases as the leaving group becomes a harder Lewis base. Stetter and Dierichs[31] studied the influence of the leaving group on the ratio of the products of the *C*- and *O*-alkylation of the sodium enolate of dihydroresorcinol in alcohol[31] (Table 15). The ratio of the *C*- and *O*-isomers diminishes by a factor of at least 100 on passing from the iodide to the toluene-*p*-sulphonate. In another study, it was established on the basis of infrared spectroscopic and NMR data that the alkylation of the potassium enolate of AcAc by methyl iodide in acetone entails the formation of the *C*-alkylation product alone, while the use of dimethyl sulphate under analogous conditions leads to the formation also of a certain amount of the *O*-isomer[122]. The employment of triethyloxonium fluoroborate as the alkylating agent has a particularly promoting effect on the formation of a considerable amount of the *O*-alkylation product. Thus the alkylation of lithium enolate derived from 4-t-butylcyclohexanone by triethyloxonium fluoroborate in methylene chloride results in the formation of 23% of the ethyl ether of the enol[123], while the potassium enolates of cyclohexanone and acetophenone give rise to 69% of the enol ether under analogous conditions in DME.[124] Kabachnik and coworkers[125] showed that, when the sodium salt of AAE is treated with triethyloxonium fluoroborate in ether, ethyl β-ethoxycrotonate is also formed in a low (~15%) yield, while the sodium salt of AcAc gives rise to 28.5% of the *O*-isomer under the same conditions.

Table 15. The alkylation of the sodium salt of dihydroresorcinol.

| RX | n-$C_4H_9I$ | n-$C_4H_9Br$ | n-$C_4H_9OTs$ |
|---|---|---|---|
| Yield of *C*-isomer, % | 43.5 | 30 | 0 |
| Yield of *O*-isomer, % | 56.5 | 70 | 100 |

The effect of the leaving group in the alkylation reactions of ambident anions can be explained within the framework of the HSAB principle by the so called symbiotic effect of the stabilisation of the transition state. It is suggested that a group of either several soft bases or several hard ligands at a saturated carbon atom of the alkylating agent should stabilise the transition state and should increase the rate of the process. In other words, the rate of reaction should increase if the entering and leaving groups are simultaneously either soft or hard bases. Pearson and Songstad adduce convincing evidence for the occurrence of the symbiotic effect in bimolecular nucleophilic substitution at a saturated carbon atom[126]. In relation to ambident enolate ions, this implies that the rate of the *C*-alkylation reaction increases if the leaving group in the alkylating agent is a soft base (iodide, bromide). The opposite effect—an increase of the rate of *O*-alkylation—is achieved when the leaving group is a hard base (toluene-*p*-sulphonate, perchlorate, fluoroborate, etc.). In certain cases such a change in the relative rates of the two processes leads to a complete change in the mode of reaction.

The ratio of the rate constants for the *C*- and *O*-alkylation of enolate anions under the influence of alkyl iodides and alkyl toluene-*p*-sulphonates characterises the degree of hardness of the two nucleophilic centres. In the *C*-ethylation of the enolate ion of α-ethylacetoacetic ester in DMF,[127] $k_{I^-}/k_{OTs^-} = 420$. In general, this is the expected result for the soft centre of the enolate ion. It was found that the rate of the competing *O*-alkylation reaction under the influence of ethyl iodide is also higher than in the reaction with ethyl toluene-*p*-sulphonate

($k_{I^-}/k_{OTs^-}$ = 13). Such a change in the rate of reaction on passing from a hard to a soft alkylating agent indicates a considerable softness of the AAE ambident anion. The same behaviour was observed a little later [128]. However, according to the latter data [128], the rate of reaction under the influence of ethyl fluorosulphonate and ethyl trifluoromethanesulphonate ("ethyl triflate") ($CF_3SO_3C_2H_5$) is much higher than for ethyl iodide, i.e. the rate of reaction does not vary in parallel with increasing softness of the leaving group. This anomaly is probably associated with the change in the nature of the interaction between the reacting species from a purely ion–dipole interaction for ethyl toluene-*p*-sulphonate, ethyl bromide, and ethyl iodide to a nearly ion–ion interaction in the case of ethyl fluorosulphonate and ethyl trifluoromethanesulphonate. The ratio of the *C*- and *O*-ethylation products decreases as usual under these conditions on passing from the iodide to the toluene-*p*-sulphonate and further to the trifluoromethanesulphonate ($CF_3SO_3^-$). Thus the fraction of the products of the *O*-alkylation of the enolate ions of carbonyl and β-dicarbonyl compounds increases as the leaving group becomes a harder base.

In other instances, for example in the alkylation of the alkali metal enolates of esters, which are apparently softer Lewis bases, *C*-alkylation products are formed exclusively even on treatment with toluene-*p*-sulphonates, fluorosulphonates, and trialkyloxonium salts. The opposite case is observed in the alkylation of the phenoxides and enolates derived from certain β-diketones (dihydroresorcinol, trifluoroacetylacetone, hexafluoroacetylacetone, etc.) when the *O*-isomer becomes the main reaction product (and sometimes the only product) even when an alkyl iodide is used. Consequently, on the basis of the symbiotic effect alone, one cannot predict in the general case the mode of alkylation of the enolate ion; it is only clear that the ratio of the *C*- and *O*-isomers will decrease as the leaving group becomes a harder base.

## V. THE INFLUENCE OF THE NATURE OF THE AMBIDENT ANION

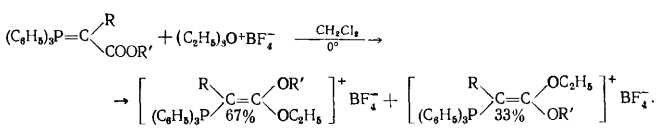
Analysis of data for the influence of the nature of the electrophile, the metal cation, and the solvent on the dual reactivity of the phenoxides and enolates derived from various carbonyl and β-dicarbonyl compounds and esters shows that there is a certain tendency in the influence of these factors. However, different systems exhibit unequal sensitivities. Certain ambident anions show an enhanced tendency towards *O*-alkylation and *O*-acylation, while for other enolate ions it has not so far been possible to detect the formation of the *O*-isomer. Hence the nature of the ambident system itself determines to an even greater extent than the electrophile the mode of reaction of the ambident enolate anion. Thus the enolates of alkyl phenyl ketones form a much larger amount of the *O*-isomer than the enolates of dialkyl ketones. According to the data of Zook et al. [12], the alkylation of the enolates of acetophenone and butyrophenone in monoglyme and diglyme by alkyl halides leads to the formation of considerable amounts of the *O*-alkylation products (Table 10). Under the same conditions, dialkyl ketones and alicyclic ketones undergo only *C*-alkylation.

The considerable influence on the mode of reaction by the nature of the ambident anion itself is manifested most clearly when data on the alkylation and acylation of the enolate ions of ketones and esters are compared. Whereas the mode of reaction can be altered selectively for the enolates of carbonyl and β-dicarbonyl compounds by choosing an appropriate medium or counter ion or by varying the "hardness" of the leaving group of the alkylating agent, the enolate ions of esters form solely *C*-alkylation and *C*-acylation products for reasons which are little understood. Lithium enolate derived from ethyl acetate and t-butyl acetate is alkylated at the carbon atom when acted upon by the diphenylcyclopropenylium cation [129], alkyl halides, methyl fluorosulphonate, and triethyloxonium fluoroborate [130]. Mainly as a result of studies by Rathke and coworkers and by Cregge and coworkers, excellent general methods have been developed for the *C*-alkylation and *C*-acylation of the lithium salts of esters and dilithium salts of carboxylic acids [131–136]. The lithium salts, obtained by treating the ester with lithium di-isopropylamide or lithium isopropylcyclohexylamide in THF at −78°C, can even be isolated in a pure form in many instances. Lithium enolates in benzene and toluene solutions are stable for several hours at least and, on treatment with an alkyl or acyl halide, give excellent yields of ester homologues or β-ketoesters [137]. A characteristic feature of these processes is the complete absence of dialkylation and diacylation products. The alkylation and acylation of lithium salts of esters is apparently the best preparative method for the synthesis of esters and β-ketoesters in a chromatographically pure form. The formation of mono-*C*-alkylation and acylation products, unaccompanied by the competing reaction involving the oxygen atom of the lithium enolate, has been observed in all cases.

Only three instances of the *O*-alkylation of ester enolates have apparently been described hitherto, among which the formation of a keten acetal was reliably demonstrated in only one case. *O*-Alkylation of an ester was observed for the first time in the intramolecular alkylation of the sodium enolate derived from the β-bromoethyl esters of cyanoacetic, malonic, acetoacetic, and *p*-nitrophenylacetic acids [138]. According to the author, of the four possible reaction pathways, only intramolecular *O*-alkylation actually occurs, leading to the formation of a keten ethylene acetal as the sole reaction product. The structure of the reaction products was demonstrated by infrared spectroscopy. Since the reaction products are derivatives of keten ethylene acetal, their structure could be demonstrated unambiguously by $^1$H NMR data, but these were not quoted [138]. If keten ethylene acetals are indeed formed in the given reaction, as suggested by the author, the intramolecular *O*-alkylation of the ester is determined exclusively by the influence of the entropy factor, since in any other case one would expect the formation of a *C*-alkylation product, bearing in mind that the bromide ion is a soft base.

In another study, the mechanism of the transesterification reaction is accounted for by postulating that the sodium enolate of methyl *O*-(tetrahydropyranyl)mandelate is alkylated at the oxygen atom of the enolate ion under the influence of benzyl and allyl halides with formation of a keten acetal, which is then converted into benzyl or allyl mandelate. The authors do not present any evidence for the formation of a keten acetal as an intermediate. Benzyl and allyl halides are traditional agents for the selective *C*-alkylation of the enolate ions derived from ketones and β-dicarbonyl compounds. The *O*-alkylation of the enolate ion of an ester under the influence of these reagents therefore appears to be an improbable reaction pathway even theoretically. Naturally, the transesterification mechanism may not in fact include a stage where a keten acetal is formed as an intermediate. The only

reliably established example of the *O*-alkylation of an ester is the reaction between triethyloxonium fluoroborate and alkoxycarbonylmethylenetriphenylphosphorane, described by Bestman et al.[140]:



In this case, a mixture of the *cis*- and *trans*-isomers of a keten acetal is formed in a nearly quantitative yield (Table 16). The structure of the reaction products was demonstrated reliably by $^1H$ NMR and infrared spectroscopic data.

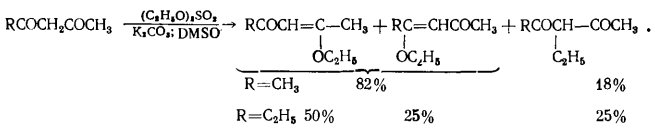
Table 16. The *O*-alkylation of alkoxycarbonylmethylenetriphenylphosphorane with triethyloxonium fluoroborate.

| R | R′ | Yield, % | R | R′ | Yield, % | R | R′ | Yield, % |
|---|---|---|---|---|---|---|---|---|
| H | $CH_3$ | 67 | $C_6H_5CH_2$ | $C_2H_5$ | 97 | $CH_2COOC_2H_5$ | $C_2H_5$ | 98 |
| H | $C_2H_5$ | 68 | $C_6H_5$ | $C_2H_5$ | 99 | $COOC_2H_5$ | $C_2H_5$ | 95 |

Appreciable differences are observed between the capacities for *C*- and *O*-alkylation in the reactions of the enolates of cyclic and acyclic carbonyl compounds. For example, the ratio of the *C*- and *O*-isomers increases by a factor of 10 on passing from 2-ethoxycarbonylcyclohexanone to the $\alpha$-ethylacetoacetic ester in the alkylation of sodium enolate by isopropyl iodide in DMSO.[141] A similar effect was observed also when data for the alkylation of the sodium salt of AAE and the sodium enolates of cyclic $\beta$-ketoesters by $\beta$-dimethylaminoethyl chloride were compared[142,143].

In a series of cyclic $\beta$-ketoesters, the ratio of the *C*- and *O*-isomers formed depends on the ring size. According to the results of Rhoads and Hasbrouck[144], the ratio of the products of the *C*- and *O*-alkylation of sodium enolates derived from 2-ethoxycarbonylcyclanones with 5–10-membered rings by isopropyl iodide in DMSO varies as follows: 1.74 ($n$ = 3); 1.34 ($n$ = 4); 15 ($n$ = 5); 7.72 ($n$ = 6); 32 ($n$ = 8). Such marked differences between the ratios of the *C*- and *O*-isomers obtained for these compounds and the enhanced tendency of the five- and six-membered systems to undergo *O*-alkylation can be caused by a wide variety of factors: the different p$K_a$ values of the $\beta$-ketoesters, conformational effects, and the different degrees of dissociation of the sodium enolates in DMSO. If the reacting species is not only the enolate ion of the 2-ethoxycarbonylcyclanone but also ion pairs, whose relative contributions for each $\beta$-ketoester may be different, the ratios of the *C*- and *O*-isomers quoted in the above study do not correspond to the dual reactivity of the free enolate ion. Finally, even a change in the formal charge in the ambident system alters markedly its capacity for reaction via two pathways. In contrast to the monoanions, the dianions of $\beta$-dicarbonyl compounds, formed when a $\beta$-diketone or a $\beta$-ketoester is treated with two equivalents of sodium amide in liquid ammonia[145] or after successive treatment with sodium hydride and butyllithium in DHF,[146] form only $\gamma$-*C*-alkylation products regardless of the nature of the alkylating agent. The alkylation of the dianions of $\beta$-dicarbonyl compounds has been investigated in detail by Hauser and coworkers (see the review of Harris and Harris[147]).

It is difficult to find a characteristic of an ambident nucleophile which might serve as a basis for correlation with the reactivity and the ratio of the *C*- and *O*-isomers, at least within the framework of ambident anions of a single class. Presumably, in the absence of steric hindrance, the p$K_a$ of the ketone of the $\beta$-dicarbonyl compound can serve as a quantity of this kind. Indeed, according to Gelin and Rouet[148], the relative yield of the *C*-isomer is somewhat higher in the alkylation of the potassium enolate of acetylpropionylmethane than in the alkylation of the potassium enolate of acetylacetone:



This is consistent with the hypothesis that the ratio of the *C*- and *O*-isomers varies in parallel with the p$K_a$ of the carbonyl compound. The data available at present show, however, that such a regularity does not occur in most instances. Thus, according to Heiszwolf and Kloosterziel[124], in the alkylation of the potassium salts of acetophenone, cyclohexanone, AAE, and AcAc by dimethyl sulphate in DMSO, the ratios of the *C*- and *O*-alkylation products are approximately the same for all the compounds enumerated, although the acidities of ketones and $\beta$-dicarbonyl compounds in DMSO differ by at least 3–7 p$K_a$ units. The ratio of the *C*- and *O*-isomers in the ethylation of the potassium enolate of diacetylacetone also differs insignificantly from the analogous quantity for the weaker acid AcAc.[148]

When data for the alkylation of enolate ions and their closest analogues—ketimines, which also contain a hard nucleophilic centre, are compared, a considerable similarity between the effects of the leaving group is observed. The fraction of the *N*-alkylation product is particularly large when the leaving group of the alkylating agent is a hard base (sulphate, toluene-*p*-sulphonate).[149] In full agreement with the influence of the symbiotic effect, *C*-alkylation predominates for a soft leaving group and a small counter ion[149–151]:

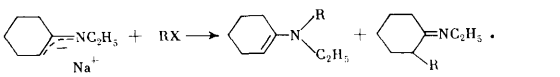
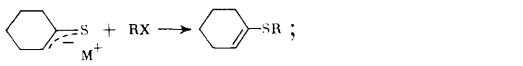


Table 17 lists the relative yields of the products of the *N*-alkylation (enamines) and *C*-alkylation of the sodium salts of certain substituted imines[149]. The ratio of the products of *N*- and *C*-ethylation is seen to be completely inverted for the anion of the acetophenone anil when ethyl iodide is replaced by triethyloxonium fluoroborate as the alkylating agent. The same effect has been observed also for other imines. Enamine is the main reaction product in the alkylation of the sodium salt of diethyl ketone *N*-ethylimine by a hard alkylating agent—dimethyl sulphate, but in the reaction involving a soft alkylating agent only the *C*-isomer was detected in the products, without an admixture of the enamine.

A completely different situation is observed in the alkylation of the sulphur analogues of carbonyl compounds and esters. As already stated, the mode of alkylation of alkali metal enolates of cyclohexanone depends mainly on the nature of the leaving group: alkyl halides form *C*-alkylation products, the *O*-isomer predominating in the reaction products on alkylation with diethyl sulphate

and ethyl toluene-*p*-sulphonate in DMSO.[75] On the other hand, alkali metal salts of tricyclohexanone are alkylated and acylated exclusively at the sulphur atom regardless of the nature of the leaving group[152]:



R = $CH_3$, $C_2H_5$, iso-$C_3H_7$, or $C_6H_5CH_2$; X = Hal or OTs.

The formation of *S*-alkyl derivatives has also been observed in the alkylation of salts of β-thioketoesters[153-155] under conditions such that the enolates of the acetoacetic and benzoylacetic esters are alkylated only at the carbon atom:

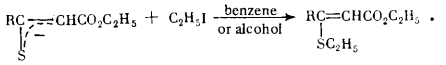
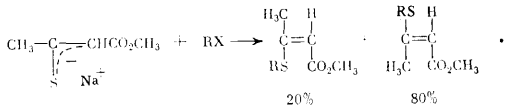


Table 17. The *C*- and *N*-alkylation of the sodium salts of *N*-substituted imines.

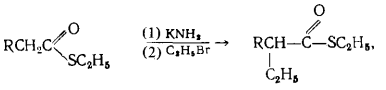
| Solvent | Imine | Alkylating agent | Reaction products, % | | | |
|---|---|---|---|---|---|---|
| | | | unchanged imine | enamine | *C*-alkylated product | poly-alkylated products |
| Diethylcellosolve | Acetophenone anil | $(C_2H_5)_3O^+BF_4^-$ | 8 | 88 | 4 | — |
| | | $(C_2H_5O)_2SO_2$ | 9 | 49 | 42 | — |
| | | $C_2H_5I$ | 5 | 5 | 90 | — |
| HMP | Cyclohexanone *N*-ethylimine | $(C_2H_5)_3O^+BF_4^-$ | 29 | 53 | 18 | — |
| | | $(CH_3O)_2SO_2$ | 11 | 75 | 10 | 4 |
| | | $C_2H_5I$ | 15 | 17 | 56 | 12 |
| HMP | Diethyl ketone *N*-ethylimine | $(C_2H_5)_3O^+BF_4^-$ | 26 | 29 | 42 | 3 |
| | | $(CH_3O)_2SO_2$ | 17 | 57 | 26 | — |
| | | $C_2H_5I$ | 20 | — | 71 | 9 |

The salts of the β-thioketothioester $CH_3CSCH_2COSC_2H_5$ react similarly[153]. The alkylation of the sodium salt of thio-AAE by alkyl bromide or iodide in alcohol results in a mixture of the *Z*- and *E*-forms of β-alkylthiocrotonates in proportions of ~1 : 4 [154]:

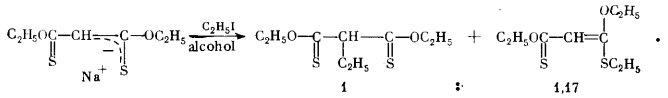


20% 80%

An enormous difference between the reactivities of enolates and enethiolates is also manifested in the alkylation of alkali metal salts of esters and their sulphur analogues. Thus, whereas the enolates of thiolo-esters form *C*-alkylation products like ordinary esters, for example[156]:

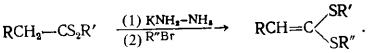


the enolates of thiono-esters[157,158] and dithioesters behave quite differently. The sodium salt of the thiono-ester of malonic acid reacts with ethyl iodide to form a mixture of the products of the *C*- and *S*-ethylation in approximately equal amounts:



1 : 1.17

The enethiolates of dithioesters are alkylated exclusively at the sulphur atom with formation of keten thioacetals in both polar and non-polar media[159,160]:



The reaction is insensitive both to the influence of the counter ion and to the effect of the leaving group. The different mode of reaction of enethiolates compared with enolates is undoubtedly due to the high polarisability or, in terms of the HSAB principle, the softness of the sulphur atom as the nucleophilic centre. However, the enormous difference in the behaviour of these two classes of ambident anions cannot be accounted for from the standpoint of a purely phenomenological approach, to which the application of the HSAB principle is in essence restricted when it is used to account for the reactivity of ambident anions. This remark applies fully also to the difference between the reactivities of the enolate ions of carbonyl compounds and esters. Evidently, in this case too the problem cannot be solved within the framework of the above concept. All these general theoretical problems require the development of a different approach to the problem of the dual reactivity of ambident systems.

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# Organic *N*-Fluoroimines

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The available information about the methods of synthesis of *N*-fluoroimines and their reactions with nucleophiles and electrophiles and with oxidants and reductants as well as pyrolytic and photolytic reactions are surveyed. The reaction mechanisms are discussed and certain aspects of the practical applications of the reactions are examined. The bibliography includes 184 references.

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## I. INTRODUCTION

Organic *N*-fluoroimines are characterised by the presence of the C=NF group in the molecule. The first information about the synthesis of fluorine–nitrogen compounds of this class was obtained at the beginning of the 1950s. In subsequent years, the number of publications steadily increased, the most vigorous research in this field having been carried out in the last decade when easy methods for the synthesis of *N*-fluoroimines were developed.

*N*-Fluoroimines exhibit a wide variety of reactivities owing to the presence of the C=N and N–F bonds. Depending on their structures, it is possible to find in the chemical properties of organic *N*-fluoroimines a definite analogy with the chemical properties of familiar classes of organic compounds such as perfluoroketones, carboxylic acid halides, and certain others. On the other hand, the chemistry of these compounds has its distinctive features, so that the study of their chemical properties is of interest both from the standpoint of the deepening of the theoretical ideas about the chemistry of carbon linked by a double bond to a heteroatom and as regards synthetic research. At the same time, compounds of this class can find extensive practical applications.

There have so far been no reviews on organic *N*-fluoroimines. Individual data on the methods of synthesis and chemical properties of these compounds can be found in a number of papers [1-5] and also in monographs [6-10]. The synthesis and reactions of perfluorinated *N*-fluoroimines with nucleophiles have been examined by Dyatkin et al. [11] The present review covers the entire fundamental literature on *N*-fluoroimine published up to May, 1976.

## II. METHODS OF SYNTHESIS

The main methods for the preparation of *N*-fluoroimines are fluorination of nitrogen compounds by elemental fluorine, dehydrofluorination of aminodifluoroalkanes, the interaction of tetrafluorohydrazine with acetylenes, and reductive dehalogenation or difluoroperhalogenoalkylamines. *N*-Fluoroimines are also obtained in reactions of bromine or iodine compounds with tetrafluorohydrazine and in the homolysis of geminal bis(difluoroamino)-derivatives. In addition, there exist examples of the synthesis of individual *N*-fluoroimines which are not general.

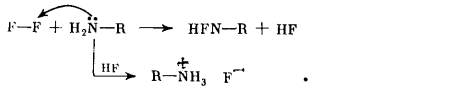
### 1. Fluorination of Nitrogen Compounds by Elemental Fluorine

As early as 1951, Haszeldine [12] fluorinated acetonitrile and trifluoroacetonitrile over gold gauze and obtained, among other products, compounds for which he proposed the structure of perfluoroiminoethane $CF_3CF{=}NF$ and perfluoroformimine $F_2C{=}NF$. The formation of $F_2C{=}NF$ was later noted in the fluorination of acetonitrile [13], methylformamide, and methyl thioisocyanate [14] in the gas phase. The formation of *N*-fluoroimino-derivatives was demonstrated also in the fluorination of perhalogenonitriles [15] and tris(trifluoromethyl)-*s*-triazines [16].

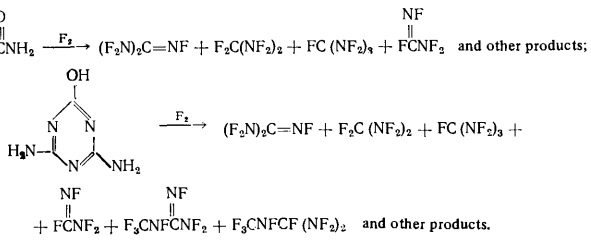
The fluorination of nitrogen compounds by elemental fluorine has become in the last decade one of the fundamental methods for the synthesis of *N*-fluoroimines. This was assisted to a considerable degree by the improvement of the fluorination technique and apparatus and, what is most important, the methods for the isolation and identification of the reaction products. The fact that many unique compounds, highly fluorinated at the nitrogen atom, such as pentafluoroguanidine, tetrafluoroformamidine, *NNN'*-trifluoroamidines, etc., can be obtained by this method has also been enormously important. Various nitrogen compounds may be fluorinated in powder form, as suspensions in an inert organic solvent, and as solutions in aqueous or organic solvents.

The solid-phase fluorination of nitrogen derivatives has been most widely investigated. In order to make the reaction conditions milder, a diluent is used as a rule. Sodium fluoride, which not only plays the role of a diluent but also combines with the hydrogen fluoride evolved in the reaction (the latter is a fluorination inhibitor), is usually employed for this purpose [17-27]. The fluorination mechanism, which is based on the attack on the nitrogen atom by the fluorine molecule [4,5,8], permits the conclusion that the successful occurrence of the process requires that the electron pair at the nitrogen atom should remain free. On the other hand, the presence of hydrogen fluoride in the reaction leads to its inhibiting the process with

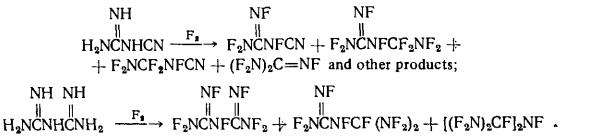
the formation of the corresponding hydrofluoride, which is incapable of further reaction with fluorine:



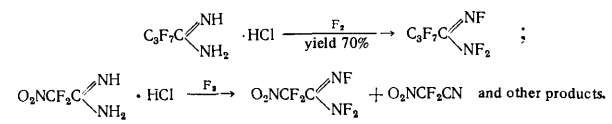
Numerous studies have been devoted to the preparation of pentafluoroguanidine by this method. Guanidine and its derivatives as well as various nitrogen compounds whose molecules contain guanidine structural fragments have been fluorinated, namely guanidinium salts (sulphate, carbonate, hydrochloride, etc.),[21,25,28,29] guanylurea and its sulphate[30-32], biguanide[32-36], ammeline and its salts[17,28,29,32,33,37,38], melamine[33], and cyanoguanidine[26,32]. Fluorination results in the formation of complex mixtures of products, for example:



The maximum yield of pentafluoroguanidine does not exceed 25% under these conditions[25]. Apart from pentafluoroguanidine, the reaction products include various difluoroamino-, fluoroimino-, and difluoroaminofluoroimino-derivatives. The formation of cyanoperfluoroguanidine[19,26,39] and perfluorobiguanide in the fluorination of their hydrogen analogues has been demonstrated[18,20,33,40]:

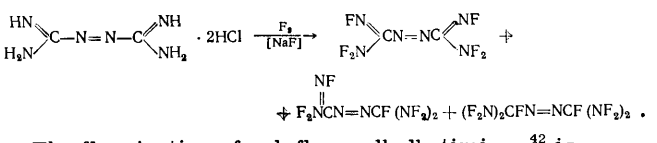


The fluorination of the hydrochlorides of tetrafluorobutyramidine and difluoronitroacetamidine is completed by the formation of the corresponding *NNN'*-trifluoroamidines[27]

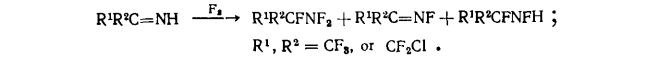


The fluorination of the *N*-fluoroamidines of perfluorocarboxylic acids[32], which can be obtained, for example, by the reaction of *N*-fluoroimidoyl fluorides with ammonia, also leads to the formation of perfluoroalkylamidines.

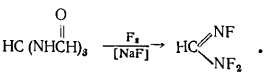
Hexafluoroazodiformamidine (in the form of three isomers), mixed with other products, is formed in the fluorination of azodiformamidinium salts in the presence of sodium fluoride[24,41]:



The fluorination of polyfluoroalkylketimines[42] is completed by the formation of the following reaction products:

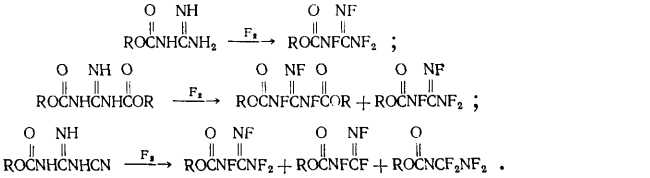


The attempts to obtain unsubstituted *NNN'*-trifluoroamidines $R_HC(=NF)NF_2$ by the solid-phase fluorination of the hydrochlorides of the corresponding amidines were unsuccessful[27]; the alkyl residue of the initial molecule is fluorinated and appreciably degraded. Only the synthesis of *NNN'*-trifluoroformamidine by the fluorination of a mixture of tri-(*N*-formylamino)methane with sodium fluoride is known[23]:



A characteristic feature of the solid-phase fluorination reaction involves the use of various metal fluorides, whose role is apparently not restricted to that of diluents and binders of hydrogen fluoride (see above). It is natural to suppose that metal fluorides behave as catalysts[43]. This property is manifested most distinctly by caesium fluoride in the fluorination of, for example, perfluoroacetone imine[43], which leads to an almost quantitative yield of the saturated perfluoroamino-derivative.

The fluorination of nitrogen compounds in solution, which is a convenient method for the preparation of difluoroaminoalkanes[44], has not found extensive applications in the synthesis of *N*-fluoroimines. However, pentafluoroguanidine has been obtained by the fluorination of aqueous solutions of guanidinium salts[45,46] at pH 8–9 in a thin layer, the formation of which was ensured by a special design of the reactor, The fluorination of alkoxycarbonylguanidines in acetonitrile at 0°C has been shown by Grakauskas and Baum[47,48] to lead to the formation of guanidines fluorinated at the nitrogen atom:



In all cases the yield of fluorination products did not exceed 15%.

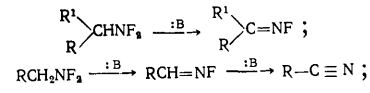
The attempt to use the fluorination of acetonitrile solutions of heptafluorobutyramidine or its hydrochloride in order to synthesis the *NNN'*-trifluoroamidine of heptafluorobutyric acid was unsuccessful[27]. Only the solvent was fluorinated in this reaction.

The possibility of employing other fluorinating agents in order to synthesise *N*-fluoroimines has not been studied systematically. There have been only individual reports of the synthesis of *N*-fluoroimines on treatment of nitrogen compounds with mercury(II) fluoride[6,49] and trifluoromethyl hypofluorite[50].

## 2. Dehydrofluorination of Difluoroaminoalkanes

Difluoroamino-compounds with hydrogen atoms in the α-position relative to the difluoroamino-group are capable of dehydrofluorination[3,5,51,52]. By virtue of the unusual amphoteric nature of difluoroaminoalkanes, the reaction can be carried out under the influence of both bases and Lewis acids[2,51]. Basic reagents are used in preparative syntheses. If the initial compound contains the $-CH_2NF_2$ group, the dehydrofluorination takes place in two stages: the first stage leads to the formation of the fluoroimino-group $-CH{=}NF$ and the second is completed by the formation of a cyano-group. If the initial

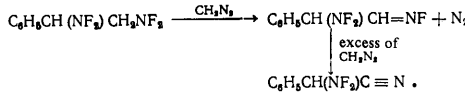
compound contains the $\rangle CHNF_2$ group, the elimination of an HF molecule from it leads to the formation of the fluoroimino-group $\rangle C{=}NF$, which is incapable of further dehydrofluorination:



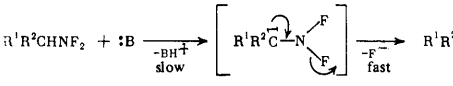
R and $R^1 \neq H$; :B = dehydrofluorinating agent.

When there are no hydrogen atoms in the $\alpha$-position relative to the difluoroamino-group, the latter is as a rule resistant to the action of bases [52,53]. When the molecule of the initial compound contains several difluoroamino-groups, products of incomplete dehydrofluorination can be obtained under certain conditions [51-54].

From the practical point of view, the dehydrofluorination of compounds containing the $\rangle CHNF_2$ group is most important for the synthesis of *N*-fluoroimine. A characteristic feature of the $\rangle CH_2NF_2$ group is its conversion into a cyano-group [51,52,55-59], although the formation of an intermediate *N*-fluoroimine cannot be ruled out, for example [51,52]:



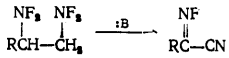
Depending on the conditions, the dehydrofluorination of difluoroamino-derivatives can proceed via different mechanisms. Bearing in mind that in the majority of studies fairly strong bases (triethylamine, pyridine, etc.) have been used for dehydrofluorination, preference should probably be given to the *E1cB* (or similar) mechanism [51, 52,60,61]:



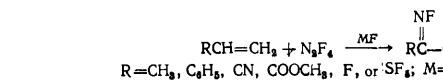
At the same time a bimolecular *E2* mechanism has been proposed for the dehydrofluorination of difluoroamino-alkanes in aqueous organic solutions [53,54,60], this being supported, according to the authors, by the large negative activation entropies and also by the absence of the isomerisation of the diastereoisomers of 2,3-bis-(difluoroamino)-butane in their dehydrofluorination reaction [54]; the latter is of pseudo-first order and has an activation energy of 13–20 kcal mole$^{-1}$ [53,54,60].

Various dehydrogenating agents are used to remove hydrogen fluoride; they can be arranged in the following sequence in terms of their activities: $C_2H_5OH < H_2O < CH_2N_2 < C_5H_5N < (C_2H_5)_3N < C_2H_5ONa$. [60] Bases such as pyridine [27,51,52,58,62-64], sodium alkoxides [65-69], triethylamine [51,52,70,71], alkali metal fluorides [55,57,59,72-77], and aqueous alkaline solutions [52,56,61,66] are used for the preparative syntheses of *N*-fluoroimines. The employment of the alkaline solutions may be complicated by a series of further reactions (the haloform decomposition, the hydrolysis of cyano-, amide, and ester groups, and decarboxylation) [52,61]. In certain cases, for example in the synthesis of bis(fluoroimino)cyclohexenes [78], specially selected dehydrofluorinating agents are used. Organic solvents, namely chlorohydrocarbons, Freons, acetonitrile, alcohols, etc. are widely used in the synthesis of *N*-fluoroimines.

When bases are allowed to act on vicinal primary-secondary bisdifluoroamino-derivatives, *N*-fluoroimino-nitriles are formed [51,52,58,72]:

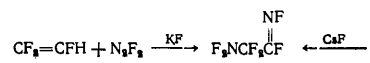


The interaction of terminal olefins with tetrafluorohydrazine in the presence of an alkali metal fluoride is a variant of this method [55,57,72]:

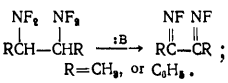


Olefins with electronegative substituents are particularly readily involved in this reaction. Addition products are probably formed initially and are then dehydrofluorinated under the reaction conditions [55].

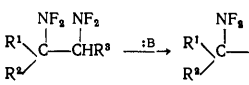
Later this reaction was extended to the synthesis of perfluoroimines [73,74]. For example, when tetrafluorohydrazine reacts with trifluoroethylene in the presence of potassium fluoride, the *N*-fluoroimidoyl fluoride derived from difluoroaminodifluoroacetic acid is formed in a yield exceeding 60%. This product is also formed when 1,2-bis(difluoroamino)trifluoroethane is acted upon by caesium fluoride [76]:



Vicinal bis(fluoroimino)alkanes have been obtained by the dehydrofluorination of vicinal and bis(difluoroamino)-alkanes [53,54,56,62,70,71,77-79], for example:

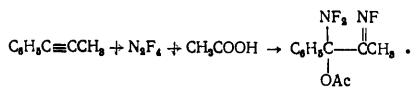


$\alpha$-Difluoroaminofluoroimines are formed from vicinal bis(fluoroamino)alkanes containing one secondary difluoroamino-group [56,65,66,68,69,71,76,80]:

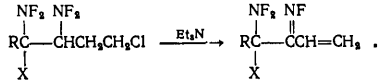


$R^1$, $R^2$=Alk, Ar, Hal, $NF_2$, or $OPO(OR)_2$; $R^3$=Alk, or Ar.

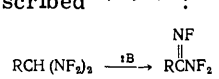
The dehydrofluorination of $\alpha$-acetoxy-$\alpha\beta$-bis(difluoroamino)-derivatives does not lead to the formation of $\alpha$-acetoxy-$\alpha$-(difluoroamino)fluoroimines [61]. Such a fluoroimine has been obtained from methylphenylacetylene, tetrafluorohydrazine, and acetic acid [81]:



*N*-Fluorovinylimines are formed as a result of the simultaneous dehydrofluorination and dehydrochlorination of vicinal bis(difluoroamino)alkanes containing the $\beta$-chloroethyl group [71]:



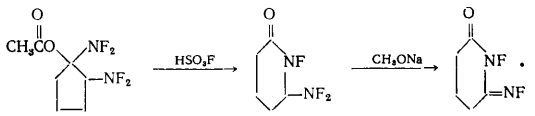
The synthesis of *NNN'*-trifluoroamidines as a result of the dehydrofluorination of geminal bis(difluoroamino)-alkanes has been described [27,53,63,64]:



A preparative method has been developed for the synthesis of compounds of this kind [27,63,64] using dehydrofluorinating

agents such as pyridine, piperidine, quinoline, and aqueous sodium hydroxide. Best yields are achieved when pyridine is used [27].

3-Fluoroimino-2-fluoro-2-azacyclohexanone has been obtained by the dehydrofluorination of 3-difluoroamino-2-fluoro-2-azacyclohexanone [67]:



The dehydrofluorination of the *cis*- and *trans*-isomers of 9,10-bis(difluoroamino)-9,10-dihydroanthracene leads to the formation of 9,10-bis(fluoroimino)anthracene [82], the *trans*-isomer splitting off hydrogen fluoride more readily than the *cis*-isomer.

When 1,1,2-tris(difluoroamino)alkanes are dehydrofluorinated, the corresponding fluoroimines are formed readily [66,68,71,80]. However, the dehydrofluorination of 1,1,3-tris(difluoroamino)cyclohexane on treatment of the latter with sodium methoxide, undertaken to obtain the corresponding fluorimine, proved unsuccessful [83], probably owing to the instability of the resulting *N*-fluoroimine, caused by the presence of the methylene group with mobile hydrogen atoms [$-C(NF_2)_2CH_2C(=NF)-$].

## 3. The Interaction of Tetrafluorohydrazine with Acetylenes

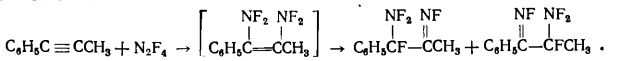
The reaction of tetrafluorohydrazine with acetylenes is a convenient method for the synthesis of $\alpha$-difluoroaminofluoroimines:



(1)

The first stage involves the formation of a bis(difluoroamino)alkene, which subsequently isomerises to the corresponding *N*-fluoroimine. The rearrangement of difluoroaminoalkenes to *N*-fluoroimines, which was first reported by Bumgardner [84], is based on the higher thermodynamic stability of the C–F and C=N bonds compared with that of the N–F and C=C bonds [85], but there is as yet no unanimous view concerning its mechanism. Many workers support a radical mechanism of this rearrangement, initiated, for example, by heat or ultraviolet light [8]. On the other hand, the stereospecificity of the rearrangement of the products of the addition of tetrafluorohydrazine to allene in the presence of fluoride ions shows that the isomerisation may be based on a heterolytic mechanism [86].

The process is as a rule carried out with heating in a solvent under pressure, best results having been obtained with higher acetylenes (no products were isolated when unsubstituted acetylene was used [85]). In most cases, the main reaction products are $\alpha$-difluoroaminofluoroimines. Bis(difluoroamino)alkenes could be isolated only in the reaction of tetrafluorohydrazine with hex-2-yne [87] and perfluoroacetylenes [86], their formation sometimes constituting the main process in the latter case. Perfluoroderivatives of 1,2-bis(difluoroamino)alkenes can isomerise to the corresponding *N*-fluoroimines on heating or irradiation [86]. When tetrafluorohydrazine interacts with asymmetric acetylenes, the intermediate bis(difluoroamino)-alkenes can arrange with formation of two products. For example, methylphenylacetylene gives rise to both isomers [85]:

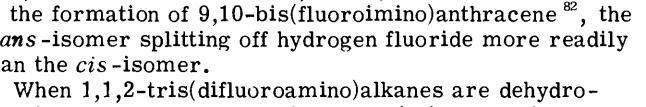


However, phenylpropiolyl fluoride yields only one rearrangement product, namely $C_6H_5CF(NF_2)C(=NF)COF$.

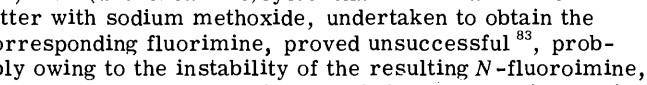
It is of interest that only one mole of tetrafluorohydrazine reacts with hexa-2,4-diyne [85]. This involves 1,2- and not 1,4-addition:



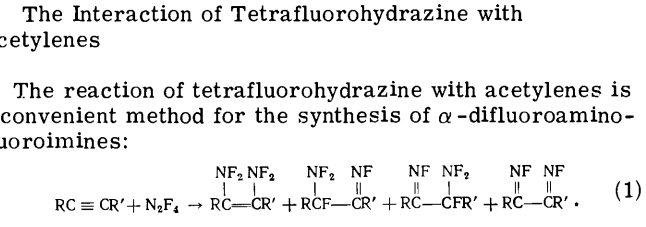
On the other hand isopropenylacetylene gives rise to 1,2- and 1,4-addition products [85]:



The formation of $\alpha$-difluoroaminofluoroimines is also observed in the reaction of tetrafluorohydrazine with allene [85,86]:



When the reaction is catalysed by fluoride ions, the rearrangement of the intermediate product (I) becomes stereospecific, since only the *syn*-isomer (II) is formed together with its dehydrofluorination product [86]:

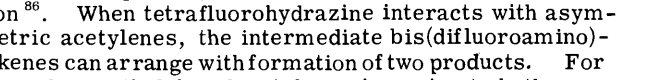


The reactions of tetrafluorohydrazine with acetylenes can also give rise to 1,2-bis(fluoroimino)alkenes [see Eqn.(1)], whose formation is favoured by prolonged heating and a higher temperature [79]. It has been shown for the synthesis of 2,3-bis(fluoroimino)hexafluorobutane and bis(fluoroimino)succinonitrile that the reaction can be regarded as a convenient method of synthesising vicinal bis(fluoroimino)-derivatives [79].

## 4. Reductive Dehalogenation of Perhalogenoalkyldifluoroamines

Perhalogenoalkyldifluoroamines containing the $NF_2$ group at a primary or secondary carbon atom are converted into *N*-fluoroimines on reductive dehalogenation. The reducing agents most often used are dicyclopentadienyliron (ferrocene) [88–91], iron pentacarbonyl [92–94], and mercury [95–98]; silver or silver nitrite [99] and potassium or tetrabutylammonium iodides [100] are more rarely used.

The process is based on the successive transfer of electrons from the reducing agent to the difluoroamino-derivative accompanied by twofold elimination of the fluoride ion [92]:



The reaction involving perhalogenoalkyldifluoroamines containing the $NF_2$ group at a secondary carbon atom stops at the stage involving the formation of the *N*-fluoroimine [89–91]. As a result of the elimination of a further two

fluoride ions, the corresponding nitriles may be formed from primary perhalogenoalkyldifluoroamines [90,92]. However, by selecting a suitable reducing agent (ferrocene is best) [88-90,101], it is possible to obtain *N*-fluoroimine in this case too:

$$R_fCF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} R_fCF{=}NF\ ;$$
$$R_f{=}C_3F_7 \text{ or } CFCl_2\ .$$

The reduction of difluoroaminotrihalogenomethanes with iron pentacarbonyl [93,94] or mercury [95-97] leads to *N*-fluorodihalogenoformimines:

$$F_nCl_{3-n}CNF_2 \xrightarrow{A} F_nCl_{2-n}C{=}NF\ ;$$
$$A{=}Hg \text{ or } (CO)_5Fe;\quad n = 0, 1, \text{or } 2.$$

Difluoroaminodichlorofluoromethane reacts best, the reactions involving difluoroaminochlorodifluoro- and difluoroaminotrichloro-methanes proceeding with more difficulty. Ferrocene does not reduce these compounds. When difluoroaminodichloroacetonitrile is reduced with mercury, 1-cyano-*N*-fluoroformimidoyl chloride is formed in a high yield [98].

There have been reports that the reduction of dichlorobis(difluoroamino)methane with silver or silver nitrite leads to dichloro-*N*-fluoroformimine [99], although as a rule the reduction of *gem*-bis(difluoroamino)perfluoroalkanes is completed by the formation of diazirines [88,102,103].

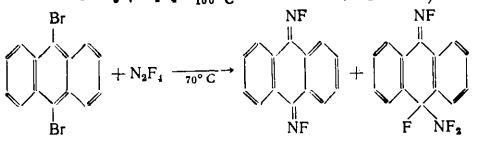
## 5. Reactions of Bromine- or Iodine-containing Compounds with Tetrafluorohydrazine

The formation of *N*-fluoroimines is observed in the reactions of tetrafluorohydrazine with certain bromine- or iodine-containing compounds. These reactions have not so far found wide-scale applications, although they frequently lead to a high yield of *N*-fluoroimines, for example, in the reaction of tetrafluorohydrazine with bromo- and iodo-perhalogenoethylenes [77,104], tribromofluoromethane [105], and 9,10-dibromoanthracene [82]:

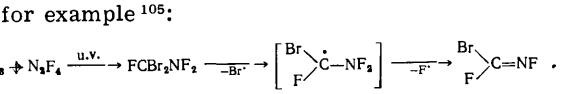
$$CBr_2{=}CBr_2 + N_2F_4 \xrightarrow{155^\circ C} CBr_2F{-}CBr(=NF) + F_2NCBrF{-}CBr(=NF)\ ;$$

$$CF_2{=}CFI + N_2F_4 \xrightarrow{100^\circ C} F_2NCF_2{-}CF(=NF) + F_2NCF_2{-}CFINF_2\ ;$$

$$CFBr_2 + N_2F_4 \xrightarrow[100^\circ C]{u.v.} BrFC{=}NF + F_2C{=}NF\ ;$$



$\alpha$-Bromo- or $\alpha$-iodo-difluoroamino-derivatives are formed in the first stages of these reactions. The homolytic elimination of a halogen atom leads to the formation of the radical species $RR^1\dot{C}{-}NF_2$, which is converted into an *N*-fluoroimine as a result of the elimination of a fluorine atom from the difluoroamino-group, for example [105]:



## 6. Homolysis of Geminal Bis(difluoroamino)-derivatives

The homolytic decomposition of difluoroamino-derivatives containing the $-C(NF_2)_2-$ group leads to the formation of *N*-fluoroimines. The reaction begins with the dissociation of the weakest C–N bond [32,106]; the resulting radical $RR^1\dot{C}{-}NF_2$ is stabilised with formation of the corresponding *N*-fluoroimine, the decomposition being usually initiated by ultraviolet irradiation [107] or heat [106,108-110]. Thus photolysis of bis(difluoroamino)-dihalogenomethanes in the presence of $N_2O$ leads to the formation of *N*-fluorodihalogenoformimines [107]:

$$XFC(NF_2)_2 \xrightarrow[N_2O]{u.v.} XFC{=}NF\ ;$$
$$X{=}F \text{ or } Cl\ .$$

The thermal decomposition of poly(difluoroamino)-halogenomethanes [32,106,109], tris(difluoroamino)methoxy-methane [109], 2,2-bis(difluoroamino)propane [110], as well as azobis(difluoroamino)fluoromethane and [bis(difluoro-amino)fluoromethylazo]trifluoroformamidine in the presence of carbon monoxide [108] has been described:

$$RC(NF_2)_3 \xrightarrow{\Delta} RC(NF){-}NF_2 \text{ and other products;}$$
$$R{=}NF_2,\ F,\ Cl, \text{ or } OCH_3\ ;$$

$$(CH_3)_2C(NF_2)_2 \xrightarrow[780^\circ C]{} CH_2CF{=}NF + (CH_3)_2C{=}NF + CH_2NF_2 + HCN + HF\ ;$$

$$(F_2N)_2CFN{=}NCF(NF_2)_2 \xrightarrow[160^\circ C]{CO} FN{=}CFN{=}NCF{=}NF\ ;$$

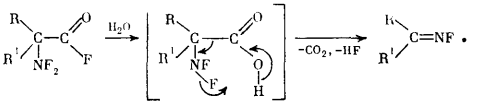
$$(F_2N)_2CFN{=}NCNF_2 \xrightarrow[120^\circ C]{CO} FN{=}CFN{=}NCNF_2\ .$$

The composition of the pyrolysis products depends both on the structure of the initial poly(difluoroamino)-compound and on temperature. Under optimum conditions, the yield of *N*-fluoroimines may reach 60–70% [106,110].

It is noteworthy that formation of *N*-fluoroimines is also observed in the pyrolysis of difluoroaminofluorodiazirine [111] and trifluoronitrosomethane [112] and in the photolysis of azofluoroiminofluoromethane [108].

## 7. Other Methods

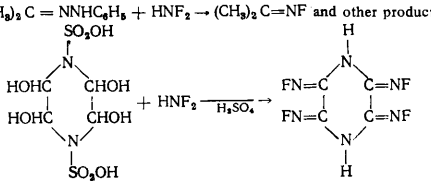
Apart from the methods discussed above, a number of reactions leading to the formation of *N*-fluoroimines merit attention. These include primarily the hydrolysis of the fluorides of $\alpha$-difluoroaminoperhalogenocarboxylic acids [113-115]. The formation of $\alpha$-difluoroaminoperhalogeno-carboxylic acid in the first stage is postulated, the acid being subsequently decarboxylated with simultaneous elimination of hydrogen fluoride. A cyclic concerted mechanism has been proposed for the decarboxylation [114,115]:



When aqueous dioxan was allowed to react with difluoro-aminodifluoroacetyl fluoride, the free acid was isolated [114]. The hydrolysis of methyl $\alpha$-cyano-$\alpha$-difluoroamino-propionate apparently proceeds via a similar mechanism with formation of *N*-fluoroiminopropionitrile [61]. When $\alpha$-difluoroaminohexafluoroisobutyryl fluoride is acted upon by caesium fluoride, perfluoroacetone *N*-fluoroimine is formed [116].

Certain *N*-fluoroimines have been obtained with the aid of difluoroamine [117,118]:

$$(CH_3)_2C{=}NNHC_6H_5 + HNF_2 \rightarrow (CH_3)_2C{=}NF \text{ and other products}$$



When sodiomalonic ester reacts with $F_2NOSO_2F$, diethyl *N*-fluoroiminomalonate is formed[119]:

$$NaCH(COOC_2H_5)_2 + F_2NOSO_2F \xrightarrow[CH_3CN]{} FN{=}C(COOC_2H_5)_2 .$$

The formation of *N*-fluoroimines is observed in the reaction of certain α-bromodifluoroamino-derivatives with liquid ammonia[120] or pyridine[48]:

$$C_6H_5CBr_2NF_2 \xrightarrow{\text{liq. } NH_3} C_6H_5CBr(=NF) ;$$

$$C_6H_5CBr(NF_2)CH_2NF_2 \xrightarrow{C_5H_5N} C_6H_5\overset{NF}{\overset{\|}{C}}CN \xleftarrow{C_5H_5N} C_6H_5CBr(NF_2)CN .$$

Treatment of a dialkylfluoroamine (III) with silica gel led to *N*-fluorobenzimidoyl fluoride[121]:

$$\underset{\text{(III)}}{C_6H_5CF_2NFCH(CH_3)CH_2CH_3} \xrightarrow[10^\circ C]{\text{silica gel}} C_6H_5CF(=NF) .$$

*N*-Fluoroimines have been isolated when $F_2NCCl_2SF_5$ was treated in succession with silver(II) fluoride and water[122] and also after the joint pyrolysis of perfluoro-2-azapropene[123] or perfluoropropene[124] with nitrogen trifluoride over caesium fluoride.

## III. PHYSICOCHEMICAL PROPERTIES

The *N*-fluoroimino-compounds known at the present time are in most cases liquids and more rarely gases or solids. They are stable on storage in dry glass vessels, but in a moist atmosphere they may gradually hydrolyse and interact with the glass.

The most complete physicochemical characteristics have been determined for pentafluoroguanidine[30]:

| | |
|---|---|
| Boiling point, °C | −2, 3 ± 1 |
| Melting point, °C | −148 to −146 |
| Density (Ref.25), g ml$^{-1}$ | 1.51 (0°C) |
| Vapour pressure equation | $\lg p = 7,322 - 1203/T$ |
| Heat of evaporation, kcal mole$^{-1}$ | 5.50 |
| Trouton's constant | 20.3 |
| Enthalpy of formation (Ref.125), kcal mole$^{-1}$ | + 23 |

Liquid column chromatography has been used to isolate pure specimens of this compound[126].

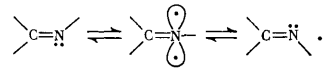
The thermodynamic characteristics of *N*-fluoroimines have been little investigated. It has been found that the enthalpy of formation of *NNN'*-trifluorohexanamidine is $-51.653 \pm 0.14$ kcal mole$^{-1}$.[127] The corresponding quantity calculated for *N*-fluoromethyleneimine by various methods is 12.4 [128] and 16.1 kcal mole$^{-1}$.[128,129] The energy of the $n-\pi^*$ transition has been calculated for *N*-fluoromethyleneimine[130] and has been found to be 6.35 eV.

The geometrical parameters of the C=NF group, calculated for the $H_2C{=}NF$, $HFC{=}NF$, $F_2C{=}NF$,[131] and $FN{=}C{=}NF$ structures[132], can serve as approximate values for the entire class of *N*-fluoroimino-compounds. It follows from the calculations that the C=N bond length is 1.26–1.29 Å, the F–N–C bond angle is in the range 108° to 118°, and the N–F bond length is approximately 1.38 Å (approximately 1.25 Å according to other data, but the authors[132] acknowledge that this value is low). The above geometrical parameters for the C=N–F group are close to the corresponding values of the same parameters for related classes of compounds[2,9,133].

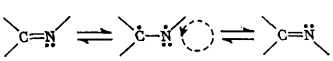
Calculation of the effective charges on the carbon and nitrogen atoms of the C=NF group[131] showed that they vary in the series of compounds $H_2C{=}NF$, $NFC{=}NF$, and $F_2C{=}NF$ from −0.034–+0.389 for the carbon atom and from −0.081 to −0.140 for the nitrogen atom. These results can probably be used, for example, in comparing the reactivities of various *N*-fluoroimines in relation to nucleophiles.

*N*-Fluoroimines containing non-identical substituents at the carbon atom of the C=NF group can exist in two isomeric forms (*syn*- and *anti*-). These isomers have been isolated in many instances. All three possible isomers of 2,3-bis(fluoroimino)butane[62] and αα-bis-(fluoroimino)bibenzyl[70] have been obtained. The *N*-fluoroimine isomers differ in their physicochemical characteristics, but the differences are small. Thus the *syn*- and *anti*-isomers of 1-cyano-*N*-fluoroformimidoyl fluoride have the following properties respectively: boiling point 2° ± 0.5°C and −3° ± 0.5°C; heat of evaporation 6.58 and 6.34 kcal mole$^{-1}$; vapour pressure equation $\lg p = -1440/T + 9.13$ and $\lg p = -1390/T + 8.01$.[55,72] The differences between the retention times of the stereoisomers in gas–liquid chromatography permit their isolation in a pure form. The structures of the *N*-fluoroimine isomers can be reliably determined by $^{19}F$ NMR and mass spectroscopy[27,47,55,62]. In certain cases, *N*-fluoroimines are formed in one (or mainly in one) of the possible isomeric forms. Sometimes this can be explained by the influence of steric factors when one of the substituents at the carbon atom of the fluoroimino-group is large (for example, t-alkyl,[53] $SF_5$, and $COOCH_3$ [55]) and in other cases by the stereospecificity of the formation of the *N*-fluoroimino-compound[47,86].

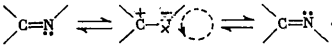
The stereoisomers of *N*-fluoroimines are fairly stable under the usual conditions and also on moderate heating[27]. Theoretical calculations showed that the energy of the isomerisation of the stereoisomers of *N*-fluoroimines is fairly high. Thus it amounts to 32.5 kcal mole$^{-1}$ for *N*-fluoromethyleneimine[134] and 22.4 kcal mole$^{-1}$ for difluorocarbodiimide[132]. These values were obtained on the hypothesis that the isomerisation mechanism involves the transfer of two non-bonding electrons from the nitrogen atom with an $sp^2$-hybrid orbital to a pure *p* orbital[134]:



Under certain conditions, for example on ultraviolet irradiation, the conversion of one isomeric form of the *N*-fluoroimine into the other may be observed. Thus irradiation of *syn*-bromofluoromethylenefluoroimine[105] and also of *syn,syn*- and *syn,anti*-2,3-bis(fluoroimino)-butanes[62] leads to their isomerisation. The conversion of the *syn*-isomers of *NNN'*-trifluoromonochloroaceto- and *NNN'*-trifluorobutyro-amidines into their *anti*-isomers is observed when the substances are kept in an ethereal solution of HCl.[135] It is suggested that in these instances isomerisation involves the formation of a single C–N bond (which permits rotation of the NF group) via mechanism (2) (on ultraviolet irradiation) or (3) (on treatment with HCl)[134]:



(2)



(3)

### NMR Spectra

The presence of the fluorine atom makes it possible to investigate *N*-fluoroimines by $^{19}F$ NMR. The $^{19}F$ NMR

spectra have been recorded for the majority of the *N*-fluoroimines describes in the literature and occupy an important place in the determination of their structures.

The chemical shift of the signal due to the $^{19}F$ nucleus in the C=NF group varies within wide limits, from +60 to −90 p.p.m. (relative to $CCl_3F$).[5,136] The upper values of this range are characteristic of *N*-fluoroimines containing the C−F bond at the fluoroimino-group. The signals for other *N*-fluoroimines are as a rule observed in weaker fields. The most intense shielding is observed in perfluoromethyleneimine $F_2C{=}NF$,[105] for which $\delta(NF)$ = +67.0 p.p.m. (relative to $CCl_3F$). The nitrogen and oxygen atoms exhibit a similar shielding effect when they are linked to the C=NF group. The CN group can probably manifest both shielding and deshielding effects[136]. The chemical shifts of the signal due to the $^{19}F$ nucleus in the *syn*- and *anti*-isomers of *N*-fluoroimines are different, which has been used to determine the stereochemistry of these compounds, particularly in combination with $^1H$ NMR spectra[27,55]. The $^{19}F$ NMR spectra of various *N*-fluoroimines have been examined in a review[136].

### Infrared Spectra

Two absorption regions in the infrared spectra are characteristic of *N*-fluoroimines, being associated with the presence in these compounds of both the C=N double bond and the N−F bond. The vibrations of the carbon–nitrogen double bond in the majority of *N*-fluorimines are manifested in the range 1600–1680 $cm^{-1}$. The same absorption region is characteristic also of other compounds with the C=N bond[133]. Hypsochromic and bathochromic shifts of the absorption band due to the multiple bond have been observed for certain *N*-fluoroimines, which is associated with the nature of the substituents at the carbon atom of the fluoroimino-group. For example $\nu$(C−N) is 1745 $cm^{-1}$ for perfluoromethyleneimine[93] and 1553 $cm^{-1}$ for *N*-fluoroiminomalonodinitrile[72].

The vibration of the N−F bond is manifested by one or two bands[55] in the range 840–1000 $cm^{-1}$. When other nitrogen–fluorine bonds are present in the *N*-fluoroimine, the absorption in this region is more complex[5].

The absorption bands corresponding to identical bonds in the geometrical isomers of *N*-fluoroimines have similar positions[53,55,62,72,79,137] and in certain cases the infrared spectra of the isomers may be identical[27].

### Mass Spectra

Mass spectrometry is being used on an increasingly wide scale as a physicochemical method for the investigation of *N*-fluoroimines[23,25,26,28,30,35,39,41,55,62,91,137–139]. However, the number of studies in which mass spectra were used as the main method for the determination of the structures of *N*-fluoroimines is extremely limited. Mention may be made of only one study[62], where mass spectrometry was used to elucidate the structure of the isomers of 2,3-bis(fluoroimino)butane.

### Explosive Properties

Organic *N*-fluoroimines exhibit explosive properties to a greater or lesser extent. Compounds containing difluoroamino-groups together with the fluoroimino-group are particularly sensitive to external influences and properties of this kind are enhanced with increase of the number of difluoroamino-groups[5]. Pentafluoroguanidine is extremely explosive[25]. Explosions of this compound have been observed on friction, impact, and following other external influences, as well as in phase transitions (this happens particularly frequently on fusion). Studies involving such compounds require special precautions.

## IV. CHEMICAL PROPERTIES

Among organic derivatives of nitrogen containing the N−F bond, *N*-fluoroimines have been found to be the most reactive. The wide variety of reactions in which these compounds may be involved is in many respects determined by the presence of the C=N double bond. These include in the first place numerous reactions with nucleophiles and electrophiles and also oxidation, reduction, etc. reactions.

### 1. Hydrolysis

The hydrolysis of pentafluoroguanidine and tetrafluoroformamidine has been investigated in greatest detail[25,30,31,126,140]. In contrast to the hydrolytically stable saturated difluoroaminoalkanes, these compounds are hydrolysed comparatively readily. Pentafluoroguanidine and tetrafluoroformamidine react particularly rapidly and exothermically with aqueous solutions of alkalis[30,140]; the reaction is accompanied by the evolution of an equivalent amount of nitrogen, which is used for the gas-volumetric analysis of these compounds[126]. The hydrolysis of pentafluoroguanidine and tetrafluoroformamidine on treatment with water proceeds over a period of several hours and the compounds react even more slowly with concentrated sulphuric acid. The hydrolysis products in the latter two cases are carbon dioxide, difluoroamine, hydrogen fluoride, and hydroxylamine. When pentafluoroguanidine reacts with concentrated hydrochloric acid, chlorodifluoroamine is also formed[140].

The hydrolysis of *N*-fluoroimidoyl fluorides of perfluorocarboxylic acids leads to the formation of the corresponding acids[16,141]:

$$R_fCF{=}NF \xrightarrow{H_2O} R_fCOOH\ ;$$

$$R_f{=}CF_3,\ \text{or}\ CF_2NF_2\ .$$

It has been shown for *N*-fluoroimidoyl fluoride derived from difluoroaminodifluoroacetic acid[11,141,142] that the first stage of the reaction involves the formation of the *N*-fluoroimidic acid (IV), whose structure has been demonstrated by $^{19}F$ NMR, infrared spectroscopy, and reaction with diazomethane. The attempts to isolate the *N*-fluoroimidic acid in a free form were unsuccessful:

$$F_2NCF_2\overset{\overset{NF}{\|}}{C}F \xrightarrow[\text{ether}]{H_2O} \left[F_2NCF_2\overset{\overset{NF}{\|}}{C}OH\right] \xrightarrow[\text{ether}]{CH_2N_2} F_2NCF_2\overset{\overset{NF}{\|}}{C}OCH_3\ .$$

(IV)

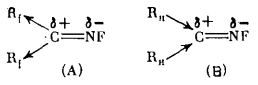
It has also been noted that *C*-chlorodifluoroformimine may be stored over water for 50 h without appreciable decomposition[93], while perfluoroketone *N*-fluoroimines do not change on contact with concentrated sulphuric or fluorosulphonic acid[11].

The hydrolysis of hydrogen-containing *N*-fluoroimines has been described in only two instances. Cyclohexanone was obtained on boiling *N*-fluoroiminocyclohexane with 2 M aqueous sulphuric acid[59]. Similarly, butyl methyl

carbonate is formed in the hydrolysis of butyl methyl *N*-fluoroiminocarbonate[57] with an aqueous-alcoholic solution of HCl.

## 2. Reactions with Nucleophiles

The reactivity of *N*-fluoroimines in relation to nucleophiles is determined by the polarisation of the C=N bond, which is responsible for the electron deficiency at the carbon atom and depends to a large extent on the nature of the substituents linked to this atom. Substituents manifesting a $-I$-effect (A) increase the reactivity of *N*-fluoroimines in relation to nucleophiles, while those with a $+I$-effect (B) reduce it:



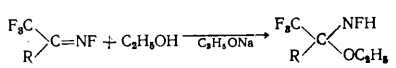
(A) (B)

Substituents such as perfluoroalkyl, $NF_2$, halogeno-, etc. ensure the highest reactivity in relation to nucleophiles.

A diminution of the nucleophilic properties of the given reactant hinders its reaction with the *N*-fluoroimine. This is shown most clearly in the interaction of *N*-fluoroimines with alcohols and amines[143,144]. In the reactions with substances showing reduced nucleophilic properties, basic catalysts are usually employed (triethylamine, pyridine, urea, etc.).

The addition of nucleophiles begins with anionic attack on the positively polarised carbon atom of the C=NF group with a simultaneous shift of the $\pi$ electrons of the C=N bond to the nitrogen atom. On treatment with nucleophiles having a mobile hydrogen atom, which are most frequently used in these reactions (for example alcohols, amines, hydrogen cyanide, nitrous acid, etc.), the corresponding *N*-fluoroamino-derivatives are formed. They are sometimes fairly stable and their presence has been demonstrated by various methods of physicochemical analysis; in other instances, these compounds undergo further reactions, which depend on their structure, reaction conditions, and other factors.

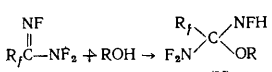
Alcohols. Perfluoroketone *N*-fluoroimines and nitriles of $\alpha$-fluoroiminoperfluorocarboxylic acids are capable of combining with aliphatic alcohols at the C=N bond in the presence of sodium alkoxide[11,142,145,146]. The resulting *gem*-fluoroaminoalkoxy-derivatives are fully stable on storage and distillation:



R=$CF_3$ or CN.

The reaction of perfluoroketone *N*-fluorimines is reversible and, on binding the alcohol (for example, with acetic anhydride) as the acetate[143], the equilibrium may be displaced towards the formation of the initial *N*-fluoroimine.

Pentafluoroguanidine[32,45,143,147-159] and perfluoroamidines[27] also give rise to the addition products (V) in reactions with alcohols:

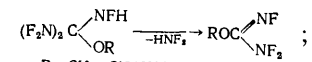


(V)

$R_f = NF_2$, $C_3F_7$, or $CF_2NO_2$.

In addition, pentafluoroguanidine is capable of forming adducts also with other compounds containing the hydroxy-group (organic acids, oximes, hydroxamic acid, amidoximes, as well as phenols with electronegative substituents, etc.)[143,154]. Methyl and ethyl alcohols, which are highly nucleophilic, react extremely vigorously with pentafluoroguanidine under the usual conditions. On the other hand, alcohols with electronegative substituents and carboxylic acids require the use of a basic catalyst (urea, triethylamine, and pyridine) for the reaction to reach completion. Trifluoroacetic acid does not react with pentafluoroguanidine under analogous conditions.

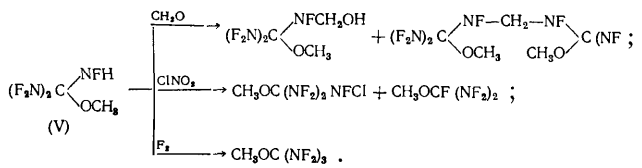
The products of the addition of alcohols to pentafluoroguanidine are converted into the corresponding alkoxytrifluoroformamidines on heating or on treatment with metal fluorides (NaF, $AgF_2$) as a result of the elimination of difluoroamine[32,143,154]. In certain other cases, this reaction proceeds spontaneously:



R=$CH_3$, $CH(CH_3)_2$, or $CH_3CO$.

The products of the addition of alcohols to perfluoroamidines are stable only in solutions, from which they cannot be isolated[27].

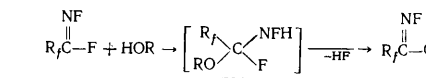
The hydrogen atom of the fluoroamino-group in compounds of type (V) is fairly mobile and capable of being substituted by other atoms or groups of atoms, for example[143]:



(V)

The last reaction has found extensive applications in the synthesis of tris(difluoroamino)methyl ethers from the corresponding bis(difluoroamino)fluoroaminoalkoxy-derivatives obtained by the interaction of pentafluoroguanidine with alcohols such as ethylene glycol, glycerol[154], methanol and ethanol[143,147,159], ethanol ammonium perchlorate[149,150,155], 2,2-dinitropropane-1,3-diol[157], tris(hydroxymethyl)nitromethane[152], 2,3-bis(hydroxymethyl)oxiran[148,151,153], tetrakis(hydroxymethyl)phosphonium chloride[45], trinitroethanol[158], alcohols containing the difluoroamino-group[154,156], and acetone oxime[143]. Ethers containing the difluoroamino-group have also been obtained by fluorinating the products of the addition of methanol to perfluoroamidines[27].

The products of the interaction of alcohols with *N*-fluoroimidoyl fluorides derived from perfluorocarboxylic acids and 1-cyano-*N*-fluoroformimidoyl fluoride are the corresponding *N*-fluoroimino-ethers[72,74,141,143,145]. It has been suggested[143] that fluoroamino-derivatives (VI) are formed as intermediates:

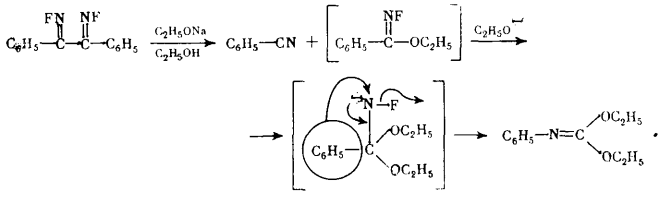


(VI)

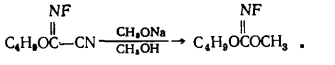
$R_f = CF_3$, $CF_2NF_2$, or CN.

*N*-Fluoroimines containing alkyl or aryl substituents at the carbon atom are less reactive in reactions with alcohols. Thus, whereas *NNN'*-trifluoroamidines derived from perfluorocarboxylic acids combine smoothly with alcohols (see above), *NNN'*-trifluoroamidines derived from non-fluorinated acids do not react with alcohols even in the presence of a catalyst[27].

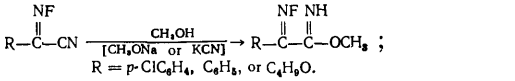
The reactions of *N*-fluoroimines containing alkyl or aryl substituents proceed as a rule in the presence of an excess of the alkoxide and may be accompanied by the rearrangement of the carbon skeleton of the molecule. Thus, on treatment of α-fluoroiminoarylacetonitriles with an excess of sodium alkoxide in alcohol, mixtures of the corresponding aryl cyanide and *N*-aryliminocarbonates are formed[57,58]. Analogous products have been obtained from αα-bis(fluoroimino)bibenzyl[70]. The reaction mechanism apparently involves a rearrangement similar to that of the Beckmann rearrangement, for example:



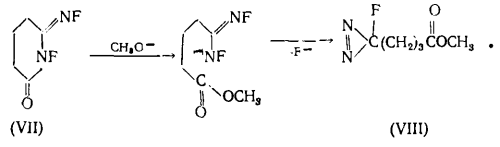
Under analogous conditions, the cyano-group of α-fluoroiminobutoxyacetonitrile exhibits pseudohalogen properties and is replaced by the methoxy-group[57]:



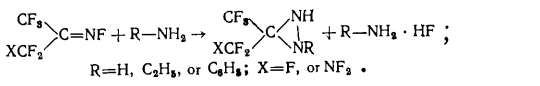
On the other hand, the reaction of α-fluoroiminoaryl- and α-fluoroiminobutoxy-acetonitriles with methyl or ethyl alcohol in the presence of catalytic amounts of potassium alkoxide or cyanide is completed by the formation of the imino-esters of α-fluoroiminocarboxylic acids as a result of the addition of the alcohol to the C≡N group and does not involve the fluoroimino-group[57]:



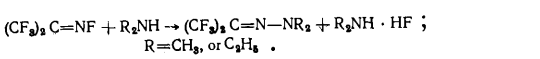
When the fluoroimine (VII) reacts with sodium methoxide, the diazirine (VIII) is formed[67]:



Amines. Perfluoroketone and *N*-fluoroimines react readily with ammonia and primary amines at a temperature as low as −78°C, forming the corresponding diaziridines[11,142,144-146]:



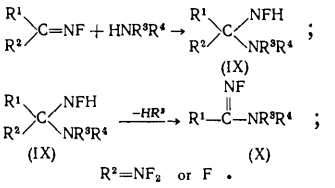
In the reactions with secondary amines, the main products are *NN*-dialkylhydrazones of perfluoroketones[11,142,144,146]:



It is suggested that these products are obtained as a result of complex reactions of the unstable geminal amino-fluoroamino-derivatives formed in the first stage[11,144]. The mechanism of these reactions has been examined in detail in a review[11].

The reactions of the nitriles of α-fluoroiminoperfluoro-carboxylic acids with amines usually lead to similar results. However, the reactions with primary amines yield, together with diaziridines, *N*-alkyl-*N'*-fluoro-amidines owing to the manifestation of pseudohalogen properties by the cyano-group[11,142].

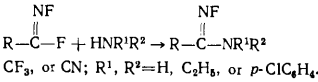
The interaction of ammonia and amines with penta-fluoroguanidine[32,144,154,159-162], perfluorobiguanide[161,162], *N*-fluoroiminomalonodinitrile[137], 1-cyano-*N*-fluoroform-imidoyl fluoride[137], cyanoperfluoroformamidine[37,137,159,160,162,163] bis(difluoroamino)fluoromethylazotrifluoroform-amidine[107], α-fluoroiminoperfluorovaleronitrile[37], tetrafluoroformamidine[144], and *N*-fluorotrifluoroacet-imidoyl fluoride[144] has also been investigated. The *N*-fluoroimines enumerated above give rise to products of type (IX) in their reactions with amines. In certain cases, these products can be converted into new *N*-fluoroimines (X) as a result of the elimination of difluoroamine or hydrogen fluoride:



The interaction of *N*-fluoroimines with amines is promoted by the use of polar solvents such as acetonitrile, dimethyl ether, and tetrahydrofuran[144].

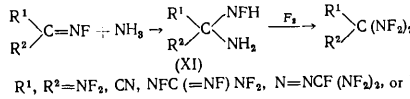
This reaction has been investigated in greatest detail in relation to pentafluoroguanidine, which proved to be reactive with respect to not only amines but also other compounds containing the N−H bond (carboxylic acid amides, imides, and amidines, nitroamines, hydrazine derivatives, etc.)[32,144,159]. The stability of the product of the addition of the amine to pentafluoroguanidine is determined by the nature of the amine involved in the reaction[144]. For example, the interaction of pentafluoroguanidine with ammonia and *p*-cyano- and *p*-trifluoromethyl-anilines gives rise to adducts which are stable at low temperatures. On being heated to room temperature, they lose difluoro-amine with formation of the corresponding trifluoro-guanidines. The products of the addition of more basic amines are unstable even at low temperatures. Thus reactions with n-butylamine and dimethylamine result in the formation of alkyltrifluoroguanidines even at −78°C.

When amines react with *N*-fluoroimidoyl fluorides, *N*-fluoroamidines are formed as a result of the elimination of HF from the intermediate addition product[55,72,144]:



On the other hand, the products of the addition of ammonia to 1-cyano-*N*-fluoroformimidoyl fluoride can apparently exist at low temperatures[128].

Among the entire wide variety of the products of the addition of amines to *N*-fluoroimines, the ammonia addition products (XI) have now found practical application. It has been shown in numerous instances that the hydrogen atoms in the amino- and fluoroamino-groups of these compounds can be substituted by fluorine atoms[37,107,137,144,159-163]:



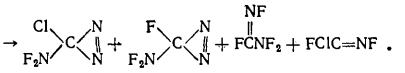
This reaction led to the synthesis of many new difluoro-amino-derivatives. The reaction with pentafluoroguanidine

yielded a compound containing the maximum possible number of difluoroamino-groups at a single carbon atom—tetrakis(difluoroimino)methane [144,159-162].

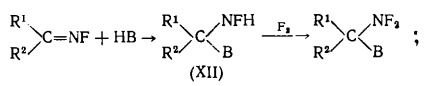
Pentafluoroguanidine reacts with acetone hydrazone and semicarbazide hydrochloride, forming a complex mixture of products as a result of the decomposition and rearrangement of the intermediates [144]:

$$(F_2N)_2C{=}NF + H_2N{-}N{=}C(CH_3)_2 \xrightarrow{25^\circ C} FC(NF_2)_2NH_2 + $$
$$+ F_2C(NF_2)NFH + HNF_2 + N_2O + (CH_3)_2C{=}O\ ;$$

$$(F_2N)_2C{=}NF + H_2NC(O)NHNH_2\cdot HCl \xrightarrow{25^\circ C} \rightarrow$$



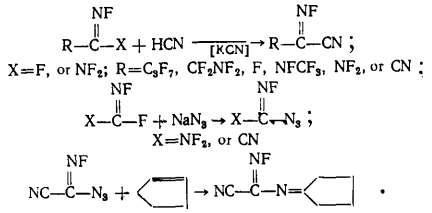
Other nucleophiles. Reactants with less pronounced nucleophilic properties such as $HN_3$, [164] HNCO, [36,165-170] HCN, [11,32,37,137,142] HBr, [138] and HF [143] have also been used in the reactions with *N*-fluoroimines. Their products are mainly the corresponding *N*-fluoroamino-derivatives (XII), which are converted into difluoroamino-compounds on fluorination with elemental fluorine [36,37,138,143,164,167-170]:



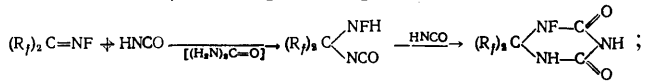
(XII)

(a) B=$N_3$; $R^1$=F, or $NF_2$; $R^2$=F, $NF_2$, $N_3$;
(*b*) B=Br, or NCO*, F; $R^1 = R^2 = NF_2$;
(c) B=CN; $R^1$=$R^2$=$CF_3$ (not fluorinated).

The reaction with a nucleophile sometimes results in the formation of a substitution and not an addition product. This happens when hydrogen cyanide reacts with pentafluoroguanidine [32,37,137], cyanotrifluoroformamidine [137], and *N*-fluoroimidoyl fluorides from perfluorocarboxylic acids [11,37] in the presence of catalytic amounts of potassium cyanide and also on treatment of tetrafluoroformamidine [171] and 1-cyano-*N*-fluoroformimidoyl fluoride [55,72] with $NaN_3$. The 1-cyano-*N*-fluoroformimidoyl azide formed in the latter case is stable only in solution; on treatment with cyclopentene, it yields 1-cyano-*N*-cyclopentylidene-*N'*-fluoroformamidine [55,72]:



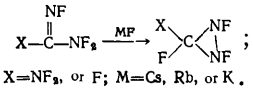
The addition of isocyanic acid to *N*-fluoroimines leads to *N*-fluoroamino-derivatives which react with a second HNCO molecule, forming cyclic products (XIII): [144,165]



(XIII)

$R_f$=$CF_3$, or $NF_2$.

On treatment with alkali metal fluorides, pentafluoroguanidine and tetrafluoroformamidine isomerise to diaziridines [35,88,172,173]:

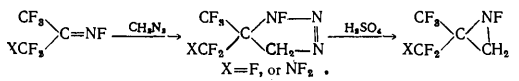


X=$NF_2$, or F; M=Cs, Rb, or K.

† The second fluorination product is $C(NF_2)_4$.

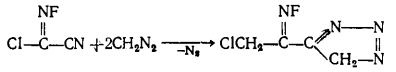
Caesium fluoride is most reactive in this process. The reaction involving tetrafluoroformamidine results in the formation, together with the diaziridine, of a dimer whose structure has not been finally established [172,173].

Perfluoroketone *N*-fluoroimines react with diazomethane even in the cold, forming triazolines, which can be converted into the corresponding aziridines [11,142]:

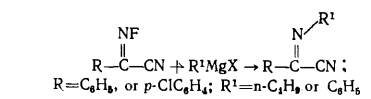


X=F, or $NF_2$.

1-Cyano-*N*-fluoroformimidoyl chloride reacts with two moles of diazomethane [11,142]:



The interaction of α-fluoroiminoarylacetonitriles with organomagnesium compounds leads to *N*-substituted α-iminonitriles in low yields [57]. α-Fluoroiminobutoxyacetonitrile does not undergo this reaction:

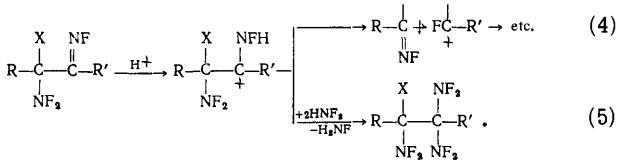


R=$C_6H_5$, or p-$ClC_6H_4$; $R^1$=n-$C_4H_9$ or $C_6H_5$

## 3. Reactions with Electrophiles

The reactions of *N*-fluoroimines with electrophiles have been less thoroughly investigated. Reactions with electrophiles are characteristic of *N*-fluoroimines in which the carbon atom of the C=NF group is linked to hydrogen-containing alkyl or aryl groups. Among these reactions, those of strong inorganic acids and Lewis acids with α-difluoroaminofluoroimines have been studied in greatest detail [65,66,69,80,174,175].

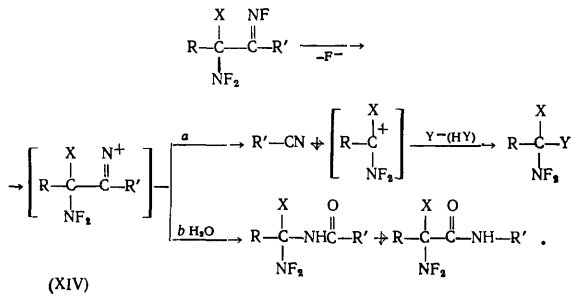
In principle, the site of attack by the electrophile may be the nitrogen atom or the fluorine atom of the fluoroimino-group. In the former case, treatment with inorganic acids should lead to the formation of the cation $\overset{+}{C}-NFH$. This cation, which has been obtained, for example, from α-(difluoroamino)fluoroimine, could decompose by mechanism (4) (similarly to the decomposition of, for example, 1-diethylphosphato-2-difluoroamino-derivatives in an acid medium [68]); in the presence of a difluoroamine, reaction via mechanism (5) is also possible [66]:



However, this mechanism has not been demonstrated experimentally, although the possibility of its occurrence under certain conditions cannot be ruled out.

It is generally accepted that the primary step in the reactions under consideration is attack by the electrophile on the fluorine atom of the fluoroimino-group, leading to the formation of a complex as a result of donor–acceptor interaction between a molecule of the *N*-fluoroimine and the electrophile [2]. The decomposition of this complex leads to the formation of a cation (XIV) with a sextet of electrons at the nitrogen atom. The carbon skeleton of

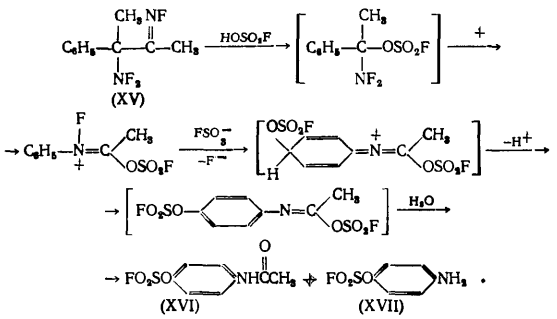
the initial molecule is then cleaved with formation of a carbonium ion (pathway *a*), whose further reaction depends on the reaction conditions. The second pathway (pathway *b*) involves a rearrangement analogous to the Beckmann rearrangement, and is completed by the formation of the corresponding amides. Cases are known where both pathways operate simultaneously:



(XIV)

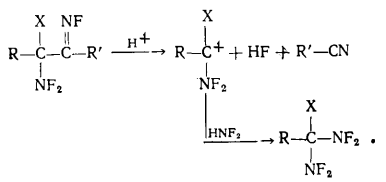
The reaction of $\alpha$-difluoroaminofluorimines with boron trifluoride[66,69] leads to compounds containing a $\rangle C(NF_2)F$ group (pathways *a*).

The mechanism of the reaction between 2-difluoroamino-3-fluoroimino-2-phenylbutane (XV) and fluorosulphonic acid is more complex[65,69,175], the product of this reaction being *p*-fluorosulphonyloxyacetanilide (XVI) and *p*-fluorosulphonyloxyaniline (XVII):



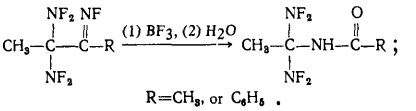
(XV) (XVI) (XVII)

The intermediate $\alpha$-difluoroaminocarbonium ion formed in the reactions is stabilised by combining with fluoride or fluorosulphonate ions. However, it can also be stabilised by reaction with other substances present in the reaction medium[176,177]. Thus difluoroamine is alkylated by the carbonium cation with formation of *gem*-bis(difluoroamino)-derivatives:

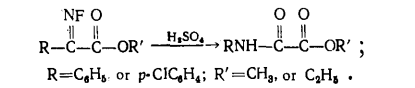


This method made it possible to synthesise many hitherto unobtainable geminal derivatives, such as 1-halogeno-1,1-bis(difluoroamino)- and 1,1,1-tris(difluoroamino)alkanes[66,174], which could not be obtained from the corresponding carbonyl compounds. Fluorosulphonic acid proved to be the most effective reagent in these reactions, but in certain cases the best yields of the final products were obtained using concentrated sulphuric acid.

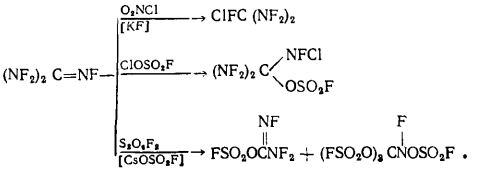
The interaction of $\alpha\alpha$-bis(difluoroamino)fluoroimines with $BF_3$ proceeds via pathway *b* with formation of the corresponding amides[66]:



The interaction of $\alpha$-fluoroiminoarylacetate esters with concentrated sulphuric acid leads to analogous results[57]:



*N*-Fluoroimines containing electronegative substituents at the carbon atom of the C=NF group (perfluoroalkyl, fluoro-, difluoroamino-, and other groups) are less reactive in reactions with electrophiles. This is indicated, for example, by the inertness of perfluoroacetone *N*-fluoroimine in relation to concentrated sulphuric acid and fluorosulphonic acid[11]. At the same time, *N*-fluoroimines of this kind can be involved in reactions with stronger electrophiles. For example, the reactions of pentafluoroguanidine with nitryl chloride[178], chlorine fluorosulphate[179], and peroxydisulphuryl difluoride[180] are known, but their mechanisms have not been elucidated:



## 4. Oxidation and Reduction Reactions

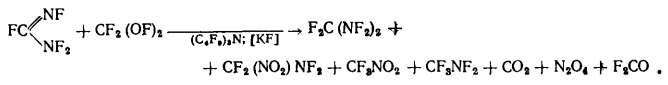
In view of the degree of oxidation of the nitrogen atom in the C=NF group, *N*-fluoroimines are capable of undergoing both oxidation and reduction reactions; reactions of the latter type are more characteristic of these compounds, owing to the presence of the relatively weak nitrogen–fluorine bond (bond energy 65–75 kcal mole$^{-1}$).

In the presence of the $NF_2$ group in the $\alpha$-position relative to the fluoroimino-group, the behaviour of each of these groups with respect to oxidants and reductants will be different, since the nitrogen atom in the difluoroamino-group is in a higher state of oxidation than in the fluoroimino-group. The first stage of the reactions of geminal difluoroaminofluoroimino-compounds with reductants therefore probably proceeds via the $NF_2$ group and that with oxidants via the =NF group.

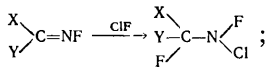
The available literature information about the oxidation of *N*-fluoroimines is mainly restricted to the reactions of pentafluoroguanidine. Under the usual conditions, pentafluoroguanidine is resistant to the action of gaseous fluorine[166] and also of solid potassium permanganate and silver vanadate[103]. Concentrated nitric acid[103] and aqua regia[99,103,140] decompose pentafluoroguanidine to carbon dioxide, hydrogen fluoride, and nitrogen oxides. In the latter case, dichlorobis(difluoroamino)methane is also formed. When pentafluoroguanidine reacts with manganese dioxide, mainly the *cis*- and *trans*-isomers of difluorodiazine are formed[95].

Talbot and Koshar investigated the oxidation of pentafluoroguanidine, trifluoro-*C*-halogenoformamidines, and perfluoroamidines by perfluoroalkyl hypofluorites in the

presence of catalytic amounts of potassium fluoride or cyanide [28,29,139]. These reactions proceed in an extremely complex manner via different pathways and involve the formation of fluorination, oxidation, and degradation products, for example:



When chlorine fluoride reacts with *N*-fluorohalogenoformimines, the corresponding (chlorofluoroamino)-halogenomethanes are formed readily as a result of the addition of a ClF molecule to the C=N bond of the initial imine [97]:

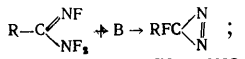


X, Y=F or Cl.

The reaction involving perfluoroacetone *N*-fluoroimine proceeds only in the presence of caesium fluoride [97].

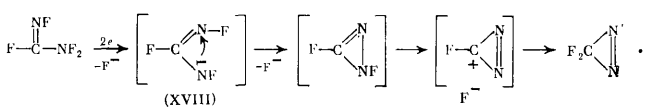
*N*-Fluoroimines readily react with various reductants. For example, they vigorously evolve iodine from aqueous solutions of potassium iodide [32,103,126], which may be used as a qualitative test for these compounds. The products of the reduction of *N*-fluoroimines in these reactions have not been determined in most cases. On the other hand, it has been shown that, when perfluoroacetone *N*-fluoroimine is treated with an aqueous acetonitrile solution of potassium iodide in the presence of acetic acid, perfluoroacetone and ammonia are formed [100].

The reduction of *N*-fluoroimines containing the trifluoroguanyl group by ferrocene [88,102,181], diphenylamine, hydroquinone [88,103,181] and potassium iodide [88,103] in various solvents leads to the formation of diazirines:



R=F, $NF_2$, $CH_3O$, CN, or NCO;
B= $(C_6H_5)_2Fe$, $(C_6H_5)_2NH$, KI, or $C_6H_4(OH)_2$.

Despite the fact that the yields of products are low, this reaction proved to be convenient for the synthesis of various diazirines [88]. The proposed reaction mechanism includes the reduction of the $NF_2$ group with elimination of the fluoride ion and the formation of the anion (XVIII) capable of cyclising to *N*-fluorodiazirine. The subsequent rearrangement, apparently via the intermediate diazirinium cation, is completed by the formation of the final product [102]:

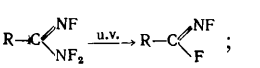


(XVIII)

## 5. Pyrolysis and Photolysis

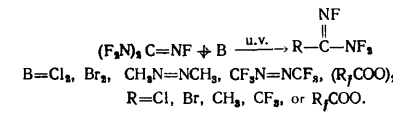
The pyrolysis of *N*-fluoroimines has been studied only in relation to pentafluoroguanidine and tetrafluoroformamidine [25,30,31]. It has been established by differential thermal analysis that these compounds are thermally less stable than the corresponding poly(difluoroamino)perfluoromethanes [30]. Rapid decomposition of pentafluoroguanidine is observed at 243°C and that of tetrafluoroformamidine at 208°C. Slow decomposition of pentafluoroguanidine begins only at 205°C. The main products of the decomposition of these compounds are $CF_4$, $NF_3$, and $N_2$.

The photolysis of *N*-fluoroimines has been studied in greater detail. Thus, it has been found that irradiation of compounds with the trifluoroguanyl group by ultraviolet light leads to the substitution of the difluoroamino-group by fluorine [38]:



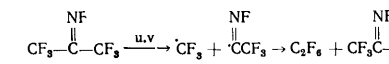
R=F, $NF_2$, or $C_2F_7$.

In the presence of compounds capable of generating a radical species such as chlorine and bromine atoms, trifluoromethyl radicals, etc., the difluoroamino-group can be substituted by them [32,38,88], which constitutes the basis of the method for the synthesis of various *NNN'*-trifluoroamidines from pentafluoroguanidine [32]:

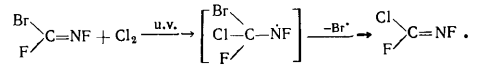


B=$Cl_2$, $Br_2$, $CH_3N{=}NCH_3$, $CF_3N{=}NCF_3$, $(R_fCOO)_2$ etc ;
R=Cl, Br, $CH_3$, $CF_3$, or $R_fCOO$.

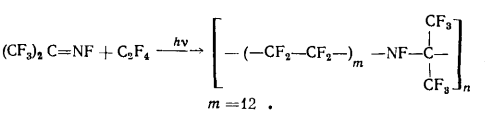
When perfluoroacetone *N*-fluoroimine was irradiated with ultraviolet light *in vacuo*, hexafluoroethane was identified in the reaction product; it may be formed via the following mechanism [91]:



The primary step in the above photolytic reactions is the decomposition of the initial *N*-fluoroimine into two radicals, one of which contains the fluoroimino-group. The recombination of this radical with other radicals leads to various *N*-fluoroimino-compounds. At the same time, the photolytic reactions of *N*-fluoroimines can proceed via a mechanism involving the initial addition of the radical species to the C=N bond. This mechanism has been proposed, for example, for the formation of *C*-chlorodifluoromethyleneimine on irradiation of *C*-bromodifluoromethyleneimine in the presence of chlorine [97]:



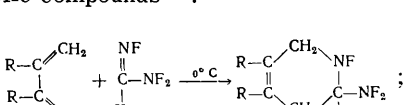
The interaction of perfluoroacetone *N*-fluoroimine with tetrafluoroethylene on $\gamma$-irradiation is completed via the formation of the corresponding copolymer [91]:



*m* =12 .

## 6. Other Reactions

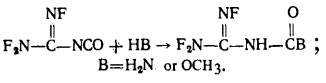
Pentafluoroguanidine and tetrafluoroformamidine readily undergo the Diels–Alder reaction with formation of heterocyclic compounds [182]:



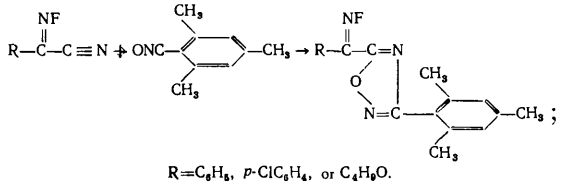
X=F or $NF_2$; R=H, $CH_3$ etc.

In the presence of catalytic amounts of caesium fluoride, perfluoroguanidine reacts with formaldehyde [183], forming the copolymer $[(F_2N)_2CNF(CH_2O)n]y$, where $n = 1-6$ and $y > 1$.

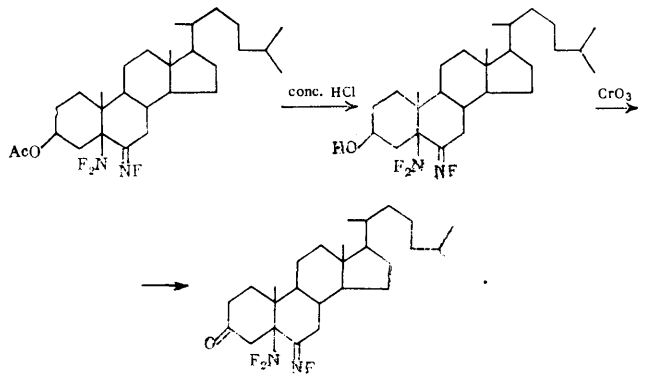
If the functional group in the *N*-fluoroimine molecule is more reactive than the C=NF group, then frequently only the former reacts, while the C=NF group remains unchanged. Thus, the reaction of trifluoroguanyl isocyanate with methanol and ammonia involves the isocyanate group [184]:



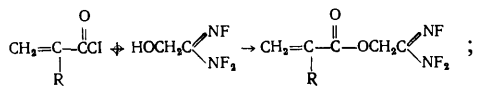
The cyano-group in α-fluoroiminoaryl- and α-fluoroiminobutoxy-acetonitriles can be involved in the 1,3-cycloaddition reactions with a nitrile oxide [57]:



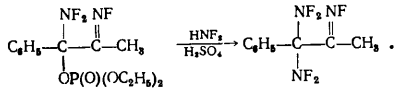
The acetoxy-group in 3β-acetoxy-5-difluoroamino-6-(fluoroimino)cholesterol can be hydrolysed to the hydroxy-group, which may be oxidised to the oxo-group [76]:



2-Difluoroamino-2-fluoroiminoethanol is acylated by acryloyl and methacryloyl chlorides [64]:



When α-(diethoxyphosphoryloxy)-α-difluoroamino-fluoroimines are treated with difluoroamine in the presence of concentrated sulphuric acid, the phosphoryloxy-group is replaced by the difluoroamino-group [66,68]:



α-Acetoxy-α-difluoroaminofluoroimines are decomposed under analogous conditions [66,68,81].

## V. CERTAIN ASPECTS OF PRACTICAL APPLICATIONS

Judging from the literature data, the interest in the synthesis of *N*-fluoroimines is mainly associated with the search for new components of rocket fuels and explosives. *N*-Fluoroimines usually serve as the starting materials for further syntheses. Pentafluoroguanidine is most frequently used for this purpose; it has led to the synthesis of compounds regarded as oxidants of rocket fuels [tetrakis(difluoroamino)methane [144,159-162], tris(difluoroamino)methyl ethers derived from nitroalcohols [152,157,158], bis(difluoroamino)fluoronitromethane [28,139], etc. as well as energetically suitable binders or plasticisers for solid rocket fuels [37,148-151,156,158,182,183]. In certain cases, *N*-fluoroimines are themselves regarded as components of rocket fuels, for example *NNN'*-trifluoroformamimidine [23], 2,3,5,6-tetrakis(fluoroimino)piperazine [118], trifluoroguanyl isocyanate and its derivatives [184], perfluorobiguanide, and 1-[bis(difluoroamino)fluoromethyl]-1,2,3,3,-tetrafluoroguanidine [18-20,40]. A mixture of pentafluoroguanidine with nitrogen oxides has been proposed as an oxidant for rocket fuels [21]. Certain *N*-fluoroimino-compounds containing a large number of oxidising groups have been suggested as explosives [23,24] or as starting materials for the synthesis of the latter [137,160-163].

Physiologically active substances have been found among *N*-fluoroimines. For example, difluoroamino-fluoroiminosteroids inhibit the growth of the prostate gland [76]. Fluoroiminocycloalkanes and fluoroiminocycloalkenes are regarded as intermediates for the synthesis of bactericidal preparations [78].

The use of *N*-fluoroimines as monomers for copolymerisation and as polymerisation initiators is of definite interest. Thus perfluoroacetone *N*-fluoroimines readily copolymerises with tetrafluoroethylene, forming a thermoplastic polymer, whose properties are close to those of Teflon [91]. 1,2-Bis(fluoroimino)-compounds are capable of initiating the polymerisation of, for example, ethylene and tetrafluoroethylene [79]. A number of patents are devoted to the employment of *N*-fluoroimines (mainly perfluoro-derivatives) for the synthesis of diazirines [35,88,99,181], which are potential monomers and sources of biradicals.

Certain *N*-fluoroimines have been suggested as corrosion inhibitors [72], bleaching agents [24], and oxidants in chemical reactions [23].

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# Organometallic Catalysis in Stereospecific Polymerisation and Nature of the Active Centres

B.A.Dolgoplosk

Experimental results on the application of individual organic compounds of transition metals for the stereospecific polymerisation of dienes are summarised, and a relation is established between the nature of the metal with its surrounding ligands and the microstructure of the polymer chain. The nature of the active centres responsible for various types of stereoregulation and the mechanism of the formation of chain units are discussed. Aspects of copolymerisation in coordinated systems are considered. Research results on the mechanism of the cleavage of cycloalkenes and the dismutation of alkenes are clarified, arguments are given in favour of a chain process and a carbene character for the active centres, and the mechanism of individual stages in the process is examined. A list of 207 references is included.

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## I. INTRODUCTION

The present paper summarises experimental results on organometallic catalysis in the stereospecific polymerisation of dienes and cycloalkenes. Research has been devoted mainly to elucidating the nature of the active centres exerting different stereospecific effects in the polymerisation of conjugated dienes, and to studying the mechanism of a novel type of chain reactions—the polymerisation of cycloalkenes and the dismutation of alkenes under the influence of carbene complexes of transition metals. The paper deals mainly with results in this field obtained in the Reviewer's laboratory. It will not be concerned with methods for the preparation of organometallic compounds of transition metals or their specific properties.

## II. POLYMERISATION OF DIENES BY ORGANIC COMPOUNDS OF TRANSITION METALS

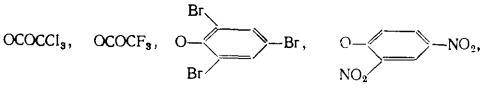
Ziegler–Natta systems, comprising mainly organoaluminium compounds and salts of transition metals, have found wide application in industry for the production of stereoregular polymers of alkenes and dienes. An immense number of scientific papers, reviews, and patents have been devoted to these questions. We shall dwell only briefly on the composition of the principal types of systems employed for the stereospecific polymerisation of dienes, and examine certain secondary reactions in the polymer chain leading to disruption of the chain structure.

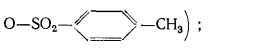
*cis*-Polyisoprene, similar in structure and properties to natural rubber, was obtained[1,2] by means of the classic Ziegler system comprising triethylaluminium and titanium tetrachloride. Various modifications of the system, containing titanium tetrachloride, have since been employed for the industrial production of *cis*-polyisoprene. This system proved insufficiently stereospecific for butadiene.[3] Later investigations have shown that systems containing titanium tetraiodide or mixed halides of titanium increase the content of *cis*-butadiene units[4-6] to 90–95%. Systems consisting of an alkylaluminium halide and a cobalt or nickel salt have also been used to obtain *cis*-polybutadiene.[7-12] Crystalline *trans*-polybutadiene and *trans*-polyisoprene were obtained in the presence of organoaluminium compounds and vanadium halides[13,14] and of higher oxides of chromium deposited on aluminium silicate[15]. Systems based on organoaluminium compounds and a tetra-alkoxytitanium or cobaltous chloride yield stereoregular 1,2-polybutadiene and 3,4-polyisoprene[12,16-19].

Ziegler–Natta systems have been used to obtain *cis*- and *trans*-polypentadienes[20,21], alternating butadiene–propene copolymers[22,23], and several other stereoregular polymers and copolymers of dienes. Many of these systems contain additional components (water, ketones, ethers, esters, Lewis acids, etc.) enhancing their efficiency and stereospecificity of action. As research into the mechanism of the action of the various systems intensified, it became increasingly obvious that the transition metals were the main factor in Ziegler catalysis, and that chain growth occurred at the bond attaching the transition metal to a carbon atom. However, the composition of the systems was too complicated for direct experimental studies of the nature of the active centres and the mechanism of stereoregulation. The most promising approach was to use individual organic compounds of transition metals, so that a direct relation could be established between the nature of the active centres and their stereospecificity. The wide range of action of such compounds is due to the possibility of varying the state of oxidation of the metal and the chemical nature of the ligands surrounding it.

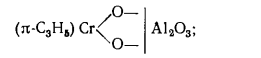
During recent years stable, hydrocarbon-soluble $\sigma$- and $\pi$-allyl compounds of various transition metals—titanium(IV and III), nickel(II), chromium(III and II), molybdenum(IV), vanadium(III), iron(III), and manganese(II)—and the derivatives listed below

1. $(\pi\text{-}C_5H_9)_3Ti$, $[(CH_3)_3SiCH_2]_3Ti$, $\left(\pi\text{-}\bigcirc\right)_3Ti$;
2. $[(CH_3)_3SiCH_2]_4Ti$, $[(CH_3)_3SiCH_2]TiCl_3$, $[(CH_3)_3SiCH_2]_2TiCl_2$;
3. $(C_6H_5CH_2)_4Ti$, $(C_6H_5CH_2)_3TiX$ (X=Cl, Br, I)
4. $\pi$-RNiX (R=$C_3H_5$, $C_4H_7$, $C_5H_9$, , X=Cl, Br, I,





5. $(\pi\text{-}C_3H_5)_3Cr$, $(\pi\text{-}C_5H_9)_3Cr$, $(\pi\text{-}C_3H_5)_2Cr{-}O{-}|SiO_2$,
$(\pi\text{-}C_5H_9)_2Cr{-}O{-}|SiO_2$, $(\pi\text{-}C_5H_9)_2Cr$;



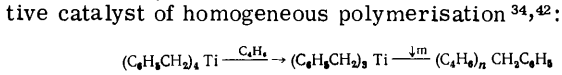
6. $(\pi\text{-}C_5H_9)_3Co$, $(\pi\text{-}C_5H_9)_3Fe$, $(\pi\text{-}C_5H_9)_2Mn$,
$(\pi\text{-}C_5H_9)_3V$;

7. $(\pi\text{-}C_3H_5)_4Mo$, $(\pi\text{-}C_3H_5)_3MoX$ (X = Cl, Br, I, OCOCCl$_3$),
$(\pi\text{-}C_5H_5)_4W$ and its derivatives

have been prepared in our laboratory[24-41], most of them for the first time. Compounds in groups 1 and 2, $\pi$-pentenyl and $\pi$-cyclohexenyl complexes of nickel, and especially $\pi$-allyl complexes of chromium chemically combined with silicon dioxide (group 5), were the most stable at 20–50°C. Examination of the catalytic activity and the stereospecificity of action of several individual organometallic compounds permitted a direct study of the nature of the active centres effecting a particular type of stereoregulation.

## 1. Organotitanium(IV) Compounds

Tetrabenzyltitanium in an aromatic solvent is an effective catalyst of homogeneous polymerisation[34,42]:



(A)

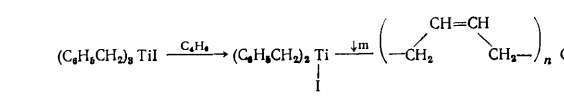
↓ m — point of entry of monomer (m).

The active centre (A) retains three benzyl groups and one growing polymer chain at various degrees of polymerisation[42,43]. Titanium remains in the quadrivalent state, which indicates that the organometallic compound is quite stable up to 50°C. In the polymerisation of butadiene the polymer chain consists mainly of 1,2-units[34,42,43], but every possible type of structure (*cis*-1,4, *trans*-1,4, 3,4, and 1,2) is formed from isoprene[44].

Table 1. Stereospecificity of action of tribenzyltitanium halides and effect of donors[43,44].

| Monomer | Catalytic system | Microstructure of chain, % | | | |
|---|---|---|---|---|---|
| | | *cis* | *trans* | 1,2- | 3,4- |
| Butadiene | $R_4Ti$ | 20 | 20 | 60 | — |
| | $R_3TiCl$ | 35 | 19 | 46 | — |
| | $R_3TiBr$ | 66 | 13 | 21 | — |
| | $R_3TiI$ | 97 | 0.5 | 2.5 | — |
| | $R_3TiI$ + 10$(C_2H_5)_2O$ | 79 | 17 | 4 | — |
| | $R_3TiI$ + 10 oxolan | 27 | 14 | 59 | — |
| Isoprene | $R_4Ti$ | 0 | 75 | 7 | 18 |
| | $R_3TiCl$ | 19 | 36 | 6 | 39 |
| | $R_3TiBr$ | 69 | 0 | 4 | 27 |
| | $R_3TiI$ | 87 | 0 | 0 | 13 |
| | $R_3TiI$ + 10$(C_2H_5)_2O$ | 16 | 37 | 2 | 45 |
| | $R_3TiI$ + 10 oxolan | 7 | 16 | 9 | 68 |

A more effective catalyst, producing ~95% of *cis*-units, is tribenzyltitanium iodide[42-44]:



(B)

The presence of the iodide anion directly at the reaction centre inverts the stereospecificity of the catalytic effect.

In the active centre (B) titanium is maintained in the quadrivalent state throughout polymerisation. These systems exhibit no fundamental differences from organometallic compounds of alkali and alkaline-earth metals, since chain growth takes place at an ordinary carbon–metal $\sigma$-bond.

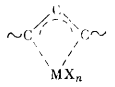
Characteristic features of benzyl derivatives of titanium(IV) will be noted below in the discussion of copolymerisation processes. Table 1 gives the chain microstructure in the polymerisation of butadiene and isoprene under the influence of various such derivatives[43,44]. The content of *cis*-1,4-units increases in the sequence

$$(C_6H_5CH_2)_4Ti < (C_6H_5CH_2)_3TiCl < (C_6H_5CH_2)_3TiBr < (C_6H_5CH_2)_3TiI.$$

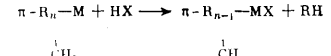
The last of these compounds is a highly selective catalyst for obtaining *cis*-polymers. Oxygen-containing solvating additives increase the content of *trans*- and 3,4-units. It is possible that the use of tribenzyltitanium iodide under especially pure conditions would have yielded only *cis*-units.

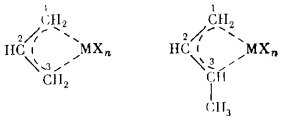
## 2. $\pi$-Allyl Complexes of Transition Metals

It is well known that alkyl derivatives of transition metals are extremely unstable, readily decomposing at the instant of formation[45]. The greater stability of the $\pi$-allyl complexes is due to donor–dative interaction involving $\pi$-electrons of the double bond and non-bonded *d*-electrons of the transition metal[46,47]. $\pi$-Allyl complexes of metals of general formula

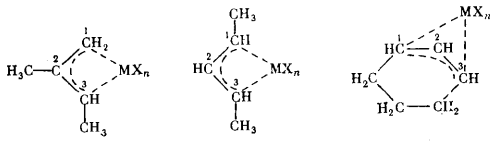


represent most closely the structures of the terminal units in an active centre during the polymerisation of dienes, so that study of the specific reactions of such complexes under model conditions is of considerable interest for an understanding of the mechanism of polymerisation: *anti*- and *syn*-configurations of the $\pi$-allyl complexes correspond to *cis*- and *trans*-states of the terminal growing unit. Organomagnesium synthesis in ethereal medium leads to the formation of poly-$\pi$-allyl derivatives $\pi$-$R_nM$, from which exchange with acids and other compounds yields[27,28,48,49] the corresponding derivatives:





(I) (II)



(III) (IV) (V)

The allyl complexes (I), (IV), and (V) are characterised by equivalence of the two carbon–metal bonds and by higher stability, especially complexes (IV) and (V), containing alkyl substituents on the atoms at positions 1 and 3.

Several of the pentenyl complexes of titanium(III), cobalt(III), vanadium(III), chromium(III), iron(II), and manganese(II) synthesised in the Laboratory of Organometallic Catalysis at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences have proved to be stable in solution at room temperature for a long time[24,25,29]. Compounds of type (II) correspond to the growing chain unit of polybutadiene, those of type (III) to the most probable conformation of an isoprene active centre, and (IV) and (V) to pentadiene and cyclohexadiene active centres respectively.

Allyl-, but-2-enyl-, pentenyl-, and cyclohexenylnickel halides have been prepared[50] from the corresponding alkenyl halides and nickel carbonyl:

$$RHal + Ni(CO)_4 \rightarrow RNiHal \ .$$

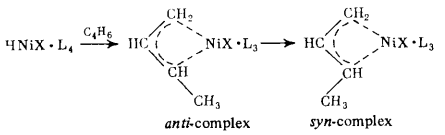
Several specific reactions characteristic of $\pi$-allyl complexes

$$(\pi\text{-}RNiX)_2 \underset{H_2O,oxolan}{\overset{a}{\rightleftharpoons}} \pi\text{-}R_2Ni + \pi\text{-}RNiX \cdot NiX_2$$
$$\downarrow b \qquad\qquad c \downarrow C_4H_6$$
$$R\text{—}R \qquad\qquad Ni + R\text{—}R$$

are of interest for understanding the chemical reactions involved in polymerisation. In the presence of water or oxolan an equilibrium is established (reaction *a*), which can be displaced to the right[51] by distilling off $\pi$-$R_2Ni$ from the system. Reaction (*b*), accompanied by formation of the recombination product R–R, takes place under the influence of various electron-accepting components, especially in aromatic solvents[52,53]. Reaction (*c*) occurs[54] in the presence of dienes with the formation of "bare" active nickel, a catalyst for the cyclic oligomerisation of dienes. Reactions (*b*) and (*c*) illustrate the possibility of the destruction of active centres by recombination during stereospecific polymerisation. This is probably why attack on a growing polymer centre by $CH_3O^3H$ and $^{14}CH_3OH$ in several cases does not result in the appearance of radioactivity in the polymer[55]. The decomposition of $\pi$-but-2-enylnickel chloride by acids leads to the formation of but-1-ene, but hydrogenolysis (and alkaline decomposition) yield *trans*-but-2-ene [56–58]:

$$\pi\text{-}C_4H_7NiX \begin{cases} \xrightarrow{HCl\,(H_2SO_4)} CH_3CH(NiX)\text{—}CH{=}CH_2 \rightarrow \text{but-1-ene (90\%)} \\ \xrightarrow{H_2} CH_3CH{=}CH\text{—}CH_2NiX \rightarrow \textit{trans}\text{-but-2-ene (96\%)} \end{cases} .$$

The point of attack and the nature of the "units" formed [but-1(or 2)-ene] depend on the nature of the reagent. Extremely important results were obtained in work[59] showing that the primary addition of butadiene at a hydrogen–nickel bond results in formation of an anti-complex, which then isomerises into the *syn*-complex:



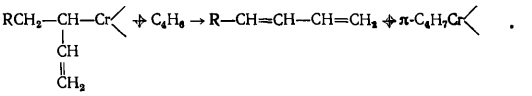

X = sulpho; L = phosphite ligand .

(*a*) Organochromium compounds

Tris-$\pi$-allyl compounds of chromium catalyse the polymerisation of dienes in hydrocarbon solutions[60,61]. All three alkenyl groups are involved in steps of chain growth:

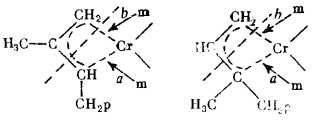
$$\pi\text{-}R_3Cr + 3n\,C_4H_6 \rightarrow [\pi\text{-}R(C_4H_6)_n]_3Cr \ .$$

Three polymer chains are formed on one chromium atom. The resulting polymers have low molecular weights owing to chain transfer to the monomer:




Every "dead" polymer molecule contains a conjugated group of double bonds at the end of the chain.

The butadiene chain contains ~80% of 1,2-units. Every possible type of unit arises in the polymerisation of isoprene. The formation of roughly the same quantities of vinyl and isoprenyl side-groups in polyisoprene (1,2 and 3,4-units) evidently indicates that the two types of centres




are equally probable, where *a* is the point of entry of the monomer into the chain at a carbon–chromium $\sigma$-bond with formation of 1,2- and 3,4-units, while *b* is the point of entry of the monomer on formation of 1,4- and 4,1-units. Hence 1,4-units are randomly arranged "head to tail" in the polyisoprene chain. The polymerisation of isoprene under the influence of $(\pi\text{-}C_5H_9)_2Cr$ in hydrocarbon solution yields a polymer containing only 1,2- and 3,4-units (in roughly equal quantities)[29]. Entry of monomer into the chain is accomplished only by path *a*.

When tris-$\pi$-allylchromium interacts with vacuum-ignited aluminium silicate, silica gel, or aluminium oxide, the organometallic compound passes quantitatively from solution to the surface[30,31]:

$$\pi\text{-}R_3Cr + HO\text{—}|SiO_2 \rightarrow \underset{R}{\overset{R}{>}}Cr\text{—}O\text{—}|SiO_2 + RH$$
(A)

$$\pi\text{-}R_3Cr + \begin{matrix} HO\text{—} \\ HO\text{—} \end{matrix}\Big|Al_2O_3 \rightarrow RCr\begin{matrix} O\text{—} \\ O\text{—} \end{matrix}\Big|Al_2O_3 + 2RH \ .$$
(B)

The reaction with aluminium silicate results in the separation of one RH molecule and the formation of an active centre (A) in which two alkenyl groups are retained by one chromium atom. An important feature is that, in contrast to the initial tris-compound, the new organochromium compound is extremely stable when kept at room temperature for a long time. Since this catalyst causes also the polymerisation of alkenes, it can reasonably be assumed that the $\sigma$-state of the chromium–carbon bond is more characteristic of this organochromium compound. This catalyst was highly stereospecific for the synthesis of *trans*-polyisoprene and *trans*-polybutadiene. Because of the great stability of chromium–carbon bonds, polymerisation takes place by a mechanism of "live" chains without destruction of active centres. Two polymer chains are formed on one chromium atom, with continuous increase in molecular weight with the degree of polymerisation. The reaction of the tris-compound with aluminium oxide produces an active centre (B) in which one carbon–chromium bond is preserved at the chromium atom. In the polymerisation of butadiene and isoprene this catalyst yields polymers containing 92–93% of *cis*-units.

It has thus been shown for chromium compounds that, depending on the electronic state of the transition metal

and the nature of the ligands surrounding it, all kinds of microstructures can be realised with great selectivity on the same metal atom. This principal, which is probably common to many transition metals, has been confirmed for compounds of titanium, niobium, cobalt, and nickel. Although the compounds $\pi$-$R_3Cr$, $\pi$-$R_3Nb$, $\pi$-$R_3Co$, etc. behave in exchange reactions as molecules containing the metal in the tervalent state, the latter is in effect present in a more reduced state, in view of its greater electronic saturation in $\pi$-allyl complexes. This principle is consistent with several specific reactions of poly-$\pi$-allyl complexes that are typical of zerovalent metals. In this sense the transitions $\pi$-$R_3M \rightarrow \pi$-$R_2MX \rightarrow \pi$-$RMX_2$ can be regarded as oxidation accompanied by increase in the positive charge on the metal atom, although the exchange equivalent remains unchanged. The systems become *cis*-stereoregulating after one or two alkenyl groups have been replaced by electronegative ligands (Table 1A).

Table 1A.

| Catalyst | Chain microstructure |
|---|---|
| $\pi$-$R_3Cr$ | 81% 1.2-[48,60,61] |
| $\pi$-$R_3Nb$ | 100% 1.2-[48] |
| $\pi$-$R_2CrOSi\equiv$ | 96% *trans*-[30,31] |
| $\pi$-RCr(O—Al≡)(O—Al≡) | 93% *cis*-[30,31] |
| $\pi$-$RCrCl_2$ | 93% *cis*-[49,60,61] |
| $\pi$-$R_2CrOCOCCl_3$ | 93% *cis*-[48,60,61] |
| $\pi$-$R_2NbCl$ | 91% *cis*-[48] |

Higher oxides of chromium ($CrO_3$) on aluminium silicate have long been known as catalysts for the polymerisation of alkenes. Their catalytic action was earlier attributed to the presence of $Cr^{4+}$, $Cr^{5+}$, and $Cr^{6+}$. Detailed investigation of this system [30,31,62] has shown that the active centre effecting polymerisation is identical with the centre (A) obtained in the reaction of $\pi$-$R_2Cr$ with aluminium silicate: i.e. chromium is present in the active centre in a more reduced state than $Cr^{3+}$. In both cases polymerisation takes place by a mechanism of "live" chains with the formation of *trans*-units, and values of the copolymerisation constants $r_1$ and $r_2$ for the pair butadiene–isoprene fully coincide.

(*b*) Organonickel compounds

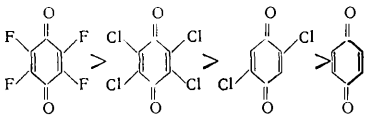
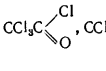
Research on the use of organonickel compounds for the stereospecific polymerisation of dienes has been published in many papers and reviews [63-65]. We shall consider only a few of the most important results of interest in connection with the mechanism of stereoregulation. The compounds $\pi$-RNiX catalyse the polymerisation of dienes in solution. The nature of the anion X has a significant influence on the stereospecificity of the catalytic effect:

1. $\pi$-RNiX (X=I, Br, Cl, O—C$_6$H$_2$Br$_3$) → Crystalline *trans*-polymers of butadiene and isoprene (Refs. 27, 28, 66-71),

2. $\pi$-RNiY (Y=$OCOCCl_3$, $OCOCF_3$, O—C$_6$H$_3$(NO$_2$)$_2$) → *cis*-Polybutadiene (Refs. 27, 28, 72).

Replacement of X by more electronegative ligands leads to a significant enhancement of the catalytic activity of the system and to a reversal of the stereospecificity. However, systems based on complexes of $\pi$-RNiCl with various electron-accepting compounds proved to be the most effective and *cis*-stereoselective (Table 2). [63,73-77]

Table 2. Complexes of alkenylnickel halides with electron acceptors.

| Complex | Electron-accepting compound (A) |
|---|---|
| $\pi$-$R\overset{(+)}{N}iCl(Br, I)$ ⋮ $A^{(-)}$ |  |
| (charge transfer complexes) | $CCl_3COCCl_3$,  ,  , $CCl_3COOH$, $CF_2COOH$, $I_2$ |
| $\pi$-$RNi^{(+)}[ClA]^{(-)}$ | $AlHal_3$, $TiHal_4$, $SnHal_4$, $ZnHal_2$, $CoHal_2$, |
| (anion-transfer complexes) |  |

Charge-transfer complexes are formed with the aid of halogenoquinones, whose effectiveness is consistent with the redox potential of the quinones, halogenated carbonyl compounds, halogenated acids, etc. Anion-transfer complexes (such as ion-pairs) are formed by various Lewis acids. The reversal of stereospecificity on passing from $\pi$-RNiI to the $\pi$-RNiI–$I_2$ system indicates directly that the effect is not due to replacement of ligands but to increase in the positive charge on the nickel atom.

Table 3. Catalytic system and structure of polybutadiene.

| Catalytic system | Chain microstructure, % | | | $[\eta]$, dl g$^{-1}$ | Physical state of polymer | Ref. |
|---|---|---|---|---|---|---|
| | 1,2- | *cis*- | *trans*- | | | |
| $\pi$-$R_3MoCl$ | 90 | 2 | 8 | 3.1 | amorphous | 37 |
| $\pi$-$R_3MoOCOCCl_3$ | 97 | — | 3 | 3.0 | amorphous | 37–39 |
| $\pi$-$R_4Mo + CCl_3COCl$ | 95 | — | 5 | 6.5 | amorphous | 38,39 |
| $\pi$-$R_4Mo$ + chloranil | 95 | — | 5 | 5.4 | amorphous | 38,39 |
| $\pi$-$R_4Mo + C_3H_5I$ | 96 | — | 4 | 2.0 | crystalline | 40 |
| $\pi$-$R_4W + C_3H_5Cl(I)$ | 95 0 | — | 5.0 | | amorphous | 41 |
| $\pi$-$R_4W + O_2$ | 99 5 | — | 0.5 | | amorphous | 41 |

Kinetic investigation of various nickel systems has thus far revealed a fractional order (0.5) with respect to the catalyst only for $(\pi\text{-RNiX})_2$, where X = I, Br, Cl, which indicates that polymerisation involves only a small quantity of monomeric forms in equilibrium with the main, inactive dimeric form [70,71]. The kinetic orders with respect to the catalyst established in *cis*-regulating systems, at least in the case of $\pi$-$RNiOCOCF_3$ and complexes with electron acceptors, indicated that the organonickel centres were fully involved in steps of chain growth [27,28,56,57,78].

(*c*) Organomolybdenum and organotungsten compounds

Organometallic compounds based on tetra-$\pi$-allylmolybdenum are highly effective catalysts for the production of amorphous and crystalline 1,2-polybutadiene [37-40] (Table 3). The high intrinsic viscosity of the polymer indicates the formation of a very small quantity of long-lived active centres. Detailed study of the $\pi$-$R_4Mo$ + $CH_2:CHCH_2I$ system, which forms crystalline 1,2-polybutadiene, has shown that the active centre is the compound $\pi$-$R_2Mo(I)$-p, which results from the interaction of the above components. Chain growth occurs at the allyl-molybdenum $\sigma$-bond, but transition of the $\sigma$-bond into the stable $\pi$-allyl form is an act of chain termination[37-40].

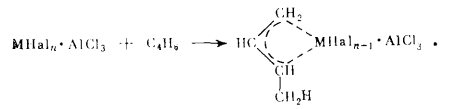
As is shown in Table 3, systems based on $\pi$-allyl derivatives of tungsten also effect 1,2-stereoregulation[41].

3. Formation of Organometallic Compounds during Polymerisation

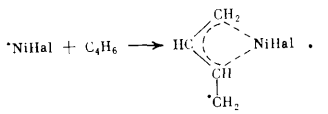
Transition-metal compounds of the $\pi$-allyl type are formed as a result of diverse reactions because of their relatively high stability. Metal hydrides in the presence of butadiene are converted into the corresponding $\pi$-but-2-enyl complexes, as was proved [79,80] with nickel, cobalt, and chromium:

$$NiH_2 + C_4H_6 \rightarrow (\pi\text{-}C_4H_7)_2Ni\ ,$$
$$CoH_2 + C_4H_6 \rightarrow (\pi\text{-}C_4H_7)_nCo\ ,$$
$$CrH_3 + C_4H_6 \rightarrow (\pi\text{-}C_4H_7)_3Cr\ .$$

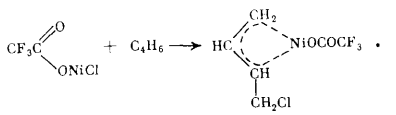
Complexes of halides of transition metals (nickel, cobalt, vanadium) with aluminium chloride cause the stereospecific polymerisation of dienes, presumably [81,82] by the reaction



Defect halide salts (subhalides) of nickel, cobalt, and niobium, obtained by heating in a vacuum, effect the polymerisation of dienes with the stereospecificity characteristic of the corresponding $\pi$-allyl complexes. It has been proved for nickel halides that formation of an organometallic active centre involves an intermediate radical-ion stage [83-85]:



Mixed salts react with dienes in several cases with the formation of $\pi$-allyl active centres [86]:



When $CF_3COONi^{36}Cl$ is used, the labelled chlorine atom is incorporated into the polymer chain [87].

In Ziegler catalysis organic compounds of transition metals are formed by exchange reactions with aluminium alkyls:

$$MX_n + R_3Al \rightarrow RMX_{n-1} + R_2AlX\ ,$$
$$MX_n + R_2AlCl \rightarrow RMX_{n-1} + RAlClX\ .$$

Addition of a diene at the alkyl–metal bond tends to stabilise the resulting organometallic compound as a $\pi$-allyl complex. With titanium(IV) halides a $\pi$-allyl active centre can be formed only after reduction to titanium(III). The alkylaluminium halides probably act subsequently as electron acceptors, forming complexes with $RMX_{n-1}$ and enhancing their effectiveness and stereospecificity, as was established above for $\pi$-allyl complexes of nickel.

4. Nature of Secondary Reactions in Polymer chains during Stereospecific Polymerisation of Dienes by Ziegler Systems

The Ziegler–Natta catalytic systems employed for the stereospecific polymerisation of dienes consist of organoaluminium compounds and halides of transition metals, mainly titanium, nickel, and cobalt. With the first of these metals appearance of the catalytic complex is preceded by reduction of the tetrahalide to the trihalide accompanied by formation of $R_2AlHal$:

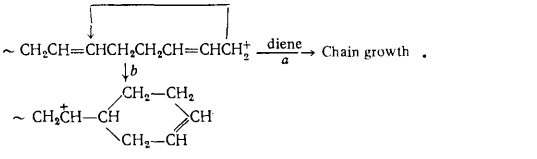
$$R_3Al + TiHal_4 \rightarrow R_2AlHal + RTiHal_3\ ,$$
$$RTiHal_3 \rightarrow {}^1/_2R_{-H} + {}^1/_2R_{+H} + TiHal_3\ .$$

Under certain conditions alkylaluminium halides and titanium(IV) chloride are catalysts for cationic processes. In catalytic systems based on nickel and cobalt halides the alkylaluminium halides and water are used in the molar proportions

$$NiCl_2\ (CoCl_2):R_2AlCl:H_2O = 1:150:10$$

In such cases the initial catalytic system is characterised by extremely high cationic activity, as is illustrated by the possible use of its components ($R_2AlCl + H_2O$) to initiate the polymerisation of isobutene [88]. The organometallic active centres that effect the stereospecific polymerisation of dienes are capable of initiating the oligomerisation and polymerisation of alkenes, which indicates the theoretical possibility that double bonds of the polymer chain are involved. The most important results of investigations on these aspects are reported below.

In anionic and coordination polymerisation conjugated dienes are considerably more reactive than the corresponding alkenes. A distinguishing feature of cationic systems is the comparatively small differences in reactivity between dienes and alkenes [89-91]. Thus isopentene ($m_1$) is more reactive than butadiene ($m_2$) on cationic copolymerisation: $r_1 = 0.90$ and $r_2 = 0.38$



Because of the great probability of reaction (*b*) cyclised polymers, less unsaturated than would be expected theoretically, are formed even at low degrees of conversion in the cationic polymerisation of dienes. In dilute solutions of natural rubber and *cis*-polybutadiene intramolecular cyclisation takes place under the influence of the $R_2AlCl$–$H_2O$ system, accompanied by diminution of unsaturation with maintenance of the molecular weights of the polymers [92-94].

It was shown for the model compound 3-methylpent-2-ene [95] that the cation-active components of Ziegler systems initiate the *cis–trans* isomerisation of isoprene

units extremely efficiently (Table 4). Analogous isomerisation effects were observed[92,96,97] in benzene solutions of natural rubber under the influence of ethylaluminium dichloride, diethylaluminium monochloride, and titanium tetrachloride; the coactivators in such processes were traces of water and other compounds.

Table 4. Variation in composition of reaction mixture and structure of 3-methylpent-2-ene (at 60°C).

| Catalyst (mole % on monomer) | Продолжительность реакции, мин | Isolated, % on initial | | Monomer structure, % | |
|---|---|---|---|---|---|
| | | monomer ($C_6$) | dimer ($C_{12}$) | *cis* | *trans* |
| $C_2H_5AlCl_2$ (3.6%) | 0 | 100 | — | 86 | 14 |
| | 25 | 68 | — | 70 | 30 |
| | 60 | 54 | 46 | 60 | 40 |
| | 90 | — | — | 48 | 52 |
| $TiCl_4$ (2.5%) | 8 | 79 | 21 | 66 | 34 |
| | 60 | 46 | 54 | 52 | 48 |
| Equilibrium | — | — | — | 42.2 | 57.8 |

Reactions of a third type occurring under the influence of cationic initiators involved the migration of double bonds in the polymer chain. Such migration takes place in polybutadiene in the presence of titanium tetrachloride and alkylaluminium chlorides[92], until conjugated systems are formed:

$$\sim CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\sim \xrightarrow{+H^+} \sim CH_2CH_2\overset{+}{C}HCH_2CH_2CH{=}CHCH_2 \sim \xrightarrow{-H^+}$$
$$\rightarrow \sim CH_2CH_2CH{=}CHCH_2CH{=}CHCH_2\sim \xrightarrow{+H^+}$$
$$\rightarrow \sim CH_2CH_2CH_2\overset{+}{C}HCH_2CH{=}CHCH_2 \sim \xrightarrow{-H^+} \sim CH_2CH_2CH_2CH{=}CH{-}CH{=}CHCH_2 \sim .$$

A detailed study of these reactions has been made[98].

Nuclear magnetic resonance spectroscopy of the *cis*-polybutadiene obtained in the presence of the $R_2AlCl$–$CoCl_2$ system showed the presence of : CH.$CH_2$.CH : groups, which characterise the first stage in the migration of double bonds[99].

Research showed the usefulness of introducing into the catalytic systems components that inhibit the development of cationic processes. Such inhibitors may be weak Lewis bases, which do not affect the rate of polymerisation, the molecular weight, or the chain microstructure in the stereospecific polymerisation of butadiene, as was shown for diphenyl ether[100].

In the absence of the monomer (a conjugated diene) migration and isomerisation of double bonds can be effected in model hydrocarbons and in polybutadiene not only by Ziegler systems containing cation-active components but also by organometallic complexes, active centres for stereospecific polymerisation. Thus at room temperature $\pi$-allyl complexes of nickel of general formula $\pi$-RNiHal effect[101,102] the chain isomerisation of hexa-1,5-diene

$$\underset{(A)}{CH_2{=}CHCH_2CH_2CH{=}CH_2} \rightarrow \underset{(B)}{CH_3CH{=}CHCH_2CH{=}CH_2} \rightarrow \underset{(C)}{CH_3CH{=}CH{-}CH{=}CHCH_3}$$

which involves the successive addition and detachment of HNiHal at the double bond. Migration of the double bond (A) → (B) is accompanied by the formation of *cis*–*trans* isomers and by the dimerisation of hexa-1,5-diene, which also involves addition of the organonickel compound at the double bond in the alkene. At room temperature the $\pi$-but-2-enylnickel chloride–chloroanil complex—an effective stereospecific catalyst for the production of *cis*-polybutadiene—causes the isomerisation of but-1-ene and but-2-ene into the equilibrium mixture[103].

Addition of an organometallic active centre at a double bond in the chain during the polymerisation of dienes should lead to the formation of branched polymers. The probability of such reactions is small, for conjugated dienes are considerably more reactive than alkenes in coordinated systems. The appearance of conjugated double bonds in a polymer chain as a consequence of acts of migration is probably one of the main reasons for the formation of branched polymers in the polymerisation of butadiene under the influence of a "cobalt" catalytic system. This system is characterised by very small differences in reactivity between butadiene and its alkyl derivatives (isoprene and 2,3-dimethylbutadiene),[104–106] and the "polymeric" diene formed may be actively involved in copolymerisation with butadiene. It has been demonstrated for cobalt, nickel, and chromium catalytic systems that the main reaction limiting chain growth is chain transfer to the monomer:

$$\sim \pi\text{-}CH_2CH{=}CHCH_2{-}MX_n \xrightarrow[a]{C_4H_6} \text{Chain growth}$$
$$b\downarrow C_4H_6$$
$$\sim CH{=}CH{-}CH{=}CH_2 + \pi\text{-}C_4H_7MX_n \xrightarrow{C_4H_6} \text{Chain growth} .$$

Reaction (*b*) is accompanied by the formation of polymer molecules containing a conjugated system of double bonds at the ends of the chains[60,61,107], whose involvement in polymerisation results in branched macromolecules.

## 5. Some Aspects of Copolymerisation in Coordination Systems and the Effect of Solvating Additives

On copolymerisation under the influence of RLi in hydrocarbon media dienes are considerably more reactive[108–111] than is styrene ($r_1 \gg r_2$). When the same monomers undergo copolymerisation in the presence of RLi in the usual solvating media or of organo-potassium and -sodium compounds in any media, under conditions leading to formation of 1,2- and 3,4-units, styrene has proved to be considerably more reactive[112,113] than dienes. Both phenomena (change in microstructure and reversal of reactivity) are genetically related to enhancement of the polarity of the carbon–metal bond. With compounds of transition metals, independently of the character of the stereoregulation, dienes are always considerably more reactive than styrene (Table 5).

Table 5. Relative reactivities of butadiene ($m_1$) and styrene ($m_2$) and the chain microstructure.

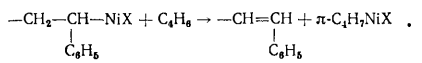
| Catalytic system | Copolymerisation constants | | Chain microstructure, % | | | Ref. |
|---|---|---|---|---|---|---|
| | $r_1$ | $r_2$ | *cis*-1,4 | *trans*-1,4 | 1,2- | |
| RLi in oxolan | 0.20 | 8.0 | 0 | 9 | 91 | 114 |
| RLi in diethyl ether | 0.11 | 1.78 | — | — | — | 114 |
| RLi in toluene | 15.0 | 0.05 | 44 | 48 | 8 | 109 |
| $\pi$-RNiCl–Acceptor | 4.6 | 0.13 | 92 | 6 | 2 | 115 |
| $(\pi\text{-}C_3H_5)_4Mo$–Acceptor | 27.5 | 0,02 | 4 | 5 | 91 | 116, 117 |
| $(\pi\text{-}C_3H_5)_4W$–Acceptor | 10.1 | 0.2 | 0 | 9 | 91 | 116, 117 |
| $(\pi\text{-}C_3H_5)_4Zr$ | 34 | 0.02 | 61 | 4 | 35 | 116, 117 |
| $(C_6H_5CH_2)_4Ti$ | 27 | 0 02 | 15 | 25 | 60 | 116, 117 |

The results indicate a coordination mechanism for the formation of any type of unit on a transition metal. $\pi$-Allyl active centres are considerably more stable than the corresponding styrene derivatives. Entry of styrene into

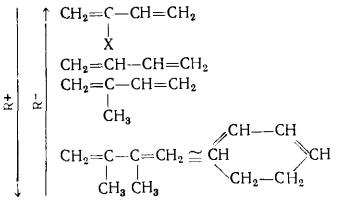
Table 6. Values of $r_1$ and $r_2$ in the copolymerisation of dienes in hydrocarbon media.

| Catalytic system | Butadiene ($m_1$), isoprene ($m_2$) | | | Butadiene ($m_1$), 2,3-dimethylbutadiene ($m_2$) | | | Butadiene ($m_1$), cyclohexadiene ($m_2$) | | | Butadiene ($m_1$), penta-1,3-diene ($m_2$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $r_1$ | $r_2$ | Ref. | $r_1$ | $r_2$ | Ref. | $r_1$ | $r_2$ | Ref. | $r_1$ | $r_2$ | Ref. |
| $R_3Al—TiCl_4$ | 1.0 | 1.0 | 104—106, 118, 119 | 2.16 | 0.39 | 126 | | | | | | |
| $R_3Al—TiI_4$ | 1.9 | 0.5 | 120 | | | | | | | | | |
| $R_3Al—TiI_4$ | 2.8 | 0.53 | 121, 122 | 6.3 | 0.15 | 121 | | | | 2.6 | 0.5 | 121, 122 |
| $R_2AlCl—CoCl_2$ | 0.9 | 1 3 | 123 | 2.7 | 1.1 | 126 | | | | | | |
| $R_2AlCl—CoCl_2$ | 2.3 | 1.15 | 104—106 | | | | | | | | | |
| $R_2AlCl—CoCl_2$ | 1.0 | 0.9 | 121, 122 | 0.74 | 0.67 | 121, 122 | | | | 1.2 | 0.3 | 121, 122 |
| $R_2AlCl—NiCl_2$ | 1.15 | 0.59 | 123 | | | | | | | | | |
| π-RNiX — Acceptor | 6.2 | 1.1 | 121, 122 | 2.8 | 0.18 | 127 | 0.4 | 0.9 | 36 | | | |
| $(π\text{-RNiI})_2$ | 0.3 | 2.35 | 124 | | | | 0.8 | 1.1 | 127 | | | |
| $π\text{-}R_2Cr—O—$ \| Aluminium silicate | 1.06 | 0.8 | 125 | | | | | | | | | |
| $CrO_3$ — Aluminium silicate | 1.04 | 0.70 | 125 | | | | | | | | | |
| RLi | 3.38 | 0.47 | 110—111 | | | | | | | | | |

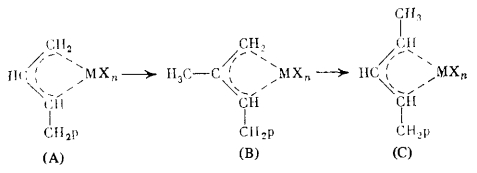
a chain therefore involves a sharp decrease in molecular weight owing to chain-transfer reactions [115]



With respect to relative activity on ionic copolymerisation dienes form the well known sequence



in which X is an electronegative substituent. This sequence breaks down with systems in which the stage of coordination of the diene with the transition metal begins to play a significant part. Table 6 gives data on copolymerisation constants of dienes in various systems. In most cases butadiene is more active than alkylated dienes, which is typical of anionic active centres, but $r_1 = r_2$ in several systems ($R_3Al–TiCl_4$, $R_2AlCl–CoCl_2$, and "chromium" systems) or even $r_2 > r_1$ in the copolymerisation of butadiene with cyclohexadiene effected by π-allyl complexes of nickel. Passage from a butadienyl (A) to an isoprenyl (B) and especially a pentadienyl (C) π-allyl centre



(A) (B) (C)

is extremely advantageous, since the stability of the organometallic compound increases in this sequence. Low values of $r_2$ for pentadiene and isoprene on copolymerisation with butadiene indicate that steric factors in the stage of coordination of the monomer on the transition metal are probably of decisive importance for the reactivity.

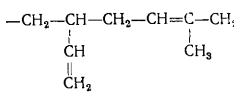
The most interesting feature of copolymerisation in coordination systems is the mutual influence of monomers on the character of the stereoregulation. This phenomenon, observed by many workers [104–106,121,122,128] and directly connected with the nature of the active centres and the mechanism of formation of units in them, can be illustrated by a few examples (Table 7). In the $R_2AlCl–CoCl_2$ system the entry of alkylated butadiene derivatives into the chain

Table 7. Microstructure of butadiene units in copolymers [121].

| Catalytic system | Second monomer (m2) | Copolymer $m_2$, mole % | Microstructure of butadiene part of chain, % | | |
|---|---|---|---|---|---|
| | | | *cis*-1,4 | *trans*-1,4 | 1,2- |
| $R_2AlCl—CoCl_2$ | isoprene | 0 | 94 | 3 | 3 |
| | isoprene | 32 | 75 | 7 | 18 |
| | isoprene | 53 | 58 | 3 | 39 |
| | 2,3-dimethylbutadiene | 27 | 44 | 7 | 49 |
| | 2,3-dimethylbutadiene | 41 | 26 | 6 | 68 |
| | penta-1,3-diene | 41 | * | * | 20 |
| | penta-1,3-diene | 53 | * | * | 50 |
| $R_3Al—TiI_4$ | isoprene | 0 | 90 | 6 | 4 |
| | isoprene | 31 | 49 | 37 | 12 |
| | isoprene | 66 | 41 | 40 | 14 |
| | 2,3-dimethylbutadiene | 35 | 76 | 19 | 5 |
| $(π\text{-RNiCl})_2 \cdot TiCl_4$ | isoprene | 0 | 90 | 8 | 2 |
| | isoprene | 10 | 77 | 19 | 4 |
| | isoprene | 26 | 71 | 24 | 5 |
| | isoprene | 68 | 50 | 39 | 11 |

*The remainders are the sums of *cis*-1,4 and *trans*-1,4 units.

is accompanied by a corresponding increase in the proportion of 1,2-butadiene units instead of the *cis*-units characteristic of a butadiene homopolymer. A decrease is observed in the number of 3,4-isoprene units relative to polyisoprene obtained on the same catalyt [104–106,121,128]. Hence linking butadiene and isoprene units in the copolymer have the structure



In the $R_3Al–TiI_4$, $R_3Al–TiI_2Cl_2$, and π-RNiX–Acceptor systems the same monomers convert the *cis*-butadiene units predominantly into *trans*-units. Similar effects are produced by electron-donating additives (ethers, esters, sulphides, amines) in the homopolymerisation of butadiene. In the $R_2AlCl–CoCl_2$ system they cause an increase in the number of 1,2-units, but in the other systems they increase the quantity of *trans*-units [129–136].

Chromium-containing systems enable stereoregular *trans*-copolymers of butadiene and isoprene to be obtained in which the structure of the units in the homopolymers is preserved. With *cis*-regulating nickel systems statistical *cis*-copolymers of butadiene and cyclohexadiene can be obtained, for which pair of monomers [36] $r_2 > r_1$.

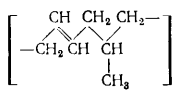
As noted above, oxygen-containing compounds increase considerably the content of 3,4-, 1,2-, and *trans*-units in the polymerisation of butadiene and isoprene under the influence of organotitanium(IV) compounds. In most cases

the change in stereospecificity in the presence of electron-donating components is accompanied by a considerable decrease in the rate of polymerisation, probably due mainly to the equilibrium

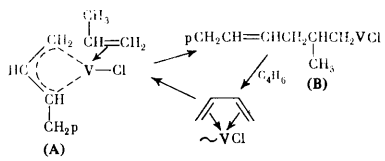
$$\overset{\text{Donor}}{\underset{\downarrow}{\text{pMX}_n}} + \text{Diene} \rightleftarrows \overset{\text{Diene}}{\underset{\downarrow}{\text{pMX}_n}} + \text{Donor} .$$

With sufficiently high concentrations of solvating components or in the case of bidentate complexing additives polymerisation ceases.

In the presence of certain oxygen-containing components at low temperatures systems containing organoaluminium compounds with vanadium and titanium halides yield[22,23] an alternating copolymer in which the butadiene units are mainly in the *trans*-configuration.



With strict alternation of butadiene and propylene units, and the same type of structure for the former, the repeating units in the main polymer chain will contain six carbon atoms instead of the four in natural rubber and in stereoregular polymers of dienes. Vanadium is assumed[22,23] to be bivalent in the active centre, and the mechanism of the process to be



In the $\pi$-allyl complex (A) vanadium retains one coordination position, which is occupied by the alkene. After the latter has entered the chain (B), bidentate coordination of the diene becomes possible. In this way a self-regulating system is established for alternation of the monomers.

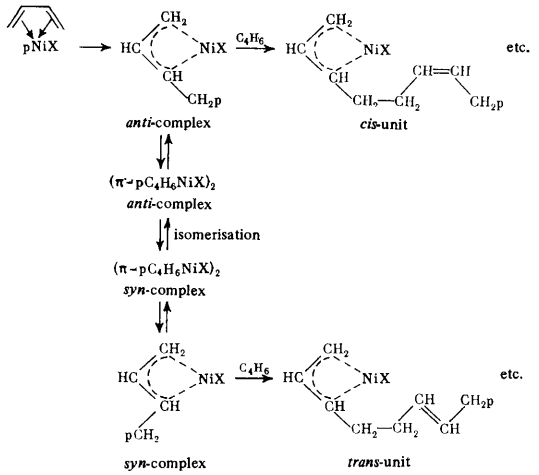
## 6. Mechanism of Stereoregulation

### (*a*) Mechanism of formation of *cis*- and *trans*-units

As noted above, the primary addition of butadiene to HNiX yields an *anti*-complex, which then isomerises into a *syn*-complex. The hydrogenolysis of $\pi$-but-2-enylnickel chloride, obtained from but-2-enyl chloride and nickel carbonyl, forms 95% of *trans*-butene with but-1-ene completely absent[58]. Hence the content of the *syn*-form at equilibrium is close to 100%. The rate of *anti–syn* isomerisation of the complex depends, of course, on the nature of the metal and of the ligands. A diene coordinates with a transition metal always as a bidentate ligand: as a unidentate ligand it would give way to the more basic monoenes. This factor is probably decisive in the formation of alternating copolymers of dienes with alkenes: in the presence of two vacancies the diene is coordinated preferentially, but in the presence of one vacancy the alkene. The especially advantageous character of bidentate coordination is illustrated by the fact that compounds of the type $-OCH_2CH_2O-$ or $\rangle NCH_2CH_2N\langle$ on coordination polymerisation are tenfold as effective as oxolan and other solvating agents in influencing the kinetics of polymerisation and the microstructure of the chain. The considerably higher activity of conjugated dienes than of styrene in copolymerisation under the influence of transition-metal compounds and of organolithium compounds in hydrocarbon medium is due to preferential coordination of the diene. In the suggested mechanism of stereoregulation dienes are coordinated as bidentate ligands in a cisoid configuration. We shall first consider systems exhibiting a fractional kinetic order with respect to the catalyst.

The rate of polymerisation of butadiene under the influence of $\pi$-RNiHal is proportional to the square root of the catalyst concentration[70]. Hence polymerisation takes place only on the monomeric forms $\pi$-RNiHal in equilibrium with the main dimeric form $(\pi\text{-RNiHal})_2$, which is not involved in the polymerisation. A dimeric state has been demonstrated[50] for the $\pi$-allyl and $\pi$-but-2-enyl complexes $\pi$-RNiHal.

Primary entry of the diene into the active centre leads to an *anti*-complex, from which the unit is then displaced into the chain as a *cis*-unit. Processes of *anti–syn* isomerisation occur mainly in the "sleeping" dimeric associate, which is not involved in polymerisation. This probably applies also to the polymerisation of dienes under the influence of organolithium compounds in hydrocarbon solution. It is well known that alkyl derivatives of lithium are present as association complexes in hydrocarbon solution. Numerous investigations have shown[137–140] that "live" polymeric organolithium compounds are present in hydrocarbon medium as the association complexes $(pLi)_n$, where $n = 2$ for styrene and $n = 4$ for butadiene and isoprene, the rate of polymerisation being proportional to the concentration $[pLi]^{1/n}$. Hence the ligitimate conclusion was drawn that the stage of chain growth involves the monomeric form of the organolithium compound, whose proportion at equilibrium is extremely small, and that association complexes are not appreciably involved in polymerisation. Recent investigations have shown[141,142] that the microstructure of polybutadiene and polyisoprene depends on the concentration of the organolithium compound in solution, and that *cis*-stereoregulation occurs at vanishingly low concentrations of the latter (Table 8).



The degree of dissociation of the association complexes $(pLi)_n$ into the monomeric forms increases with dilution and with rise in temperature. This suggests that *cis*-units are formed only in the monomeric form pLi, but other types of units in associated forms of pLi, in which the carbon–metal bond is more strongly polarised. The autosolvation effect in association is due to enhancement of the polarity of this bond, and the participation of association complexss in polymerisation should yield structures typical of solvates of pLi with electron-donating

components. It has recently been shown[143] that the polymerisation of dienes from the vapour phase on crystalline ethyl-lithium is very slow, with preferential formation of 3,4-, 1,2-, and *trans*-units. It is therefore highly probable that stereoregulation during polymerisation in hydrocarbon media is accomplished by the scheme[144]

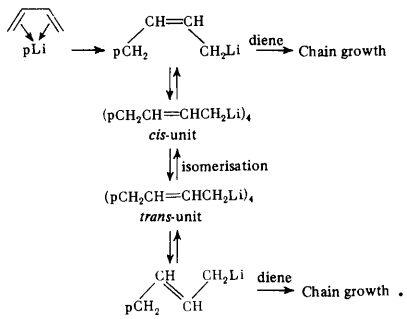
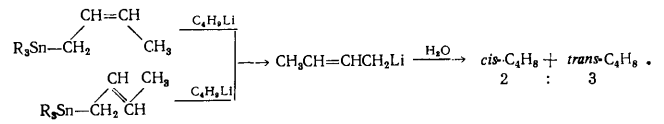



Table 8. Effect of RLi concentration on chain microstructure (in n-heptane at 20°C).

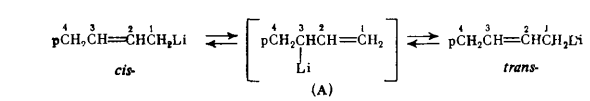
| Monomer | [RLi], M | Microstructure of chain, % | | | | Ref. |
|---|---|---|---|---|---|---|
| | | *cis* | *trans* | 1,2- | 3,4- | |
| Isoprene | 0.061 | 74 | 18 | — | 8 | 141 |
| | 0.001 | 78 | 17 | — | 5 | 141 |
| | 0.0001 | 84 | 11 | — | 5 | 141 |
| | 0.00008 | 97 | — | — | 3 | 141 |
| Butadiene | 0.073 | 30 | 46 | 24 | — | 141 |
| | 0.0124 | 44 | 46 | 10 | — | 141 |
| | 0.0003 | 47 | 45 | 8 | — | 141 |
| | 0.000054 | 70 | 28 | 2 | — | 141 |
| | 0.00001 | 86 | 10 | 4 | — | 142 |

Decomposition with water of but-2-enyl-lithium, formed from butyl-lithium and *cis*- or *trans*-but-2-enyltrialkyltin in ether, is a mixture of *cis*- and *trans*-butenes[145] in the proportion 2 : 3:

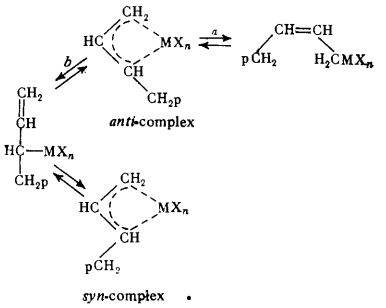



This ratio of *cis*- and *trans*-units, corresponding roughly to the composition of polybutadiene obtained under the same conditions, is probably close to the equilibrium value for the but-2-enyl-lithium–diethyl ether solvate.

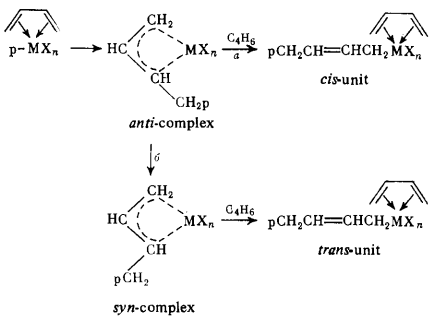
The maximum tendency to coordinate develops on the monomeric forms of pLi (and pNiX), and the diene behaves as a bidentate ligand. Primary acts of addition to the monomeric form of pLi yield a *cis*-unit, but formation of other types of structure is due mainly to isomerisation of the active centre in association complexes, although the latter may to some extent be involved in polymerisation with formation of secondary structures (3,4-, 1,2-, and *trans*-units). Isomerisation of a unit in a solvate would probably involve a stage of migration of lithium to the third carbon atom from the end of the chain




since direct *cis*–*trans* transitions are improbable. In association complexes lithium is able to migrate as a result of intermolecular transitions. The probability of isomerisation in solvates and aggregates increases with the polarisation of the carbon–lithium bond and the degree of charge delocalisation. A content of ~5–10% of 1,2- and 2,3-units when butadiene and isoprene are polymerised under the influence of RLi in hydrocarbon media indicates the presence of reactive structures (A) during polymerisation. An analogy exists between *cis*–*trans* isomerisation during anionic polymerisation and *anti*–*syn* transitions in π-allyl complexes of transition metals. In the latter case isomerisation can evidently take place only through π–σ transitions:




The π–σ equilibrium (*b*) leads to *anti*–*syn* isomerisation. Most catalytic systems based on compounds of transition metals are characterised by the kinetic first order of polymerisation with respect to the catalyst, and the whole of the catalyst, present mainly in the monomeric state, usually takes part in acts of chain growth. In this case the ratio of *cis*- and *trans*-units in the chain should be determined by the ratio of rates of chain growth on the active centre (reaction *a*) and of *anti*–*syn* (*cis*–*trans*) isomerisation of the active centre (reaction *b*):




Although there are at present no direct quantitative data on *anti*–*syn* isomerisation processss, several experimental rules are consistent with the above mechanism of stereoregulation.

(*b*) Effect of monomer concentration on chain microstructure

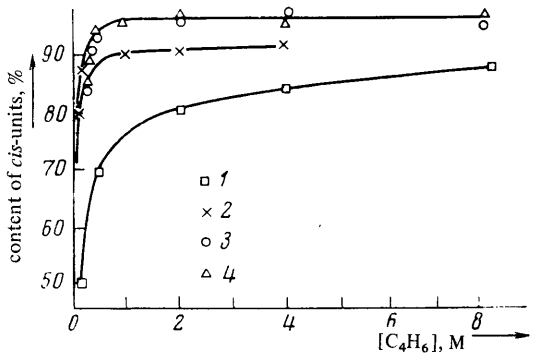
It follows from the above scheme that, in *cis*-regulating catalytic systems in which the rate of chain growth is proportional to the monomer concentration, fall in the latter should be accompanied by increase in the quantity of *trans*-units. The influence of butadiene concentration on chain microstructure has been studied[146,147] in various systems

1) $R_3Al + TiI_2Cl_2$ 2) $R_2AlCl + CoCl_2$
3) π-RNiCl · $(CCl_3COO)_2Ni$ 4) π-RNiOCOCF$_3$

characterised by first-order polymerisation with respect to the monomer. Systems (1) and (2) are of Ziegler type

and the individual organonickel compounds (3) and (4) are stereoselective for the *cis*-polymerisation of butadiene.

The diagram shows that at low monomer concentrations the quantity of *trans*-units increases considerably at the expense of *cis*-units in all cases. Such *cis–trans* conversion can be explained by variation in the relative rates of chain growth and isomerisation. In cases in which the monomer undergoing coordination affects also the rate of *anti–syn* isomerisation no relation may be observed between monomer concentration and chain microstructure.




Dependence of content of *cis*-1,4 units in polybutadiene on initial concentration of butadiene in the presence of: 1) $TiI_2Cl_2$ + (iso-$C_4H_9)_3Al$; 2) $CoCl_2$ + $R_2AlCl$; 3) $\pi$-$C_5H_9$. .NiCl.Ni$(OCOCCl_3)_2$; 4) $\pi$-$C_3H_5NiOCOCF_3$.

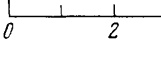
(*c*) Relative rates of chain growth in *cis*- and *trans*-regulating systems

Previous investigations in our laboratory of individual organometallic compounds—of titanium, nickel, chromium, niobium, and cobalt—have shown that all kinds of microstructures can be produced with high selectivity on the same transition metal depending on the nature of the ligands surrounding it[48,49,60,61,63]. From the suggested scheme of stereoregulation it might have been expected that on a given metal *cis*-regulating systems would generally be characterised by considerably higher rates of chain growth than would *trans*-regulating systems. Relative rates of chain growth have been compared[148] in such systems based on chromium(III), nickel(II), and titanium(IV) compounds.

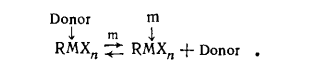
The polymerisation of dienes under the influence of the active centre $R_2Cr–O–|SiO_2$, resulting from the interaction of $\pi$-$R_3Cr$ with hydroxy-groups or ignited aluminium silicate, takes place by a mechanism of "live" chains and yields *trans*-polymers[30–32]. The molecular weight of the polymer is given by the formula $M_b = m/2n$, where $m$ is the quantity of monomer polymerised and $n$ the concentration of the organochromium compound. The active centre formed from $\pi$-$R_3Cr$ and ignited aluminium oxide is a catalyst for *cis*-polymers of isoprene and butadiene. A characteristic feature of this system is the formation of products of very high molecular weight at low degrees of conversion, as a consequence of the high rate of chain growth.

Comparison of molecular weights at a low degree of conversion indicates the ratio $v_a/v_b$ of the rates of chain growth in the systems (Table 9). Published kinetic data[43,56,57,70] have been used to calculate such ratios for nickel and titanium compounds. For systems in which the rate of polymerisation was proportional to the square root of the concentration of the transition metal it was arbitrarily assumed that the quantity of monomeric active centres was 1% of the total quantity of catalyst. Table 9 shows that with a given transition metal inversion of stereospecificity from *cis*- to *trans*-regulating is accompanied by a sharp drop in the rate of chain growth. Any factors tending to "jam" the end-group of a growing chain in an active centre entail increase in the proportion of *anti–syn* isomerisation and hence in the content of *trans*-units in the polymers.

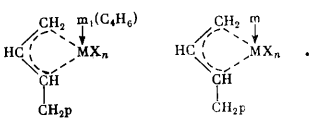
Table 9. Ratio of rates of growth in *cis*- and *trans*-regulating systems.

| No. | Catalytic system | Monomer | Microstructure, % | | | | $v_a/v_b$ |
|---|---|---|---|---|---|---|---|
| | | | *cis* | *trans* | 1,2- | 3,4- | |
| 1a |  | isoprene | 95 | 0 | 0 | 5 | ~$10^3$ |
| 1b |  | isoprene | 0 | 95 | 0 | 5 | |
| 2a | $\pi$-RNiCl·$(CCl_3COO)_2Ni$ | butadiene | 97 | 0 | 3 | — | $7.8\cdot10^2$ |
| 2b | $(\pi\text{-RNiI})_2$, $v=k[Ni]^{0.5}$ | butadiene | 0 | 95 | 5 | — | |
| 3a | $(C_6H_5CH_2)_3TiI$, $v=k[Ti]^{0.5}$ | butadiene | 95 | 2 | 3 | — | $7.4\cdot10^3$ |
| 3b | $(C_6H_5CH_2)_4Ti$ | butadiene | 20 | 20 | 60 | — | |

The inversion of stereospecificity from *cis* to *trans* under the influence of electron-donating compounds coordinated with the transition metal is evidently due to increase in the "lifetime" of the terminal unit in conformity with the equilibrium




As noted above, such inversion is accompanied by a considerable decrease in the rate of polymerisation. The mutual influence of monomers on chain microstructure in coordination copolymerisation observed in several investigations can be explained, in terms of the above mechanism of stereoregulation, by variation in the rate of entry of the monomers into the chain

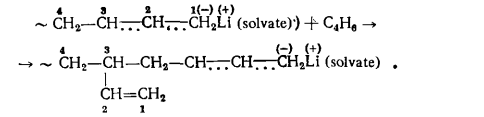



If the rate of entry of $m_2$ (isoprene, pentadiene, etc.) is lower than the rate of entry of butadiene, the "lifetime" of the terminal $\pi$-but-2-enyl unit is increased, as well as the probability of *anti–syn* isomerisation.

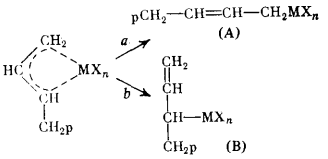
(*d*) Mechanism of formation of 1,2- and 3,4-units

Numerous investigations have established that organolithium compounds in the presence of various solvating compounds (oxolan, etc.), and organopotassium and organosodium compounds in hydrocarbon media, lead to

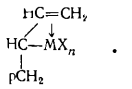
preferential formation of 1,2- and 3,4-units in the polymerisation of dienes [149-154]. Nuclear magnetic resonance spectroscopy in perdeutero-oxolan has been used [155,156] to study the charge distribution in the terminal unit of polybutadienyl-lithium and polyisoprenyl-lithium. In the absence of the monomer the charge in "live" chains is localised mainly on the terminal carbon atom. In the formation of 1,2- and 3,4-units, however, the reaction centre is established on the third carbon atom from the end of the chain:



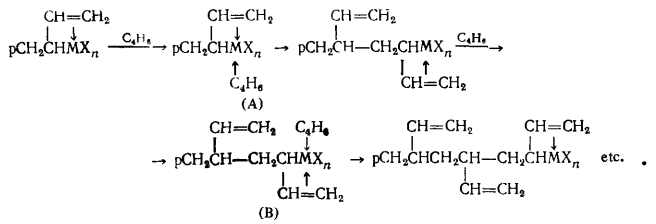
In model reactions with water, alcohol, and other compounds the but-2-enyl anion reacts in conformity with the charge distribution to form an equilibrium mixture of butenes containing only ~3% of but-1-ene. [116,117,157] Hence migration of the reaction centre to the third carbon atom evidently occurs under the influence of the monomer. A similar effect is probable in the radical polymerisation of dienes, since the content of 1,2- and 3,4-units in the polymers considerably exceeds the equilibrium value and is independent of the temperature of polymerisation, whereas the ratio of *cis*- and *trans*-structures varies with temperature, approaching the equilibrium value. As noted above, formation of a carbon–metal σ-bond precedes entry of the monomer into the chain in coordination systems:



The formation of 1,2- and 3,4-units evidently corresponds to the case in which the α-form (B) is more advantageous than (A), which may be favoured by coordination of the transition metal with electron-donating solvating components, as in "cobalt" catalytic systems, and by the formation of π-complexes of vinyl groups with the transition metal



This provides an explanation for the preferential formation of syndiotactic units in the polymerisation of butadiene under the influence of various compounds of transition metals—cobalt, molybdenum, tungsten:



The complexes (A) and (B), formed alternately during chain growth, differ sterically in the position of the π-coordinating double bonds and the monomer. With π-allyl complexes of molybdenum crystalline syndiotactic 1,2-polybutadiene is formed [38-40]. It is noteworthy also that poly-π-allyl complexes of general formula $\pi$-$R_nM$ usually cause predominant formation of 1,2-units, as has been shown for

$(\pi\text{-}C_3H_5)_4Cr$ [60,61], $(\pi\text{-}C_5H_9)_2Cr$ [29], $(\pi\text{-}C_4H_7)_3Ti$ [158], $(\pi\text{-}C_5H_9)_3Ti$ [24], $(\pi\text{-}C_3H_5)_3Nb$ [48].

An exception is $\pi$-$R_3Rh$, which is stereospecific for the production of *trans*-units [48].

## III. CLEAVAGE OF CYCLOALKENES

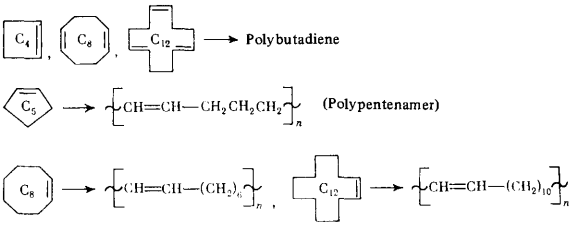
### 1. Mechanism of Dismutation

The cleavage of cycloalkenes is a novel route in coordination catalysis, revealing prospects for the synthesis of rubbers and other polymeric materials that cannot be obtained by the usual methods of polymerisation. The reaction was first described in Refs. 159 and 160. For some time the study of coordination catalysis developed in parallel and independently in the dismutation of alkenes and in the cleavage of cycloalkenes, until their completely identical nature was established with the possibility of initiation by the same systems. The catalysts used consisted mainly of organoaluminium compounds and halides of certain transition metals (tungsten, molybdenum, etc.). These catalytic systems (individual examples are given in Table 10) are closely similar in composition to Ziegler catalysts used for the stereospecific polymerisation of dienes and alkenes, but ineffective for the cleavage of cycloalkenes. An indispensable condition for Ziegler catalysis is formation of an organometallic compound in which chain growth takes place at the carbon–metal bond. It will be shown below that the cleavage of cycloalkenes and the dismutation of alkenes involve a new type of active centres.

Table 10. Systems used for the dismutation of alkenes and the cleavage of cycloalkenes.

| Catalytic system | Ref. | Catalytic system | Ref. |
|---|---|---|---|
| $RAlCl_2+MoCl_3(NO)_2\cdot(PPh_3)_2$ | 161 | $R_4Sn+WCl_6$ | 166 |
| $RAlCl_2+WCl_2(NO_2)\cdot(PPh_3)_2$ | 161 | $R_2Al+ReCl_5$ | 167 |
| $RAlCl_2+WCl_6$ | 162, 163 | $Mo(CO)_6+Al_2O_3$ | 168 |
| $R_3Al(R_2AlCl)+WCl_6$ | 164 | $MoO_3/Al_2O_3$ | 168 |
| $R_3Al+MoCl_5$ | 164 | $Re_2O_7/Al_2O_3$ | 169 |
| $RLi+WCl_6$ | 165 | | |

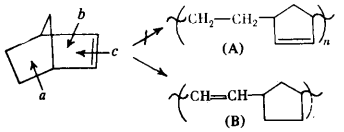
The polymerisation of cycloalkenes with homogeneous systems, which occurs very rapidly at low temperatures, yields products of high molecular weight that preserve the unsaturation of the initial cycloalkene:



The cleavage of cyclobutene, cyclo-octadiene, and cyclododecatriene yields polybutadiene. The possibility of obtaining *cis*-polybutadiene from cyclo-octadiene attracted the attention of research workers in connection with the

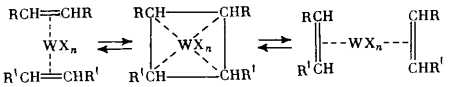
small heat of reaction (~8 kcal mole$^{-1}$). The fission of cyclopentene results in *cis*- and *trans*-polymers containing chains of five carbon atoms in the repeating unit and exhibiting rubberlike elasticity [170]. Depending on the ratio of *cis*- and *trans*-units either amorphous rubbers or crystalline *trans*-polymers melting at 73 and 83°C respectively are obtained from the cleavage of cyclo-octene and cyclododecene. The copolymerisation of different rings gives amorphous rubbers containing after completion of the reaction a random distribution of monomeric units in proportions corresponding to the composition of the initial mixture of monomers, independently of their relative reactivities. The reason is that the unsaturated polymer molecule also takes part in redistribution reactions [171-174].

It was supposed initially that cleavage of a cycloalkene results from rupture of a carbon–carbon bond adjacent to the double bond [175]. A study of the structure of polynorbornene.

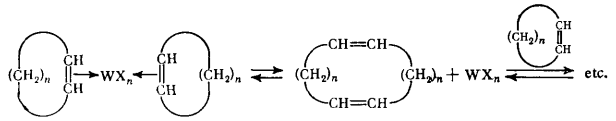



was adduced in support of such a mechanism. Cleavage of norbornene with rupture of a carbon–carbon bond in direction (*a*) should lead to formation of a polymer containing unsaturated five-membered rings (structure A). From the usual ideas on the nature of active centres of radical and ionic character it might have been assumed that this mode of rupture was the most advantageous, for the active centre would then be conjugated with the double bond. However, experimental data showed that the polymer had structure (B), which led to the conclusion [175] that the reaction followed path (*b*). It has since been established unambiguously [176,177] that ring cleavage takes place in direction (*c*): i.e. the polymerisation of cycloalkenes with ring fission is a particular case of the general reaction of alkene dismutation.

The mechanism suggested [178] for the dismutation of alkenes involved the formation of a "quasi-cyclobutane" intermediate complex of two alkene molecules in the coordination sphere of the transition metal:



This mechanism was transferred [179] to the polymerisation of cycloalkenes:




The above scheme entails a stepwise mechanism of polymerisation, in which dimers, trimers, etc. of comparable reactivity with the initial monomer (in the case of relatively unstrained rings) are formed successively. Hence in the initial stage of polymerisation the reaction system should comprise mainly oligomeric products of low molecular weight.

A chain process differs fundamentally from a stepwise process in the possible formation of products of high molecular weight even in the earliest stage of polymerisation, with a low yield of oligomeric forms. However, investigations of the polymerisation of various cycloalkenes have shown [173,174,180,181], that at the very start of the process—at degrees of conversion of 5–10%—polymers of very high molecular weight are formed (Table 11). The quantity of oligomeric products is small, and they are formed not by polymerisation but by cyclodegradation of polymers. Initial formation of products of high molecular weight is an indication of a chain mechanism and the appearance of extremely active centres effecting the chain process [173,174,182,183]. This conclusion must evidently be extended to the dismutation of alkenes. It is necessary to examine the individual stages of this process.

Table 11. Intrinsic viscosities of polymers obtained from cycloalkenes [173,177,180,181].

| Cycloalkene | Catalytic system | Conversion, % | $[\eta]$, dl g$^{-1}$ |
|---|---|---|---|
| Norbornene | $AlBr_3$—$WCl_6$—thiophen | 13 | 5.5 |
| | $(iso\text{-}Bu)_3Al$—$WCl_6$ | 11 | 2.4 |
| | $(iso\text{-}Bu)_2AlCl$—$WCl_6$ | 9 | 1.8 |
| Cyclopentene | $Si(C_6H_5)_4$—$WCl_6$ | 7.5 | 6.0 |
| | $LiCH_2SiMe_3$—$WCl_6$ | 15 | 5.0 |
| | $PhCHN_2$—$WCl_4$ | 10 | 7.8 |
| Cyclo-octa-1,5-diene | $AlBr_3$—$WCl_6$—thiophen | 12 | 2.3 |
| | $(iso\text{-}Bu)_3Al$—$WCl_6$ | 11 | 1.5 |
| | $(iso\text{-}Bu)_2AlCl$—$WCl_6$ | 12 | 0.9 |
| | $PhCHN_2$—$WCl_6$ | 6 | 4.2 |
| Cyclo-octene | $(iso\text{-}Bu)_2AlCl$—$WCl_6$ | 10 | 0.8 |
| Cyclododecene | $(iso\text{-}Bu)_2AlCl$—$WCl_6$ | 5 | 0.7 |

Table 12. Polymerisation of cycloalkenes under the influence of carbene complexes (at 20°C).

| Catalytic complex | Monomer (m) | $\frac{[m]}{[W]}$ | $\frac{[RCHN_2]}{[W]}$ | Duration of reaction, min | Yield of polymer, % | $[\eta]$, dl g$^{-1}$ |
|---|---|---|---|---|---|---|
| $C_6H_5CH:WX_n$ | cyclopentene | $10^3$ | 0.1 | 1 | 18.2 | 9 |
| | cyclopentene | $10^2$ | 0.005 | 1 | 10 | 7.8 |
| | cyclo-octa-1,5-diene | $5\cdot10^2$ | 0.01 | 1 | 6 | 4.2 |
| $C_2H_5OCOCH:WX_n$ | cyclopentene | $10^3$ | 1 | 15 | 65 | 0.77 |
| | cyclopentene | $10^3$ | 0.2 | 20 | 62 | 0.82 |
| | cyclo-octa-1,5-diene | $5\cdot10^3$ | 3 | 20 | 62 | 1.33 |

## 2. Initiation

All hitherto known active centres for chain polymerisation—free radicals, ions, ion-pairs, the usual coordination systems involving organometallic compounds—are ineffective for the cleavage of cycloalkenes and the dismutation of alkenes. We have undoubtedly met active centres of a novel type in the chain cleavage of cycloalkenes, which were regarded hypothetically [182,183] as complexes of carbenes with transition metals. An argument in support of their carbene nature was the formation of cyclopropane and methylcyclopropane when ethylene was kept over a dismutation catalyst [168]. Experimental results have been cited [180,184] that can be regarded as direct proof that monocarbene complexes are able to initiate the chain cleavage of cycloalkenes. The decomposition of phenyldiazomethane and ethyl diazoacetate in the presence of tungsten chlorides initiates the chain cleavage of cyclopentene and cyclo-octadiene with the formation of polymers of very high molecular weight. In the case of phenyldiazomethane the reaction occurs almost instantaneously at room temperature (Table 12).

The decomposition of diazo-compounds in the presence of salts of copper and certain other metals is a classical method for obtaining carbenes. The formation of products of very high molecular weight ($[\eta] = 4$–$9$ dl g$^{-1}$) indicates that the reaction involves very small quantities of long-lived active centres. Ordinary carbenes are extremely reactive in solution, adding non-selectively at C–H, C=C, etc. bonds. Their reactivity diminishes in the sequence

$$RCH:,\ C_6H_5CH:,\ (C_6H_5)_2C:,\ ROC(=O)CH:,\ (ROC(=O))_2C:\ \text{etc.}$$

In several cases carbenes exhibit roughly the same selectivity on incorporation at tertiary, secondary, and primary carbon–hydrogen bonds [185] as do alkyl free radicals in abstracting the hydrogen atom.

Carbenes are stabilised to the greatest extent by coordination with transition metals. Thus many complexes of carbenes with zero- or uni-valent metals—chromium(0), molybdenum(0), tungsten(0), tellurium(0), manganese(I), rhenium(I), rhodium(I)—containing one or two oxygen, nitrogen, or sulphur atoms at the reaction centre $(RO)_2C:M$ are crystalline compounds stable at ordinary temperatures [186,187]. This indicates that coordination with a transition metal is energetically favourable to the formation of carbenes. The selectivity of carbene active centres towards the cleavage of cycloalkenes and the dismutation of alkenes is evidently connected primarily with their stabilisation on the transition metal.

The main types of redox systems involving transition metals and generating free radicals are well known:

$$\left.\begin{aligned} &ROOH + M^n \rightarrow M^{n+1} + RO^{\cdot} + OH^-\\ &ROOH + M^{n+1} \rightarrow M^n + RO_2^{\cdot} + H^+\\ &ROH + M^{n+1} \rightarrow M^n + RO^{\cdot} + H^+\\ &RH + M^{n+1} \rightarrow M^n + R^{\cdot} + H^+ \end{aligned}\right\} \quad (1)$$

$$A + M^{n+2} \rightarrow M^n + B: \quad (2)$$

The formation of free radicals (1) involves one-electron transitions in the course of oxidation or reduction of the metal. Reaction scheme (2) entails the possible formation of a carbene centre by the transfer of two electrons in a single step. Such a redox system, effective for the polymerisation of cycloalkene down to −70°C, has been studied [181,188] in the reactions of certain organolithium compounds—trimethylsilyl- and trimethylgermanyl-methyl-lithium—with tungsten hexachloride. The composition of the reaction products in benzene and $\alpha\alpha\alpha$-trideuterotoluene at 20°C is indicated [181,188] in Table 13. The appearance of trimethylsilyl and trimethylgermanyl chlorides is due to decomposition of an organotungsten compound accompanied by formation of a carbene complex:

$$(CH_3)_3Si\,(Ge)\,CH_2WCl_5 \rightarrow$$
$$(CH_3)_3Si\,(Ge)\,Cl + [CH_2:WCl_4]\ .$$

The absence of deuteromethyltrimethylsilane on decomposition in $\alpha\alpha\alpha$-trideuterotoluene indicates that formation of this compound does not involve the trimethylsilylmethyl radical, which may result from homolytic breakdown of the organotungsten compound. Tetramethylsilane and tetramethylgermane may result [181,188] from disproportionation of two groups:

$$(CH_3)_3SiCH_2{-}WCl_4{-}CH_2Si(CH_3)_3 \rightarrow (CH_3)_4Si + [(CH_3)_3SiCH:WCl_4]\ .$$

This correlates with the increase in the yield of tetramethylgermane produced by raising the ratio of organolithium compound to tungsten(VI) chloride (Table 13).

The systems usually employed for the cleavage of cycloalkenes and the dismutation of alkenes—carbene active centres—can be formed in particular by isomerisation of the $\pi$-alkene complex:

$$\begin{matrix} RCH \\ \| \\ RCH \end{matrix} \rightarrow MX_n \longrightarrow \begin{matrix} RC:MX_n \\ | \\ RCH_2 \end{matrix}\ .$$

Such a scheme was suggested [189] to explain the formation of certain stable carbene complexes of platinum. Lower chlorides of tungsten (IV and V) by themselves initiate the polymerisation of cyclopentene when the catalyst is exposed to ultraviolet radiation [190]. The above mechanism for the generation of carbenes may operate in this case. In systems containing alkylating organic compounds of aluminium, tin, or other metals a carbene complex may be produced by the reaction

$$CH_3CH_2WCl_5 \rightarrow CH_3CH:WCl_4 + HCl \xrightarrow{R_3AlCl} RH + RAlCl_2\ .$$

This mode of decomposition can occur only in systems in which carbene formation becomes energetically advantageous as a consequence of stabilisation by coordination with a transition metal. Alkyl derivatives of many other transition metals—nickels, chromium, cobalt, etc.—break down [45,191,192] by a mechanism of disproportionation:

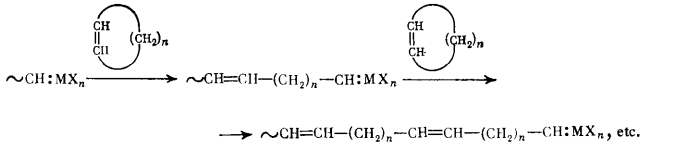
$$2RMX_n \rightarrow 2MX_n + R_{-H} + R_{+H}\ .$$

Table 13. Composition of reaction products.

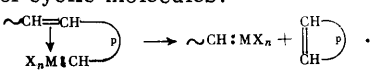
| RLi / $WCl_6$ | Products isolated | Yield from RLi, mole %, in $C_6H_6$ | Yield from RLi, mole %, in $C_6H_5CD_3$ |
|---|---|---|---|
| 1:1 | $(CH_3)_3SiCl$ | 29—33 | 25 |
| | $(CH_3)_4Si$ | 24—26 | 28 |
| 1:1 | $(CH_3)_3GeCl$ | 44 | — |
| | $(CH_3)_4Ge$ | 11 | — |
| 2:1 | $(CH_3)_3GeCl$ | 34.5 | — |
| | $(CH_3)_4Ge$ | 24.0 | — |

## 3. Mechanism of Chain Growth

A mechanism suggested [180,182,183] for chain growth under the influence of carbene complexes

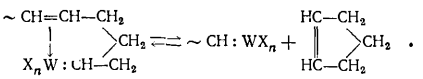


involves the formation of linear polymer molecules. As the monomer concentration decreases, reaction of the carbene active centre with double bonds in the chain itself becomes more probable, leading to degradation and the formation of cyclic molecules:



In cases in which complex formation between the transition metal and the nearest double bond in the polymer chain is sterically highly probable, a polymer–monomer

equilibrium is established, as has been found for cyclopentene [193]:



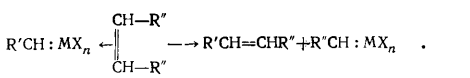
The position of equilibrium depends on the structure of the terminal unit. It lies closer to the monomer in the case of a *cis*-unit than with a *trans*-unit [194]. *cis*-Polypentenamer has been obtained under the influence of the system comprising tetra-allylsilane and tungsten hexachloride. With other cycloalkenes reaction of the active centre with a double bond in the actual chain yields a set of unstrained oligomeric cyclic molecules, the proportion of which increases with fall in the concentration of monomer and polymer in the solution. In dilute solutions linear polybutadiene of high molecular weight and polycyclo-octadiene undergo rapid cyclodegradation in the presence of above catalysts to form a set of cyclic oligomeric molecules (Table 14) [171,172,195]. In several systems equilibrium is established within 10–15 min, its position being determined by the polymer concentration in the solution. Cyclodegradation is characterised by the formation of oligomers having a very wide molecular-weight distribution ($\bar{M}_w/\bar{M}_n > 4$), which is consistent with results obtained by Stockmayer et al. [196] for ester polycondensation.

| Catalytic system | Polymer | Polymer concn., wt.% | $\bar{M}_n$ of initial polymer | Time, min | $\bar{M}_n$ of polymer |
|---|---|---|---|---|---|
| $WCl_6$—$EtAlCl_2$ | *cis*-polybutadiene | 4 | 127 000 | 120 | 3 400 |
| $WCl_6$—$EtAlCl_2$ | *cis*-polybutadiene | 8 | 220 000 | 25 | 9 000 |
| $W(OR)_2Cl_4$—$EtAlCl_2$ | *cis*-polybutadiene | 8 | 220 000 | 30 | 1 000 |
| $W(OR)_2Cl_4$—$EtAlCl_2$ | polyoctadienamer | 8 | $[\eta] = 2.5$ | 30 | 0.20 dl g$^{-1}$ |

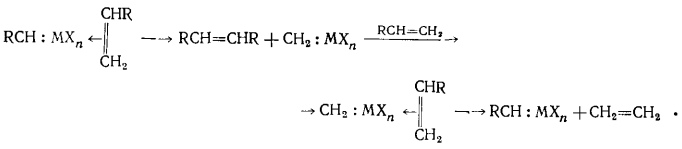
The general rules of the usual processes of radical or ionic copolymerisation are determined by the relative reactivities of the monomers and the corresponding active centres. No data are yet available that would enable us to estimate the relative reactivities of different carbenes coordinated with a transition metal. The nature of the active centres remains unchanged during the copolymerisation of unsubstituted cycloalkenes, since their entry into the chain is always accompanied by regeneration of the same type of active centre $\sim CH : MX_n$. According to their relative reactivities on copolymerisation $r_1$ and $r_2$ these compounds form the sequence [197–199]



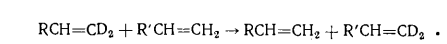
The dismutation of unbranched alk-2-enes, like the copolymerisation of cycloalkenes, involves carbene centres of the same type without thermal effects:



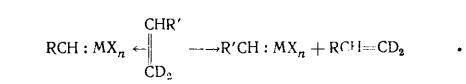
Under the influence of homogeneous catalytic systems this reaction is extremely rapid, as already noted. The dismutation of alk-1-enes in the same systems is very slow. The significance of this phenomenon is [188,200] that redistribution of alk-1-enes can take place only via alternating stages of transfer from secondary to primary carbene complexes:



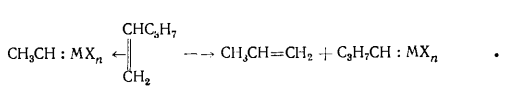
If the secondary carbene complex is rather less reactive than the primary complex, this should lead under conditions of a chain process to marked retardation of dismutation. Alk-1-enes are redistributed even more rapidly than are alk-2-enes with internal double bonds [201,202], but reaction is accompanied only by exchange of methylene groups:



Such a process occurs only with secondary carbene complexes:

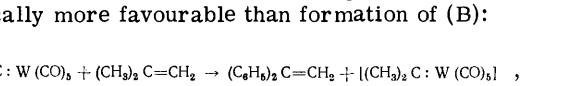


Experimental confirmation of the kinetic role of this factor has been obtained from investigation of the primary products of the codismutation of pent-1-ene and but-2-ene present in equimolecular proportions [203]. The homodismutation of pent-1-ene, involving alternating stages of primary and secondary active centres, should yield ethylene. Codismutation via secondary carbene centres seems more advantageous, and in the presence case should give propene:



The investigations [203] have shown that the chief primary reaction product is propene, with hardly any ethylene formed. When competing directions are possile, reaction occurs along the energetically most advantageous path.

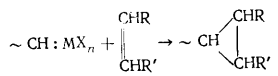
Interaction of the carbene complex $(CO)_5W : C(C_6H_5)_2$ with isobutene gives only 1,1-diphenylethylene, not 2-methyl-1,1-diphenylpropene. The reason can be understood on the basis that formation of the product (A) is energetically more favourable than formation of (B):



The complex (A) then decomposes to form propene. It has since been found [205] that, in the analogous reaction of the carbene complex $(CO)_5W : C(C_6H_4CH_3)_2$ with pent-1-ene, the yield of 1,1-ditolylethylene (and hence of the secondary carbene complex) exceeds 600-fold the yield of 1,1-ditolylpent-1-ene (and of the methylene complex B). It is important to note that diphenyl- and ditolyl-carbenes occupy a single coordination position on the tungsten atom, displacing one carbonyl group.

4. Possible Modes of Termination of Chain Dismutation

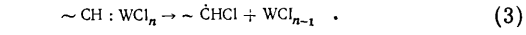
The problem of chain termination in dismutation must be considered in terms of the reactions of carbenes. The most specific reaction in solution is the formation of cyclopropane groups:



Such reactions occur also with coordinated carbenes. It has been shown[206] for various cyclopropane derivatives (n-pentyl, phenyl, n-butoxy) that under the influence of tungsten hexachloride and other components of catalytic systems they isomerise rapidly into the corresponding alkenes and conversion products of the latter. Thus the formation of cyclopropane groups results in chain termination. The appearance of linear alkenes during the polymerisation of cycloalkenes also lowers the molecular weight of the polyalkenamers, because such alkenes are involved in codismutation reactions.

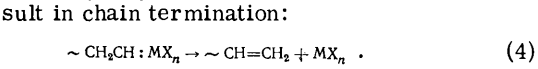
As in chain reactions of radical and ionic character, the cleavage of cycloalkenes and the dismutation of alkenes may be expected to be retarded or completely inhibited if the system is contaminated with alkenes capable of forming more stable carbene complexes. Possible examples of such compounds are alkyl vinyl ethers and 1,1-diphenylethylene, which are able to form centres of the type $ROCH:MX_n$ and $(C_6H_5)_2C:MX_n$. We have shown[184] that benzoylphenyldiazomethane, whose decomposition with the evolution of nitrogen is catalysed by tungsten(VI) chloride, does not initiate the polymerisation of cyclopentene.

Chain termination might occur also by reduction of the transition metal accompanied by formation of a free radical:



(3)

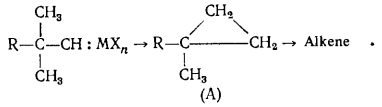
Migration of a hydrogen atom in the carbene complex will also result in chain termination:



(4)

The fundamental possibility of such a reaction has been demonstrated by Fisher[207] on alkyl-phenylcarbene–pentacarbonyltungsten model compounds.

The formation of polymers of very high molecular weight from cyclopentene in the presence of a diazocomponud and a tungsten halide[180] indicates that the role of reactions (3) and (4) is probably slight. But the probability of reaction (4) is increased by the presence of methyl substituents on the second carbon atom:



(A)

With the above secondary carbene in solution the yield of product (A) reaches 92–97%.[185]

The above ideas on possible ways in which a chain process initiated by a carbene complex can be terminated are based solely on analogies with the behaviour of carbenes in solution. Coordination with transition metals may change the picture significantly, and the specific reactions of such complexes have not yet been studied.

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# Organosiloxazanes—A New Line of Advance in the Chemistry of Hetero-organic Oligomers and Polymers

K.A.Andrianov and V.N.Emel'yanov

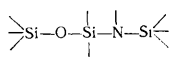
Organosiloxazanes synthesised by the beginning of 1977 have been classified for the first time (according to their structure and molecular weight). For each of the three main groups—(1) cyclic, (2) linear and cyclolinear, and (3) polymeric—the main methods of preparation and the physicochemical characteristics are surveyed. In conclusion several fields of practical application of the new compounds and materials based on them are considered. [A list of 114 references is included.]

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## I. INTRODUCTION

The development of the chemistry of organosilazanes, especially during the past 10–15 years, has been accompanied by a considerable growth in the interest taken in organosilicon compounds containing both organosilazane and organosiloxane groups, i.e.



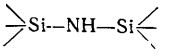
segments. The trend to a systematic study of compounds of this type originated from the wish to combine the characteristic features of organosiloxanes and organosilazanes. The new compounds show greater possibilities than organosiloxanes for the controlled modification of properties, both from the introduction of an additional element (nitrogen) into the molecules and by variation in the nature of the organic radical attached to the nitrogen atoms.

Organosiloxazane compounds that have been obtained to date can be divided into three main groups—(1) cyclic, (2) oligo-organosiloxazanes of linear or cyclolinear molecular structure, and (3) polyorganosiloxazanes varying in the structure of the molecular chains—according to structure and molecular weight. The present Review surveys the preparation, chemical and physical properties, and possible applications of organosiloxazane compounds in preparative chemistry and in industry.

## II. ORGANOCYCLOSILOXAZANES

Synthesis of the first individual organocyclosiloxazanes, which initiated the development of the new trend in the chemistry of hetero-organic oligomers and polymers, was accomplished in our country. Investigating the aminolysis of organo-$\alpha$-$\omega$-dichlorosiloxanes, Sokolov[1] was the first to isolate and identify six- and eight-membered heterocycles containing both silazane and siloxane groups in the molecule.

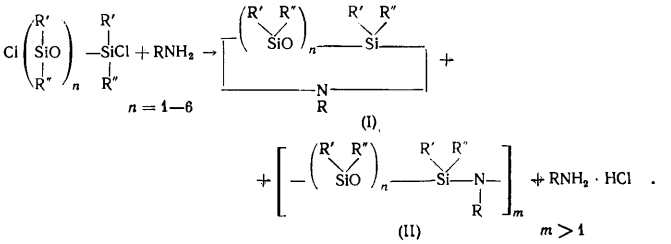
More than 60 six-, eight-, ten-, and twelve-membered heterocycles have now been described, as well as representatives of spiran organocyclosiloxazanes. The homologous series of dimethylsilyl organocyclosiloxazanes is most fully represented in the literature, with reports of all kinds of structural isomers with six and eight atoms in the ring, containing one, two, or three



groups, and several compounds having larger ring skeletons have been synthesised (Tables 1–3).

### Methods of Preparation

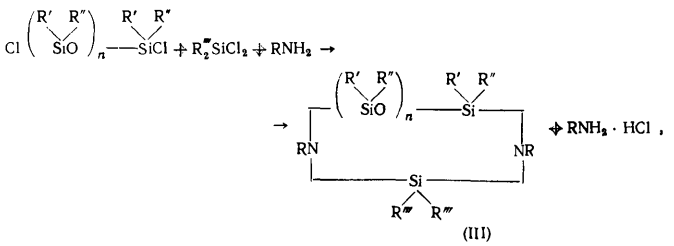
The most widely used methods for obtaining organocyclosiloxazanes are the ammonolysis[1-11] and the aminolysis[2,5,12,13,15] of individual organo-$\alpha\omega$-dichlorosiloxanes or their mixtures with organodichlorosilanes[14-17]:



Ammonolysis or aminolysis, effected by passing the amine into a solution of the dichlorosiloxane, takes place either by an intramolecular mechanism to give heterocycles (I) containing a single silazane bond or by an intermolecular mechanism giving cyclic compounds (II) comprising two or more siloxazane units. Formation of oligomeric and polymeric as well as cyclic products has been observed in these reactions[7,10,11,13].

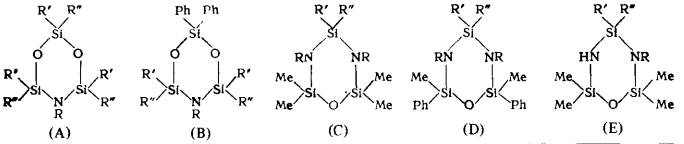
In the coammonolysis (coaminolysis) of mixtures of polychloro-organosiloxanes and diorganodichlorosilanes

the desired products are compounds formed by an intermolecular mechanism and containing two or more silazane bonds[14-18]:



(III)

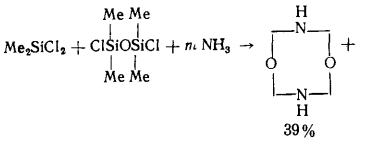
Table 1. Properties of six-membered organocyclosiloxazanes.



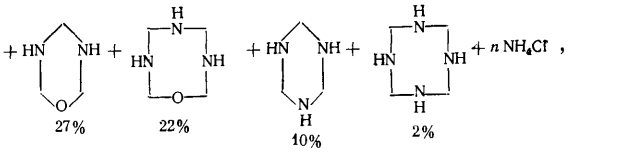
(A) (B) (C) (D) (E)

| R | R′ | R″ | M.p., °C | B.p., °C (*p*, mmHg) | $n_D^{20}$ | $d_4^{20}$ | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | (A) | | | |
| H | Me | Me | 9.5—10 | 151 (760) | 1.4088 | 0.9313 | 1,2,5—7,9,10 |
| Me | Me | Me | — | 163 (760) | 1.4100 | 0.9254 | 13,20 |
| Et | Me | Me | — | 41 (1—2) | 1.4153 | 0.9343 | 12 |
| n-Bu | Me | Me | — | 31 (0.5—1) | 1.4244 | 0.9235 | 2,5,22 |
| Ph | Me | Me | 80 | — | — | — | 15 |
| $C_6F_5$ | Me | Me | 42 | 66 (0.2) | — | — | 21,36 |
| $SiMe_3$ | Me | Me | — | 135 (44) | 1.4488 | — | 30,41 |
| H | Me | Ph | 113—115 | 169—172 (0.25) | — | — | 2,5,19 |
| Me | Me | Ph | 111—112 | 184—189 (10.5) | — | — | 13 |
| Et | Ph | Ph | 170—171 | — | — | 1.195 | 38 |
| Me | Ph | NHMe | —20 | 196—198 (1) | 1.557 | 1.153 | 25 |
| Et | Ph | NHEt | —24 | 223 (1) | 1.546 | 1.129 | 25 |
| Pr | Ph | NHPr | —45 | 250—255 (1) | 1.534 | 1.082 | 25 |
| $C_6H_{11}$ | Ph | $NHC_6H_{11}$ | 15 | 345—347 (1) | 1.545 | — | 25 |
| Ph | Ph | NHPh | 84 | 352—354 (1) | — | — | 25 |
| | | | | (B) | | | |
| H | Me | Me | 99—100 | 119—135 (0.05) | — | — | 2,32,35 |
| Et | Me | Me | — | 117—119 (0.07) | — | — | 15,32 |
| | | | | (C) | | | |
| H | Me | Me | —4÷—5 | 100 (75) | 1.4292 | — | 17,41 |
| Me | Me | Me | —14 | 75 (11) | 1.4326 | 0.9244 | 31,32 |
| Me | Me | Vin | —21 | 80—81 (0.5) | 1.4380 | 0.9184 | 27 |
| Me | Cl | Cl | 38 | 89 (10) | — | — | 27 |
| Me | Br | Br | 45—46 | 63 (0.2) | — | — | 27 |
| Ph | Me | Me | 109—110 | — | — | — | 15 |
| $C_6F_5$ | Me | Me | 168—170 | — | — | — | 36 |
| $SiMe_3$ | Me | Me | — | 111 (5) | 1.4589 | — | 30,41 |
| $Si(Me_2)OSiMe_3$ | Me | Me | — | 88 (0.25) | — | — | 41 |
| | | | | (D) | | | |
| H | Me | Me | 63.5 | 172—174 (6) | — | — | 26 |
| H | Cl | Cl | 80—82 | — | — | — | 26 |
| | | | | (E) | | | |
| $SiMe_3$ | Me | Me | — | 81 (5) | 1.4330 | — | 30,41 |
| $Si(Me_2)OSiMe_3$ | Me | Me | — | 81 (1) | — | — | 41 |

Products of separate amination—organocyclosiloxazanes (I) and organocyclosilazanes—are also formed. Thus chromatography indicates[17] that the composition distribution of products of the simultaneous ammonolysis of dimethyldichlorosilane and tetramethyldichlorodisiloxane is



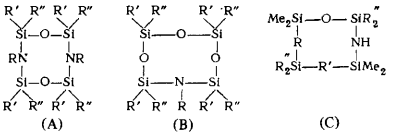
39%



27% 22% 10% 2%

where each corner in a ring represents a dimethylsilylene group.

Table 2. Properties of eight-membered heterocycles.



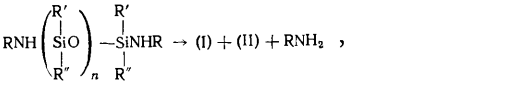
(A) (B) (C)

| R | R′ | R″ | M.p., °C | B.p., °C (*p*, mmHg) | $n_D^{20}$ | $d_4^{20}$ | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | (A) | | | |
| H | Me | Me | 37—40 | 206—208 (760) | — | — | 1,2,6—10, 17,32,33 |
| Me | Me | Me | 24.5—28 | 232—234 (760) | 1.4321 (30°) | 0.9463 (30°) | 4,13,20,32, 33 |
| Et | Me | Me | — | 95—96 (1—2) | 1.4410 | 0.9470 | 12 |
| Bu | Me | Me | — | 95—98 (0.25) | — | — | 2 |
| $C_6F_5$ | Me | Me | 107—108 | 170—175 | — | — | 21,36 |
| $SiMe_3$ | Me | Me | — | 126 (5) | 1.4571 (22°) | — | 24,74 |
| H | Me | Ph | 134—136 | 200—206 (0.1) | — | 1.215 | 2,39 |
| Me | Me | Ph | 1) 115—118* 2) 136—137* | 228 (0.4) | — | — | 13 |
| Me | OMe | OMe | — | 173—175 (0.05) | — | — | 29 |
| Me | Ph | NHMe | 5 | 257—260 (1) | 1.573 | 1.163 | 25 |
| Et | Ph | NHEt | 10 | 275—278 (1.5) | 1.559 | 1.151 | 25 |
| Pr | Ph | NHPr | 7 | 257—260 (1) | 1.082 | 1.550 | 25 |
| Me | Ph | $OSiEt_3$ | — | 285 (1) | 1.4998 | — | 90 |
| | | | | (B) | | | |
| H | Me | Me | 20—20,5 | 190—191 (760) | 1.4151 | 0.9921 (26°) | 2,5—7,10 |
| Me | Me | Me | — | 84—85 (8) | 1.4202 | — | 4 |
| H | Ph | Me | — | 192—202 (0.15) | — | — | 2,5 |
| $Me_3Si$ | Me | Me | — | 90 (4.5) | 1.4316 (25°) | — | 41 |
| | | | | (C) | | | |
| NH | O | Et | — | 70 (0.5) | 1.4308 | — | 1,8,9 |
| NH | NH | Me | 63 | — | — | — | 16—18 |
| O | NH | Me | 46 | — | — | — | 16 |

* Isomers.

Several studies on the synthesis of organocyclosiloxazanes have examined the variation of the yield of products with temperature[4], nature of solvent[5,15], proportions and mode of introduction of reactants[4,12,19,20], catalysts[5,20], etc.[13] Thus the aminolysis by aniline of $\alpha\omega$-dichlorohexamethyltrisiloxane[15] yields in most solvents merely linear diamino-derivatives. Nor could cyclic organosiloxazanes be obtained by the reaction of $\alpha\omega$-dichlorodimethylsiloxanes with pentafluorophenylaniline[21]. Only the use of dimethylformamide enables the reaction to be directed towards formation of *N*-phenylated six-membered rings[15].

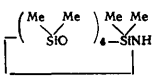
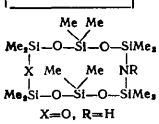
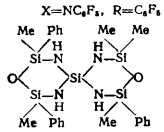
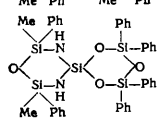
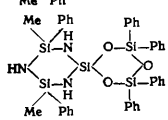
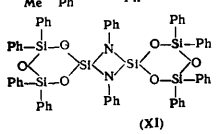
Owing to the formation of linear organosiloxanes having terminal amino-groups[3,12,19,22,23] the homocondensation of amino-derivatives has acquired greater importance in the synthesis of cyclic organosiloxazanes:



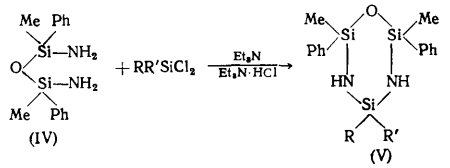
where R = H or Alk. Not only heterocycles of types (I) and (II) but also polymeric products have been obtained by homocondensation[19,10]. In the absence of a catalyst

$\alpha\omega$-diamino-derivatives of organosiloxanes readily undergo homocondensation only when the terminal amino-groups are primary[25]. When they are secondary, such reactions either do not take place or give only a low degree of conversion[4,6,7,10,13,19,22]. Ammonium chloride, copper(I) chloride, and certain other catalysts have been used in these reactions[2,4,13,20,22].

**Table 3.** Properties of organocyclosiloxazanes.

| Compound | M.p., °C | B.p., °C (*p*, mmHg) | $n_D^{20}$ | $d_4^{20}$ | Ref. |
|---|---|---|---|---|---|
|  | — | 115—119 (13) | 1.4125 | 0 9683 | 2, 3, 5 |
|  | | | | | |
| X=O, R=H | — | 58—60 (1) | 1.4122 | 0.9690 | 2, 3, 5 |
| X=NH, R=H | —12 | 148—150 (2) | 1.4269 | 0.9756 | 2, 5, 9 |
| X=NH, R=SiMe$_3$ | — | 94 (0.5) | — | — | 41 |
| X=NSiMe$_3$, R=SiMe$_3$ | 57—58 | 106 (0.5) | — | — | 41 |
| X=NC$_6$F$_5$, R=C$_6$F$_5$ | 117—118 | — | — | — | 21, 36 |
|  | 134—136 | 212—230 (0.02) | — | — | 26 |
|  | 134—135 | 265—270 (0.02) | — | — | 26 |
|  | 170 | 299—301 (0.02) | — | — | 26 |
|  (XI) | 261 | — | — | — | 58 |
| | 230—231 | — | — | — | 58 |

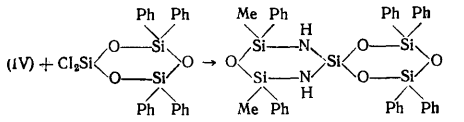
Heterofunctional condensation of organo-$\alpha\omega$-diaminosiloxanes with diorganodihalogenosilanes and tetrachlorosilane yields heterocycles of type (III). Thus the corresponding six-membered organosiloxazanes have been obtained[26,27] by treating tetraorganodisiloxane-1,3-diamines with dimethyldichlorosilane, methylvinyldichlorosilane, and tetrachlorosilane in the presence of triethylamine:



(IV) + RR′SiCl$_2$ $\xrightarrow[Et_3N\cdot HCl]{Et_3N}$ (V)

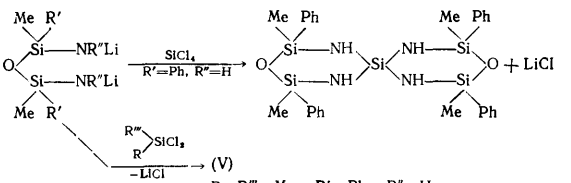
R=R′=Me; R=R′=Cl; R=Me, R′=Vin.

Use of an organodichlorocyclosiloxane instead of a dialkyldichlorosilane in such a reaction yielded a spirosiloxazane[26]:



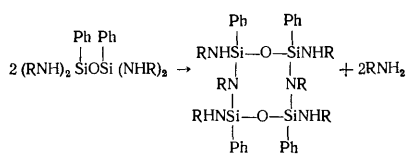
Replacement of (IV) by dimethyldiphenyldisilazane-1,3-diamine led to the formation of a spiro-compound comprising a silazane ring and a siloxane ring[26].

Rings of type (V) have been obtained from dilithium derivatives of (IV) with dimethyl- or methylvinyl-dichlorosilane without the use of a tertiary amine as acceptor of hydrogen chloride, but condensation with tetrachlorosilane gives a symmetrical bicyclic methylphenylspirosiloxazane[26]:

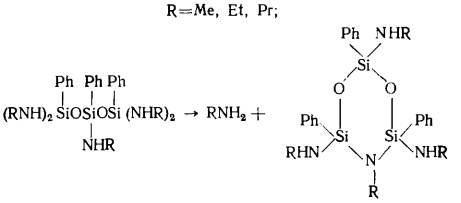


R=R″=Me, R′=Ph, R″=H;
R=Me, R‴=Vin, R′=R″=Me.

Six- and eight-membered organocyclosiloxazanes containing one amino-group on every silicon atom[25] are the chief products of the homocondensation of organosiloxane-tetra(and penta) amines[19,28]:

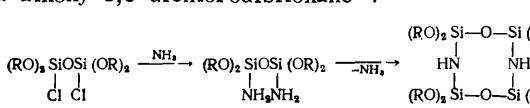


R=Me, Et, Pr;

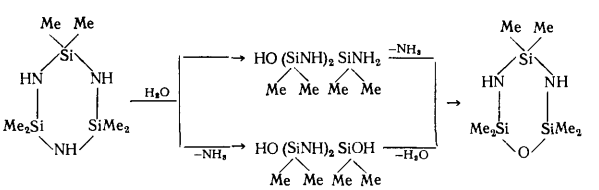


R=Me, Et, Pr, Ph, $C_6H_{11}$.

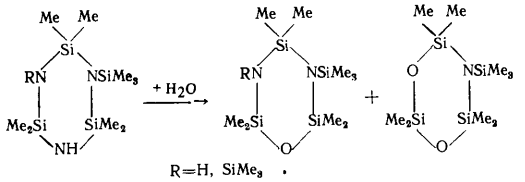
Cyclisation predominates in the condensation of such compounds, as evidenced both by the high yields of individual cyclic compounds and by the absence from the reaction mixture of insoluble polymers having a three-dimensional macromolecular structure. An eight-membered organosiloxazane containing two alkoxy-groups on every silicon atom was first obtained in 1963, from a tetra-alkoxy-1,3-dichlorodisiloxane[29]:



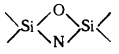
Organocyclosiloxazanes have been obtained also by hydrolysing hexamethylcyclotrisilazane[17]:



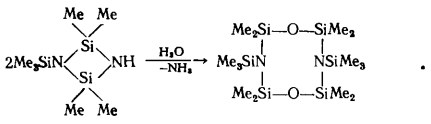
Partial hydrolytic condensation of organocyclosiloxanes in diglyme gave *N*-silylated six-membered organosiloxazanes[30]. This method enabled two of the three silazane groups in the ring to be replaced by oxygen:



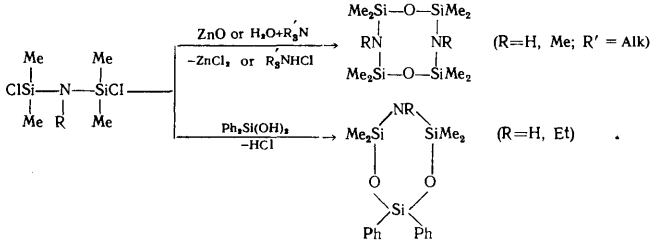
In contrast to the above reactions the partial hydrolysis of a tetramethyldisilazane ring results in the formation not of a four-membered ring



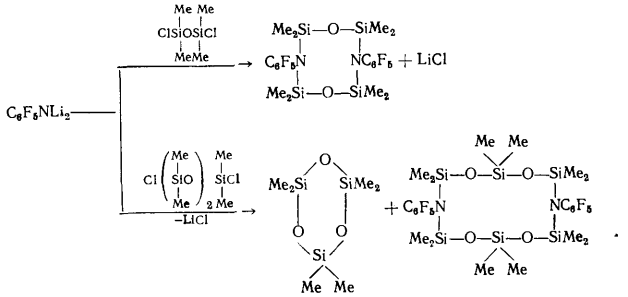
but of the symmetrical eight-membered 1,1,3,3,5,5,7,7-octamethyl-4,8-bistrimethylsilylcyclo-1,3,5,7-tetrasil-2,6-dioxa-4,8-diazane[24,74]:



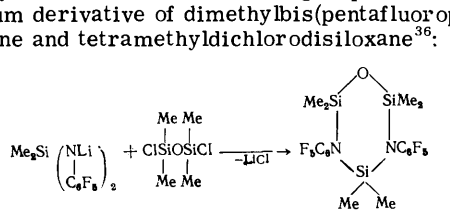
When linear organosilazanes containing halogen attached to the silicon atoms are used to obtain cyclosiloxazanes, the silazane bonds are unaffected, and siloxane units result from the action of water[31-33], zinc oxide[34], or a disubstituted silanediol[35] on the terminal halogen atoms:



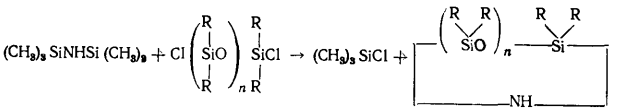
Six-, eight-, and twelve-membered organocyclosiloxazanes have been obtained[21,36] by cyclising $\alpha\omega$-dihalogenated organosiloxanes by the action of $N,N$-dilithium derivatives of amines·



A six-membered organocyclosiloxazane having two perfluorophenyl radicals in the silazane groups is formed from the dilithium derivative of dimethylbis(pentafluorophenylamino)silane and tetramethyldichlorodisiloxane[36]:

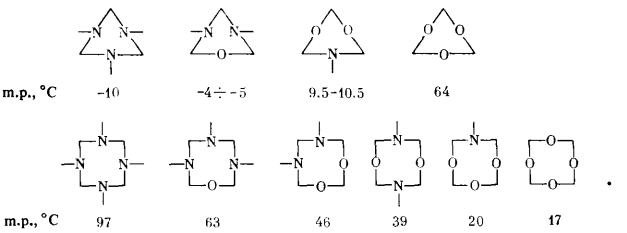


It has been claimed also[37] that linear $\alpha\omega$-dihalogenated organosiloxanes can be converted into cyclic siloxazanes by exchange between the chlorosilyl group and hexamethyldisilazane[37]:



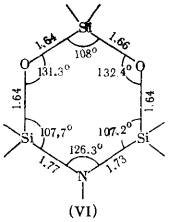
## Physicochemical Properties

Melting points. Tables 1–3 list several physical properties of monocyclic organosiloxazanes. In structural analogues such properties depend on the ratio of the total numbers of Si–O–Si and Si–N–Si bonds in the molecules. This is typified by the variation in melting point in the two homologous series of dimethylsilylene six- and eight-membered ring compounds (with one hydrogen atom attached to every nitrogen atom):

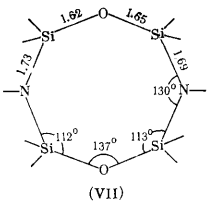


In the first series hexamethylcyclotrisilazane melts 74 deg below hexamethylcyclotrisiloxane, but in the second series the melting point of the dimethylsilylene eight-membered cyclosilazane is lower than that of the corresponding siloxane by 80 deg. The overwhelming majority of heterocycles are readily soluble in aromatic solvents but less soluble in alkanes.

Structure. Among crystalline organocyclosiloxazanes one six-membered ring[38] and one eight-membered ring[39] have been subjected to structural analysis: *N*-ethylhexaphenylcyclo-1,3,5-trisil-2,4-dioxa-6-azane (VI) and 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclo-1,3,5,7-tetrasil-2,6-dioxa-4,8-diazane (VII) have the structures



(VI)



(VII)

Monoclinic, space group $P2_1/a$; $a = 17.412$; $b = 16.287$; $c = 13.752$ Å; $\beta = 116°31'$;

Orthorhombic, space group $Pbca$, $a = 11.652$; $b = 19.798$; $c = 12.833$ Å; $V = 2960.5$ Å$^3$.

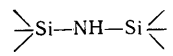
The cyclic skeleton of (VI) departs slightly though definitely from planar and gravitates towards the "boat" form in structure. Compound (VII) has the "chair" conformation. The mean silicon–nitrogen bond length is rather shorter in the eight-membered than in the six-membered ring (1.71 and 1.747 Å). No less interesting is the difference in silicon–carbon bond lengths, obviously due to $p_\pi$–$d_\pi$ interaction of electrons of exocyclic substituents with vacant *d* orbitals of silicon and to hyperconjugation in the

siloxazane ring (Table 4). The position of the phenyl group in (VII) with respect to the siloxazane ring (perpendicular) is regarded[39] as optimal in terms of maximum overlap of the $\pi$-electron systems of the phenyl rings with $3d_{z^2}$ orbitals of silicon, so that the remaining $3d$ orbitals of the silicon atom may be involved in delocalisation of the electron cloud of the siloxazane ring.

Table 4.

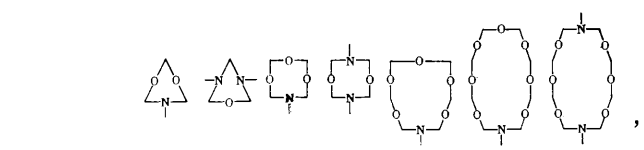
| Compound | Si-C bond length, Å | |
|---|---|---|
| | Ar | Alk |
| (VI) | 1.875 | – |
| (VII) | 1.85 (2) | 1.91 (1) |
| Arylsilanes | 1.843 | – |
| Alkylsilanes | – | 1.875 |

Infrared spectra. The infrared absorption band corresponding to asymmetric siloxane-stretching vibrations is sensitive to variation in the dimensions of the ring. As example, the homologous series of dimethylsilylated cyclosiloxazanes containing one silazane bond



with respectively 2–5 siloxane bonds exhibits a shift in $\nu_{as}$(Si.O.Si) from 983–1023 to 1067–1090 $cm^{-1}$ on passing from six- to eight-, ten-, and twelve-membered heterocycles[2,10,40]. Analogous shifts are exhibited by other six- and eight-membered organocyclosiloxazanes[25,41]. A shift in this band towards higher frequencies occurs with increase in ring size effected not only by additional siloxane groups but also by the introduction of a new silazane bond[2,10,25,40,41].

The series of *SiSi*-dimethylated cyclosiloxazanes suggests that the $\nu_{as}$(Si.N.Si) band is extremely sensitive both to change in the ring size and to the number of cyclic silazane bonds. A regular displacement of this band to higher frequencies is observed either when the number of silazane bonds is increased at the expense of a diminished number of siloxane bonds in a ring of unchanged size or when the ring is expanded while the number of silazane groups remains constant. This is demonstrated by the homologous series



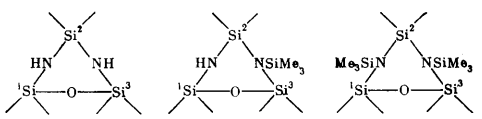

where the corners represent dimethylsilylene groups, and one hydrogen atom is attached to each nitrogen atom.

In contrast to an *Si*-substituent, whose effect on the position of the Si.O.Si vibrational band is little apparent in the infrared spectra of most of the organocyclosiloxazanes studied, radicals attached to the nitrogen atom of a silazane group cause characteristic and considerable shifts in the $\nu_{as}$(Si.N.Si) band. In the homologous series of hexamethylcyclo-1,3,5-trisil-2,oxa-4,6-diazanes having the structural formula



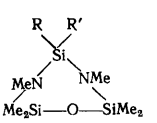
variation in the inductive effect of one or two substituents—in the sequence R = H, $Si(CH_3)_3$, $Si(CH_3)_2OSi(CH_3)_3$—led to a shift in the $\nu_{as}$(Si.N.Si) absorption band from 930 to 979 $cm^{-1}$.[41] Similar changes had been observed previously in the spectra of four-membered organodisilazane compounds[42], as well as for other *N*-alkylated (or *N*-arylated) organocyclosiloxazanes[25]. Radicals having a negative inductive effect, such as phenyl, lower the $\nu_{as}$(Si.N.Si) frequency to 907–910 $cm^{-1}$ when attached to the nitrogen atom[15,25].

Nuclear magnetic resonance spectra. The structure of the $^1H$ n.m.r. spectra of cyclic organosiloxazanes is more complicated than with cyclosiloxanes and silazanes. As the spectra became more complex, however, the information potential also became greater, revealing finer structural features. Thus the effect of a trimethylsilyl group on the hydrogen atoms of the dimethylsilylene groups gradually decayed with distance[41]. The following data




show that replacement of a hydrogen atom in an SiNHSi group by trimethylsilyl has different effects on the signals of neighbouring and more remote dimethylsilylene groups. Introduction of a second trimethylsilyl group has the strongest effect on a methyl group attached to $Si_{(2)}$, lying between the two added radicals. Substitution of phenyl for the hydrogen atoms of both silazane groups shifted the signal only of methyl groups located at $Si_{(2)}$ (to $\tau$ = 9.82), while the position of the second signal in the spectrum remained unchanged ($\tau$ = 9.94).[15] An analogous effect was observed furthermore when silazane hydrogen in six-membered rings was replaced by methyl or pentamethyldisiloxanyl substituents, as well as in the case of eight-membered homologues[41].

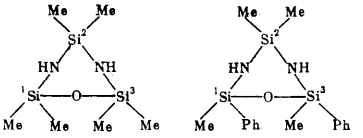
Radicals attached to the silicon atoms have an appreciably more marked effect on the proton magnetic resonance than on the infrared spectra. Thus the spectra of a series of *NN'*-dimethylcyclotrisiloxazanes of general formula



reveal a tendency for the signal to move down field with decrease in the $+I$ effect of the substituents R and R':

| R, R' | Me, Me | Br, Br | Cl, Cl | Vin, Me |
|---|---|---|---|---|
| τ, ppm | 9.93 | 9.85 | 9.83 | 9.73 |

The signal of the methyl hydrogen atoms in methylphenylsilyl derivatives is usually displaced down field in comparison with the dimethylsilyl analogues. This is characteristic also of cyclic organosiloxazanes[26,41]:



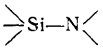
| | | |
|---|---|---|
| $Me(Si^1)$ | 9,92 | 9,66 |
| $Me(Si^2)$ | 9,93 | 9,93 |
| $Me(Si^3)$ | 9,92 | 9,66 |

These values of $\tau$ (ppm) show that, when two dimethylsilylene groups are replaced by methylphenylsilylene radicals, the position of the signal corresponding to the hydrogen atoms of the dimethylsilylene group remains unchanged, whereas the signal of the methyl hydrogen atoms in a methylphenylsilylene group is displaced by >0.2 ppm. Nuclear magnetic resonance data have been published also for several other organocyclosiloxazanes[4,10,12,17,31,35].

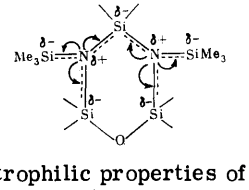
Mass spectra. Among other physical methods, mass spectrometry has also been used to analyse organocyclosiloxazanes[43].

Interpretation of physicochemical properties and reactivity. The approach to interpreting e.g. the ability to polymerise under the influence of nucleophiles is usually more cautious with organocyclosiloxazanes than with cyclic organosiloxanes and organosilazanes, most probably because of the additional effects arising from the combination of siloxane and silazane groups. Despite the comparatively few data that have accumulated, we can distinguish some of the most important factors governing such properties of cyclosiloxazanes as thermal and hydrolytic stability, ability to rearrange or polymerise.

Firstly may be mentioned the inductive and mesomeric effects of substituents attached to the silazane nitrogen. For the series of substituents—hydrogen, methyl, trimethylsilyl, phenyl—the inductive effect changes sign from positive to negative, corresponding to diminished electron density on the nitrogen and enhanced resistance of the

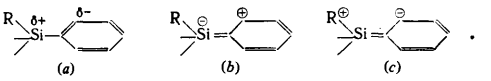


bond to hydrolysis, which usually involves protonation of the nitrogen[44]. Since moreover the negative mesomeric effect of the trimethylsilyl group ($p_\pi$–$d_\pi$ interaction of exocyclic groups with nitrogen) lowers the electron density on the nitrogen and increases it on the silicon atoms, we can explain the high hydrolytic and thermal stability of trimethylsilylated heterocycles. The scheme



shows that the electrophilic properties of silicon are weakened by the above negative mesomeric effect with simultaneous decrease in the basic strength of the nitrogen. Basic properties are completely absent from tris-trimethylsilylamine $((CH_3)_3Si)_3N$.[45]

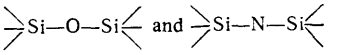
Another important factor—the influence of groups attached to the silicon atoms—can also be considered in terms of mesomeric and inductive effects. In the case of an *Si*-phenyl substituent, for example, the inductive effect guides electrons from the silicon orbitals to the phenyl ring (*a*), whereas the mesomeric effect resulting from interaction of $\pi$ electrons of the phenyl ring with vacant (*b*) orbitals of the silicon atom has the opposite direction (*b*) or transmits electric charge to the *ortho*- and *para*-positions by hyperconjugation (*c*) and thus strengthens the inductive effect[46]:



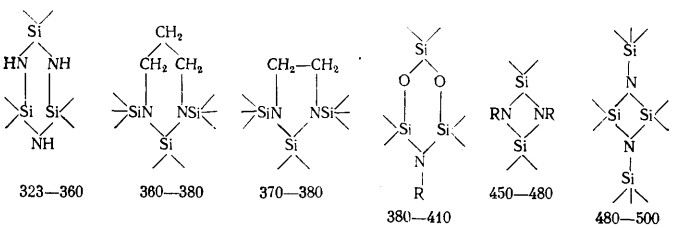
(*a*) (*b*) (*c*)

Depending on the steric disposition of the phenyl group, $p_\pi$–$d_\pi$ conjugation may be either strengthened or weakened[39].

A no less important factor determining the reactivity and the physical properties of organocyclosiloxazanes is hyperconjugation (pseudoaromatisation) within the siloxazane ring, which depends on the size of the ring, its conformation, the regularity of alternation of

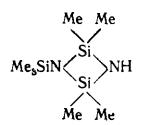


units, etc. Study of this problem is not yet sufficient to permit unambiguous interpretation of many regular changes in properties on passing from cyclic organosiloxanes to organocyclosilazanes or organocyclosiloxazanes. Judging from the variation in bond lengths and angles[38,39] and also the diminished basicity of the silazane nitrogen[24] due to its involvement in delocalisation of the electron cloud within the ring, however, hyperconjugation interactions have a considerable influence on the stability and other properties of the compounds. Indeed, in the series of organosilicon heterocycles[47]



323—360 360—380 370—380 380—410 450—480 480—500

(the temperature ranges of decomposition (°C) are indicated below the formulae) four-membered cyclodisilazanes are the most thermostable. Thus in 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane

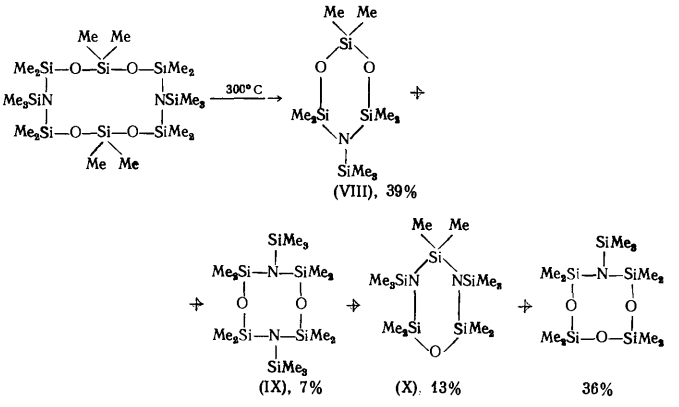


the proton attached to the second nitrogen atom exhibits enhanced acidity (and the nitrogen atom is correspondingly less basic), which indicates a considerable contribution to conjugation within the ring by the nitrogen electrons, including those bonding the hydrogen atom with the nitrogen[24].

Thermal stability. Study of organocyclosiloxazanes as a novel type of heterocycles showed[44,48,49] that the thermal stability of organocyclotetrasildioxadiazanes exceeded those of cyclic organosilazanes and organosiloxanes. Perfluorophenylated derivatives of six- and

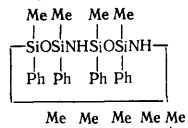
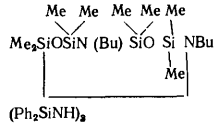
eight-membered heterocycles begin to decompose[21] over the temperature range 400–450°C. The start of the decomposition of hexaphenylcyclotrisiloxazane also lies above 410°C.[50]

Comparison of the thermal stability of *N*-silylated *SiSi*-dimethylated twelve-, eight-, and six-membered cyclosiloxazanes has revealed[41] the extraordinary stability of the six-membered 2,2,4,4,6,6-hexamethyl-5-trimethylsilylcyclotrisil-1,3-dioxa-5-azane (VIII) to isothermal heating at 300°C: whereas the *N*-trimethylsilylated twelve-membered heterocycle underwent the rearrangement




after being heated in a sealed ampoule at 300°C for only 13 h, compound (VIII) remained unchanged after 260 h at the same temperature. Heating (IX) under the same conditions for 120 h led to the formation of approximately equal quantities of (VIII) and (X) (totalling ~90%). The heterocycle (X) suffered only slight losses after the same treatment.

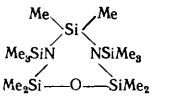
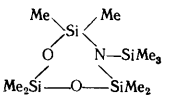
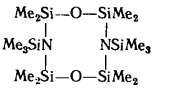
Table 5.

| Compound | $\nu_{as}$(Si.N.Si), cm$^{-1}$ | Rate of disappearance of band at 25°C |
|---|---|---|
| $(Me_2SiNH)_3$ | 925 | 1 h |
| $(Me_2SiNH)_4$ | 941 | 1 h |
| $Ph_2SiOSiMe_2OSiMe_2NH$ | 898 | 1 h |
| $Me_2SiOSiMe_2N(H)SiMe_2OSiMe_2NH$ | 947 | slight changes after 13 h |
|  | 941 | no change after 25 h, slight changes after 7 days |
|  | 904 | no change after 7 days |
| $(Ph_2SiNH)_3$ | 952 | no change after 7 days |

Hydrolytic stability. The resistance of organocyclosiloxazanes to hydrolysis is governed mainly by the nature of the silazane bond, being considerably affected by the substituent on the nitrogen atom. This factor was noted in one of the first preparations of the heterocycles[2]. Table 5 gives relative rates of hydrolytic cleavage of the silazane bond in cyclic organosilazanes and siloxazanes determined from the disappearance of the $\nu_{as}$(Si.N.Si) band from the infrared spectra of 0.25 M solutions of the heterocycles in dimethylformamide containing 5% of water.

Later work has established the great hydrolytic stability of cyclosiloxazanes containing an *N*-phenyl[15] or an *N*-perfluorophenyl[21] group. The accompanying data show that the nature and the bulk of substituents attached to the silicon atoms may also have a considerable influence on the rate of hydrolysis.

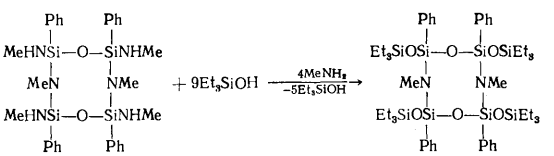
Table 6.

| Compound | Time of hydrolytic cleavage of ring, h | | Rate constant, $k$, h$^{-1}$ |
|---|---|---|---|
| | 50% | 95% | |
|  | — | 20 | — |
|  | 132 | 400 | $5.2\cdot10^{-3}$ |
|  | 66 | 200 | $1.2\cdot10^{-2}$ |

*N*-Trimethylsilylated compounds are among the hydrolytically most stable organosiloxazanes. Parallel tests of the hydrolytic stability of organosilazanes and organosiloxazane heterocycles, made under homogeneous conditions in a boiling solvent (dimethoxyethane) containing excess of water (relative to the silazane bonds), demonstrated rapid breakdown of the cyclosilazanes, whereas the cleavage of *N*-trimethylsilylated organosiloxazane rings occurs considerably more slowly[41] (Table 6).

The resistance of organocyclosiloxazanes and also of cyclic organosilazanes is greater in neutral and alkaline than in acid media[8]. The main hydrolytic condensation products are oligomeric and cyclic organosiloxanes[10].

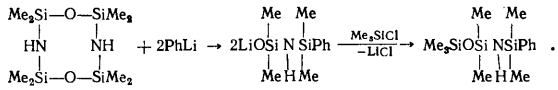
Triethylsilanol acts on organocyclosiloxazanes containing *Si*-amino-groups at temperatures up to 130°C predominantly at these groups[51]:




The cleavage of heterocycles at the silazane bond under the influence of organic primary amines[12] can be regarded as displacement to the left of the equilibrium formation of cyclic organosiloxazanes from organosiloxane-$\alpha\omega$-diamines.

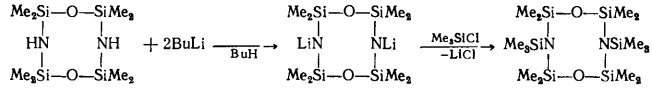
Several investigations have been made on the metallation of organocyclosiloxazanes at the secondary amino-group by means of metal aryls or alkyls[10,41,52–54]. Treatment of symmetrical octamethylcyclotetrasildioxadiazane with phenyl-lithium in ethereal solution at room temperature led to fission of the siloxane bond[10], but

subsequent reaction of the lithium silanolate with trimethylchlorosilane gave the corresponding trimethylsilyl derivative:

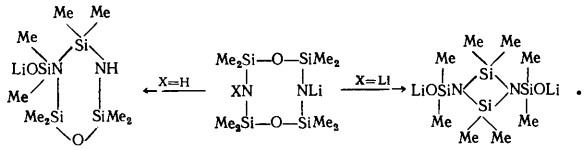


A cyclosiloxazane undergoes a similar reaction with sodamide.

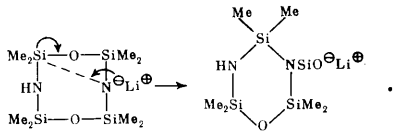
The action of butyl-lithium on the same organocyclosiloxazane has been examined in greater detail[41,53,54]. At low temperatures cleavage of siloxane bonds is not effected, and at −60°C metallation occurs smoothly, to yield mono- or di-*N*-trimethylsilylated products after treatment of the *N*-lithium derivatives with trimethylchlorosilane:



If, however, the di- or mono-lithium derivative is left at a higher temperature (from −30 to +20°C) for some time, it undergoes rearrangement with contraction of the ring, when the dilithium compound passes into a cyclodisilazane, and the monolithium compound into a six-membered organocyclosiloxazane:



The mechanism of the rearrangement most probably involves nucleophilic attack by $N^-$ on silicon, leading to cleavage of the siloxane bond and formation of a new silazane bond:



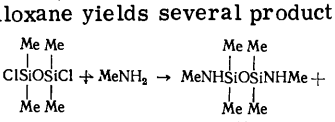
Rearrangements of this type are transannular interactions, and occur rapidly in 1,2-dimethoxyethane and oxolan; they are far slower in ether and in hexane[53].

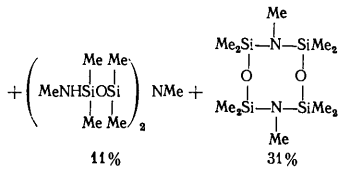
The preparation and certain properties of cyclic organosiloxazanes have been discussed also in several other references[55-57].

## III. OLIGO-ORGANOSILOXAZANES—LINEAR, CYCLO-LINEAR, AND SPIROCYCLIC

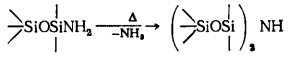
### Methods of Preparation

The methods used are more diverse than for organocyclosiloxazanes. The ammonolysis and aminolysis of organochlorosiloxanes, as well as the homocondensation of organosiloxanes containing *Si*-amino-groups, are common to the two classes of products[6,7,13,58,59]. Thus the introduction of methylamine into a solution of 1,3-dichlorotetramethyldisiloxane yields several products[13]:



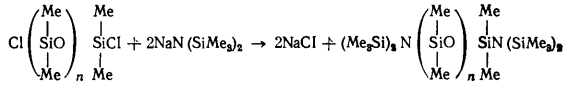


The tendency for heterocycles or linear products to be formed in such reactions depends on the structure of the initial compounds and on the experimental conditions. Homocondensation processes for obtaining such linear oligo-organosiloxazanes take place according to the general scheme[6,7,59,60]



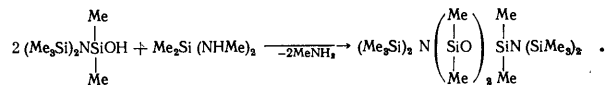
Certain properties of the resulting oligomers are listed in Table 7.

Linear oligo-organosiloxazanes having terminal bistrimethylsilylamino-groups have been synthesised by the action of bistrimethylsilylsodamide on organo-$\alpha\omega$-dichlorosiloxanes[59,61]:

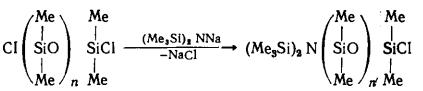


$n = 3, 5, 7, 13.$

In this reaction both halogen atoms are smoothly replaced by bistrimethylsilylamino-groups only in halogenated siloxanes containing four or more siloxane units[59]. The oligomer of this homologous series having three siloxane units has been obtained by condensing dimethylbismethylaminosilane with bistrimethylsilylaminodimethylsilanol[62]:



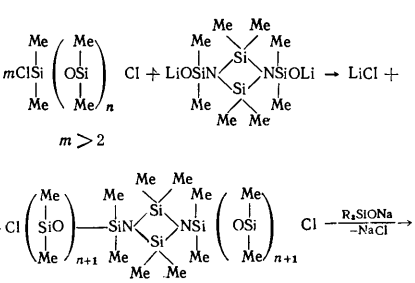
When the proportion of bistrimethylsilylsodamide is lowered to equimolecular relative to the organodichlorosiloxane, monosubstituted compounds are formed in yields up to 70%:[6,7,59,61]

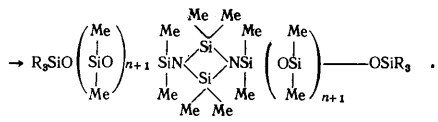


$n = 1, 2, 3, 6.$

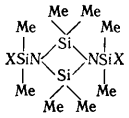
Various derivatives—hydroxysilyl, aminosilyl, etc.—have been obtained from $\alpha$-bistrimethylsilylamino-$\omega$-chlorodimethylsiloxanes.

Exchange of mono- or di-lithium derivatives of cyclodisilazanediols with dimethyldichlorosilane or organo-$\alpha\omega$-dichlorosiloxanes has been used to obtain a series of oligomers containing organodisilazane rings in the molecular chains[63-65]; the terminal halogenosilyl groups in the resulting oligomers were then blocked by means of alkylated (or arylated) silanolates[63]:



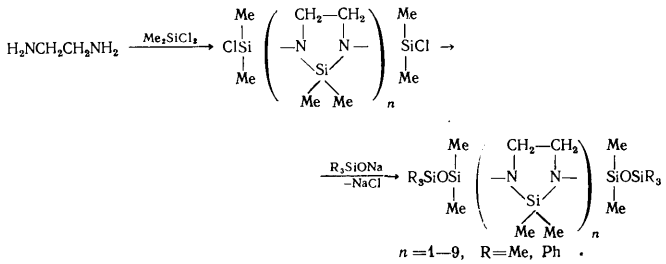


Other methods of heterofunctional condensation used to prepare analogous products include the reactions of organocyclodisilazane derivatives

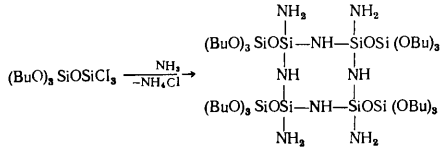


($X = NR_2$ or Cl) with alkyl(aryl) silanols or the corresponding silanolates[66,67].

The same processes based on exchange reactions underlay the method of obtaining "mixed" oligomers of cyclocarbosiloxazane type. Diazasila-alkane rings and polycyclolinear products formed by the action of ethylene-1,2-diamine on dimethyldichlorosilane were used as starting materials[68,69]; treatment of the bischlorosilyl derivatives with trimethylsilanol or triphenylsilanol hence gave cyclolinear carbosiloxazanes having terminal triorganosiloxy-groups:

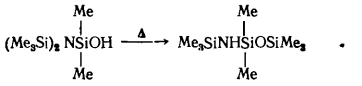


Among oligomers containing eight-membered silazane rings with siloxane units in exocyclic groups the tetrafunctional 1,3,5,7-tetrakistributoxysiloxycyclo-1,3,5,7-tetrasilazane-1,3,5,7-tetramine has been synthesised[70]:

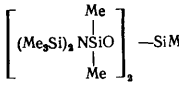


Besides the above condensation methods, oligo-organosiloxazanes can be obtained by cleaving the siloxane bonds in organocyclosiloxazanes by the action of phenyl-lithium or sodamide and then treating the resulting lithium or sodium silanolates with alkylchlorosilanes[10] (see fourth last equation in Section II).

An interesting laboratory preparation of a linear organosiloxazane involved rearrangement[71]: contrary to expectation, when bistrimethylsilylaminodimethylsilanol was heated to 200°C, neither heterofunctional condensation of hydroxysilyl and aminosilyl groups nor homocondensation of hydroxy-groups was observed, but the isomerisation

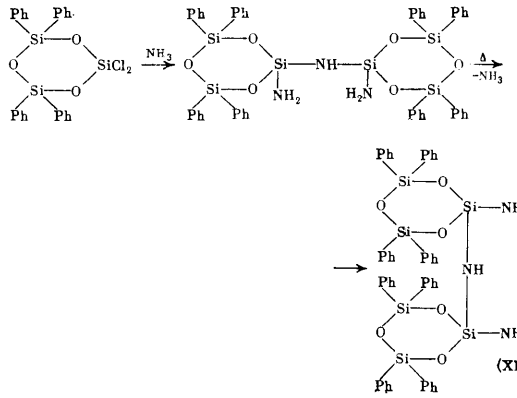


Yet with dimethylbismethylaminosilane the same reactant gave a 57% yield of the expected linear siloxazane[62]



The above type of rearrangement goes smoothly in the presence of basic catalysts; catalytic additions of sulphuric acid gave bistrimethylsilylaminopentamethyldisiloxane.

The ammonolysis of organopolychlorosiloxanes followed by homocondensation of the amino-derivatives has recently been used[58,72] to synthesise polycyclic systems consisting of fused organosiloxane and organosilazane rings:

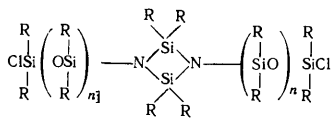


(XI)

## Physicochemical Properties

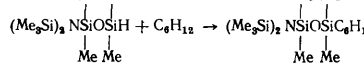
Table 7 shows that most of the oligo-organosiloxanes are liquids that can be distilled in a vacuum. Their viscosity increases with increase both in molecular weight and in the number of cyclic units and phenyl groups in the molecule. All known oligomers containing triphenylsilyl radicals are crystalline compounds melting in the range 100–200°C. The solubility of oligo-organosiloxazanes in polar and non-polar solvents depends on the content of aliphatic and aromatic radicals in the molecule, as well as on the structure and composition of the cyclic segements.

Controlled hydrolysis of oligomers of general formula $((CH_3)_3Si)_2N.[SiR_2.O]_n.SiR_2Cl$ in the presence of acceptors of hydrogen chloride enables the corresponding hydroxy-derivatives to be isolated[6,7,59]. The ammonolysis of oligomers containing an $\alpha$-chlorine atom and an $\omega$-bistrimethylsilylamino-group gives silylated amines with chloro in the above formula replaced by amino, which can be selectively hydrolysed only at one of the silicon–nitrogen bonds[73]. Hydrolysis of oligomers of the series



has enabled the corresponding organosiloxazane-$\alpha\omega$-diols to be obtained[63,65,75] as oily liquids.

The hydride addition of an *SiSi*-dimethylated siloxazane containing a free hydrogen atom to hex-1-ene proceeds smoothly in the presence of chloroplatinic acid to give the expected product—1-bistrimethylsilylamino-3-hexyltetramethyldisiloxane[62]:



The most specific feature of the infrared spectra of oligo-organosiloxazanes is the absorption band corresponding to asymmetric stretching vibrations of the silazane bond. Its spectral position permits reliable identification

**Table 7. Properties of oligo-organosiloxazanes.**

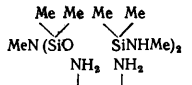
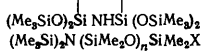
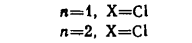
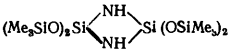
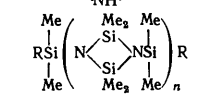
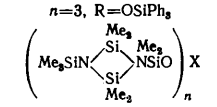
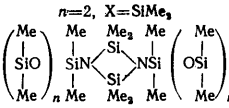
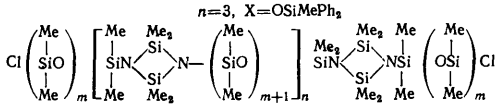
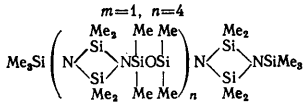
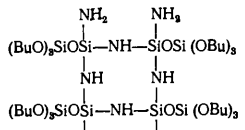
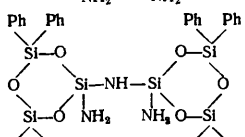
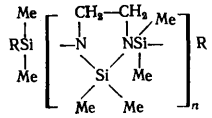
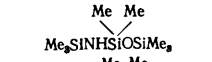
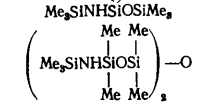
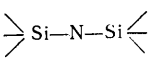
| Compound | M.p., °C | B.p., °C (*p*, mmHg) | $n_D^{20}$ | $d_4^{20}$ | Ref. |
|---|---|---|---|---|---|
|  | — | 90—94 (0.8) | 1.4280 (24°) | — | 13 |
|  | — | 117—119 (3) | 1.4119 | 0.9338 | 60 |
|  | | | | | |
| *n*=1, X=Cl | — | 109,5—110,5 (10) | 1.4440 | 0.9446 (25°) | 59 |
| *n*=2, X=Cl | — | 106—107 (2.5) | 1.4365 | — | 59 |
| *n*=3, X=Cl | — | 123—124 (2) | 1.4333 | 0.9493 | 6,7,59,61 |
| *n*=6, X=Cl | — | 208—210 (2) | 1.4179 | 0.9684 | 61 |
| *n*=1, X=$NH_2$ | — | 75—76 (2) | 1.4409 | 0.9122 (25°) | 59 |
| *n*=2, X=$NH_2$ | — | 91—92 (1.5) | 1.4346 | 0.9123 (27°) | 59 |
| *n*=3, X=$NH_2$ | — | 98—99 (1) | 1.4297 | 0.9237 (26°) | 6,7,59 |
| *n*=2, X=OH | — | 102—104 (2) | 1.4370 | 0.9346 (25°) | 59 |
| *n*=3, X=OH | — | 103—104 (1.5) | 1.4288 | — | 6,7,59 |
| *n*=1, X=H | — | 73 (3) | 1.4340 (25°) | — | 62 |
| *n*=1, X=Me | — | 71 (2) | — | — | 62 |
| *n*=1, X=$C_6H_{13}$ | — | 118 (1.5) | — | — | 62 |
| *n*=2, X=N($SiMe_3$)$_2$ | — | 138 (1) | — | — | 62 |
| *n*=3, X=N($SiMe_3$)$_2$ | — | 159—161 (1) | 1.4453 | 0.9362 | 59,61 |
| *n*=13, X=N($SiMe_3$)$_2$ | — | 290 (2.5) | — | — | 61 |
| *n*=5, X=N($SiMe_3$)$_2$ | — | 213 (2) | 1.4361 | 0.9415 | 61,59 |
| *n*=7, X=N($SiMe_3$)$_2$ | — | 218 (1.5) | 1.4262 | 0.9449 | 6,7,59,61 |
|  | | | | | |
| *n*=2 | — | 196—198 (1.6) | 1.4417 | — | 59 |
| *n*=3 | — | 196—198 (1) | 1.4437 | — | 6,7,59 |
|  | 103 | 180—183 (4) | — | — | 60 |
|  | | | | | |
| *n*=1, R=$OSiMe_3$ | — | 105 (1) | 1.4247 | — | 41,67 |
| *n*=1, R=$OSiMe_2Ph$ | — | 178—180 (0.02) | 1.4869 | — | 66 |
| *n*=1, R=$OSiMePhI_2$ | — | 225 (0.01) | 1.5338 | — | 67 |
| *n*=1, R=$OSiPh_3$ | 189—191 | — | — | — | 67 |
| *n*=2, R=$OSiMe_3$ | 3 | 146 (0.05) | 1.4425 | — | 67 |
| *n*=3, R=$OSiMe_3$ | 18 | 205 (0.01) | 1.4581 | — | 67 |
| *n*=2, R=$OSiMePh_2$ | 39 | 274 (0.001) | 1.5219 | — | 67 |
| *n*=2, R=$OSiPh_3$ | 95 | 320—330 (0.002) | — | — | 67 |
| *n*=3, R=$OSiPh_3$ | 106 | — | — | — | 67 |
|  | | | | | |
| *n*=1, X=$SiMe_3Cl$ | — | 132 (14) | 1.435 | — | 64 |
| *n*=2, X=$SiMe_3$ | — | 125 (0.04) | 1.4462 | — | 64 |
|  | | | | | |
| *n*=1, X=Cl | — | 82 (0,001) | 1.4355 | — | 63 |
| *n*=2, X=Cl | — | 104 (0.005) | 1.4281 | — | 63 |
| *n*=3, X=Cl | — | 146 (0.005) | 1.4235 | — | 63 |
| *n*=2, X=OH | — | — | — | — | 63,75 |
| *n*=3, X=OH | — | — | — | — | 63 75 |
| *n*=1, X=$NEt_2$ | — | 133 (0.005) | 1.4413 | — | 63 |
| *n*=2, X=$NEt_2$ | — | 162 (0.005) | 1.4328 | — | 63 |
| *n*=1, X=$OSiMePh_2$ | 26 | 230 (0.005) | 1.5091 | — | 63 |
| *n*=2, X=$OSiMePh_2$ | 1—3 | 246 (0.005) | 1.4925 | — | 63 |
| *n*=3, X=$OSiMePh_2$ | — | 257 (0.005) | 1.4808 | — | 63 |
|  | | | | | |
| *m*=0, *n*=2 | — | 207 (0.005) | 1.4538 | — | 63 |
| *m*=0, *n*=4 | — | 280 (0.005) | 1.4525 | — | 63 |
| *m*=1, *n*=2 | — | 198—201 (0.001) | 1.4415 | — | 63 |
| *m*=1, *n*=4 | — | 291—305 (0.001) | 1.4404 | — | 63 |
|  | | | | | |
| *n*=1 | 15—16 | 125 (0.04) | 1.4462 | — | 63 |
| *n*=2 | 25—27 | 193—195 (0.005) | 1.4485 | — | 63,65 |

Table 7 (continued).

| Compound | M.p., °C | B.p., °C (*p*, mmHg) | $n_D^{20}$ | $d_4^{20}$ | Ref. |
|---|---|---|---|---|---|
|  | — | 220—222 (0.5) | 1.4250 | — | 70 |
|  | 128—130 (decomp.) | — | — | — | 58 |
|  *n*=1, R=OSiMe$_3$ | — | 80 (0.03) | 1.4295 | — | 69 |
| *n*=2, R=OSiMe$_3$ | — | 153 (0.02) | 1.4505 | — | 68,69 |
| *n*=3, R=OSiMe$_3$ | — | 205—206 (0.02) | 1.4622 | — | 68,69 |
| *n*=4, R=OSiMe$_3$ | — | 255 (0.01) | 1.4697 | — | 68,69 |
| *n*=5, R=OSiMe$_3$ | — | 280—300 (0.02) | — | — | 68,69 |
| *n*=1, R=OSiMePh$_2$ | — | 226 (0.02) | 1.5420 | — | 68,69 |
| *n*=2, R=OSiMePh$_2$ | — | 275 (0.02) | 1.5325 | — | 68,69 |
| *n*=1, R=OSiPh$_3$ | 132—133 | — | — | — | 68 |
|  | — | 56—57 (8) | 1.4085 | — | 71 |
|  | — | 126—127 (0.5) | — | — | 73 |

of the structure of the silazane segments[59,66]. Thus linear oligomers containing silazane bonds in terminal bistrimethylsilylamino-groups are characterised by a doublet in the range 940–920 cm$^{-1}$;[59] in the infrared spectra of oligoorganosiloxazanes in which the



units forms a disilazane ring the $\nu_{as}$(Si.N.Si) band is observed in the range 895–870 cm$^{-1}$.

The size and composition of the cyclic segment has an appreciable influence on the position of signals of protons in cyclic dimethylsilylene groups in the $^1$H n.m.r. spectra of the cyclolinear organosiloxazanes studied (~20 compounds). Thus the shift of the peak corresponding to a dimethylsilylene group forming part of a disilazane ring is $\tau$ = 9.70–9.76 ppm.[63] The analogous shift of the peak corresponding to the dimethylsilylene group in a diazasilacyclopentane segement was $\tau$ = 9.86 ppm.[69] No perceptible effect of exocyclic siloxazane or other groups on the position of this signal has been observed.

## IV. POLYORGANOSILOXAZANES

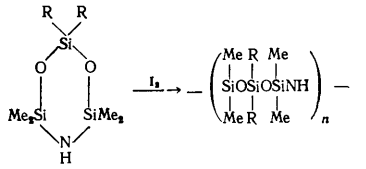
Polyorganosiloxazanes have been synthesised with various molecular structures—(1) linear macrochains having an irregular distribution of siloxane and silazane bonds, and also monochain polymers with cyclic segments, (2) branched and three-dimensional macromolecules, and (3) ladderlike or partly ladderlike.

Polymers containing organosiloxazane segments in the macromolecular chains are obtained by the catalytic polymerisation of cyclic compounds, by the condensation of $\alpha\omega$-diamino- or polyamino-organosiloxanes or cyclo-organosiloxazanes containing functional groups attached to silicon atoms, or by hydride migration.

Attempts to apply to cyclo-organosiloxazanes well known methods of polymerisation using potassium hydroxide as catalyst unexpectedly did not yield polymers of high molecular weight[76]. In the action of this alkali on *SiSi*-dimethylated six-, eight, and ten-membered cyclosiloxazanes (5% of alkali on the weight of the heterocycle) at temperatures above 100°C the increase in viscosity of the reaction products was accompanied by the evolution of ammonia and methane[78]. The formation of these gases indicated the simultaneous occurrence of degradation and polycondensation processes at Si–Ni–Si and Si–C bonds. Subsequent heating of the reaction mixture entailed a fall in viscosity, obviously owing to breakdown of oligomeric chains. In contrast to the above processes the use of caustic potash as catalyst in combination with solvating additives such as dimethyl sulphoxide facilitated the synthesis of polymers of high molecular mass[76].

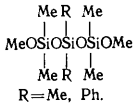
Tetramethylammonium hydroxide, iodine[76,77,79], and ammonium chloride[10] have also proved effective catalysts for the polymerisation of organocyclosiloxazanes. Study of the mechanism of polymerisation in the presence of

catalytic quantities of iodine showed that the process was highly specific involving cleavage only of silazane bonds:



R=Me, Ph

The intrinsic viscosity of the resulting polymers was $[\eta] = 1.25$.[76,77] Evidence of this course of polymerisation was the formation of a single product—a hexasubstituted 1,5-dimethoxytrisiloxane

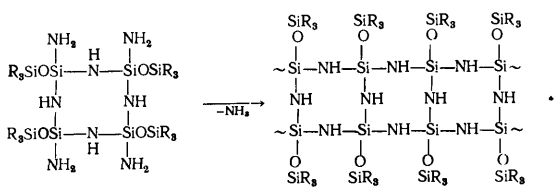


R=Me, Ph.

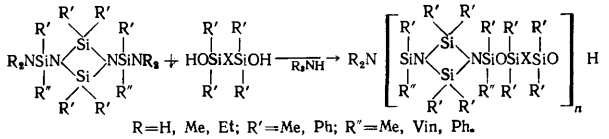
as a result of complete methanolysis of the silazane bonds in the resulting polymer. Chromatographic analysis of analogous methanolysis products from the polymer obtained from hexamethylcyclotrisildioxazane in the presence of tetramethylammonium hydroxide as catalyst indicated also the formation of dimethoxydimethylsilane, 1,3-dimethoxytetramethyldisiloxane, and higher homologues $CH_3O[Si(CH_3)_2O]_nCH_3$ ($n$ = 3–5). The presence of these products was regarded[76] as evidence of the statistical development of polymerisation involving both silazane and siloxane bonds. Individual studies revealed that, among six-membered cyclo-organosiloxazanes, rings in which methyl and phenyl groups were attached to the silicon atoms were least active with respect to polymerisation in the presence of iodine as catalyst[77].

Elastomers of high molecular weight with various contents of silazane groups have been obtained also by the copolymerisation of two eight-membered rings—octamethylcyclotetrasiloxane and octamethylcyclotetrasiltrioxazane—with tetramethylammonium hydroxide as catalyst[80].

The homocondensation of $\alpha\omega$-diamino-, $\alpha\omega$-bismethylamino-, and $\alpha\omega$-bisethylamino-diorganosiloxanes[3,19,23] and of polyamino-organosiloxanes[81] yields polymers in the absence of catalysts. However, no data have appeared on the use of this method to obtain products of high molecular weight. Eight-membered organosilazane rings containing exocyclic siloxane units and a primary amino-group on every silicon atom in the ring are considerably more reactive. When redistilled, they evolve ammonia and form a polymeric organosiloxazane, to which a ladder structure was assigned[70]:



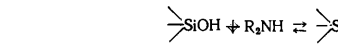
Rather more publications have appeared on the synthesis of cyclolinear organosiloxazanes by heterofunctional condensation. This has most often involved the reaction of cyclodisilazane compounds containing aminosilyl groups with $\alpha\omega$-diol derivatives:



R=H, Me, Et; R′=Me, Ph; R″=Me, Vin, Ph.

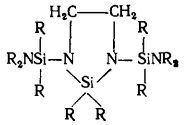
Compounds containing an *SiSi*-dimethylated[47,82–86] or *SiSi*-diphenylated[47,84,86,87] disilazane ring and amino-, dimethylamino-, or diethylamino-silyl groups have been used as cyclic component. The $\alpha\omega$-diols were dimethyl- or diphenyl-siloxane oligomers of various chain lengths[82,84,85], $p$-bishydroxydiorganosilylated benzenes[47,83,86,87], or analogous derivatives of diphenyl ether[86]. The viscosity of the final polymers obtained by the above reaction scheme depended on the reaction conditions and on the nature of the reactants[82]. However, prolonged heating or raising the temperature of the reaction mixture might result in gelation of the polymers.

The probability of the formation of polyorganosiloxazanes having three-dimensional macromolecules is regarded[82] as directly proportional to the probability of cleavage of the disilazane ring (and also the appearance of additional functional groups) under the influence of nucleophilic species formed according to the scheme



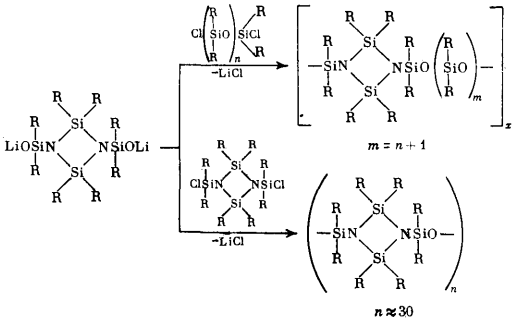
The probability of the appearance of such nucleophilic species should increase with the basicity of the amine, accelerating gel formation by the macromolecules. In the reactions studied a corresponding increase in rate of formation of insoluble polymers has actually been observed according to the nature of R in the sequence $v_H < v_{CH_3} < v_{C_2H_5}$. Reaction between analogous disilazane rings and $p$-bisdiphenylhydroxysilylbenzene in diglyme or xylene goes practically to completion and is not accompanied by fission of cyclic silazane bonds[47].

Polymers have been synthesised by a similar procedure from azasilacycloalkanes of general formula



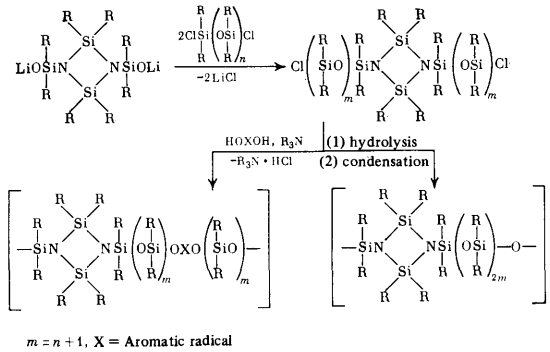
and disubstituted silanediols[88], tetraphenyldisiloxane-1,3-diol, or $p$-bisdiphenylhydroxysilylbenzene[89].

Cyclolinear polymers have been obtained not only by the silanediamine–silanediol type of heterocondensation but also by exchange reactions of cyclic lithium silanediolates with *SiSi′*-dichlorinated cyclodisilazanes or organo-$\alpha\omega$-dichlorosiloxanes[47,65]:



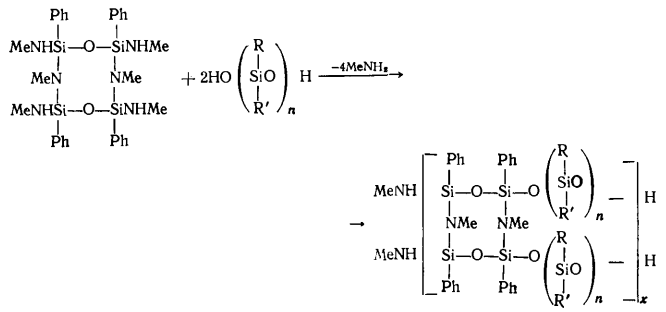
$m = n + 1$

$n \approx 30$



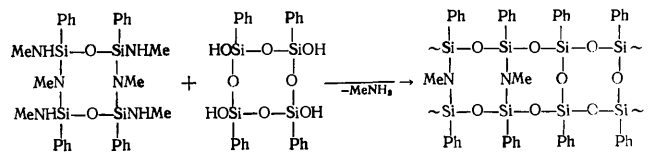

$m = n + 1$, X = Aromatic radical

The use as initial compounds of cyclo-organosiloxazanes of higher functionality ($f = 4$) enables polymers to be synthesised with branched macromolecules or ladderlike siloxazane segments[51]:



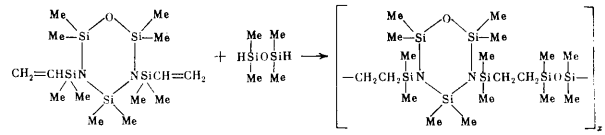

The hydroxylated monomers and oligomers used in these reactions were diphenylsilanediol, tetraphenyldisiloxane-1,3-diol, 1,3-dimethyl-1,3-diphenylsiloxanediol, tetramethyldisiloxane-1,3-diol, decamethylpentasiloxane-1,9-diol, and dimethyl(methylphenyl)siloxane-$\alpha\omega$-diols in which the number average of siloxane units in the molecules was ~100. The nature of the siloxane-$\alpha\omega$-diol—primarily the length and the rigidity of the chain—determined both the course of polycondensation and the structure of the macromolecules. Short and rigid molecules, such as those of diphenylsilanediol and tetraphenyldisiloxane-1,3-diol, caused polycondensation without formation of insoluble polymers having a three-dimensional structure. The use of organosiloxanediols having a very flexible siloxane chain for condensation with cyclic 4,8-dimethyl-1,3,5,7-tetrakismethylamino-1,3,5,7-tetraphenylsil-2,6-dioxa-4,8-diazane, because of the greater mobility of the branches, facilitated long-range intermolecular interaction leading to gel formation. Soluble polymers obtained by this method had molecular weights in the range $(25-30) \times 10^3$.

A polyphenylsiloxazane polymer having a high content of ladderlike segments in the macromolecular chains is formed by the polycondensation of two tetrafunctional cyclic compounds[51]:

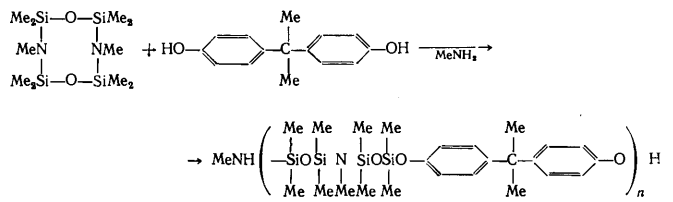



The reaction goes almost to completion. Despite the high functionality of the initial monomers, the resulting polymer is a powder readily soluble in aromatic solvents. Light scattering indicates that its molecular weight is $(100-200) \times 10^3$. The use of various organocyclosiloxazanes having functional amino-groups and diphenylpropane-*pp'*-diol has been claimed[90] for obtaining polyphenylated carbosiloxazane polymers by a similar method.

Processes for obtaining polymeric organosiloxazanes by hydride addition have been claimed in the patent literature. In one case this involved reaction of cyclosiloxanes containing vinylsilyl groups with linear or cyclic organosilazanes containing free hydrogen atoms in the presence of chloroplatinic acid[91]. In another process linear organosiloxanes containing terminal hydrogen atoms were heated with vinylsilylated cyclosiloxazanes or cyclo-organosilazanes in the presence of the same catalyst[52]:

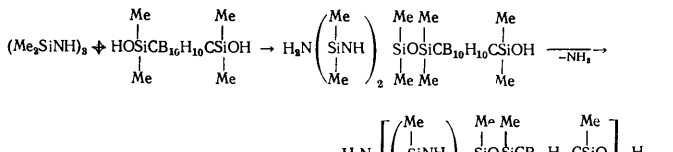


Organosiloxazanes of high molecular weight have been synthesised by splitting some of the silazane bonds in an eight-membered cyclo-organosiloxazane by means of a phenolic hydroxyl[13]:




The elastomeric polycarbosiloxazane obtained had an intrinsic viscosity of 2.7. Polymeric carbosiloxazanes have been synthesised similarly using as hydroxylated compounds fused aromatic diols, bisnitrophenyl sulphone derivatives, and tetraphenylcyclotetrasiloxane-1,3,5,7-tetraol, but polycyclic silazanes were employed together with cyclo-organosiloxazanes[92]. The reduced viscosity of the polymers of this series (0.5% solutions in toluene) lay in the range 0.1–0.95.

The same principle of the partial utilisation of silazane bonds in heterocycles to build up polymer chains underlay the preparation of carborane–siloxazane polymers[108,109]. The reactions of 1,7-bisdimethylhydroxysilylcarborane studied with various heterocycles—hexamethylcyclotrisilazane, octamethylcyclotetrasilazane, hexamethylcyclotrisil-2-oxa-4,6-diazane, octamethylcyclotetrasil-2,6,-dioxa-4,8-diazane, octamethylcyclotetrasil-2,4,6-trioxa-8-azane, and dodecamethylcyclohexasil-2,4,8,10-tetraoxa-6,12-diazane—involved ring cleavage followed by condensation of the linear aminosiloxazanol. With cyclotrisilazane as example the reaction can be written




The rate of cleavage of the heterocycles by the hydroxysilylcarborane is significantly affected by the strain in the ring and its content of silazane bonds: the reactivity of the molecule diminished with increase in size of the cyclo-organosiloxazane and decrease in the number of silazane bonds. The specific viscosity of the resulting polymers (1% solutions in benzene) was 0.2–0.3.

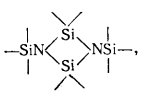
The segmental mobility and the elasticity of linear siloxazane macromolecules in which one silazane unit alternated with two siloxane units were closely similar to those for polyorganosiloxanes. Nuclear magnetic resonance data indicated that segmental mobility in a polymer containing the $Si(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2NH$ unit began around −100°C, but in polydimethylsiloxane it began at about −130°C. The energies of viscous flow for these polymers were respectively 4.3 and 3.4 kcal.[79]

The molecular structure of branched cyclic, ladderlike, and three-dimensional polyorganosiloxazanes has been studied by X-ray diffraction, enabling the rigidity of the polymer chain to be assessed[51] from the interplanar spacing $d_1$. The largest spacing $d_1 = 12.0$Å is characteristic of a molecular chain comprising only cyclic tetrasiloxazane and siloxane units (see fourth last equation and polymer formula above). Replacement of the siloxane ring in this reaction by linear organosiloxane-$\alpha\omega$-diols produced a gradual decrease in $d_1$ to 7.5Å with increase in the length and flexibility of the chain of linear organosiloxanes.

Investigation of the stabilising influence of silazane bonds on the thermo-oxidative degradation of organosilicon polymers[93] revealed that the Si–NH–Si group has a significant stabilising effect on the main chains of siloxazane molecules, with considerably less effect on the rate of degradation of organic groups surrounding the main chains. Such a unit serves as a barrier to depolymerisation of the main chain; in its presence, furthermore, fairly intense oxidation of methyl groups attached to silicon atoms has been observed, leading to branching, three-dimensional cross-linking of the polymer, and thus an additional thermostabilising effect.

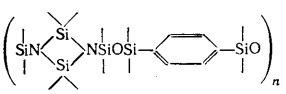
However, a silazane unit containing a secondary nitrogen atom is less stable than Si–NR–Si (R = Alk or Ar) and $Si–N(SiAlk_3)–Si$ groups not only to hydrolytic cleavage but also in the thermo-oxidative degradation of polyorganosiloxazanes. The presence of organosilazane groups having a secondary nitrogen atom is evidently one reason for the relatively low thermal stability in air of several polycarbosiloxazanes[92].

Cyclodisilazane groupings of the type



when introduced into siloxane chains, not only prevent the development of degradative processes involving stepwise cyclisation but also are "suppressors" of hydroxy-groups appearing during thermo-oxidative reactions. Interaction of one hydroxysilyl group with a cyclodisilazane segment does not entail breakdown of the main molecular chains. In a series of polymers whose macromolecules consist of dimethylsiloxane chains separated by tetramethyldisilazane rings thermo-oxidative degradation begins over the temperature range 400–450°C.[82]

Perphenylated polymers having a minimal content of linear chains remain as yet the most stable polyorganosiloxazanes to both thermal and thermo-oxidative treatment. Examples are cyclodisilazane polymers[47] of general formula



and polymers whose macromolecules have predominantly a ladder structure (see fourth last equation above)[51]. Thermal degradation of the former polymers (in nitrogen at 2.8 deg $min^{-1}$) and thermo-oxidative degradation of the latter (in air at 2.7 deg $min^{-1}$) began in the region of 500°C.

## V. PROSPECTS FOR PRACTICAL APPLICATION

Polyorganosiloxazanes have been tested as protective coatings in the electronics industry[94] and on solar energy installations[95]. The stability of the optical properties of organosiloxazane varnishes on prolonged exposure to light and weathering, combined with good adhesion, moisture resistance, and durability, has permitted these coatings to be recommended for protecting the working surfaces of photocells and concentrators in solar energy technology[95]. Polymers containing organocyclodisilazane segments are among the most thermostable types of binders for paint technology.

Organosiloxazane varnishes and coatings are promising protective materials, exhibiting not only high thermal stability but also the ability to harden under normal conditions by interaction with atmospheric moisture[95,96]. The increasing density of three-dimensional cross-linking of macromolecules during hardening is an obstacle to complete disappearance of silazane groups from the polymeric binder. Several features of film formation by the replacement of some of the silazane bonds by siloxane bonds have been investigated[97]. The drying times in air of coatings used in solar energy technology[95] and recommended for the protection of semiconductor materials and instruments[96] are 0.5–5 h. The adhesion of varnishes to steel and copper surfaces reaches 47 kg $cm^{-2}$ after the coatings have been kept at room temperature for 5 days. The adhesion parameters of the materials can be somewhat improved by heat-treatment. Both Soviet[98–100] and foreign[87,89,101–103] patents indicate not only individual characteristics of the coatings but also fields of application—electrical engineering, electronics, the paper, textile, and leather industries, the protection of glass and silicate surfaces, etc.

Organosiloxazane elastomers are less well represented in the literature. Elastomeric copolymers containing Si–NH–Si units are considerably more thermostable than siloxane rubbers with similar radicals attached to the silicon atoms, but are inferior to the latter in resistance to hydrolytic cleavage[80]. Replacement of secondary-nitrogen silazane bonds in the elastomers by tertiary-nitrogen or especially trisilylamine bonds should improve considerably the resistance of such materials to moisture and to water. Filled organosiloxazane elastomers whose macromolecules contain also carborane and trifluoropropylsilyl groups are distinguished by long fatigue life over the temperature range 300–350°C.[104] Methods for obtaining elastomeric siloxazane materials and for their vulcanisation have been given in patents[5,83,86].

It has been proposed to introduce compounds of boron, phosphorus, titanium, iron, and certain others into organosiloxazane binders to enhance the heat resistance and improve the physicomechanical characteristics[105,106]. On the other hand, additions of methylphenylsiloxazane polymers to stabilising mixtures in the manufacture of polyamides tend to increase the resistance of articles to heat and light[107].

The advisability of using organosiloxazane compounds, primarily organocyclosiloxazanes, to obtain polymeric

organosiloxanes has been noted repeatedly both in the periodical and in the patent literature. In most cases the synthesis is accomplished by the heterocondensation of silazane groups with dihydric phenolic derivatives[110-114].

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# Some Aspects of the Coordination Chemistry of the Lanthanides

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A systematic account is given of data (mainly for the period 1965-1975) on the coordination chemistry of the lanthanides: the synthetic, phsysicochemical, and structural aspects of lanthanide complexes, mainly with organic oxygen- and nitrogen-containing ligands are examined. Attention has been concentrated on the application of the physical and physicochemical research techniques in the chemistry of lanthanide complexes.
The bibliography includes 484 references.

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## I. INTRODUCTION

Since the publication of the monograph of Yatsimirskii et al.[1], extensive data have accumulated on the coordination chemistry of the lanthanides, their publication being associated not only with theoretical research but also and mainly with the significant expansion of the applications of the lanthanides and their complexes. During the last 10–12 years, reliable methods have been developed for the isolation of all the lanthanides in a pure state[2,3], which extended the possibility of their practical applications in technology in those cases where the purity of the lanthanides is the main requirement (laser and semiconducting materials, glasses of different kinds, ceramics, etc.)[2]. Coordination compounds of lanthanides in general and chelate complexes in particular are used in liquid media lasers (europium and terbium chelates)[4,5]. Lanthanide complexes are used successfully as chemotherapeutic preparations, including anticancer agents[6], although lanthanides (Ln) are not "metals of life"[7]. The use of lanthanide compounds as paramagnetic shift reagents (PSR) assisted the development of NMR spectroscopy[8-11]. Coordination compounds of the lanthanides are also used in Mössbauer spectroscopy[12-13].

Even a brief list of the advances in the employment of lanthanide complexes in various branches of science and engineering demonstrates the necessity for an account of the achievements of the coordination chemistry of the lanthanides during the last 10 years. At the same time the reviews on PSR already published (see, for example, Refs. 8–11) are concerned to only a very limited extent with this field, which is closely related to lanthanide

complexes. This review is virtually not concerned with the problems of complex formation and extraction of the lanthanides and their analytical chemistry. Despite their urgency, these are too broad for inclusion in this review, which is devoted to advances in the synthesis and the study of the physicochemical properties and structure of lanthanide complexes achieved during the 1965–1975 decade.

## II. CHARACTERISTICS OF THE COMPLEX FORMATION REACTIONS

Whereas in the 1950's it was believed that the ability to form complexes is not a characteristic property of the lanthanides, the data which have accumulated during the last two decades created a new chapter in coordination chemistry—the chemistry of lanthanide complexes[14-17].

Certain features of the coordination chemistry of the lanthanides were examined previously by Yatsimirskii[1], Muller[2], Spitsyn and Martynenko[17], and Forsberg[16]. The majority of experimental data on the splitting of the energy levels of the 4*f* electrons of lanthanide ions on complex formation are nowadays interpreted in terms of the parameters of the semiempirical crystal field theory (CFT). The distinctive features of the states of *f* electrons in lanthanide complexes are associated primarily with the fact that they are to a large extent shielded from the ligand theory by the outer *s*, *p*, and *d* electrons and are therefore less subject to its perturbing influence. In those cases the spin–orbital interaction is much more pronounced than for *d* electrons. An unusual version of a weak crystal field therefore arises for *f* electrons, being weaker than the interelectron and spin–orbital interactions[18].

In order to determine the energy states of the lanthanide ion in the crystal field, it is necessary to begin by considering its states with allowance for interelectron and spin–orbital interactions, which are characterised for each state with the given orbital ($L$) and spin ($S$) quantum numbers by the additional quantum numbers $J$ of the total momentum operator. The distribution of the electron cloud in compounds with a total momentum $J$ and the splitting of the levels of the latter under the influence of the electrostatic effect of the ligand field must be calculated by methods of perturbation theory or determined qualitatively by methods of group theory[18]. Quantitative calculations of the splittings of the energy states of *f* electrons are performed similarly to those for *d* electrons[19], but attempts to calculate the CFT parameters for lanthanide compounds with a known structure[20] have demonstrated the impossibility of achieving a satisfactory agreement between the non-empirical values of the CFT parameters and the experimental data.

In the 1960's an attempt was made to describe more realistically the nature of the chemical bonds between lanthanide ions and ligands on the basis of the molecular orbital (MC) theory, which makes it possible to take into account the degree of covalence of the bonds under consideration. It is noteworthy that the accuracy of the calculations performed hitherto is low. Nevertheless it is believed to be an established fact[18,21] that a considerable (if not the major) component of the splitting of the energy levels of the 4*f* shell is due to the influence of the overlapping of the 4*f* orbitals of the lanthanide and the ligand orbitals. The overlap integral between the 4*f* orbital of the lanthanide ion and the valence $np$, $ns$ ligand orbital is an order of magnitude smaller than the overlap integral between the outer vacant orbitals[21]. One may therefore expect that the influence of the overlap of the wave functions of the lanthanide ion and the ligands on the structure of the 4*f* shell is slight.

The influences of the external electrostatic field and the overlap of the 4*f* orbitals with ligand orbitals on the splitting of the energy levels of the 4*f* shell have been compared[20-24]. The *f* electrons shielded by *d* electrons in the lanthanide complexes have been shown to form weak covalent bonds with the ligands. The covalent bonds between lanthanide ions and ligands are formed mainly as a result of the mixing of the occupied ligand orbitals with partially occupied 4*f* orbitals and vacant 6*s*, 6*p*, and 5*d* orbitals of the lanthanide ions. The vacant 6*s*, 6*p*, and 5*d* orbitals are located outside the occupied $5s^2$ and $5p^6$ shells; the pair integrals for the overlap of the orbitals considered with the ligand orbitals are approximately 0.1. Calculations by the MO method in terms of the Wolfsberg–Helmholtz approximation (MWH), for example, for the tetra-acetatoeuropate anion[25], make it possible to infer the properties of the valence shell of the lanthanide. Calculations have been made[25] on the two complex ions $[EuO_8]^-$ and $[EuO_8]^{5-}$ and it was found that the excess charge is concentrated mainly at the oxygen atoms without altering significantly the orbital population of the europium atom. The MO method usually yields a somewhat high covalent contribution to the chemical bond, "equalising" the charges on the atom; nevertheless it can be regarded as established that the charge of the valence shell is quite capable of influencing appreciably the splitting of the energy levels of the 4*f* shell[26].

When the influence of the overlap of the 4*f* orbitals and the valence shell orbitals of the ligand on the splitting of the energy levels of the 4*f* shell is considered within the framework of the LCAO-MO method, it is believed useful[21] to distinguish two effects: the covalent mixing of a partially occupied *f* orbital of the lanthanide ion ($f_\alpha$) with a fully occupied group orbital of the ligand ($\Phi_\alpha$) and the change in the energy of the molecular orbital of the complex ($\psi_\alpha$) owing to the overlap of the $f_\alpha$ and $\Phi_\alpha$ orbitals. Calculation[26] of the energy of the antibonding orbital taking into account both effects yields values in agreement with the observed experimental splitting.

In terms of the MWH approximation, it is also possible to estimate the relative positions of the energy levels of the 4*f* orbitals as a function of the structure of the coordination polyhedron. In conformity with theory[26], an admixture of covalent bonding in an ionic bond should favour the formation of coordination polyhedra with vertices distributed in the direction of the maxima of the hybrid $sp^3d^n$ orbitals. This requirement is satisfied primarily by the nine-coordination polyhedron with $D_{3h}$ symmetry. Among the polyhedra with a coordination number (C.N.) of 8, the dodecahedron with $D_{2d}$ symmetry, in which the σ bonds are formed via the $sp^3d^4$ hybrid orbitals, and the square antiprism ($D_{4d}$ symmetry), where the $sp^3d^4$ or $p^3d^5$ valence orbitals are hybridised, are preferred. There is also the possibility of a nine-coordination polyhedron with $C_{4v}$ symmetry[27].

Calculations[28] have shown that the contribution of the *f* orbital to a coordinate bond is sometimes very high (between 34.8 and 46.2%) and the difference between the contributions of the *f* and *d* orbitals to the structure of the polyhedra diminishes with increasing atomic number of the element in the series of lanthanides. The relation between the existence of three regions of crystal-chemical instability in the series of lanthanides and the extrema on the energy curves of 4*f* orbitals has been discussed[29]. The first region usually corresponds to Pr, Nd, and Sm, the

second to Gd, and the third to Dy, Ho, and Er. The change in structure in the first region of crystal-chemical instability can be accounted for by a sharp decrease of the energies and effective radii of the 4*f* orbitals, calculated [30] by the Thomas–Fermi method. The possibility of the involvement of heavier lanthanides in bonds formed via *f* orbitals is also postulated [29].

It can be regarded as established that the symmetry of the coordination spheres of lanthanide ions sometimes deviates significantly from that predicted for the purely electrostatic model. The characteristics of the geometry of the ligand the capacity of the coordination sphere for mixing play an important role under these conditions: for example, when solvent molecules or those of some other inorganic or organic ligand are coordinated simultaneously in addition to the primary organic ligand.

The study of the relative geometries of lanthanide complexes has also proved convenient in the application of the MO method in terms of the angular overlap approximation [31]. The method is based on the assertion that the destabilisation of the central atom owing to the formation of covalent bonds is proportional to the square of the angular component of the overlap integral, which depends strongly on the geometry of the complex. Since the bonding orbitals in lanthanide complexes are located mainly at the ligands and the antibonding orbitals at the central atom (c.a.), the antibonding effects assume principal importance in the formation of covalent bonds in lanthanide complexes. Thus there is a possibility of estimating the influence of the antibonding effects on the symmetry of the complex. For lanthanide complexes with the $f^0$, $f^7$, and $f^{14}$ electronic configurations, the antibonding effects do not influence the symmetry of the complex, which depends only on the electrostatic metal–ligand interaction.

When the bond between the central atom and the ligand is predominantly ionic, higher coordination numbers, permitted by the relative dimensions of the central atom and the ligand, are preferable (depending on the size of the ligand, coordination numbers of 8–12 and sometimes [14–16] higher are possible for lanthanide compounds); for a given coordination number, the polyhedron with triangular faces is preferable, since it constitutes a closer approximation to the sphere. Thus, whereas for the lanthanides with the $f^0$, $f^7$, and $f^{14}$ configurations the symmetry of the complexes depends only on the ion–dipole electrostatic interaction, for the remaining lanthanides complexes having the composition $LnL_6$, for example, where L is the ligand, are formed comparatively rarely and have the structure of an octahedron and not a trigonal prism (in the latter case, the antibonding effect is a minimum [31]). A detailed consideration [32] has also shown that the antibonding effects for lanthanide complexes with different coordination numbers may determine the fine structure of their coordination polyhedra.

The partly covalent nature of the bond in lanthanide complexes is also to some extent demonstrated by the results of physical measurements: the study of luminescence spectra, absorption spectra in different wavelength ranges [31], Mössbauer spectra [12,22], and the deviation of the symmetry of the complexes revealed by X-ray diffraction analysis from the predictions based on the electrostatic model [18]. The partly covalent nature of the chemical bond in the coordination compounds necessitates the classification of the latter as labile and not as inert complexes. The lability of the lanthanide complexes and the ability of lanthanide ions to form complexes with variable and high coordination numbers create difficulties in the study of coordination compounds of the lanthanides in both the solid state and in solution.

In conclusion yet another interesting feature of the coordination chemistry of the lanthanides must be pointed out. Although the most characteristic oxidation state of the lanthanides is 3+, certain lanthanide ions, namely those of europium(III), ytterbium(III), and samarium(III), exhibit a tendency towards reduction to the bivalent state [33], the europium(III) ion showing the highest electron affinity and being most readily reduced to europium(II). It is thus not fortuitous [34] that europium(II) complexes of *NN*-bis-(1-acetonylethylidene)ethylenediamine have been isolated on a preparative scale.

All the foregoing factors illustrate the complexity and wide variety of the problems involved in the study of the coordination compounds of the lanthanides and demonstrate the necessity for the employment of many methods in the synthesis and physicochemical study of such complexes.

## III. SYNTHESIS OF COORDINATION COMPOUNDS

The isolation of individual lanthanide complexes requires a careful selection of solvents and appropriate variation of the molar ratios of the reactants and the pH of the medium. In water, one of the commonest solvents [4,16,17] for the synthesis of coordination compounds of the lanthanides, complexes are formed mainly with weakly basic chelating organic ligands. This conclusion has been confirmed by numerous examples: chelate lanthanide complexes have been formed with complexones [1,14,35–38], β-diketones [39,40], pyrazolones and their derivatives [41], 8-hydroxyquinoline *N*-oxide [42], as well as complexes of certain monodentate ligands (urea [43], thiourea [44], guanidinium hydrogen carbonates [45]), etc. [1,14,46,47]. As a rule, in addition to the organic ligand, solvent (water) molecules are coordinated at the same time, but complexes without solvent molecules can be isolated from an aqueous medium [48,49].

Similar results can be obtained also in aqueous organic media, since the sequence of solvents in terms of their electron-donating properties relative to the lanthanides ("hard acids") [48] indicates an appreciable stability of the hydrates of lanthanide compounds [50,51]. At the same time anhydrous lanthanide complexes or complexes with a mixed ligand environment can be isolated from aqueous organic media prepared on the basis of oxygen-containing solvents with a higher electron-donating activity than that of water [for example, dimethyl sulphoxide (DMSO) or dimethylformamide (DMF)] [49]. The atomic number of the lanthanide, the nature of the organic solvent, and the component ratio in the water–organic solvent mixture used as a medium for the synthesis of the complexes have a significant influence under these conditions on the composition of the coordination sphere. One of the most suitable media for the synthesis of lanthanide complexes is a water–ethanol mixture in which complexes of lanthanides with complexones [1,6,17] and oxygen-, nitrogen-, and phosphorus-containing ligands [1,14–17,52–55], including tetramethyl sulphoxide [52], salicylidenehydrazine [56], *N*-salicylideneanthranilic acid [54], hexafluoroacetylacetone, 4-methylpyridine [55], chloro-derivatives of *o*-hydroxyacetophenone [58], etc. [1,16,17,49], have been obtained. Crystalline holmium bisdipivaloylmethanate [57] and trisdipivaloylmethanate [58,59], whose existence in solution had been

postulated in an earlier study [60], were synthesised in the same solvent mixture in an alkaline medium from holmium nitrate and dipivaloylmethane.

Table 1. Compositions of lanthanide coordination compounds [72-219].

| Formula | L | X, $n$ | References |
|---|---|---|---|
| $LnL_nX_3$ | Pyridine, 1,2-propylenediamine, 2,4,6-tri-α-pyridyl-1,3,5-triazine, thioxane oxide, tetramethylene sulphoxide | X = Cl, $NO_3$, $ClO_4$; $n$ = 2—9 | 72—78 |
| $LnL_6X_3 \cdot nH_2O$ | Antipyrine, o-phenanthroline, *NN'*-ethyleneurea, tetramethylurea, 1,3-, and 1,1-dimethylurea | X = Cl, Br, I, $ClO_4$, $NO_3$, NCS; $n$ = 0—3 | 79—84 |
| $LnL_8X_3$ | Urea, *NN*-dialkylamide | X = I, NCS | 85—88 |
| $LnL_4X_3 \cdot nH_2O$ | Hydrazine, 1,10-phenanthroline, urea, alkylthiourea, dimethylformamide, dimethylacetoacetamide, *NNN'N'*-tetramethylmalonamide | X = Cl, $NO_3$, $SO_4$, $ReO_4$, NCS, $ClO_4$, $C_2O_4$; $n$ = 0—2 | 89—104 |
| $LnL_3X_n$ | Hydrazine, pyridine, glycolate, acetylacetonate, benzoate, propionate, alkylphosphonothioate, dipivaloylmethanate, α-aminoacids, β-diketones, Schiff bases, cyclopentadiene | X = $H_2O$, EtOH, MeOH; $n$ = 0—4 | 65—67, 105—141 |
| $LnL_2X_3 \cdot n$Solv | 1,10-phenanthroline, 2,2'-bipyridyl, hydrazine, uropropine, antipyrine, α-aminoacids, α-furoin oxime, alkyldiantipyrylmethane, tributyl phosphate, isocyanate | X = Cl, F, I, $SO_4$, $C_2O_4$, $ClO_4$, $NO_3$, SCN, SeCN; Solv = $H_2O$, EtOH, MeOH, $n$ = = 0—5 | 142—154 |
| $LnL_2X \cdot nH_2O$ | Dipivaloylmethanate, phthalocyanine, diphthalocyanine | X = Cl, Br; $n$ = 0—2 | 57—155 |
| $Ln(L)X_m \cdot nH_2O$ | 4,4'-diamino,3,3'-dimethylbiphenyl, 4,4'-di-pyridylbenzimidazole, α-aminoacids, malonate, butyrate, tartrate, hydroxyethyl iminodiacetate | X = Cl, $NO_3$; $m$ = = 0—3, $n$ = 1—6 | 156—169 |
| $LnL \cdot nH_2O$ | Ethylenediaminetetra-acetate, nitrilotriacetate, citrate, alkylphosphonate, trimellitate | $n$ = 0—8 | 170—183 |
| $LnL_3L'_n$ | L = β-diketone, chlorosalicylate, 2-hydroxy-3-naphthoate, 2,2,6,6-tetramethylheptane-3,5-dionate; L' = picoline, pyridine, 1,10-phenanthroline, quinoline, triphenylarsine oxide | $n$ = 1,2 | 184—194 |
| $LnL_3(NO_3)_2(ClO_4)_2$ | 2,2'-bipyridyl | — | 195 |
| $LnL_2X_3 \cdot nH_2O$ | 1,10-phenanthroline, 4,4'-bipyridyl, 2,2'-bi-pyridyl, tetrahydrofuran, thiourea, triglycine | X = Cl, $NO_3$, SCN, SeCN, $C_2H_3O_2$; $n$ = = 0—6 | 196—216 |
| $Ln_2L_3 \cdot nH_2O$ | Malonate, picolinate, quinolinate, diethylmalonate, dihydroxymalonate | $n$ = 1—8 | 217—219 |

Absolute benzene, which exhibits a weak solvating capacity, is frequently used to synthesise anhydrous lanthanide complexes. However, the low solubility of lanthanide salts in benzene makes it necessary to carry out the synthesis using lanthanide alkoxides. Sparingly soluble chelate complexes of the lanthanides with *o*-hydroxyazomethines have been synthesised in the same solvent [61-64]. Complexes of the lanthanides with Schiff bases can be obtained from the lanthanide chlorides in methanol [65-67].

The method whereby lanthanide complexes are obtained in the absence of solvents is extremely convenient. Comparatively unstable complexes of a series of lanthanides with monodentate acids [1,68-71] and nitrogen-containing ligands [16], for example with organic acids [68-70] and aliphatic heterocyclic amines [1,16], are synthesised by this procedure. However, although we believe it is extremely promising as a method for the preparation of non-solvated lanthanide complexes, it has not so far been adequately used in the coordination chemistry of the lanthanides.

When the molar ratio of the reactants (lanthanide salts and ligands) is varied, it is possible to obtain complexes having different compositions and coordination numbers ranging from 6 to 12 (Table 1). [79-219] It has been shown [220] that, for different reactant ratios (1 : 4, 1 : 5, and 1 : 7), the same ligand (antipyrine) in methanol can give rise to the complexes $Y(Ant)_n(NCS)_3$, where $n = 4-6$, and, when the ratio is 1 : 3, the complex is $Y(Ant)_3(NCS).2CH_3OH$. The composition of lanthanide complexes of hydrazine also depends significantly on the reactant ratio [221].

Control of the pH of the medium in which the complexes are obtained is important for the synthesis of lanthanide complexes. Allowance for this factor is particularly necessary when the synthesis is carried out in an aqueous medium: the ligands must be weakly basic compounds incapable of precipitating the lanthanide hydroxide or hydroxo-salt [222-226]. This is why it is impossible to isolate from aqueous and aqueous organic solutions lanthanide complexes with amines which have high $pK_a$ values [16].

The influence of $pK_a$ on the formation of lanthanide complexes with nitrogen-containing ligands was noted by the present authors [169]: $LnCl_3$ (Ln = Sm or Eu) reacts with benzimidazole ($pK_a$ = 5.53) to form the complexes $LnCl_3.L.6H_2O$ in aqueous methanol, while the reaction with imidazole ($pK_a$ = 7.05) results in the formation of lanthanide hydroxides. This is apparently why it is comparatively easy to synthesise lanthanide complexes of weakly basic [227] and oxygen-containing ligands [200-226] in water-containing media. Strict control of the pH of the medium is necessary not only to prevent the possible formation of lanthanide hydroxides but also for the specific synthesis of lanthanide complexes of a particular type. Metal chelates are usually synthesised in weakly alkaline media [1,35,36,42,56,71,228,229], the required pH values being attained by the addition of ammonia or alkali; molecular lanthanide complexes of the type $LnX_3.mL.pS$olv (Table 1) are isolated from nearly neutral solutions; together with adducts of the above type, protonated lanthanide complexes are formed in acid media [230-233].

Reliable synthetic procedures and comprehensive study of the physicochemical properties of a wide variety of lanthanide salts [234-237] made it possible to obtain various coordination compounds of the lanthanides with oxygen- and nitrogen-containing ligands (Table 1) and to determine the influence of many factors on the composition of the complexes and the coordination number of the lanthanide. The highest coordination numbers are attained in lanthanide complexes with neutral ligands when the lanthanide salt anion is a pseudohalide species [108,152,202] or perchlorate [238]. For example, $Ln(phen)_4(ClO_4)_3$ and $Ln(terpy)_3.(ClO_4)_3$ with coordination numbers of 8 and 9 respectively have been synthesised [72,74]. Tris-complexes with bipyridyl and phenanthroline [152,202] have been obtained using the anions $NCS^-$ and $SeCN^-$: according to infrared spectroscopic data [108], the coordination number in such complexes is 9. On the other hand, when the anion is $Cl^-$ or $NO_3^-$, bis-complexes are formed and a coordination number greater than 6 is attained as a result of the binding of solvent molecules [89]. Analysis of X-ray diffraction data for lanthanide complexes with isoelectronic and tetrahedral ($ClO_4^-$, $SO_4^{2-}$, $PO_4^{3-}$, and $SiO_4^{4-}$) and triangular ($NO_3^-$, $CO_3^{2-}$, and $BO_3^{3-}$) anions demonstrated [238] a decrease of the coordination number of the lanthanide with increase of the formal charge of the oxo-anion. At the same time

the coordination number in the series of lanthanide complexes with $EO_4^-$ anions decreases from 9 to 6, while in the case of $EO_3^-$ the decrease is from 12 to 8.

The influence of the nature of the lanthanide on the coordination numbers of the complexes has been discussed in detail by Aslanov and Porai-Koshits[238]. The tendency towards a decrease of the coordination numbers of the lanthanides from lanthanum to lutetium has been known for a long time[1,14,16,17]. The authors[238] note that the coordination numbers of the lanthanides in compounds belonging to the same series (sulphates, phosphates, hypophosphites, and silicates) are higher for the lighter lanthanides than for the heavier lanthanides. This tendency has also been observed for lanthanide complexes with nitrate, carbonate, carboxylate, and also borate anions and with organic acid amides. Having explained these trends, Aslanov and Porai-Koshits, emphasised justifiably that the coordination numbers of the lanthanides and the composition of their complexes depend significantly on the nature of the ligand.

Chelating ligands stabilise complexes with a constant coordination number of the lanthanide regardless of the atomic number of the latter. In this case the coordination number is determined primarily by the geometrical characteristics of the ligand system: the number of members in the metal-containing rings and the number of such rings, the rigidity of their configuration, and other factors resulting from the stability of the metal chelates [239]. Among the factors enumerated, the number of members in the metal-containing rings assumes a particularly important role[238]: four-membered rings promote the formation of lanthanide complexes with coordination numbers of 8–12; five-membered rings lead to complexes with constant coordination numbers (9 for light lanthanides and 8 for heavy lanthanides); six-membered rings give rise to complexes with coordination numbers of 8 (light lanthanides) or 7 (heavy lanthanides).

A constant composition of the complexes over the entire series of lanthanides can arise also for compounds with bulky monodentate ligands (for example a coordination number of 6 is obtained for lanthanide complexes with *NNN'N'*-tetramethylurea)[238]. Extensive reviews of the formation of crystalline lanthanide complexes have been published in monographs[240,241]. Methods of synthesis characteristic of $\pi$-complexes of transition metals predominate in the chemistry of $\pi$-complexes of the lanthanides[242,243].

## IV. THERMODYNAMICS OF COMPLEX COMPOUNDS

After the publication of the monograph of Yatsimirskii et al.[1], numerous studies demonstrating the validity of the approach of these workers to the interpretation of the thermodynamics of lanthanide complexes with a wide variety of ligands were carried out; this makes it possible to take into account, in estimating the stability of lanthanide complexes, the fine structure of the ligand system and the influence of a number of factors on the complex formation process (i.e. on the number and types of reactions) namely the composition of the complex and other factors[244–250].

Calorimetric measurements of the enthalpies of stepwise complex formation, which have many advantages compared with the usual methods for estimating formation constants[244], have recently become important. The calorimetric titration method[245], whereby it is possible to obtain information in many cases about the number and type of reactions occurring simultaneously in the system and also about the concentrations of various reactants involved, is of particular interest. Furthermore, the method permits the determination of the values of $\Delta H$, $\Delta S$, and $\Delta G$ solely on the basis of calorimetric data. For example, a linear correlation between $\Delta H$ and $\Delta S$ has been observed for lanthanide fluoride complexes[247], which makes it possible to regard $LnF^{2+}$ complexes as compounds with predominantly ionic bonds. Positive and fairly high entropies of formation (18–20 e.u.) lead to the conclusion[246–248] that lanthanide fluoride and sulphate complexes have an inner-sphere structure.

All the thermodynamic characteristics of the complex formation reactions of the lanthanides (except promethium) with various organic ligands are now known, namely for propionate, isobutyrate[251], $\alpha$-hydroxyisobutyrate[252], acetate[39], lactate[252], glycolate[251], mercaptopropionate[253], diglycolate[39], ethylenediaminetetra-acetate (EDTA), ethyl sulphate[253,254], nitrilotriacetate (NTA),[255] diethylenetriaminetetra-acetate (DTRA),[256,257] triethylenetetramine[16], triaminotriethyleneamine[258], threonine and hydroxyproline[259], and thioglycolic acid[260], and others.

Examination of the above studies reveals certain general characteristics in the variation of the thermodynamic functions of the complex formation reactions of the lanthanides. The higher values of $\Delta H$ for lanthanide glycolates compared with the acetates, propionates, and isobutyrates can probably be accounted for by the formation of an additional bond with the hydroxy-group of the glycolate anion. Replacement of the oxygen atom by a sulphur atom reduces the stability of the complexes and the $\Delta H$ and $\Delta S$ for the lanthanum, samarium, and erbium thioglycolates, which have been investigated, are very close to those for the lanthanide acetates[252]. The thermodynamic parameters of the lactates and $\alpha$-hydroxyisobutyrates are close to the corresponding parameters of the glycolates:

| | $\Delta H$, kcal mole$^{-1}$ | |
|---|---|---|
| | La | Lu |
| Lactates (Ref.252) | —1.58 | —2.19 |
| α-Hydroxyisobutyrates (Ref.252) | —1.96 | —1.11 |
| Glycolates (Ref.252) | —0.85 | —0.65 |
| Glycolates (Ref.24) | —0.63 | —0.29 (Yb) |

Assuming that diglycolate complexes are formed mainly as a result of the disruption of the hydration shell of the hydrated lanthanide ion, the authors[253] showed that a sharp change in the entropy and hence the disruption of the hydration shell begin approximately in the middle of the lanthanide series.

The heat of the reaction $Ln^{3+} + L^{3-} \rightarrow LnL$, where $H_3L$ = NTA, has been measured for the lanthanides except lanthanum[254]. The heat of formation of LaNTA has been measured by Milyukov and Polenova[255]. In the lanthanum, gadolinium, and lutetium series, there is a maximum (or minimum) in the absolute heat of formation corresponding to gadolinium, as for simpler organic ligands. $\Delta S$ is constant for lanthanides of the cerium group, while in the yttrium group it increases.

The $\Delta H$ for lanthanide complexes of EDTA increase from lanthanum to neodymium, decrease on going to terbium, then increase again, i.e. the overall variation is the same as for other complexes[256,257]. However, there is a significant difference: the dependence of the heat of formation and $\Delta S$ on the atomic number of the lanthanide in LnEDTA has a minimum corresponding to gadolinium (as for LnCDTA complexes[258]). This is most probably associated with the different structures of the complexes

formed by the lanthanides of the cerium and yttrium groups. Data for the variation of entropy in the series of these complexes are consistent with the above hypothesis[259]. The maximum entropy change is observed for the LnCDTA complexes (up to 80–105 e.u.)[258]. The deviation of the $\Delta H$ for the complexes in the lanthanum, gadolinium, and lutetium series from the monotonic variation shows that the complexes LnEDTA are stabilised when the lanthanide belongs to the cerium group and are destabilised when it belongs to the yttrium group.

The available data[249,250,258] show that the variation of the thermodynamic functions with the atomic number of the lanthanide is non-monotonic for all the complexes. There is a definite parallelism in the variation of both thermodynamic functions ($\Delta H$ and $\Delta S$) of lanthanide complexes with the same ligand, but the $\Delta H$ and $\Delta S$ for ligands having different structures and different numbers of binding sites can vary similarly in the given series. Consequently the nature of the variation of the thermodynamic functions is determined by the variation of the properties of the central atoms and not the ligands. The non-monotonic S-shape of the curve relating the enthalpy to the atomic number of the lanthanide is evidence against the view that the interaction between lanthanide ions and ligands is predominantly electrostatic. According to some data[244–246], the variation of the thermodynamic functions in the series of lanthanides may be determined by the variation of the structure of the complex, particularly by the variation of the coordination number and probably the contribution of the *f* orbitals to the formation of the coordinate bond[260].

In the formation of lanthanide complexes with valine (an $\alpha$-aminoacid)[261] in an aqueous medium, the stability constant $K_1$ varies at temperatures from 15° to 55°C in the range from lanthanum to lutetium with a break corresponding to gadolinium. The dependence of $\lg K_1$ on the atomic number of the lanthanide is represented by a convex curve with a maximum in the cerium group, which can be explained by the partial formation of a covalent bond, when account is taken of the extra stabilisation energy, and by the variation of the coordination number in the series of lanthanides. Inner-sphere coordination of the metal and ligand with disruption of the hydration shell of the former has been suggested for lanthanide complexes of glycine and histidine[262,263]. However, these studies[262,263] were performed at high ionic strengths (2 and 3.0 M $NaClO_4$ respectively). One may therefore presume that an increase of the overall concentration in the medium ($NaClO_4$ + ligand) entails a greater degree of disruption of the hydration shell of the metal ion with displacement of solvent molecules from its inner sphere. At an ionic strength of 0.1 (KCl), the hydration shells of the metal ions are not disrupted for cerium-group elements but are involved in the reaction to some extent for the yttrium-group elements, which entails a rapid increase of $\Delta S$ with the atomic number of the lanthanide.

A steady increase of stability from lanthanum to lutetium has been observed for lanthanide complexes of $\beta$-phenyl-$\alpha$-alanine, tyrosine, and tryptophan[264], *NN*-biscarboxymethyl-2-aminoalkanoic acids[265], 1,3-diamino-5,5-dimethylcyclohexane[266], methyl 3-mercaptopropionate[267], and ethylene-*NN'*-diaminediglutaric acid[268]. The observed steady increase of stability from lanthanum to lutetium can be accounted for by the fact that the ionic radius decreases in the La–Lu series and there is a corresponding increase in the electron affinity of the element, which increases in its turn the degree of coordination of the lanthanide to the nitrogen atom (in the $NH_2$ group of the aminoacid).

The stability of the complex is known to be inversely proportional to the dissociation constant of the ligand ($K_d$). This rule is valid also for lanthanide complexes. The stability constants of lanthanide acetates are higher than those of the monochloroacetates, while the $K_d$ of acetic acids increase with increase of the number of chlorine atoms[269]. The same rule has been noted for lanthanide salicylates, anthranilates, acetylacetonates, and 8-hydroxyquinolinates[210,270–286], as well as a wide variety of lanthanide complexonates. For complexes with certain carboxylic acids (for example lanthanide malonates, succinates, and fumarates[286–293]), a linear relation has been observed between $\lg K_1$ and $pK_1$ (for monocarboxylates) and $pK_2$ (for dicarboxylates) of the ligands. This behaviour can break down: thus lanthanide complexes of dinitrosalicylic acid (DNS) are more stable than the lanthanide chloroacetates (CA), although $K_d(\text{DNS}) > K_d(\text{CA})$. The anomaly has been explained[269] by the formation of chelate rings in the lanthanide complexes of DNS. The replacement of carboxy-groups (lanthanide nitrilotriacetates) by the less acidic alcoholic groups (lanthanide hydroxyethyliminoacetates) leads to a decrease rather than an increase of the stability constants of the complexes, which has been attributed[294] to a change in the number of members in the chelate ring.

The number of members and the lack of steric rigidity of the chelate ring are important factors influencing the stability of lanthanide coordination compounds. The stability of complexes of ethylenediamine-*NN'*-disuccinic and ethylenediamine-*NN'*-dimalonic acids is higher than that of ethylenediamine-*NN'*-diglutarates, since the former two complexones form with the lanthanides stable five- and six-membered chelate rings respectively, while ethylenediamine-*NN'*-diglutarates give rise to comparatively unstable seven-membered chelate rings[268]. Europium(III) complexes of cyclohexylenediaminetetraacetic acid (CDTA)[295–298] are formed in the presence of a larger excess of the ligand than, for example, the analogous complexes with ethylenediaminetetra-acetate, which has been attributed to the rigidity of the CDTA structure, hindering the incorporation of the second ligand in the inner sphere of the metal. Because of this, $\lg K_2 \simeq$ const. in the Gd–Lu series for the 1 : 1 complexes with salicylhydroxamic acid[247], 8-hydroxyquinoline, and some of its 5,7-disubstituted derivatives[248], while the variation of $\lg K_1$ exhibits the usual regularities: an increase from La to Sm and from Gd to Lu, $\lg K_1$ for Gd being lower than for Sm.

The values of $K$ for the complexes of 5-sulphosalicylic acid (SSA) with the compositions Ln(Y)$(SSA)_2$, where Y = EDTA–OH, EDTA, or CDTA (*trans*-1,2-cyclohexylenediamine-*NNN'N'*-tetra-acetate), and Ln(Y)$(SSA)_2$, where Y = IMDA (iminodiacetate) or NTA in alcoholic solutions (pH 10.7–11.0) indicate an enhancement of the chelating effect in the EDTA–CDTA–OH (1 : 1 : 1 complexes) and the NTA–HIMDA (hydroxyethyliminodiacetate)–IMDA (1 : 1 : 2 complexes) series[299].

It is of interest to compare the enthalpies $\Delta H_1$ of formation of the 1 : 1 chelate lanthanide complexes of EDTA with the enthalpies of formation $\Delta H_2$ of the 1 : 1 : 1 lanthanide chelates incorporating mixed ligands, namely, EDTA–TP (triphosphate) or ATP (adenosine triphosphate)[300]. The $\Delta H_2$ for the formation of complexes of the Gd–Tm heavy lanthanides are more exothermic than the

values for the corresponding 1 : 1 lanthanide complexes of EDTA; on the other hand, the $\Delta H_2$ for the complexes of light lanthanides, with the exception of lanthanum(III), are less exothermic than the $\Delta H_1$, which can be accounted for by the formation of supercoordinate bonds when heavy lanthanides interact with EDTA (1 : 1 complexes), ATP, or TP. The formation of complexes with mixed ligands by the lighter lanthanides should also be accompanied by a more exothermic $\Delta H_2$, but the energy evolved on abstraction of strongly bound coordinated water and ligand groups diminishes $\Delta H_2$ in this instance. The entropies of formation $\Delta S_2^0$ of 1 : 1 : 1 chelates are relatively small and more negative than the entropies of formation $\Delta S_1^0$ of 1 : 1 chelate lanthanide complexes of EDTA, evidently owing to the repulsive interaction between the negatively charged mixed chelate lanthanide–EDTA complexes formed with the ATP or TP anions, bearing four or five charges. The entropies of formation of the latter increase from La to Pr and then decrease to Tb, increasing subsequently to Er and decreasing again to Tm, which has also been attributed to differences in the degrees of hydration of the lanthanide ion in the above series. As was to be expected, the entropies of formation of the lanthanide complexes with mixed ligands, EDTA–ATP or TP, in the gas phase are much more positive than in solution.

There is relatively little information on the influence of the nature of the electron-donating centre in the ligand molecule on the stability of lanthanide complexes. It is known [13], however, that in terms of their tendency to form complexes with the lanthanides, which are hard acids, electron-donating atoms can be arranged in the sequence O > N > S. This sequence has been confirmed by the difficulty of synthesising lanthanide complexes of nitrogen-containing ligands [16] compared with oxygen-containing donors [1,17,39] and by the virtual absence of reports of lanthanide complexes with ligand systems in which the electron-donating atoms are those of "soft" sulphur, tellurium, phosphorus, and arsenic. The above factor precludes the estimation of the relative "hardness" of lanthanide ions from the standpoint of the concept of hard and soft acids and bases [48]. In order to solve this problem as well as the problems of competitive coordination [301], it is necessary to have information about the stability of lanthanide complexes for a series of ligands containing variable electron-donating centres: O > S > Se and N > P > As, and quantitative estimates of the Lewis acidities of lanthanide salts must be made [302].

The determination of the stepwise complex formation constants for the lanthanides in mixed aqueous organic solutions and non-aqueous media has been attracting increasing attention of investigators: the results of studies of the stability of lanthanide acetate complexes in aqueous ethanol solutions, dioxan, and aqueous dioxan solutions [281–283], of lanthanide salicylate and anthranilate complexes in methanol [270,280], of lanthanide complexes of acetylacetone in methanol and dioxan solutions [281,284], and of the complexes of 8-hydroxyquinoline in 50% n-propyl alcohol [274] are available. These data permit inferences about the variation of the dissociation constants when both the ionic strength of the solution and the composition of the mixed solvent are varied.

Computer calculations of the stepwise stability constants have shown [276] that, with increase of the atomic number of the lanthanide, the stability of its complexes increases monotonically. However, there is no simple relation between the overall stability constant and the stepwise stability constant: in lanthanide solvato-complexes, the complex-formation effect can be divided into the contributions of the inner-sphere and outer-sphere interactions [270–274]. The contribution of the inner-sphere complex formation process depends on the composition of the mixed solvent [271] and the overall complex-formation effect also depends on the nature of the lanthanide salt anion. There exist fairly well developed methods whereby one can calculate the stability constants for the stepwise formation of acid (protonated) lanthanide complexes [295–297, 303–314].

In the presence of an equimolar ratio of neodymium and ethylenediaminediacetic acid (EDDA), there exist in the pH range 5.19–6.01 the aquo-ion and the protonated and normal 1 : 1 complexes, while in the presence of a fivefold excess of the ligand the 1 : 2 complex is present [304]. For comparison with potentiometric pH measurements [315], the stability constants of $NdL^+$ and $NdL^-$ were adjusted to an ionic strength of 0.1. The values $\lg K^{NdL^+} = 6.8 \pm 0.15$ and $\lg K^{NdL^-} = 4.97 \pm 0.08$, found by Bertha and Choppin [314], are lower than those quoted by Thompson [315] (8.06 and 5.63 respectively), possibly because no account was taken in the calculation of the formation of protonated complex. The latter has also been confirmed by a comparison of other data [316,317]. The calculated stability constants of the protonated complexes of hexamethylenediaminetetraacetic and iminodiacetic acids were compared with the stability constants calculated as the arithmetical mean values from three titration curves (the confidence limits of the $\lg K$ did not exceed 0.1) [303]. The similarity of the stabilities of the lanthanide complexes of the above acids shows that the ligands have the same numbers of binding sites; comparison of the data of Kurkina et al. [303] with those of Galaktionov and Astakhov [318] and Kornev and Konyukhov [319] is difficult, because the ionic strengths are not known and because of the different pH values and [Ln] : [L] ratios employed.

The values of $\lg K$ increase, while those of $\lg K_p$ (the logarithms of the protonation constants) steadily decrease in the series of lanthanides from La to Lu. Both effects have been attributed [320,321] to the changes in the effective ionic potential in the same series. The arrest of the increase of stability in this series at gadolinium, which is usual for lanthanide complexes, has also been observed, although the break is not very marked.

Certain general characteristics of the formation of lanthanide complexes have been interpreted [322,323] from the standpoint of the so called tetrad effect.

In conclusion mention must be made of the attempts to employ modern microwave spectroscopic (NMR) and quantum-chemical methods in the determination of the stability constants of lanthanide complexes, the lanthanide–EDTA–Cit (citrate) system has been investigated by $^1H$ NMR. [324] The value $\lg K = 1.2 \pm 0.1$ has been determined from the shift of the signal due to the ethylene protons of EDTA on formation of the mixed complex Lu(EDTA)Cit in the pH range 4–7. This is smaller by two orders of magnitude than the logarithm of the stability constant of the analogous neodymium complex and smaller by an order of magnitude than the logarithm of the stability constant of the complex Lu(EDTA)IMDA ($\lg K = 2.5 \pm 0.4$).

Comparison of the values measured by a potentiometric method at an ionic strength of 0.1(KCl), at 25° ± 0.1°C, and for the ratios [Ln] : [L] = 1 : 2 and 1 : 4 with the values calculated [325] from quantum-chemical data for the charge distribution on the ligand atoms and the mutual polarisability of the lanthanide ion and the ligand atoms [326,327] revealed a satisfactory correlation (Table 2).

## V. INVESTIGATION OF THE MOLECULAR STRUCTURES OF THE COMPLEXES

### 1. X-Ray Diffraction Analysis

Many lanthanide complexes have different types of crystal lattices and transitions from one type to another are observed in different parts of the lanthanide series: for neodymium and gadolinium [328], ytterbium and terbium [329], etc. The lanthanides form a less perfect coordination polyhedron than in the complexes of *d* transition elements with the same ligand: an octahedral configuration, which is extremely characteristic of *d* element complexes, cannot be as a rule achieved in lanthanide complexes (particularly for polydentate ligands [17]), since the large size of the lanthanide ion makes the structure of the inner coordination sphere extremely strained. It has been established that the formation of the crystal structure is influenced by the duration of storage of specimens. Certain coordination compounds of lanthanides are amorphous to X-rays, for example protonated, neutral, and polynuclear species, as well as the dehydration products of many lanthanide complexes [166,218,329]. The hydroxyethyliminodiacetates of yttrium-subgroup lanthanides [329] are amorphous to X-rays with the exception of the europium complexes which has a crystal structure similar to that of other compounds of the cerium-subgroup elements [163].

Table 2. The measured and calculated values of $\lg K_1$ (Feige et al. [325]).

| Ln | Dipeptide (expt.) | Diglycine (calc.) | Tripeptide | | L-Pro-Gly (expt.) |
|---|---|---|---|---|---|
| | | | expt. | calc. | |
| Nd(III) | 2.32 | 2.36 | 1.95 | 2.16 | 2.75 |
| Er(III) | 2.57 | 2.46 | 2.50 | 2.26 | 3.10 |
| Gd(III) | 2.39 | 2.50 | 2.10 | 2.30 | 3.00 |
| Ho(III) | 2.46 | 2.63 | 2.20 | 2.43 | 3.25 |
| Yb(III) | 2.80 | 2.70 | 2.40 | 2.50 | 3.50 |

Comparison of diffractometer traces has shown that the lanthanides form groups having the same structures, whose number depends on the nature of the ligand. Thus X-ray diffraction analysis of the thiourea complexes of the lanthanides [168] $Ln(C_2H_5C_2)_3.CS(NH_2)_2.nH_2O$, where Ln = La or Ce ($n$ = 2), Pr, Nd, or Eu–Yb ($n$ = 1), and Sm or Lu ($n$ = 0.5), has shown that the complexes can be divided into two series with identical structures: La–Pr and Nd–Eu or Y, each of which gives rise to characteristic diffractometer traces. The thiourea complexes of the yttrium sub-group lanthanides [329] $Ln(C_3H_5C_2)_3.CS(NH_2)_2.nH_2O$, where Ln = Tb, Dy, Ho, Er, or Y ($n$ = 3.5), Tm or Yb ($n$ = 3), and Lu ($n$ = 1), form two groups with the same structures: Tb–Tm or Y and Yb–Lu. Starting with Yb, the crystal lattice of the complexes changes, while the crystal structure of the yttrium compound is close to that of the complexes formed by the elements of the Tb–Tm series.

The nonahydrates of lanthanide benzenesulphonates [223] can be divided into three groups with the same structures: one includes complexes of the elements ranging from La to Nd, the other Sm and Eu complexes, and the third the complexes of the elements ranging from Gd to Lu, including yttrium benzenesulphonate. Four groups with the same structures can be distinguished among the hydrated complexes with a low water content: the first includes La, Ce, Pr, and Nd salts, the second Sm, Eu, Gd, and Tb salts, the third Dy, Ho, Tm, and Y salts, and the fourth Er, Yb, and Lu salts. Comparison of the diffractometer traces for different hydrated benzenesulphonates of the same lanthanide has shown that they are identical for the free ion and the dihydrates of lutetium, cerium, and praseodymium benzenesulphonates and for the free ion and the trihydrate of neodymium benzenesulphonates[223]. Seven molecules (six in the case of neodymium) of the water of crystallisation are apparently not involved in the formation of the crystal structure. On the other hand, the diffractometer traces for the hydrated benzenesulphonates of the lanthanides ranging from Sm to Lu, including yttrium benzenesulphonate, with different water contents, are sharply different, which indicates the involvement of the entire water of crystallisation in the formation of the structure.

In solid lanthanide complexes, there are usually intermolecular hydrogen bonds, which decrease the flexibility of the metal-containing rings. The structure of the hydrates of the protonated complexes changes in the series of lanthanides [107], while the structure of the neutral complexes remains constant. This phenomenon has been attributed [330,331] to the polarising action of the outer-sphere cations.

Calculation of the crystallographic parameters of lanthanide complexonates makes it possible to isolate groups having the same structures in the La–Lu series [331].

### 2. X-Ray Diffraction Analysis

The amorphous behaviour in relation to X-rays or polycrystallinity as well as the extremely low solubility of lanthanide complexes frequently prevent the formation of single-crystal specimens. Nevertheless Porai-Koshits and Aslanov [240,331] have now examined series of compounds with the same structures belonging to 100 structural types: studies have been made of the problems of the relative roles of the Coulombic and covalent components in the stereochemistry of lanthanide complexes, statistical data have been published on their coordination numbers and their coordination polyhedra, a relation has been demonstrated between the latter and the nature of the lanthanide and the ligand, the stereochemistry of lanthanide complexes with six- ($\beta$-diketonates) and four-membered rings (nitrates, carbonates, and sulphates) has been investigated, and a comparative analysis of the stereochemistry of the lanthanides and *d*-transition metals in $\beta$-diketonates, carboxylates, and many other chelate complexes has been carried out.

The structural aspects of six-membered metal-containing lanthanide rings have been elucidated in X-ray diffraction studies on lanthanide diketones [332-340]. Lanthanide tetra-$\beta$-diketonates can exist in two forms: as complex acids and as salts of organic bases [332,334]. The unit cell parameters of the crystals of the $\alpha$-form of piperidinium tetrabenzoylacetonatoeuropate [335] agree satisfactorily with the results of Il'inskii et al. [332] This form may be called a salt, since it contains the cation $Hpip^+$ (pip = piperidine) and the anion $[Eu(BA)_4]^-$. The second compound, described [336] as a solvate, is an acid, in agreement with a number of facts described in the literature [336,337]. In $\beta$-diketonates with electron-donating substituents, the

coordination polyhedron is as a rule a tetragonal antiprism, while in β-diketonates with electron-accepting groups it is a dodecahedron. The conversion of one polyhedron into another is difficult, which conflicts with the view [338] that the solvent plays a decisive role in the formation of the coordination polyhedra of lanthanide tetra-β-diketonates.

Comparison of the structures of tetra-β-diketonates has led to the conclusion [334] that the symmetry of the immediate environment of lanthanide ions depends on the electronic properties of the ligands: in the presence of non-fluorinated ligands [332,339], the characteristic coordination polyhedron of the lanthanide is a tetragonal antiprism, while in the case of fluorinated ligands [339,340] the polyhedron is a dodecahedron. It has been suggested [334] that this type of dependence of the form of the coordination polyhedron on the nature of the ligand can be accounted for by the degree of overlap of the orbitals of the lanthanide atoms and ions.

There have been so far few data concerning the absolute configurations of organic compounds coordinated to lanthanide ions. The study of Porai-Koshits et al. [341], who analysed the geometry of the EDTA anion in complexes and simple salts, merits most attention in this connection. Analysis reveals three configurational possibilities for the ligand: two with the *cis*-disposition of the nitrogen atoms of ethylenediamine (en) (the *gauche*-configuration of the en-ring) and one with the *trans*-configuration of ethylenediamine (planar en-ring). The first group (*E*, *G*/*R* conformation) with the non-planar structure of the en-ring (C.N. = 6–8) has the following polyhedra: octahedron, pentagonal bipyramid, and Chord's dodecahedron. Complexes with the configuration of a single-cap trigonal prism (C.N. = 7) are characteristic of the second group (*E*, *R*/*G* conformation). One of the consequences of the transition *E*, *G*/*R* → *E*, *R*/*G* is the flattening of the $O_RO_GC_GC_GO_R$ tetragon. The *E*, *R*/*G* configuration obtains in the lanthanide complexes of EDTA; the transition to coordination numbers of 9 and 10 entails a further decrease of the endocyclic angles at the metal atom.

The results of X-ray diffraction analysis of lanthanide complexes permits the conclusion that lanthanide(III) ions in the compounds have high and variable coordination numbers. In lanthanide complexes, the coordination number is usually 9 (Table 3). [342–356] Amongst the factors influencing the coordination number, the strength of the Ln–ligand bond and the steric characteristics of the ligand systems have been noted. In particular, it has been suggested [343] that the Ln–O interaction in the hexamethanol complexes of lanthanide nitrates is so pronounced that the coordination number is ≤ 8. However, for the majority of lanthanide complexes of dimethyl sulphoxide [342–344,357,358], where a very strong interaction can also be postulated, no changes have been observed in the coordination number of the metal, contrary to the view of Ramalingam and Saundararajan [359].

X-Ray diffraction data have been used to solve the problem of the location of the coordinate bond in ambident bi- and poly-dentate ligands. As expected [301], only a "hard–hard" interaction takes place with O- and N-donors (in lanthanide nicotinates) [345,360,361], in contrast to the complexes of *d*-transition elements [301,362], and the Ln–C bond is formed. The latter has also been detected in the infrared spectra of lanthanide nicotinates [363].

Analysis of the X-ray diffraction data has shown that chain and isolated group ("island") structures are characteristic of lanthanide complexes. It has been shown that the chains of the complexes are frequently linked together by hydrogen bonds, formed both between coordinated water molecules and with participation of the donor (N, O, and S) atoms of the anions [346,360,364].

Certain regularities in the Ln–A interatomic distances (A is a donor atom) as a function of the nature of Ln–A and the ligand system are known (see Table 3 and the data analysed in the literature [240,331]). The average $Ln-C_{NC_3}$ interatomic distances in the hydrates (2.65 Å) and the dimethyl sulphoxide complexes of lanthanide nitrates (2.64 Å) are approximately equal [357]. However, the $Ln-O_{DMSO}$ distances are much shorter than $Ln-O_{H_2O}$, which cannot be accounted for solely by the lanthanide contraction, which is very slight on passing from Pr to Nd.

The large (compared with the water molecule) negative charge on the oxygen atom in the DMSO molecule apparently enhances the $Ln-O_{DMSO}$ interaction, which leads to a shortening of the bond. The $Ln-O_{DMSO}$ interatomic distances in the $Nd(NO_3)_2.(DMSO)_4$, [343] $Er(NO_3)_3.(DMSO)_3$, [344] and $Lu(NO_3)_3.(DMSO)_3$ structures are on average 2.26 Å, which is significantly less than the $Ln-C_{NC_2}$ bond length

Table 3. The structures of coordination compounds of the lanthanides (the interatomic distances are quoted for the compounds of the underlined lanthanide).

| Composition of complex | Ln(III) | C.N. | Symmetry | Average interatomic distance, Å | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | | Ln–$O_{lig}$ | Ln–$O_{NO_3}$ | Ln–$O_{H_2O}$ | Ln $N_{lig}$ | |
| $Ln(NO_3)_3(DMSO)_3$ | Nd, Er, Lu | 9 | $C_3$ | 2.26 | 2.50 | — | — | 342–344 |
| $Ln(OOCC_5H_4N)_3 \cdot 2H_2O$ | Pr, Er | 8 | $C_2$ | 2.29 (bridge) | — | 2.33 | — | 345–346 |
| | | | | 2.42 (ring) | — | — | — | — |
| $Ln(NO_3)(NCS)_2 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ | Nd, Er | 9 | — | 2.65 | — | — | 2.40 | 346 |
| $Eu(terpy)_3(ClO_4)_3$ | — | 8 | $D_3$ | 2.40 | — | — | 2.64 | 347 |
| $Ho(thd)_3(4\text{-pic})_2$ | — | 9 | $C_2$ | 2.27 | — | — | 2.53 | 348 |
| $La(NO_3)_3(2,2\text{-dipy})_2$ | — | 8 | $D_2$ | — | 2.61 | — | 2.66 | 349 |
| $HLn(BA)_4 \cdot Pip$ | La—Gd | 8 | $D_2$ | 2.36 | — | — | — | — |
| $HLn(BA)_4NHEt_2$ | La—Gd | | | 2.38 | — | — | — | 332 |
| $HPip[Ln(BA)_4]$ | La—Lu | 8 | $D_2$ | 2.38 | — | — | — | 332 |
| $Ln_3mal_3 \cdot 8H_2O$ | Nd, Eu | 9 | — | 2.47 | — | — | — | 350,351 |
| $Ln(HOCH_2COO)_3 \cdot 2H_2O$ | La, Gd, Er | 8 | — | 2.31 | — | — | — | 352 |
| $Ln(C_4H_5O_4N)(H_2O)_3Cl$ | Pr—Lu | 8 | — | — | — | — | — | 353 |
| $Na_3[Ln(C_7H_3NO_4)_3] \cdot 13H_2O$ | Nd, Yb | 9 | — | 2.39 | — | — | 2.52 | 354,355 |
| $Na_3[Ln(C_7H_3NO_4)_3]NaClO_4 \cdot 10H_2O$ | Nd, Yb | 9 | — | 2.38 | — | — | 2.43 | 356 |

(2.50 Å), suggesting that the Ln–$O_{DMSO}$ bond in compounds of this class is stronger than the Ln–$O_{NO_3}$ bond. The Ln–O interatomic distances in lanthanide carboxylate complexes [361,365-367] obey the same rule: the lengths of the bonds between the oxygen atoms of the cyclic bidentate carboxy-group and the lanthanide atoms are longer than the distances between the lanthanide atom and the oxygen atoms of the bidentate bridging carboxy-group.

## VI. SPECTROSCOPIC STUDIES

### 1. Fluorescence Spectra

The coordination compounds of the lanthanides are classified into three groups according to the nature of their fluorescence. The first group includes lanthanum(III), gadolinium(III), and lutetium(III) complexes, which exhibit the fluorescence of the non-metallic ions. The second group comprises dysprosium(III), samarium(III), europium(III), and terbium(III) complexes, which exhibit the characteristic intense fluorescence of the metal ions; each ion has an excited state whose energy is close to that of the triplet level of the ligands. Praseodymium(III), neodymium(III), holmium(III), erbium(III), ytterbium(III), and thulium(III) complexes, which exhibit a weak fluorescence of the metal atoms, constitute the third group; each [metal?] ion in this group has closely spaced energy levels.

Since the electrons of the 4*f* orbitals of the lanthanides are shielded from the action of the ligand field by the $5s^2 5p^6$ electron cloud, the following regularity is observed as regards the intensity of the influence on the lanthanide ion: crystal field < spin–orbital coupling < interelectron repulsion [18].

Theoretical analysis of the symmetry in the lanthanide complexes makes it possible to interpret their fluorescence spectra [368-371]. Europium(III) chelate complexes are most frequently investigated, because in this case the low value of the quantum number $J$ for the most intense lines in the emission spectrum ($^5D_j \rightarrow {}^5F_j$; $J = 0, 1$; $J' = 0, 1, 2$) gives rise to a smaller number of energy levels than the number observed for the majority of other lanthanide ions. The transitions from the $^5D_0$ state are used to investigate the symmetry of the coordination compounds because this energy-emitting state ($J = 0$) cannot be split by the ligand field. Thus the transitions from $^5L_0$ to various $F_j$ states are usually well separated and the transitions to the $J$ states are frequently satisfactorily resolved. The interpretation of the fluorescence spectra of the europium complexes from the standpoint of symmetry agrees with the molecular structure of the complexes [338-349].

The study of the fluorescence spectra of 33 chelate complexes (pyridine derivatives of lanthanide tetrakis-1,3-diketonates) [331] showed that all eight oxygen atoms in the 1,3-diketone are directly linked to the lanthanide, which is confirmed by the analysis of the observed fluorescence spectra from the standpoint of the possible symmetry of the ion in complexes of different compositions which have been investigated. Analysis of the fluorescence spectra yields valuable information about the nature of the interaction of the lanthanide with organic ligands [372-379], the nature of the bond in lanthanide complexes [369-372,380-382], the symmetry of the complexes, and the conformation of the ligands [382-386].

A relation has been established between the probability of the energy transfer ($k_t$) and the degree of overlap of the electron clouds of aromatic ketones and lanthanide ions (Table 4). [387] The probability of energy transfer in the case of benzophenone, acetophenone, and benzoylpyridine (Table 4) reflects the similar changes in their capacity for complex formation, the differences being due to the differences in the donor–acceptor properties of the ketones and the overlap integrals for the spectra. The distinct increase of $k_t$ for ketones having the $^3\Gamma(n,\pi^*)$ state compared with the analogous ligands with the $^3\Gamma(\pi,\pi^*)$ levels constitutes clear confirmation of the role of the overlap of the electron clouds of the excited ketone and the lanthanide ion in energy transfer. Energy transfer with participation of lanthanide ions to the triplet level of organic molecules and away from the latter proceeds via an exchange-resonance mechanism [388].

Table 4. The probabilities of energy transfer from aromatic ketones to lanthanide ions [387] ($T$ = 383 K, acetone, air).

| Ketone | $10^{-3}k$, $M^{-1}$ $s^{-1}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Ce^{3+}$ | $Pr^{3+}$ | $Nd^{3+}$ | $Sm^{3+}$ | $Eu^{3+}$ | $Gd^{3+}$ | $Tb^{3+}$ | $Dy^{3+}$ | $Ho^{3+}$ | $Yb^{3+}$ |
| Acetophenone | 4 | 3 | 8 | 0.5 | 2 | 0.10 | 0.66 | 0.6 | 0.6 | 0.8 |
| Benzophenone | — | 5 | 17 | 1.0 | 6 | 0.01 | 0.1 | 0 8 | 0.8 | 0.76 |
| Benzoylpyridine | — | 4.5 | 5.4 | 0.6 | 3 | — | 0.26 | 0.6 | 0.6 | 0.5 |

The luminescence spectra of more than one hundred europium, terbium, and gadolinium complexes with different ligands have now been investigated [373-377]: $Eu(TTA)_4P$, $Eu(BTFA)_4P$, $Eu(o\text{-Cl-5-BTFA})_4Pyrr$, $Eu(DBM)_4P$, $Eu(BTFA)_4DMA$, $Tb(A)_4P$, $Eu(DFDBM)_3$, $Eu(DFDBM)_4P$, etc., where TTA = thenoyltrifluoroacetone, BTFA = benzoyltrifluoroacetone, DBM = dibenzoylmethane, P = piperidine, I = imidazole, Pyrr = pyrrolidine, DMA = dimethylamine, and DFDBM = decafluorodibenzoylmethane. Analysis of the splitting of the lines in the spectra has led to certain conclusions about the symmetry of the crystal field of the lanthanide complexes. If the crystal field has a threefold symmetry axis, three lines correspond to the $^5D_0 \leftarrow {}^7F_2$ transition and two components with the intensity ratio 2 : 1 (the inner coordination sphere is an octahedron with a $D_3$ symmetry axis) correspond to the $^5D_0 \rightarrow {}^5F_1$ transition. For a lower symmetry, the line due to the $^5L_0 \rightarrow {}^7F_1$ transition is split into three components with approximately equal intensities, and there is a weak $^5D_0 \rightarrow {}^7F_0$ transition. Solvent (water) molecules are not linked to the central atom, which is surrounded by six oxygen atoms. On the other hand, in the spectra of the di- and tri-hydrates of europium(III) tri- and tetra-acetylacetonates the line of the $^5D_0 \rightarrow {}^7F_1$ transition is split into three components and that due to the $^5D_0 \rightarrow {}^7F_2$ transition, into five components: the cubic environment, comprising eight oxygen atoms, is distorted to a tetragonal antiprism with a $C_2$ symmetry axis. The degree of hydration has a significant influence on the intensity, width, and Stark splitting of the luminescence bands of the ion in the chelate complexes.

Comparison of the results of the analysis of the luminescence spectra of europium nitrates combined with aromatic amines [358] with X-ray diffraction data showed that the luminescence spectra yield an average pattern of

the charge distribution, so that the real pattern in the structure of the complexes can be obtained solely with the aid of additional data.

The luminescence spectra of europium complexes of aromatic acids [389], complexones [390], and β-diketones [391] have been investigated in very great detail. Analysis of the luminescence spectra of europium β-diketonates using CFT led to the conclusion [391] that the vacant (*in vacuo*) 5*d*-orbitals of the lanthanides are involved in the Eu(III)–L bond.

The use of europium as a luminescence probe is of particular interest [390]. Several types of complexes of Schiff bases, in which covalent bonds are formed between europium and the ligands, were isolated by this method.

The formation of lanthanide complexes with various electron-donating solvents has been studied by the taumetric method based on the phenomenon of the radiationless energy transfer in the fluorescence spectra. It was shown [388] that, when inner-sphere lanthanide complexes are formed, the decisive factors are the relative electron-donating properties of the solvent and the competing ligand, and in outer-sphere complex formation the dielectric constant of the medium is of decisive importance.

## 2. The Absorption Spectra of Lanthanide Complexes

The absorption spectra of lanthanide ions have been investigated in fair detail in solutions of complexes [392-427]. Studies have been made on the intensities and positions of the absorption bands as a function of the nature of the lanthanide, the ligand environment, and the solvent.

In the far ultraviolet (210–300 nm), the ions of certain lanthanides have absorption bands corresponding to the allowed $4f-5d$ transitions; in the visible region, absorption bands associated with the $4f-4f$ transitions of the electrons are observed [392]. In conformity with theory [392, 393], the oscillator strengths $P$ of the $4f-4f$ absorption bands are small, but the intensity of certain bands may increase as a function of the environment.

When the environment of the $Ln^{3+}$ ion is altered, appreciable oscillator strengths are observed only for certain absorption bands, corresponding to the $4f-4f$ electron transitions—the so called hypersensitive transitions (HST). The absorption bands of lanthanide(III) ions corresponding to HST have been listed [392,394,398-415]. The appearance of HST has been explained [385,393] by the influence of the covalent nature of the $Ln^{3+}$–ligand bond (nephelauxetic shift [415-419]) and may be characterised by the CFT parameters.

In the spectra of many complexes of aromatic acids [405], the intensity of the $^7F_0 \rightarrow {}^5D_2$ and $^7F_1 \rightarrow {}^5D_1$ HST bands increases to the same extent (by factors of 1.8 and 1.62 respectively). The oscillator strength $P_{exp}$ of the $^7F_0 \rightarrow {}^5D_2$ transition has been frequently determined as a function of the solvent (water, methanol) [405,406], the lanthanide ion [395,401-405], and the nature of the anion and the ligand [395,404]. Thus $P_{exp} = 0.0004$ for the $^7F_0 \rightarrow {}^5D_2$ transition in an aqueous $Eu(NO_3)_3$ solution, which is smaller by a factor of six than for a $Eu(NO_3)_3$ solution in methanol. The intensity of the $^7F_0 \rightarrow {}^5D_2$ transition increases even more in europium salicylate: $P_{exp}$ is sixty times greater than for the aquo-ion. Consequently the field strength in methanol is greater than in water, and among all the complexes investigated [402-405] it is a maximum for europium salicylate [405].

It has been established that the intensity of the HST absorption bands and the oscillator strengths of lanthanide ions involved in complex formation depend on the chemical nature [395,406-410] and the molecular weight [406] of the ligand. Thus they increase for neodymium(III) and erbium(III) complexes of 8-hydroxyquinoline and its dihalogeno-derivatives (5-chloro-7-iodo-8-hydroxyquinoline and 5,7-di-iodo-8-hydroxyquinoline) with increase of the molecular weight of the ligand [405]. The same behaviour is characteristic of mixed lanthanide complexes formed as a result of the additional coordination of organic ligands [407-410].

Analysis of the intensities of the HST absorption bands of lanthanide ions is an effective means of determining the symmetry [415-421]. A general trend towards a decrease of the symmetry of the solvated lanthanide ions on passing from methanol to 1-propanol has been established [413,419] and the symmetries of many lanthanide complexes in different solvents [420,421] and the changes in the latter on passing from the crystalline phase to the solution [421] have been determined. Comparison [414] of the changes in the HST intensities in the luminescence spectra with the changes observed in the absorption spectra shows that the two sets of quantities are proportional. Thus the influence of the ligand field, which determines the HST intensities, is manifested to approximately the same extent in both absorption and luminescence spectra.

Not only the intensities but also the positions of the bands in the electronic absorption spectra of lanthanide complexes depend significantly on the nature of the ligand (the electron-donating atom) and the nature of the lanthanide cation and anion. The shift of the bands in the spectra of lanthanide complexes is determined by the immediate ligand environment of the central ion. A linear relation between the positions of the spectral bands and the average $R_{Ln-O}$ distance has been observed for lanthanide complexes with ligands coordinated via oxygen atoms [420,422,423]. The positions of the bands in the electronic spectra of lanthanide complexes have been investigated as a function of the nature of the complexones and aminoacids [424-426]. The presence of a single band ($^4I_{9/2} \rightarrow P_{1/2}$ transition) in the spectra of the neodymium complexes with the above ligands [424] and of two bands in those of the erbium complexes [425] permitted the conclusion that the lanthanides are bound in different ways in the complexonates: rigid incorporation of neodymium(III) in the chelating unit of the complexones, which is always of the same type, and different types of binding of erbium(III) to different electron-donating groups of the ligand system. The same data combined with NMR data have been used [426] to determine the location of coordinate bonds in the complexonates.

The influence of the anion of the lanthanide salt on the spectra of the complexes has been investigated in relation to the behaviour of $LnX_3$ (Ln = Nd, Ho, or Er; X = Cl, Br, or $NO_3$) in *NN*-dimethylacetamide [420] and of the solvato-complexes of $EuCl_3$ and $Eu(NO_3)_3$ in water, ethanol, and acetic acid [427]. It was found [427,428] that, when the anion is altered in the sequence $Cl \rightarrow Br \rightarrow NO_3$, a bathochromic shift of the HST bands is observed.

In conclusion we may note that a correlation has been found between the results derived from the electronic and $^1H$ NMR spectra of the lanthanide–complexone complexes investigated [424,425]: the shift of the absorption bands ($\Delta\lambda$) in the electronic spectra and the chemical shift ($\Delta\delta$) of the protons in the $^1H$ NMR spectra increase on formation of a bond between the lanthanide and a nitrogen atom and

diminish from La to Lu when the lanthanide is coordinated to an oxygen atom. This observation may be used to characterise the bonds in lanthanide complexes with ON-ligands and to determine the distance between the lanthanide and the donor centre.

## 3. Infared Spectroscopy of Lanthanide Complexes

The infrared spectra of lanthanide complexes have been studied over a wide wavelength range (40–4000 $cm^{-1}$), mainly in the crystalline phase [422-446]. The long-wavelength region (40–600 $cm^{-1}$) has been studied in order to assign the frequencies, to determine the spectroscopic parameters of the Ln–X bonds (X = Cl, Br, I, O, N, or S), and to discover the location of the coordinate bond. Since lanthanide chlorides belong to the $L_{3h}$ symmetry point group [115], the unit cell may be defined as a double trigonal antiprism. Consequently, four fundamental frequencies, $\nu_1(A_1')$, $\nu_2(A_2'')$, $\nu_3(E_1')$, and $\nu_4(E')$, may be expected for the vibrations of the Ln–Cl bond, the first of which should be inactive in the infrared spectra, since it is the frequency $\nu_S$ of the stretching vibration of the Ln–Cl bond. The observed vibration frequencies and calculation [115] led to the isolation of the following bands active in infrared spectra: $A_2'$ (237 $cm^{-1}$); $E_1'$ (318 $cm^{-1}$); $E'$ (285 $cm^{-1}$). The vibrations of the Ln–Cl bond in bipyridyl and phenanthroline complexes are active in the range 200–260 $cm^{-1}$, while the frequencies of the vibrations of the Ln–Br bond are significantly lower (140–155 $cm^{-1}$).[429]

The vibrational spectra of the complex anions $LnX_6^{3-}$ (Ln = Nd, Eu, Gd, Dy, Er, or Yb; X = Cl or Br) have been investigated in detail using calculated data [430]. In the calculation, the force fields of the molecules were analysed; among these, a modified valence-force field proved to be the most effective and, in the region of stretching vibrations, also a modified Urey–Bradley field. The $LnX_6^{3-}$ anion has six vibrations active in the range 50–260 $cm^{-1}$; the experimental and calculated data have been tabulated in a review [430]. It has been established that (a) the strength of the $LnCl_6^{3-}$ bonds is greater than that of the $LnBr_6^{3-}$ bonds and that (b) the force constant $K_{Ln-Cl}$ of the chlorides decrease in the sequence Yb > Er > Dy > Gd > Nd as the ionic radius of the lanthanide increases; in the case of the bromides, two groups were isolated in terms of the $K_{Ln-Br}$, namely Yb < Er < Dy < Gd and Eu < Nd; finally, (c) the force constant $f$, characterising the repulsion between non-bonded atoms, increases from Cl to Br as the ionic radius of the lanthanide increases.

The vibrations of the Ln–N bonds are active in the range 200–500 $cm^{-1}$ for bipyridyl and phenanthroline [198], 350–380 $cm^{-1}$ for ethylenediamine chelates [450], and 270 to 350 $cm^{-1}$ for isocyanate complexes of the type $[Et_4N]_3.[M(NCO)_6]$. [431] There are so far relatively few data for the vibrations of the Ln–O bonds [129]: in the spectra of praseodymium, neodymium, europium, gadolinium, dysprosium, and erbium acetylacetonates, they are active in the vicinity of 420–432, 304–322, and 620–650 $cm^{-1}$. The bond force constants $f_{Ln-O}$ increase with decrease of the Ln–O bond length. Although the Ln(III)–O bond is believed to be ionic, it has been suggested [129] that the increase of the Ln–O stretching frequencies is due to a slight increase of the degree of covalence in the acetylacetonate complexes as a result of $\pi$-bonding and the increase of the mass of the central ion.

The values of $f_{Ln-O}$ calculated by an empirical method [130] (for example, $f_{Pr-O}$ = 2.98–2.41 mdyn $Å^{-1}$) differ from those ($f_{Pr-O}$ = 2.10) obtained [129] by the more rigorous Urey–Bradley method. It is very likely that the vibrations active at 268–296 and 353 $cm^{-1}$ in the spectra of the tetraethylammonium isocyanate complexes mentioned above [431] are due to the Ln–O bond of the M–OCN group. The "hard–hard" interaction of lanthanides with ambident pseudohalide ions usually leads to the same conclusion [48,301].

The infrared spectra of lanthanide complexes in the range 600–4000 $cm^{-1}$ have been investigated mainly in order to discover the donor centre in the molecules of bi- and poly-dentate ligands (competitive coordination [301]). Infrared spectroscopic data were used to determine its location in lanthanide complexes with many ambident organic ligands: tetramethylene sulphoxide (oxygen atom of the S=O group) [52], salicyl hydrazide (secondary amide nitrogen atom) [53], salicylidene- [54] and naphthylidene-anthranilic acids [228] (O–O rings), $\alpha\beta$-unsaturated $\beta$-ketoimines (NC-chelates) [434], 1,2-ethylenebisdiphenylphosphine and arsine oxides (bridging groups involving the phosphoryl and arsenyl oxygen atoms) [435], *N*-oxides of quinaldinic acid (NO linkage) [436] and of *o*-hydroxyquinoline (the oxygen atom in the hydroxy- and N → O groups) [437], *o*-hydroxyacetophenone [56], and salicylaldehyde (metal-containing OC-ring [437,438], thiourea (S atom) [44], 2,2′-bipyridyl *N*-monoxide (Ln–O bond absorbing at 324 $cm^{-1}$), [439] urea [439] and diphenylformamide [103,441,442] (oxygen atom), butyl phosphate (phosphoryl and ester oxygen atoms) [356, 443-445], protonated methyl iminodiacetates (oxygen atom of the acetyl group and possibly of the non-protonated carboxy-group) [446], various nitrogen-containing six- [16] and five-membered [169] heterocycles (nitrogen atoms of the pyridine type), and aliphatic and aromatic amines (nitrogen atoms of the amino-groups) [16].

With increased interest in the lanthanide complexes of aminoacids and complexones, numerous studies have been made in order to assign the vibrations of the carboxy-group [218,447-452] and to determine the amount of its ionic and covalent character [447,449] as well as the possibility of employing the different $\Delta\nu = \nu^{as}_{CCO} - \nu^{s}_{CCO}$ in order to characterise the relative strength of the Ln–O bond [128,449, 450]. The study of the infrared spectra also proved to be extremely useful in the solution of the problem of the formation of acid or neutral lanthanide salts of aminoacids and complexones [448-452].

## 4. Microwave Spectroscopic Studies

The NMR method is widely used in the coordination chemistry of the lanthanides in order to investigate the composition of the complexes, the mode of coordination, [453-463] the exchange kinetics, and the fine structure of the ligands [459-464]. NMR data have shown that [456] the interaction of the lanthanides with complexones is accompanied by the formation of 1 : 1 and 1 : 2 (La, Lu) complexes; hydroxo-complexes are formed in the alkaline region [451] and protonated complexes are formed in the acid region. The kinetic data obtained in NMR investigations of ligand exchange in lanthanide complexes of a number of nitrogen-containing donors [16] [4,4′-di-n-butylpyridine [462] and tri-($\beta$-aminoethyl)amine [463]] made it possible to determine the parameters of the transition state, the order of the exchange reaction, and structural isomers of the ligands. It was established that the reaction with di-n-butylpyridine [462] is of second order: $\Delta H^{\neq}$ = 10.6 ± 1.3 kcal $mole^{-1}$ and $\Delta G^{\neq}$ = 17.6 kcal $mole^{-1}$.

The kinetics of ligand exchange, including transsolvation, have been studied in detail [457,458]. For ratios $SmCl_3$ : EDTA ≥ 1 : 2, slow exchange is observed between

the free and bound ligand species:

$$SmL + H_nL_1 \rightleftarrows SmL_1 + H_nL \quad (1)$$

$$HSmL + H_nL_1 \rightleftarrows HSmL_1 + H_nL \quad (2)$$

where $n$ is the degree of protonation of EDTA. The entropies, activation energies, and rate constants $K$ for exchange for a ligand containing between two and four protons were determined for reactions of type (1). It was shown that $K$ increases in the sequence $HL < H_2L < H_3L < H_4L$.[464]

It was established[54] that lanthanides are coordinated to the water molecule and the chloride ion in the complexes $[Ln(LH)_2(H_2C)Cl]$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, or Lu and L = *N*-salicylideneanthranilic acid.

Polycrystalline hydrates having the composition $MLnEDTA.nH_2O$, where M = Na(I), K(I), Rb(I), or Cs(I), Ln = La(III), Lu(III), Nd(III), Eu(III), Gd(III), Dy(III), Er(III), or Yb(III), and $n = 3-9$, were investigated by the low-resolution $^1H$ NMR method[465] at temperatures between $-100°$ and 250°C. In all the cerium-subgroup lanthanide compounds in the range from 0° to 60°C, two groups of water molecules, differing in their mobility in the crystal lattice, were detected; a group of three water molecules is in a rigidly fixed state, while the proton–proton vectors of the remaining molecules are distinguished by a fairly considerable mobility in the crystals. Comparison of the $^1H$ NMR and optical absorption spectroscopic data in the visible region indicates the incorporation of three water molecules in the inner coordination sphere of the lanthanide, which agrees well with X-ray diffraction data. The structure of the hydrates of lanthanide complexonates has also been discussed in other studies[466,467]. The $^1H$ NMR, optical spectroscopic, and X-ray diffraction data led to the conclusion that the number of inner-sphere water molecules in the solid hydrated lanthanide–EDTA complexes decreases in the La–Lu series: whereas three water molecules are incorporated in the inner coordination sphere in the complexes of light lanthanides, ytterbium(III) forms a complexonate with a single molecule of inner-sphere water.

The $^1H$ NMR spectra of europium complexes as well as measurements of magnetic circular dichroism of the praseodymium and neodymium complexes of azomethines obtained from aspartic acid and aromatic aldehydes (pyridoxal, *o*-vanillin, 5-nitro-*o*-vanillin, and 5-bromosalicylaldehyde)[468] are different when optically active aspartic acid and the racemate are used, which shows that each lanthanide ion is linked to more than one ligand molecule.

The employment of NMR data makes it possible to determine the configuration of the coordinated ligand[469,470] and also the geometry of the complexes in solution. $Ln^{3+}$ ions forms complexes and induce in NMR spectra both positive and negative paramagnetic shifts, yielding information about the structure of the ligands and about the contact and pseudocontact mechanism of the shifts. One of the methods developed for the separation of the pseudocontact and contact contributions to the overall shift of the signal in the NMR spectrum makes it possible to investigate the geometry of the complex (in accordance with McConnell's equation[471]). In particular, a conformation has been proposed[472] for the Ln(III) complexes of indoline-3-acetate (Ln = Pr, Nd, Eu, Gd, Tb, Dy, or Ho), in which the carboxylate behaves as a bidentate ligand and the $Ln^{3+}$ ion is located on the bisector of the OCO angle; the calculated Ln–O distance varied in the range 2.2–2.5 Å.

The possibilities of the above method in the determination of the ligand configurations were illustrated by data[473] obtained in the determination of the configurations of the isomers of 2-methoxycarbonyl-4-methyl-5-phenylpenta-2,4-dienecarboxylic acid with melting points of 117°C (I) and 153°C (II), which could not be done by analysing the infrared and ultraviolet spectra recorded under the usual conditions. Analysis of the pseudocontact shifts induced by $Ln^{3+}$ ions in NMR spectra showed that isomer (I) has the *E*,*E* configuration while isomer (II) has the *Z*,*E* configuration. Similar studies involving the analysis of NMR spectra of solutions (in $D_2O$) of α-azetidine-2-carboxylic acid in the presence of praseodymium(III), neodymium(III), and europium(III) nitrates established[474] that the four-membered ring of the azetidinecarboxylic acid has a folded configuration with a dihedral angle of 25°, the carboxy-group occupying the equatorial position. The fact that the above investigations were undertaken is evidence for a considerable interest in the study of the structures of the ligands and the geometry of lanthanide complexes in solutions by analysing NMR spectra. The method[471] based on the analysis of NMR spectra in terms of McConnell's equation is simpler and its accuracy is comparable to that of X-ray diffraction analysis.

Apart from NMR spectra, ESR and Mössbauer spectroscopic data have been used to investigate lanthanide complexes. ESR signals of europium(II) have been detected at frequencies of 9 and 35 GHz in solutions at 25°C; a hyperfine structure due to the europium nuclei appears in the spectra of frozen solutions[475]. The *g*-factors and the temperature variation of the line width in the ESR spectra of gadolinium(III) ions introduced into $Ln(C_2H_5SO_4)_3.9H_2O$ single crystals, where Ln = La, Pr, Nd, Sm, Tb, Dy, Ho, Er, Yb, or Lu, have been discussed[476]. The introduction of $Gd^{3+}$ ions into the above single crystals as well as $Nd_2(SO_4)_3(NH_4)_2.8H_2O$ single crystals[477] makes it possible to observe at room temperature the ESR spectra of two magnetically non-equivalent gadolinium(III) complexes, the symmetry of these centres being tetragonal with unusually low values of the crystal field parameters. A decrease of temperature to 77 K results in the resolution of the gadolinium(III) spectra either owing to a stronger crystal field, leading to a greater zero-point splitting, or owing to a crystallographic phase transition in the above temperature range. As a result of the maximum splitting of the states characterised by the quantum number $J$, the magnetic susceptibilities of the majority of lanthanides in crystals and in solutions differ little from the values in the free state.

Relatively few instances are known in which magnetic resonance was observed in an excited state[478]. Such observations are possible if the difference between the energies of the excited and ground states is less than $kT$. For lanthanides with an odd number of electrons, the Kramers doublet occupies the lowest energy level owing to the presence of an axial crystal field and the spin–orbital interaction. However, the intense spin–orbital interaction in the excited states implies a strong interaction with the environment. For this reason, even in this case the recording of the ESR signal usually requires a temperature of 20 K or less. In lanthanides with an even number of electrons, the crystal field with $C_{3v}$ or $C_{3h}$ symmetry splits each state into singlets and doublets. The splitting associated with the Jahn–Teller effect is usually slight and does not remove the residual degeneracy. It is therefore postulated that the system symmetry is still $C_{3h}$ or $C_{3v}$.

ESR studies of relatively simple systems provide a satisfactory answer to the question of the symmetry of the ion and its distortion. In complex systems, an unambiguous result may require much effort[478].

The spectra of europium[139] in weak, moderate, and strong external magnetic fields have been investigated by the Mössbauer method[479,480] at temperatures in the range 1.2–77 K. The form of the lineas in the Mössbauer spectra (MS) has been discussed on the basis of the relaxation theory and comparisons with calculation have been made: the MS parameters and the properties of the complexes are interrelated. The absence of a magnetic hyperfine structure in MS at temperatures in the range 1.2–77 K indicates the absence of magnetic ordering in $[Eu(NH_3)_6]^{3+}$ even at 1.2 K. The calculated rate of spin–lattice relaxation ($50 \times 10^6$ $s^{-1}$) and other experimental data confirm the $4f^7$ configuration of europium(III). In the europium chelates $EuL_4X$, where L = PhC(O)CH(O)Ph and X = $Et_4N$ (III), $Et_2NH_2$ (IV), or piperidine (V), and in the mixed chelate $EuL_3Phen$, where L = PhC(O)CHC(O)Me (VI), an appreciable Mössbauer effect was not observed at room temperature[22]. The isomeric shifts relative to $Eu_2O_3$ in compounds (III)–(VI) are respectively −0.58, −0.60, −0.50, and −0.58 mm $s^{-1}$ and are independent of temperature. The shifts confirm that $5d$, $6s$, and $6p$ europium orbitals participate in the formation of partly covalent bonds in compounds (III)–(VI). The isomeric shifts in the Mössbauer spectra of europium(III) complexes with nitrogen- and oxygen-containing ligands[12] reveal the following regularity: coordination compounds with N-donors are characterised by lower shifts than compounds with O-donors.

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The data which have accumulated during the last decade and which have been discussed in this review, indicate a significant progress in the coordination chemistry of the lanthanides.

At the same time there is still little information about lanthanide complexes in which the oxidation state of the lanthanide is other than three and lanthanide oxide halide and dioxide halide complexes, while the methods of preparation of these halogen-containing compounds are fairly well known[234]. Polydentate macrocyclic ligands (porphyrins[481–483] and crown-ethers[484]) have begun to be used comparatively recently in the synthesis of lanthanide coordination compounds and their promise is evident.

The problems of "competitive coordination"[301] and of the Lewis acidity of lanthanide salts[302] have been inadequately investigated in the coordination chemistry of the lanthanides.

It is of interest to study the equilibria involved in the formation of lanthanide complexes of different types, particularly mixed and polynuclear complexes, to carry out quantum-chemical calculations, and to investigate further the physicochemical properties of lanthanide coordination compounds. The development of research on these and other fields traditional for the chemistry of complexes is the task for the immediate future.

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# The Synthesis, Reactivity, and Physicochemical Properties of Compounds with a Tin-Nitrogen Bond

Yu.I.Dergunov, V.F.Gerega, and O.S.D'yachkovskaya

Data on the methods of preparation, properties, and practical applications of organotin compounds with an Sn-N bond are reviewed.
The bibliography includes 343 references.

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## I. INTRODUCTION

Organotin compounds with a covalent tin–nitrogen bond have attracted in recent years the continuous attention of investigators and workers in the field of applied chemistry. The study of their properties led to the discovery of new types of processes, for example the reaction involving the insertion of isocyanates in the Sn–N bond. The fields where these compounds have found practical applications are continuously expanding [1-9]. Several reviews [10-17] and a separate chapter in a monograph [18] have been devoted to this problem and the data have been partly surveyed in a book [19].

The aim of this paper is to review the available data on the synthesis, reactivity, physicochemical properties, and applications of organotin compounds with a tin–nitrogen bond, contained in monographs, journal articles, and patents published up to 1975. The main task is to draw the attention of Soviet chemists to this rapidly developing field of organoelemental chemistry, which is promising from both theoretical and practical points of view. The characteristics of the structures, physicochemical properties, and possible applications of nitrogen-containing organotin products have still been inadequately investigated.

These compounds can be divided into two groups [18]. The first includes aminostannanes $\equiv Sn-NR_2$ and the second organotin pseudohalides $\equiv Sn-N-R$ (R = C, N, or P). Compounds belonging to the first and second groups are synthesised by similar methods, but their physicochemical properties and reactivities are very different in certain cases.

The synthesis and properties of aminostannanes have been investigated in detail, while the studies which have been carried out on organotin pseudohalides are much less satisfactory.

## II. THE SYNTHESIS OF COMPOUNDS WITH A TIN–NITROGEN BOND

Organotin amines of the type $R_{4-n}Sn(NR'R'')_n$ ($n = 1-4$) cannot be synthesised by the reactions of amines with organotin halides, in contrast to the corresponding silicon and germanium compounds. The explanation is that the complexes formed in this reaction decompose on heating into the initial reactants [20-21]. The cases where the thermal stability of the complex is high are an exception. For example, triphenylstannylpurine can be synthesised from triphenylstannyl chloride and purine [22].

Organotin amines are obtained by transmetallation and transamination reactions as well as addition and exchange reactions.

### 1. Transmetallation Reactions

Whereas the syntheses of secondary and tertiary aminostannanes have been satisfactorily developed, an acceptable method for the synthesis of primary organotin amines of the type $R_3SnNH_2$ was not proposed until 1974 for t-butyl derivatives [23]. It involves the treatment of tris-(t-butyl)phenylstannane with a solution of potassium amide in liquid ammonia:

$$t\text{-}Bu_3SnPh + KNH_2 \xrightarrow{NH_3} t\text{-}Bu_3SnNH_2 + PhK \quad .$$

Secondary and tertiary aminostannanes are readily obtained by the reaction of lithium salts of amines with organotin halides [4,8,22,24-37]:

$$R_{4-n}SnX_n + n\,LiNR'R'' \rightarrow R_{4-n}Sn(NR'R'')_n + n\,LiX \quad ,$$

where R, R′, and R″ are alkyl or aryl groups and X is a halogen. The reaction proceeds readily and with high yields of the desired products in a dry inert solvent. At the same time the general method has certain characteristic features to which attention must be drawn. In particular, only the reaction of monolithium salts of primary aromatic amines leads to the formation of secondary organotin amines [27,38]:

$$R_3SnX + LiNHR' \rightarrow R_3SnNHR' + LiX \quad .$$

When organotin alkyl derivatives and salts of aliphatic amines were used, the products were the corresponding distannazanes. This can probably be accounted for by the successive transformations of (alkylamino)trialkylstannane:

$$\begin{aligned} 2R_3SnNHR' &\rightarrow (R_3Sn)_2NR' + H_2NR' \quad , \\ R_3SnNHR' + R_3SnX &\rightarrow (R_3Sn)_2NR' + HX \quad . \end{aligned} \qquad (1)$$

Lithium nitrides or amides are used in the synthesis of tris(trialkyl- and triarylstannyl)amines or hydrazine derivatives [33,39-41]:

$$3Me_3SnCl + Li_3N \rightarrow (Me_3Sn)_3N + 3LiCl \quad .$$

Different organotin amines and amides, including derivatives of sulphonamides and heterocyclic compounds (imidazoles, triazoles, etc.) are obtained via the corresponding sodium, potassium[2-4,42-45], and silver[46] salts and dialkylaminomagnesium bromide[47]. Together with organotin halides, the corresponding nitrates and acetates[48] as well as oxide derivatives[49,50] are used:

$$R_3SnX + MNH_2 \xrightarrow{NH_3} (R_3Sn)_3N \quad , \qquad (2)$$
$$X=Cl,\ OR,\ or\ OSnR_3;\ M=Li,\ Na,\ or\ K;$$

$$R_3SnCl + R'NAg \rightarrow R_3Sn{-}\underset{NO_2}{\underset{|}{N}}{-}R' + AgCl \quad ;$$

$$R_3SnCl + R'_2NMgBr \rightarrow R_3SnNR'_2 + MgBrCl \quad ;$$

Together with the tertiary amine, the secondary amine $(R_3Sn)_2NH$ was obtained in reaction (2).[51] The simultaneous formation of secondary and tertiary aminostannanes was also noted in the reaction of tricyclohexylphenylstannane and hexacyclohexyldistannane with potassium amide[52-54]:

$$2R_3SnC_6H_5 + KNH_2 \xrightarrow{NH_3} (R_3Sn)_2NH + C_6H_6 \quad ,$$

where R is the cyclohexyl group.

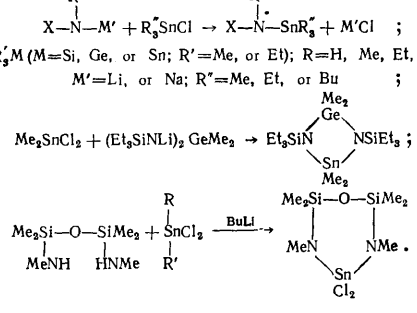
The use of organometallic derivatives and salts for the synthesis of aminostannanes is not restricted to Group I and II metals. Four- and six-membered cyclostannazanes[55] and dichlorostannoazosulphonylarenes, the first compounds containing a Sn–N bond[56], have been synthesised via tin(II) chloride:

$$ArSO_2NCl_2 + SnCl_2 \rightarrow ArSO_2{-}\underset{Cl}{\underset{|}{N}}{-}SnCl_3 \xrightarrow{SnCl_2} [ArSO_2N(SnCl_3)_2] \rightarrow$$
$$\rightarrow ArSO_2N{=}SnCl_2 + SnCl_4 \quad .$$

However, there is some doubt about the existence of such products, which are allegedly fairly stable under the usual conditions. From our point of view, these derivatives probably have dimeric or trimeric structures [see reaction (3)].

The transmetallation reaction is widely used also in the synthesis of mixed organotin–organosilicon amines of the type $X{-}\underset{R}{\underset{|}{N}}{-}Y$,[29-31,36,57-61] including cyclic derivatives containing organoelemental germanium and silicon fragments[29,62]:

$$X{-}\underset{R}{\underset{|}{N}}{-}M' + R''_3SnCl \rightarrow X{-}\underset{R}{\underset{|}{N}}{-}SnR''_3 + M'Cl \quad ;$$
$$X=R'_3M\ (M=Si,\ Ge,\ or\ Sn;\ R'=Me,\ or\ Et);\ R=H,\ Me,\ Et,\ or\ X;$$
$$M'=Li,\ or\ Na;\ R''=Me,\ Et,\ or\ Bu \quad ;$$



$$Me_2SnCl_2 + (Et_3SiNLi)_2GeMe_2 \rightarrow Et_3SiN\ \underset{\displaystyle Me_2Ge}{\overset{\displaystyle NSiEt_3}{\diagup\ \diagdown}}\ Sn\ \diagup\ \diagdown\ Me_2 \quad ;$$



Mixed organosilicon aminostannanes can be obtained also by the converse reaction, i.e. from the lithium salts of organic aminotin compounds and trialkyl derivatives of the chlorides of Group IVB elements[63] or from trialkylstannyl-lithium and *N*-bromohexamethyldisilazane[48].

Exchange reactions are quite suitable also for the synthesis of organotin pseudohalides. Trialkyl- and triaryl-stannyl isocyanates[64-68], trialkyl- and triarylstannyl isothiocyanates[64,69,70], dialkyl- and diaryl-tin di-isothiocyanates[71-74], the di-isocyanates, di-isothiocyanates, and hydroxide isothiocyanates of tetra-alkyldistannoxanes $R_2(SCN)SnOSn(NCS)R_2$ and $R_2(SCN)SnOSn.R_2(OH)$,[6,71,75] and triphenylstannyl *N*-selenocyanate[76] have been obtained in this way from organotin halides and cyanates or sodium, potassium, silver, and ammonium thiocyanates. Trialkylstannyl isocyanides, which are converted into isothiocyanates on heating with elemental sulphur[77], have been obtained via potassium cyanide[69]. Triphenyl- and tributyl-stannyl isocyanates may be synthesised also by treating organotin chlorides in xylene with a suspension of sodium *N*-ethylcarbamate[65]:

$$R_3SnCl + NaNHCOOC_2H_5 \rightarrow [R_3SnNHCOOC_2H_5] \rightarrow R_3SnNCO + C_2H_5OH \quad .$$

Trialkyl- and triaryl-stannyl azides[24,43,44,78,79,80,81] and hexa-alkyl-1,5-diazidotristannoxane $N_3Sn(R)_2{-}OSn(R)_2{-}OSn(R)_2N_3$[82] have been obtained by a corresponding procedure via azide salts.

Imino-derivatives of organotin compounds may be synthesised from trialkyltin salts and cyanoiodo-derivatives[28]:

$$Et_3SnLi + Me_2\underset{CN}{\underset{|}{C}}I \rightarrow Et_3SnN{=}C{=}CMe_2 + LiI$$

or from immonium salts and organotin halides[83-85]. Triphenyl- and trimethyl-stannyldicyanamides and bis-(dicyanomido)dimethylstannane have been obtained similarly[41,86,87]:

$$Me_2SnCl_2 + 2NaN(CN)_2 \rightarrow Me_2Sn[N(CN)_2]_2 + 2NaCl \quad .$$

In order to elucidate the structure of organotin compounds containing the carbodi-imide fragment, *NN'*-bis-(triphenylstannyl)carbodi-imide was synthesised via the sodium salt of cyanamide, but the conditions of this reaction and the constants of the products are not quoted by the authors[43]. The syntheses of the corresponding alkyl derivatives[88-91] and of the tetrameric dibutylcarbodi-imidostannane were achieved subsequently[92]:

$$2Me_3SnCl + X_2NCN \rightarrow Me_3SnNCNSnMe_3 + 2XCl \quad ;$$
$$X=H,\ Na,\ or\ Ag \quad .$$

Organotin hyponitrites have also been obtained by the above procedures, but Beck et al.[93] are inclined to the idea, based on dipole moments and infrared spectra, that these compounds do not contain an Sn–N bond and the problem has therefore not been finally solved.

## 2. The Transamination Reaction

Organotin amines are frequently synthesised by exchange reactions between dialkylaminostannanes and secondary aliphatic amines, which proceed readily and quantitatively[26,27]:

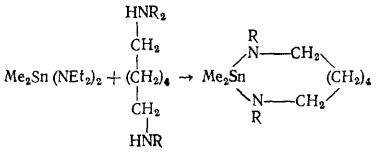
$$R_3SnNR'_2 + HNR''_2 \rightarrow R_3SnNR''_2 + HNR'_2 \quad ;$$
$$R,\ R'\ R''\ =\ alkyls.$$

The order of substitution of the amino-groups in simple aliphatic aminostannanes is[27]

$$NBu_2 > NEt_2 > NMe_2 \quad .$$

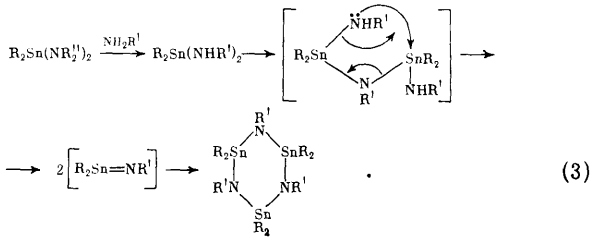
This method has also been used on a preparative scale to synthesise not only linear but also cyclic organotin

amines [94-99], for example:



Dialkylaminostannanes are transaminated by primary amines [26,27]. When t-butylamine and aniline were used in this reaction, t-butyl- and phenyl-aminostannanes were isolated respectively [100]. On the other hand, the reaction with methyl- or ethyl-amine leads to the formation of only the corresponding distannazanes even in the presence of an excess of the amine. This confirms yet again that the condensation of organotin amines of the type $R_3SnNHAlk$ to distannazanes via reaction (1) proceeds rapidly and irreversibly.

An interesting example of intramolecular transamination is the synthesis of six-membered [24,26,101] and four-membered [102] cyclostannazanes via primary amines. In the former case, the reaction is a four-stage process involving the transamination proper, intermolecular condensation, and nucleophilic 1,3-rearrangement with subsequent elimination and cyclopolymerisation:



(3)

Like amines, ammonia can be used successfully in the transamination reactions in order to obtain tertiary organotin amines, the ease of substitution decreasing in the sequence [27,103] $H_2N > RNH > R_2N$, where R is an alkyl group.

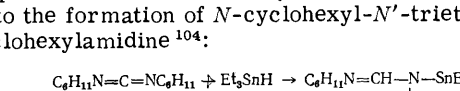
### 3. Reactions Involving the Addition of Organotin Compounds to Multiple Bonds

The addition of organotin compounds to multiple bonds is a preparatively convenient method of synthesis of organotin formamides, carbamates, amino- and imino-derivatives, substituted ureas, and related products. This section deals mainly with insertion reactions via the mdchanism

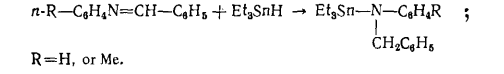
$$\equiv Sn{-}X + N{-}Y \rightarrow \equiv Sn{-}N{-}Y{-}X \quad ,$$

where N–Y is an unsaturated nitrogen compound and X = H, O, N, P, or As. These reactions can be conveniently considered separately for different X.

(a) Insertion in the Sn–H bond. The interaction of triethylstannane with dicyclohexylcarbodi-imide in the presence of azobisisobutyronitrile or zinc chloride leads to the formation of *N*-cyclohexyl-*N'*-triethylstannyl-*N'*-cyclohexylamidine [104]:

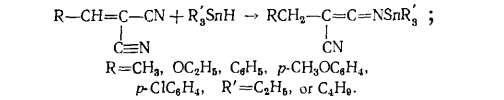


The reaction with azomethines containing aromatic substituents proceeds similarly [104-107]:

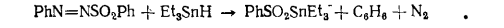


R=H, or Me.

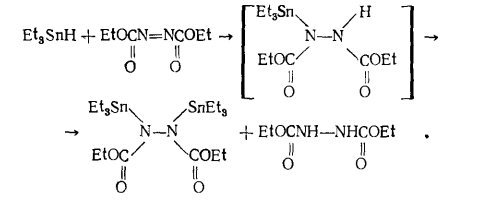
Similar reactions of azocarboxylic acid nitriles [28] and the dinitriles of alkylidenemalonic acids [108,109] also lead to the formation of an Sn–N bond:



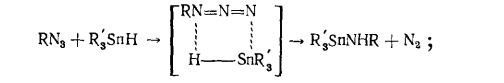
Triphenyl- and triethyl-stannanes react with azeobenzene in different ways. While the former gives rise to *NN'*-diphenyl-*N*-triphenylstannylhydrazine, the corresponding addition product derived from the latter was not isolated. When aromatic azocompounds of the type RN=NXR' and RXN=NXR' (where X = $SO_2$ or $OCH_2$) are used in this reaction, there is no addition of triethylstannane [110], for example:



In the reaction of triethylstannane with diethyl azodicarboxylate, the primary 1,2-addition product disproportionates to hydrazinedicarboxylate and bis(triethylstannyl)-bis(ethoxycarbonyl)hydrazine [111]:



The synthesis of trialkylstannylaniline and *N*-tributylstannylarenesulphonamides by the reaction of incompletely substituted stannanes with benzene- and arene-sulphonyl azides [63,112] is an example of the intermediate formation of products resulting from addition to the unsaturated nitrogen–nitrogen bond in the molecule of the incompletely substituted stannane:



R=$C_6H_5$, *p*-$CH_3C_6H_4SO_2$, *p*-$CH_3OC_6H_4SO_2$, *p*-$NO_2C_6H_4SO_2$, or $SO_2C_6H_5$; R' = $C_2H_5$, or $C_4H_9$.

The analogous reaction of benzoyl azide is accompanied by the Curtius rearrangement and the formation of phenyl isocyanate, which in its turn gives rise to a urea derivative on interaction with the incompletely substituted stannane [113]. In contrast to the foregoing, when incompletely substituted arylstannanes were allowed to react with triphenylstannane azide, compounds with an Sn–N bond were not isolated [114]. There is no doubt that such products are formed as intermediates [16], but the authors apparently did not select conditions necessary for their isolation.

The reactions of trialkyl- and triaryl-stannanes with isocyanates and isothiocyanates are of greatest interest from the preparative and theoretical standpoints [115-117]. The composition of these products showed that, depending on the nature of the reactant, different types of addition are observed. The reaction between trialkylstannanes and aromatic isocyanates leads to the formation of

trialkyl-*N*-arylformamidostannanes [116]:

$$ArNCO + R_3SnH \rightarrow R_3SnN(Ar)\overset{\overset{O}{\|}}{C}H \ ;$$
$$Ar = C_6H_5,\ p\text{-}ClC_6H_4,\ \text{or}\ p\text{-}NO_2C_6H_4;\ R = C_2H_5,\ \text{or}\ C_4H_9.$$

The reactions of diethylstannane with two moles of phenyl isocyanate and of two moles of triethylstannane with *p*-phenylene di-isocyanate proceed similarly.

The same behaviour has been observed in the reactions of aliphatic isocyanates. For example, the addition of triethylstannane to cyclohexyl isocyanate leads to the formation of compounds with an Sn–N bond [118], although in an earlier study [115] the author believed that the process results in the formation of *N*-cyclohexylcarbamoyltriethylstannane only.

Allyl isocyanate reacts with tributylstannane, this being accompanied by the possible formation of a formamide derivative, which decomposes to tributylstannyl isocyanate and propene [119]. Alkyl and aryl isothiocyanates react with triethylstannane to form alkylstannylthiomethyleneimines. The hydrostannylation of arenesulphonyl isocyanates by tributylstannane takes place similarly [120]. It has been shown by infrared spectrophotometry and thermographically that the *N*-(tributylstannyloxymethylene)-arenesulphonamide (A) is involved in a tautomeric equilibrium with *N*-tributylstannylarenesulphonylformamide (B) [120]:

$$\underset{(A)}{ArSO_2N{=}C(H)OSnBu_3} \rightleftharpoons \underset{(B)}{ArSO_2N(SnBu_3)C(O)H} \ .$$

The use of an excess of triarylstannane in the reaction with aromatic isocyanates leads to the decomposition of the resulting organotin formamide and ultimately to the reduction of the isocyanates to *N*-arylformamides [121].

The study of the mechanism of the hydrostannylation of organic isocyanates and isothiocyanates has demonstrated the occurrence of nucleophilic attack by stannane hydrogen on the carbon atom of the isocyanate in the rate-determining stage of the reaction [117]. It is believed that the reaction proceeds via a polar mechanism [122,123]:

$$R_3SnH + R'N{=}C{=}X \rightarrow \left[\begin{array}{c} R'{-}N{\cdots}C{\cdots}X \\ \vdots \quad\ \vdots \\ H \quad\ SnR_3 \end{array}\right] \rightarrow$$
$$\rightarrow R_3Sn^{(+)} + \begin{array}{l} R'{-}\overset{(-)}{N}{-}CH{=}X \\ R'{-}N{=}CH{-}\overset{(-)}{X} \end{array} \longrightarrow \begin{array}{l} \xrightarrow{X=O} R'{-}N(SnR_3){-}C(O)H \\ \xrightarrow{X=S} R'{-}N{=}CH{-}S{-}SnR_3 \end{array} .$$

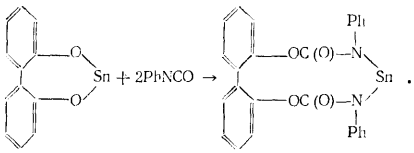
The proposed mechanism cannot apparently be unambiguous, because it does not take into account the possible tautomeric transformations of the products.

(b) Insertion in the Sn–O bond. These reactions are not of preparative importance alone. They are important for the understanding of the problem of the mechanism of the catalytic interaction of alcohols with isocyanates in the presence of organotin compounds, which still remains controversial [124–126].

The interaction of isocyanates and alkoxy-derivatives of organotin compounds results in the formation of *N*-stannylcarbamates [118,127–130]:

$$R_3SnOR' + R''NCO \rightarrow R_3SnN(R'')C(O)OR' \ ;$$
$$R = \text{alkyl};\ R' \text{ and } R'' = \text{alkyl or aryl.}$$

Ethyl and phenyl isocyanates react similarly with dibutyldimethoxystannane. The reaction proceeds stepwise with formation of 1 : 1 and 2 : 1 adducts in the first and second stages respectively. The latter adduct disproportionates on heating with dibutyldihalogenostannane, forming halogeno-substituted carbamates [131]. The synthesis of new heterocycles in which tin is bivalent constitutes an interesting example of the insertion of phenyl isocyanate in the Sn–O bond [132]:




The authors [132] give preference to the carbamate form of this compound.

It is noteworthy that the structure of the corresponding organotin imide rather than the carbamate has been attributed to the adduct of acetyl isocyanate and methoxytripropylstannane [133]:

$$CH_3{-}C{=}N{-}C(O)OCH_3 \ .$$
$$\quad\ |$$
$$\quad OSn(C_3H_7)_3$$

Presumably the imide is a result of the isomerisation of the carbamate form to the imide form as a result of the migration of the trialkylstannyl fragment. This idea has been put forward [118,129] but without any evidence for its occurrence. The possibility of the tautomeric transformations of organotin carbamates into imides was confirmed for products of the interaction of arenesulphonyl isocyanates and tributylmethoxystannane [134]:

$$p\text{-}RC_6H_4SO_2NC(O)OCH_3 \rightleftharpoons p\text{-}RC_6H_4SO_2N{=}C\overset{OSn(C_4H_9)_3}{\overset{|}{\underset{OCH_3}{|}}} \ ;$$
$$\quad\ |$$
$$Sn(C_4H_9)_3$$
$$R = H,\ CH_3,\ OCH_3,\ \text{or Cl.}$$

Organotin urea derivatives can be readily synthesised by the reaction of hexa-alkyldistannoxanes and alkyl or aryl isocyanates. The initial step involves the formation of trialkylstannyl *N*-alkyl(or aryl)-*N*-trialkylstannylcarbamates, which are decarboxylated to dialkyl(diaryl)-*NN'*-bis(trialkylstannyl)ureas and stannoxanes on heating [135–137]:

$$(R_3Sn)_2O + R'NCO \rightarrow R_3SnNR'C(O)OSnR_3 \ ;$$
$$2R_3SnNR'C(O)OSnR_3 \xrightarrow[-CO_2]{} R_3SnNR'{-}CO{-}NR'SnR_3 \ ;$$
$$R \text{ and } R' = \text{alkyl or aryl.}$$

Stannylureas are obtained also by the reaction of organotin carbamates with isocyanates on heating [137,138]:

$$R_3SnNR'C(O)OSnR_3 + R''NCO \rightarrow R_3SnNR'{-}CO{-}NR''SnR_3 + CO_2 \ .$$

When the reaction is carried out at room temperature, hexa-alkyldistannoxanes and organic isocyanurates are formed [125,138]. It is of interest that this type of reaction apparently constitutes the basis of the catalytic trimerisation of isocyanates, which occurs in the presence of organotin compounds [125,126].

Like the reactions of arenesulphonyl isocyanates with incompletely substituted stannanes and alkoxy-derivatives, the reaction of the above isocyanates with tributyltin oxide results in the isolation of a mixture of tautomeric compounds to which the structures of the corresponding carbamates and stannoxymethyleneimines [scheme (4)] has been attributed to the basis of infrared spectra. When the isocyanate and the oxide were used in proportions of 2 : 1, it was possible to obtain organotin disulphonylureas [139]:

$$n\text{-}RC_6H_4SO_2NCO + (Bu_3Sn)_2O \longrightarrow \begin{array}{l} \xrightarrow{\quad} n\text{-}RC_6H_4SO_2N(SnBu_3)C(O)OSnBu_3 \\ \xrightarrow{\quad} n\text{-}RC_6H_4SO_2N{=}C(OSnBu_3)_2 \end{array} \ ;$$
$$R = H,\ CH_3,\ OCH_3,\ \text{or Cl.} \qquad (4)$$

The attempt to synthesise triethylstannyl *N*-phenylcarbamate from triethyltin hydroxide and phenyl isocyanate was unsuccessful[136]. On the other hand, the reaction of arenesulphonyl isocyanates with triethyl- and triphenyltin hydroxides proceeds readily and in the case of the ethyl derivative results in formation of organotin arenesulphonamides and, in the presence of the phenyl derivative, a mixture of the corresponding arenesulphonamides and arenesulphonylcarbamates[140].

Organotin ureas can also be obtained by the interaction of hexa-alkyldistannoxanes or alkoxy-tin derivatives with carbodi-imides[94,141]. The latter are more reactive than isocyanates and isothiocyanates. Nitriles containing strong electron-accepting groups react with oxygen-containing organotin compounds to form substituted imides with an Sn–N bond[9,94,131]:

$$Bu_3SnOMe + CCl_3CN \rightarrow Bu_3SnN{=}C(CCl_3)OMe \ .$$

Diarylsulphodi-imides and *N*-sulphinamides readily react with alkylstannoxy derivatives; one or two N=S bonds are ruptured and intermediate products resulting from insertion in the Sn–O bond are formed[142-144]:

$$ArN{=}S{=}NAr + (Bu_3Sn)_2O \rightarrow Bu_3SnN(Ar)SON(Ar)SnBu_3 \ ;$$
$$ArSO_2NSO + R_3SnOR' \rightarrow R_3SnN(SO_2Ar){-}SO{-}OR' \ ;$$
$$Ar = C_6H_5, \text{ or } p\text{-}CH_3C_6H_4 \ .$$

The organotin sulphinyl diamides, sulphimates, and other compounds formed in these reactions are as a rule thermally unstable.

Finally, fairly stable t-butyl *N*-alkyl-*N*-triphenylstannylperoxycarbamates, $Ph_3SnN(Alk)C(O)OOBu\text{-}t$, have been obtained as a result of the reaction of t-butyl triphenylstannyl peroxide with alkyl isocyanates[145].

(c) Insertion in the Sn–N bond. The addition of unsaturated compounds to the Sn–N bond is the most typical example of the insertion reaction. It is used to synthesise organotin ureas, imines, imides, sulphinic diamides, and other compounds from aminostannanes and isocyanates, isothiocyanates, organic cyano-derivatives, carbodi-imides, and sulphinyl derivatives[12,26,108,146-149]:

$Me_3SnNMe_2$ + PhNCO → $Me_3SnN(Ph)C(O)NMe_2$
+ PhCN → $Me_3SnN{=}C(Ph)NMe_2$
+ PhNCNPh → $Me_3SnN(Ph)C(=NPh)NMe_2$
+ PhNSO → $Me_3SnN(Ph)S(O)NMe_2$
+ PhNCS → $Me_3SnN(Ph)C(S)NMe_2$ .

The reactions proceed under mild conditions with nearly quantitative yields. Aromatic isocyanates are less reactive in these processes than the aliphatic compounds.

Phenyl isocyanate is capable of adding to *N*-tributylstannyl-*N*-methylformamide and *N*-tributylstannylacetamide, but the adduct obtained as a result of the latter reaction decomposes to tributylstannyl isocyanate and acetanilide[7,150]:

$$Bu_3SnNHC(O)Me + PhNCO \rightarrow [Bu_3SnN(Ph)C(O)NHC(O)Me] \rightarrow$$
$$\rightarrow Bu_3SnNCO + PhNHC(O)Me \ .$$

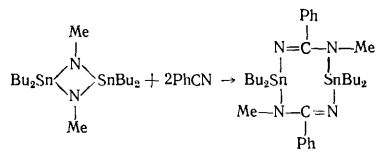
The reactions of aminostannanes with aromatic *N*-sulphinylsulphonamides[143] and of phenyl isocyanate with diethylaminodimethylstannyl chloride[151] also proceed with formation of unstable adducts. The interaction of alkyl or aryl isocyanates and isothiocyanates with *N*-tributyldiphenylmethyleneiminostannane leads to the formation of the corresponding organotin ureas and thioureas[152]:

$$Bu_3SnN{=}CPh_2 + RNCX \rightarrow Bu_3SnN(R)C(X)N{=}CPh_2 \ ;$$
$$R = Me, Et, Bu, \text{ or } Ph;\ X = O \text{ or } S \ .$$

The addition of heptamethylsilylstannazane to isocyanates and isothiocyanates has been studied in a number of investigations and it has been shown that the structures of the products thus obtained are different[12,153]. Thus the reaction with methyl isocyanate gives rise mainly to the iminoester

$$R_3SnN(CH_3)C\langle {}^{NCH_3}_{OSiR_3} \ ,$$

while the reaction with phenyl isocyanate gives rise to the urea derivative $R_3SnN(Ph)CON.(CH_3)SiR_3$. The reaction of silylstannazane with phenyl isothiocyanate leads to an equilibrium mixture of products with both structures. The reaction involving the insertion of isocyanates in the Sn–N bonds of organotin cyanamides has been used to synthesise organotin cyanoureas, which exhibit biological activity[154]. An interesting example of the addition reaction of the above type is the synthesis of eight-membered organotin heterocycles by the reaction of benzonitrile with diazostannetidines[102]:




A simple method has been proposed for the synthesis of trimethylstannyl *N*-methyl(trimethylstannyl)carbamate by passing carbon dioxide through a solution of heptamethyldistannazane[155]:

$$(Me_3Sn)_2NMe + CO_2 \rightarrow Me_3SnN(Me)C(O)OSnMe_3 \ .$$

(d) Insertion in the Sn–P and Sn–As Bonds. The interaction of isocyanates, isothiocyanates, and phenyl azide with triphenylstannyldiphenylphosphine and triphenylstannyldiphenylarsine may be classified as insertion reactions of the above type[156-158]:

$$Ph_3SnPPh_2 + PhNCX \rightarrow Ph_3SnN(Ph)C(X)PPh_2 \ ;$$
$$X = O \text{ or } S;$$
$$Ph_3SnYPh_2 + 2PhN_3 \rightarrow Ph_3SnN(Ph)Y(=NPh)Ph_2 \ ;$$
$$Y = P \text{ or } As;$$
$$Ph_3SnAsPh_2 + 3PhN_3 \rightarrow Ph_3SnN(Ph){-}As(Ph){-}N(Ph)SnPh_3 \ .$$
$$\|$$
$$NPh$$

## 4. Exchange and Substitution Reactions of Organotin Compounds

Exchange reactions of organotin oxides and hydroxides with nitrogen-containing reagents having an active hydrogen atom have been proposed for the synthesis of compounds with an Sn–N bond, which are fairly resistant to hydrolysis:

$$(R_3Sn)_2O + 2HN\langle \rightarrow 2R_3SnN\langle + H_2O \ .$$

Organotin derivatives of pyrrole, imidazole, benzotriazole[22,43-45], amido-compounds[118,159], nitroamines[46], and trialkylstannyltoluenesulphonamide[42,150] have been obtained via this mechanism. The reaction is used in the preparative methods for the synthesis of organotin isocyanates and isothiocyanates involving the interaction of trialkyl- or triaryl-tin oxides and hydroxides with urea,

## III. REACTIVITY OF COMPOUNDS WITH A TIN–NITROGEN BOND

It has been suggested that the reactions of organotin compounds with an Sn–N bond be divided into these with protic reagents, reactions with organoelemental hydrides, and exchange decomposition and addition reactions [18].

### 1. Reactions with Protic Reagents

The most characteristic property of organotin amines [33,44,47,147,182,190], imines [83,191,192], ureas [130,136], carbamates [127,128,129,145], triazenes [193], amides [112,140,159,182], sulphinic diamides [142], and triphenylstannyldicyanamide [86] is their hydrolytic instability:

$$\equiv Sn{-}N\!\!<\; + H_2O \rightarrow \equiv Sn{-}OH + HN\!\!<\;\; .$$

Aminostannanes containing less bulky substituents are more readily hydrolysed by water as a result of the steric factor [30]. When these reactions are performed in air, hydrolysis is accompanied by carboxylation of the aminostannanes, leading to organotin carbonates [33,47,106,155,194].

Various organotin amino-derivatives are readily cleaved at the Sn–N bond by hydrogen chloride or hydrochloric acid [47,49,145,147,194], hydrogen sulphide [127,129], and hydrogen cyanide [195]. The last reaction is used to synthesise organotin cyanides:

$$R_{4-n}Sn(NEt_2)_n + 2n\,HCN \rightarrow R_{4-n}Sn(CN)_n + n\,HNEt_2\cdot HCN\;;$$
$$R{=}Me,\ Et,\ or\ Bu,\ Ph;\ n = 2,\ 3.$$

When stannylamines [194,196], trialkylstannylketenimines [192], organotin carbamates [127,129,134,139], *NN'*-bis(trialkylstannyl)-sulphinic amides [142], and *NN*-bis(tributylstannyl)benzenesulphonamide [182] react with acetic acid, organotin acetates are formed quantitatively.

Alcohols react readily with aminostannanes [34,141,147,182,194,197,198], *N*-trialkylstannylketenimines [191,192], *NN'*-diaryl-*NN'*-bis(trialkylstannyl)sulphinic diamides [142], and stannyl carbamates [126,129,136,139,175,193] at the Sn–N bond under mild conditions, which leads to the formation of organotin alkoxides and amines. Such reactions are used, for example, to synthesise pure methoxytrimethylstannane [197]:

$$R_{4-n}Sn(NR'_2)_n + n\,R''OH \rightarrow R_{4-n}Sn(OR'')_n + n\,R'_2NH\;\; .$$

Butaneselenol [199,200], butanethiol [201], and silanol [34] react with aminostannanes similarly to alcohols.

The reactions of alcohol with organotin carbamates are particularly interesting from the standpoint of the explanation of the mechanism of the catalysis of the synthesis of urethanes by the latter [129,202]:

$$Bu_3SnOEt + PhNCO \rightarrow Bu_3SnN(Ph)C(O)OEt \xrightarrow{EtOH} Bu_3SnOEt + PhNH{-}C(O)OEt$$

or

$$PhNCO + EtOH \xrightarrow{Sn^{IV}} PhNH{-}C(O)OEt\;\; .$$

However, the lack of quantitative data, on the basis of which the rates of the known catalytic reactions put forward by Bloodworth and Davies [129] could be compared, precludes unambiguous inferences concerning this mechanism. One can only add that a different version of the mechanism of the catalytic formation of urethanes has been considered [124] and its validity demonstrated.

Organic hydroperoxides and peroxides react similarly with aminostannanes. The reaction of t-butyl hydroperoxide with a dialkylaminotrialkylstannane yields the trialkyl-t-butylperoxystannane and the dialkylamine. The main products of the reaction with benzoyl peroxide were the trialkylstannyl benzoate and the *NN*-dialkyl-*O*-benzoylhydroxylamine. The latter reaction does not have a free-radical mechanism despite the use of a typical free-radical generating agent–benzoyl peroxide [203].

Reactions involving the transamination of aminostannanes have already been partly discussed in Section II. It is of interest to consider here the interaction of methyl *N*-phenyl-*N*-tributylstannylcarbamate with ethylamine, the products of which are tributylmethoxystannane and *N*-ethyl-*N'*-phenylurea instead of the expected transamination products [129] [Eqn. (6)]. According to the authors [129], the reaction can proceed via two equally probable pathways. From our point of view, the second pathway is preferable, because the tributylethylaminostannane formed via the first pathway should condense with liberation of distannazanes [Eqn. (1)], which were not detected in the reaction:

$$Bu_3SnN(Ph)C(O)OMe + EtNH_2 \begin{cases} \rightarrow Bu_3SnNHEt + PhNH{-}C(O)OMe \\ \rightarrow MeOH + Bu_3SnNPh{-}CO{-}NHEt \end{cases} \rightarrow$$
$$\rightarrow PhNH{-}CO{-}NHEt + Bu_3SnOMe\;\; . \qquad (6)$$

When stannyl *N*-stannyl-*N*-sulphonylcarbamates react with diethylamine, the corresponding substituted ureas and tributyltin oxide are also obtained [139]. The transamination of bis(tributylstannyl)benzenesulphonamide with diethylamine proceeds in the standard manner [182]:

$$Bu_3Sn\,N(PhSO_2)C(O)OSn\,Bu_3 + Et_2NH \rightarrow PhSO_2NH{-}CO{-}NEt_2 + (Bu_3Sn)_2O\;;$$
$$(Bu_3Sn)_2NSO_2Ph + Et_2NH \rightarrow Bu_3SnNHSO_2Ph + Bu_3SnNEt_2\;\; .$$

Stannylamines react with halogenohydrocarbons in different ways depending on the nature of the halogen and the structure of its derivative. Thus when a dialkylaminotrialkylstannane was acted upon by chloroform, bromoform or chloroethylene derivatives, trihalogenomethyl derivatives of tin were obtained [131,204–207]:

$$R_3SnNR'_2 + HCX_3 \rightarrow R_3SnCX_3 + R'_2NH\;;$$
$$R{=}Me,\ Et,\ Bu,\ or\ Ph;\ R'{=}Me\ or\ Et;\ X{=}Cl\ or\ Br.$$

The synthesis of pentafluorophenyltrimethylstannane was achieved by the reaction of dimethylaminotrimethylstannane with pentafluorobenzene in boiling benzene [208]. However, this reaction does not occur with iodo-, fluoro-, or mixed chlorofluoro-derivatives of methane of the type $HCFCl_2$.

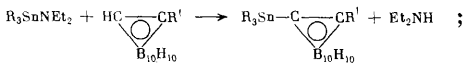
The reaction of aminostannanes with acetylene and its derivatives constitutes a preparative method for the introduction of an unsaturated bond into the molecule of an organotin compound. The reaction proceeds quantitatively which is promoted by the possibility of the effective elimination of the volatile alkylamine formed as a product [147,148,194,208,209,210,211]:

$$R_{4-n}Sn(NR'_2)_n + n\,HC{\equiv}CR'' \rightarrow R_{4-n}Sn(C{\equiv}CR'')_n + n\,HNR'_2\;;$$
$$n{=}1{-}4$$
$$R,\ R',\ and\ R''\ =\ hydrocarbon\ groups.$$

In the reactions with amines of the type $R_2Sn(NR'_2)_2$ acetylene gives rise to a polymeric complex [147,194]. Cyclopentadiene, indene, and their derivatives react with aminostannanes similarly to acetylene [147,194,212].

Other compounds containing an active hydrogen atom attached to a carbon atom (nitriles, nitromethane) are also capable of involvement in proton exchange reactions with aminostannanes [194]. Thus diazomethane reacts with dimethylaminotrimethylstannane, which is followed by the substitution of two hydrogen atoms by organotin fragments [186,213,214], the reactivity of diazomethane derivatives

increasing in the sequence $MeCHN_2 < CH_2N_2 < CH[C(O).OEt]N_2$.[214-216]. *o*-, *m*-, and *p*-Carboranes react similarly[217,218]:



$R = Et$, or Bu; $R' = H$, $CH{=}CH_2$, or $SnR_3$ .

Although decaborane contains an active hydrogen atom, it reacts with aminostannane to form only a complex of the type $[Me_3Sn]^+[B_{10}H_{13}\cdot Me_2NH]^-$.[219] The mechanism of the reactions of aminostannanes with protic reagents has not been elucidated. However, one may postulate that it is based on electrophilic attack by the hydrogen atom of the protic reagent HA on the nitrogen atom of the aminostannane $\equiv Sn-N\lessdot$ followed by the coordination of the A fragment to the tin atom[18].

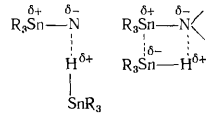
## 2. Reactions of Amino-Derivatives of Tin with Organoelemental Hydrides

Organotin hydrides react with aminostannanes[220-228], stannylhydrazines[117], and amides[111,226,229] to form di- and poly-stannanes in almost quantitative yields, for example:

$$R_3SnNEt_2 + R'_3SnH \rightarrow R_3SnSnR'_3 + Et_2NH \quad ;$$

$$n\,R_2Sn(NEt_2)_2 + n\,R_2SnH_2 \rightarrow (-SnR_2)_{2n} + 2n\,Et_2NH \quad .$$

The relative reactivity of $R_3SnH$ depends on R and increases in the following sequences[222,224]: t-Bu < iso-Bu < Bu < Ph and $R_3SnSnR_2H < R_3SnH < R_2SnH_2$. On the other hand, the reactivity of aminostannanes in these reactions increases with increasing basicity of nitrogen: $R_3SnNHR'' < R_3SnNR''_2$.[222] The study of the kinetics of the reaction of diethylaminotriethylstannene with triethylstannane showed that it is of second order overall and of first order with respect to each reactant[230]. $S_E2$ and $S_Ei$ mechanisms have been proposed for polar and non-polar solvents respectively[220], the intermediate states being of the following form:



The main reaction is sometimes accompanied by an exchange side reaction, which, however, may be reduced to a minimum[220,222,224]. For example, in the synthesis of compounds with more than two tin atoms, it is best to employ dialkylstannanes and not diaminostannane, because exchange reactions are more probable in the $R_3SnH/R'_2.Sn(NEt_2)_2$ system[224].

Typical examples of the synthesis of compounds with a tin–element bond are the reactions of trialkyldimethylaminostannanes with triphenylgermanes[223,228], phosphines[147,194], arsines[103,147,231], and stibenes[103]:

$$R_3SnNR'_2 + Ph_nXH \rightarrow R_3SnXPh_n \quad ;$$

X = P, As, Sb, or Ge, $n = 2,3$.

The reaction has been used to synthesise tin–germanium derivatives with functional groups by treating tin–germanium amines with water, phenols, acetylene derivatives, and other reagents[228]. At the same time, aminostannanes do not react with trialkylgermanes and trialkyl(or triaryl)silanes, apparently as a consequence of the lower activity of the hydrogen atom in these compounds[157,222,228].

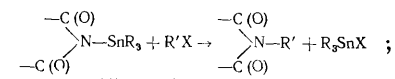
Carbonyl and cyclopentadienyl derivatives of chromium, molybdenum, vanadium, manganese, rhenium, rhodium, platinum, and other metals containing active hydrogen also react with aminostannanes, which makes it possible to synthesise organometallic compounds containing Sn–Cr,[232,233], Sn–Mo,[232-235], Sn–W[232,233,236], Sn–Rh[79,233], Sn–Mn, Sn–Fe, Sn–Co, and Sn–Ni bonds[235]:

$$(\pi\text{-}C_5H_5)(CO)_3M{-}H + R_3SnNR'_2 \rightarrow (\pi\text{-}C_5H_5)(CO)_3M{-}SnR_3 + HNR'_2 \quad ;$$

M = Cr, Mo, or W.

## 3. Substitution Reactions

The substitution reactions of aminostannanes involving the dissociation of the Sn–N bond can be regarded as amination reactions and the organotin amines can therefore be treated as aminating agents[18,237]. Reactions of this type include the alkylation or acylation of organotin derivatives of imides (phthalimide, succinimide, imidazole, and isatin) with the aid of alkyl or acyl halides[238], selective substitution of tributylstannyl groups in organotin tetrazoles by methyl iodide[239], and the synthesis of tris(benzoyl)isocyanurate on treatment of an organotin isocyanurate with benzoyl chloride[193,238]:



R = Alk; R' = Alk, or Ac; X = Hal.

The interaction of tin-containing amino-derivatives with halogenohydrocarbons depends on the nature of the reactants. Thus the explosive reaction of bis(dimethylamino)dimethylstannane with carbon tetrachloride has been reported[240]. When tributyldiethylaminostannane was allowed to react with butyl chloride, tributylamine, triethylamine, and dibutylethylamine were isolated together with butyldiethylamine[241], while the reaction involving dimethylaminotrimethylstannane proceeds with dehydrochlorination and the formation of *cis*- and *trans*-but-2-enes[242]. This was also observed when pentachloroethane[204] and chloromethylacetylene were used[219]. On the other hand, on reaction with fluoroalkanes (or fluoroalkenes) and other fluorine compounds, aminostannanes behave in the usual manner[101,196,237,241,243-246]:

$$Me_3SnNMe_2 + YF \rightarrow Me_3SnF + YNMe_2 \quad ;$$

$Y = C_6F_5$, $C_6F_4Br$, $C_6F_4CN$, CF=CFCl, $BF_2(OC_2H_5)_2$, $PF_2$, $AsF_2$, $SbF_2$, or $TiF_3$.

Organoelemental and inorganic chloro-, bromo-, and iodo-derivatives react similarly[79,196,237,241,242,247]. In contrast to the reactions of aminostannanes with organoelemental hydrides discussed above, which lead to the formation of an element–element bond, metal hydrides and certain hydrogen-containing boron, aluminium, and silicon derivatives give rise to hydrogen-containing stannanes[46,196,237,242,248]:

$$R_{4-n}Sn(NR'_2)_n + R''H \rightarrow R_{4-n}SnH + R''NR'_2 \quad ;$$

R = R' = Alk; R'' = $Et_3N\cdot BH_2$, $B_2H_5$, $Bu_4Al_2H$, or $Ph_2SiCl$.

Substitution reactions between aminostannanes and organoelemental alkyl and alkoxy-derivatives are known[49,196,237,249]:

$$R_3SnNMe_2 + R'_nM \rightarrow R_3SnR' + Me_2NMR_{n-1} \quad ;$$

M = Li, R' = Me, $n = 1$; M = Al, R' = Et, $n = 3$; M = B, R' = Bu, Ph, or OMe, $n = 3$.

The synthesis of disubstituted organoelemental alkylstannanes of the type $R_3SnC{\equiv}CMR_3$ (R = Me, Et, or Ph; M = Si, Ge, or Pb) on heating a mixture of a dialkylaminotrialkyl(or triaryl)stannane, sodium acetylide, and organic derivatives of the chlorides of Group IVB elements can also be included among the reactions of the type under consideration[250].

The interaction of a trialkyldiethylaminostannane with bis(trimethylsilyl)mercury, which leads to the formation of the hexa-alkyldistannane, the diethylaminotrimethylsilane, and metallic mercury is unusual[251].

Aminostannanes also react with esters, but these reactions have not been studied in detail and have not been fully explained[148,196,249,252]. It has been shown that the reactions with methyl methacrylate and alkyl and aryl acetates involve exchange and the dissociation of the bond between the carbon atom of the carbonyl group and the alkoxy-fragment[196,249]:

$$R_3SnNMe_2 + R'C(O)OR'' \rightarrow R_3SnOR'' + R'C(O)NMe_2;$$
R, R' = alkyl or aryl groups.

The similar reaction with vinyl acetate proceeds with formation of the trialkylstannyl acetate and the dissociation of the C–O bond in the alkoxy-group[252]. When aminostannanes were allowed to react with isopropenyl acetate, a trialkylstannyl acetate and dimethylacetamide were obtained[194,253]:

$$Et_3SnNMe_2 + MeC(O)OC(CH_3){=}CH_2 \rightarrow Et_3SnCH_2C(O)Me + CH_3C(O)NMe_2.$$

Certain aldehydes are also involved in the exchange reactions. Thus chloral cleaves the Sn–N bond in a dialkylaminotrialkylstannane, forming the trialkyl(trichloromethyl)stannane and the dialkylformamide[254,255]. The interaction of *N*-phenylhexabutyldistannazane with acetaldehyde proceeds under mild conditions with substitution of the oxygen of the carbonyl group and the formation of ethylideneamine[100]:

$$(R_3Sn)_2NR' + R''CH{=}O \rightarrow \left[\begin{array}{cc} R_3Sn{-}O & SnR_3 \\ | & | \\ R''CH{-}NR' & \end{array}\right] \rightarrow (R_3Sn)_2O + R''CH{=}NR'.$$

## 4. Addition Reactions of Aminostannanes

This section gives a systematic account of the reactions of stannylamines with unsaturated compounds which involve the cleavage of the Sn–N bond and the insertion of the unsaturated compounds in accordance with the general mechanism[26,148,155,249]:

$$\equiv Sn{-}N\!\!<\!\!\!\!\diagdown + A \rightarrow \equiv Sn{-}A{-}N\!\!<\!\!\!\!\diagdown$$
A = compounds with a multiple bond.

It has been shown that different versions of the reaction are possible, including 1,1-, 1,2-, 1,3-, and 1,4-insertion reactions.

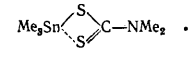
The interaction of dimethylaminotrimethylstannane with *p*-tolyl isocyanide is an example of the 1,1-insertion reaction[148,157]:

$$Me_3SnNMe_2 + p\text{-}CH_3C_6H_4N{=}C \rightarrow p\text{-}CH_3C_6H_4N{=}C\!<\!\!\!\!\diagdown^{SnMe_3}_{NMe_2}.$$

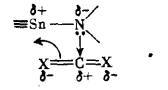
1,2-Insertion has been much more thoroughly investigated. The reactions of aminostannanes with carbon and sulphur dioxides, carbon disulphide, and carbon oxide sulphide are typical; they take place at room temperature and are accompanied by the formation of the corresponding organotin carbamates, thiocarbamates, and related products[26,146,151,155], for example:

$$Me_3SnNMe_2 + CX_2 \rightarrow Me_3SnXC(X)NMe_2;$$
X=O, or S.

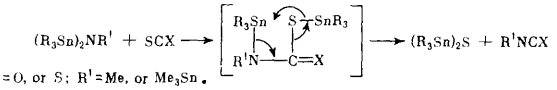
The oxygen-containing compounds are polymers in which the tin atom is coordinated to oxygen. The thioanalogues of carbamates are monomeric in benzene solution, but the tin in these compounds is likewise in a five-coordinated state:



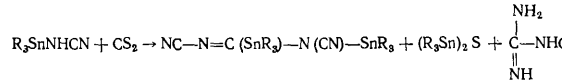
The reactivity of *N*-arylaminostannanes is much lower compared with that of the alkyl derivatives. For example, trimethylphenylaminostannane reacts with carbon dioxide much more slowly and trimethyldiphenylaminostannane does not react with $CO_2$ and $CS_2$ at all. This is consistent with the hypothesis that the mechanism of the insertion reaction involves initial nucleophilic attack by the nitrogen atom of the stannylamine on the positively charged carbon atom of the 1,2-dipole (in the present instance, O=C=O or S=C=S). The aromatic substituent delocalises the free electron pair of the nitrogen atom and hence hinders attack by this atom[146,155]:



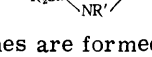
At the same time one should note that in certain cases these reactions do not stop at the first stage involving the formation of the insertion product. Thus the reaction of trimethylphenylaminostannane with carbon disulphide results in the formation of bis(trimethylstannyl) sulphide and *syn*-diphenylthiourea, while *N*-methylhexamethyldistannazane and tris(trimethylstannyl)amine react with COS and $CS_2$ to form bis(trimethylstannyl)sulphide and the corresponding organic or organotin isocyanates and isothiocyanates. It has been suggested that an unstable 1,2-adduct is formed only in the first stage of the reaction[155,254,256,257]:




The use of trialkyl(or triaryl)stannylcyanamide in these reactions leads to unexpected products[167]:

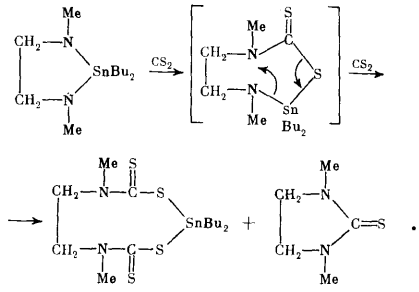



Bis(dialkylamino)stannanes reacts with carbon dioxide and carbon disulphide to form the corresponding biscarbamates and bisthiocarbamates. Tetrakis(dimethylamino)stannane reacts similarly with $CS_2$.[135] When the latter adds to diazostannetidines,

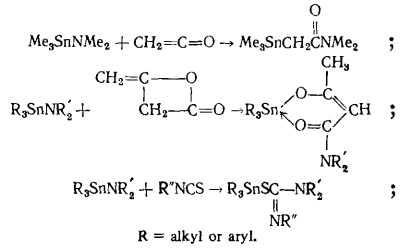


stable dithiostannetanes are formed[102]. The interaction of cyclic diaminostannanes, for example, a 2,2-dialkyl-1,3-diaza-2-stannacyclopentane, with carbon disulphide

proceeds via a 1,2-insertion mechanism, but is accompanied by the simultaneous decomposition of the 1,2-adduct to diazacyclopentanes [258]:

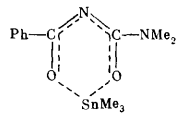


The reactions of amino-derivatives of tin with ketenes [18,146,253,259], diketen [260,261], isothiocyanates [26,146,148,262], isocyanates, and carbodi-imides [149,263,265] are also examples of the 1,2-insertion reaction:



R = alkyl or aryl.

The reaction of dimethylaminotrimethylstannane with benzoyl isocyanate, *N*-benzoyl-*N'*-t-butylcarbodiimide [149,263,264], and thiobenzoyl isocyanate [265] leads to six-membered rings owing to the intramolecular coordination of oxygen with the tin atom:



Processes involving the addition of stannylamines to double and triple carbon–carbon bonds activated by strong electron-accepting substituents belong to insertion reactions of the same type. Acrylate esters, acrylonitrile, acrolein, crotonaldehyde, diethyl acetylenedicarboxylate, 1-chloro-2-diphenylacetylene, etc. have been investigated as the activated reagents [148,243,249,252]. As a rule, the amino-group adds to the $\beta$-carbon atom and the organotin fragment adds to the $\alpha$-atom. The reactions proceed under mild conditions and give high yields of the desired products:

$$CH_2{=}CHC(O)OCH_3 + R_3SnNR'_2 \rightarrow R'_2NCH_2CH(SnR_3)C(O)OCH_3 \quad ;$$

$$C_6H_5C{\equiv}CCl + R_3SnNR'_2 \rightarrow R'_2NC(C_6H_5){=}C(Cl)SnR_3 \quad ;$$

R=R' — alkyl groups.

However, aldehydes with strong electron-accepting substituents add to stannylformamides and stannylureas with dissociation of their C=O bond [138,150]:

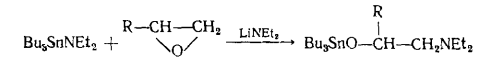
$$R_3SnN(R')C(O)R'' + CX_3C(O)H \rightarrow R_3SnOCH(CX_3)-N(R')C(O)R'' \quad ;$$

R=Bu, R'=Me, R''=H, X=Cl, or Br;

R=Et, R'=Ph, R''=H, X=Br; R=Bu,

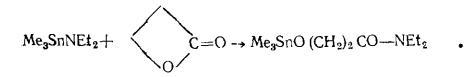
R'=H, R''=Me, X=Br.

Stannylamines and stannyl carbamates can also give rise to a 1,2-insertion product on interaction with acetic anhydride, but it could not be isolated [129,196,252]. Under certain conditions, the extremely weak Sn–N bond can be dissociated by ketones. Here the interaction is complex, as shown by the formation of a hexaalkyldistannoxane, organic amines, mesityl oxide, a trialkylstannylacetone, and other products in the reaction of alkylaminostannanes with acetone [194,296]. The possible pathways in this reaction and the influence on the latter by steric and electronic factors have been investigated [267]. On the other hand, hexafluoroacetone reacts with aminostannanes to form 1,1-adducts [268]. Analogous 1,2-addition products have been obtained in the reaction of trialkyldiethylaminostannane with cyclopentanone and cyclohexanone [244,269]. 1,3-Insertion reactions of aminostannanes have been observed in their interaction with epoxy-derivatives, including epoxybutane, phenyloxiran (styrene oxide), and epoxycyclohexane [270]:



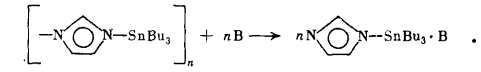
Thi-iran and methylthi-iran give rise to $R_3SnSCH(R'')CH_2.NR'_2$, where R = R' = R'' = Me or Et respectively [243].

The interaction of diethylaminotrimethylstannane with $\gamma$-butyrolactone and $\beta$-propiolactone, which involves ring opening, is an example of 1,4-insertion [271–273]:



## 5. Other Reactions of Aminostannanes

Aminostannanes can exhibit both electron-accepting (tin atom) and electron-donating (nitrogen atom) properties and can thus function both as aprotic acids and aprotic bases. However, such reactions are not characteristics of these compounds and few are known owing to the low strength of the Sn–N bond. *N*-Tributylstannylimidazole forms complexes with basic ligands [18,274] in which tin has a coordination number of five and behaves as a Lewis acid:

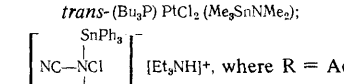


Another example of compounds in which tin exhibits electron-accepting properties is provided by organotin derivatives of nitroamine, which have a chelate structure [46].

The properties of aminostannanes as Lewis bases are characterised by the formation of complexes [18,256,275,276]:

$(Me_2N)_4Sn \cdot VOCl_3$; $[(Me_3Sn)_4N]^+Br^-$;

*trans*-$(Bu_3P)PtCl_2(Me_3SnNMe_2)$;



EtCO, Bz, MeOCO, EtOCO, or $PhSO_2$.

The reactions involving the photochemical decomposition of aminostannanes, whose study has only just begun, constitute a group separate from those enumerated above. It has now been shown that the photochemical decomposition of diethylaminotrimethylstannane, investigated by ESR, proceeds with the dissociation of the nitrogen–tin bond and

is a complex multistage process leading ultimately to the formation of hexamethyldistannane, diethylamine, and *N*-ethyliminoethane[277]:

$$Me_3SnNEt_2 \xrightarrow{h\nu} \begin{cases} Me_3SnH + MeCH{=}NEt \\ Me_3Sn^{\cdot} + Et_2N^{\cdot} \end{cases}$$
$$Me_3SnH + Me_3SnNEt_2 \rightarrow (Me_3Sn)_2 + Et_2NH$$
$$2Me_3Sn^{\cdot} \rightarrow (Me_3Sn)_2$$
$$2Et_2N^{\cdot} \rightarrow Me{-}CH{=}NEt + Et_2NH$$
$$Me_3Sn^{\cdot} + Et_2N^{\cdot} \rightarrow Me_3SnH + Me{-}CH{=}NEt \ .$$

## IV. CHEMICAL PROPERTIES OF ORGANOTIN PSEUDOHALIDES WITH A TIN–NITROGEN BOND

Bearing in mind the appreciable differences between the reactivities of aminostannanes and tin pseudohalides, we thought it useful to consider in this Section the specific chemical properties of typical examples of the latter, including organotin azides, isocyanates, isothiocyanates, carbodi-imides, imines, and related compounds.

Investigators noted in the first place the high thermal stabilities of the pseudohalides. Thus triphenylstannyl azide decomposes at a high temperature (>200°C), in contrast to organic analogues, with formation of tetraphenylstannane as the only tin-containing product[278]. Aromatic and aliphatic organotin isocyanates of the type $R_3SnNCO$ are distinguished by an enhanced stability. The latter are stable when acted upon by oxygen, ultraviolet radiation, and prolonged heat up to 200°C. The thermal decomposition of such isocyanates is a complex process, which probably involves both homolytic and heterolytic reactions. The decomposition of tributylstannyl isocyanate takes place at 250°C with the liberation of butane, butene, carbon dioxide, and carbon monoxide and the formation of metallic tin. In the decomposition of triphenylstannyl isocyanate, both disproportionation to tetraphenylstannane and diphenylstannyl di-isocyanate and its decomposition with formation of carbon dioxide and an organotin carbodi-imide were observed[91,163,279]:

$$(C_4H_9)_3SnNCO \begin{cases} \rightarrow C_4H_8 + C_4H_{10} + N_2 + Sn + CO \\ \rightarrow (C_4H_9)_3SnNCNSn(C_4H_9)_3 + CO_2 \end{cases} ;$$
$$(C_6H_5)_3SnNCO \begin{cases} \rightarrow (C_6H_5)_4Sn + [(C_6H_5)_2Sn(NCO)_2] \\ \rightarrow (C_6H_5)_3SnNCNSn(C_6H_5)_3 + CO_2 \end{cases} .$$

Organotin pseudohalides react in different ways with protic reagents. Under the influence of hydrogen chloride, the Sn–N bond in triphenylstannyl isocyanate is cleaved, but only triphenylstannyl chloride (44%) and tetraphenylstannane (33%) could be isolated from the reaction mixture[163]. On the other hand, *NN'*-bis(tributylstannyl)-carbodi-imide is involved in exchange processes with HCl and acetic and benzoic acids under mild conditions, forming the corresponding organotin derivatives and cyanamide[91,280,281]:

$$Bu_3SnNCNSnBu_3 + 2HX \rightarrow 2Bu_3SnR + H_2NCN \ ;$$
$$X{=}Cl,\ MeC(O)O,\ or\ PhC(O)O.$$

In contrast to aminostannanes, typical organotin pseudohalides (monoisocyanates and carbodi-imides) are as a rule comparatively resistant to hydrolysis, which makes it possible to synthesise them via reactions involving the elimination of water. Nevertheless, the hydrolysis of butyl and phenyl organotin di-isocyanate derivatives leads to high-molecular-weight compounds of the type $Bu_8Sn_4(NCO)_4O_2$, $Bu_8Sn_4(NCO)_2(OH)_2O_2$, and $Ph_4Sn(NCO)_2 \cdot (OH)_2$.[65]

Tributylstannyl isocyanate is wholly hydrolysed with formation of tributyltin hydroxide and urea derivatives only when acted upon by boiling water in the course of 28 h. Alkalis appreciably accelerate this process[91]. The Sn–N bond in *NN'*-bis(tributylstannyl)carbodi-imide is cleaved by water under the same conditions[282].

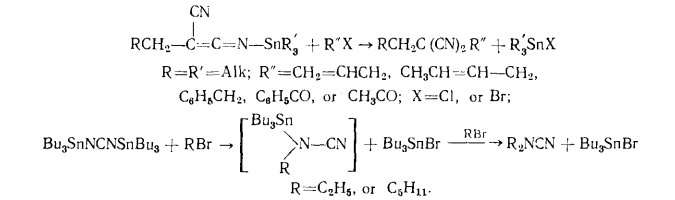
However, dimethyltin di-isocyanate is readily and completely decomposed by water[283]:

$$Me_2Sn(NCO)_2 + 3H_2O \rightarrow (Me_2SnO)_n + CO_2 + 2NH_3 \ .$$

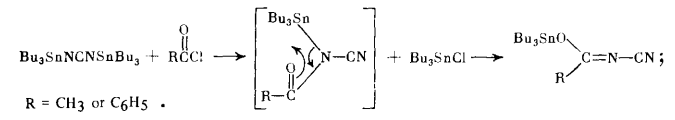
The report that tributylstannyl isocyanate reacts with alcohols and phenols to form organotin carbamates has been confirmed experimentally[160]. It was subsequently established that the adduct obtained when the isocyanate reacts with an excess of methanol or butanol contains the urethane group according to infrared spectroscopic data, but is unstable on heating and cannot be isolated by vacuum distillation[91,284]. When butaneselenol reacts with $Bu_3SnNCO$ in proportions of 2 : 1, the cleavage of the tin–nitrogen bond is accompanied by addition to the isocyanate group and the formation of butylselenourethane[285]:

$$Bu_3SnNCO + 2BuSeH \rightarrow BuSeSnBu_3 + BuSeCNH_2 \ .$$
$$\qquad\qquad\qquad

The reactions of tin pseudohalides with various halogeno-derivatives are of interest. Thus alkyl derivatives of organotin isocyanates exchange the isocyanate group for the halogen on heating with alkyl halides. On the other hand, the phenyl analogues are decomposed by ethyl bromide to triphenylstannyl bromide, the isocyanate fragment undergoing complex transformations, whose nature was not elucidated [133,163]. Chlorotrimethylsilane is involved in an exchange interaction with triphenylstannyl isocyanate, giving a high yield of the corresponding silyl isocyanate [172]. *N*-Trialkylstannylketenimines and *NN'*-bis(tributylstannyl)carbodi-imide react vigorously with organic halogeno-derivatives [91,191,280]. The reactions apparently proceed with transfer of the reaction centre:



When a stannylcarbodi-imide and equimolecular amounts of acetyl or benzoyl chloride are used, only one Sn–N bond in the carbodi-imide is cleaved and there is a simultaneous migration of the organotin group to the oxygen atom. As a result, *N*-[tributylstannoxy(methyl or phenyl)-methylidene]cyanamides were obtained instead of the expected *N*-acetyl(or benzoyl)-*N*-(tributylstannyl)cyanamides [289]:

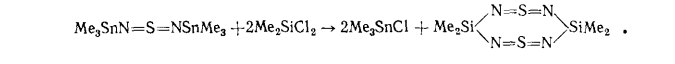


It is of interest that in the case of benzenesulphonyl chloride, azide, and isocyanate which exhibit pseudohalide properties, this process involves the exchange of only one $R_3Sn$ fragment regardless of the proportions of the reactants [181,290]:

$$Bu_3SnNCNSnBu_3 + PhSO_2X \rightarrow Bu_3SnX + PhSO_2NCNSnBu_3 \quad ;$$
$$X = Cl,\ N_3,\ or\ NCO.$$

It has been shown [291] that the interaction of bis(triphenylstannyl)carbodi-imide with organic halogeno-derivatives proceeds somewhat differently. On heating with benzyl bromide, this reagent yields an isomerisation product—dibenzylcyanamide. When chlorotriphenylmethane, which has three bulky substituents, is used, the process is accompanied by the formation of a non-isomeric compound—*NN'*-bis(triphenylmethyl)carbodi-imide.

The usual exchange processes take place when *NN'*-bis(trimethylstannyl)sulphodi-imide is treated with chlorotrimethylsilane and dichlorodimethylsilane. In the latter case, the product is an eight-membered cyclic compound containing silicon, sulphur, and nitrogen atoms [179,292]:



Group II–IV metal chlorides react with *NN'*-bis(triethylstannyl)carbodi-imide, forming triethylstannyl chloride and metal-cyanamides. The reaction is accelerated in the presence of water [282]:

$$Et_3SnNCNSnEt_3 + MCl_2 \xrightarrow{H_2O} 2Et_3SnCl + MNCN \cdot n\,H_2O \quad ;$$
$$M = Cu,\ Cd,\ Zn,\ Ca,\ or\ Sn;\ n = 1\text{–}3.$$

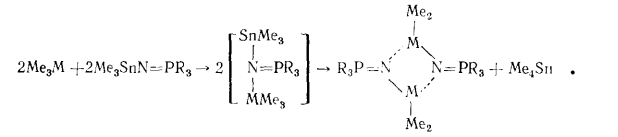
The interaction of organotin imines of the type $Me_3SnN{=}C(CF_3)_2$ with platinum, rhodium, and iridium halides is accompanied by the formation of metal alkylideneimides [293]. In contrast to this, triphenylstannyl azide forms 1 : 1 adducts with $BBr_3$ and $SnCl_4$. [294]

The reactions of trialkyl(aryl)stannyl azides with aliphatic and aromatic phosphines, which as a rule take place with formation of organotin phosphineimines, have been investigated in fair detail [79,295–297]:

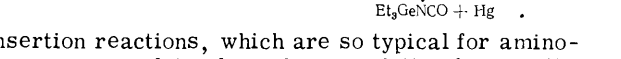
$$R_3SnN_3 + PR'_3 \rightarrow R_3SnN{=}PR'_3 + N_2 \quad ;$$
$$R,\ R' — \text{alkyl or aryl groups.}$$

The reaction of $Me_3SnN_3$ with methyl-, ethyl-, and phenyl-phosphines is complicated by disproportionation reactions and also leads to the formation of *N*-azidodimethylstannyl(phosphine)imine, $Me_3Sn(N_3)N{=}PR_3$, and and tetramethylstannane [295]. Under mild conditions, $Ph_3SnN_3$ does not react with $Ph_3X$ (X = P, As, or Sb). [80]

Organotin phosphine imines are readily decomposed by triethylaluminium, triethylgallium, and triethylindium, which leads to the formation of the dimeric trialkyl-[(dimethylmetal)imino]phosphorane [298].



Bis(triethylgermyl)mercury undergoes an exchange interaction with tributylstannyl isocyanate [299]:



Insertion reactions, which are so typical for aminostannanes, are relatively uncharacteristic of organotin pseudohalides. An example of such reactions is the addition of phenyl isothiocyanate to $Ph_3SnNCNSnBu_3$ and of phenyl isocyanate to $Bu_3SnNCNSnBu_3$, which is accompanied by the formation of the corresponding 1,2-insertion adducts [291,300]. In the latter case, further successive cycloaddition of a second and third isocyanate molecule is observed, which ultimately leads to the formation of an organotin triphenylisoammelide. The addition of tributylstannyl azide to the triple bonds of nitriles and acetylenedicarboxylate esters has been fairly thoroughly investigated, but the reaction proceeds without the cleavage of the Sn–N bond and the function of the azide group under these conditions does not differ from that in organic azides [185,186,301].

In order to investigate the reactivity of the biradical $Ph_3SnN^{\cdot}$, a study was made of the photolysis of aromatic organotin azides, which proceeds with the cleavage of the Sn–N bond and not the N–N bond as suggested by Jappy and Preston [302]. Finally a characteristic property of trialkylstannyl isothiocyanates and dialkyltin di-isothiocyanates is their capacity for complex formation [71,303], with, among others, pyridine, 2,2-bipyridyl, 1,10-phenanthroline and other bases [233,304–306].

The different properties of the pseudohalides and amino-derivatives of tin examined can probably be accounted for by electron redistribution between the tin atom and the $-\ddot{N}{=}C<$ group, which is highly unsaturated and has lone electron pairs. As a result, the trialkylstannyl fragment passivates the N=C bond in nucleophilic substitution reactions. The addition of a second isocyanate group to the tin atom or of an electron-donating substituent to the nitrogen atom diminishes the degree of

redistribution and thereby increases the reactivity of the Sn–N bond in pseudohalides, which approaches that in aminostannanes. Examples of reactions of these compounds were given above. It is noteworthy that detailed studies have not been made of the influence of different substituents on the Sn–N=A linkage, where A = C, O, P or other elements. The available physicochemical data for the strength of the Sn–N bond are summarised in the next section.

## V. PHYSICOCHEMICAL PROPERTIES AND STRUCTURES OF NITROGEN-CONTAINING ORGANOTIN COMPOUNDS

Systematic investigations of the physicochemical properties of organoelemental compounds containing an Sn–N bond were begun comparatively recently. It is therefore not surprising that the published data are sometimes incomplete and contradictory. There are only isolated publications on many key problems concerning the molecular structures of these derivatives (the geometrical configurations of the molecules, the quantum-mechanical description and determination of the energetic parameters of the Sn-N bond). As a result, the available information about the mechanisms of reactions involving compounds of the above type is extremely limited. The physical characteristics quoted in papers on the synthesis of aminostannanes (melting and boiling points, refractive indices, and densities) can serve only for the estimation of the degrees of purity of the products. These parameters have been arranged systematically [18] and additional data have been published elsewhere [307,308].

The majority of nitrogen-containing organotin compounds are volatile liquids, which permitted the conclusion, also on the basis of infrared, Raman, and NMR spectroscopic data, that the Sn–N bond is covalent in products of this kind [33,103,198,309]. However, the problem of the degree of delocalisation of the unshared electron pair of nitrogen owing to the $d_\pi$–$p_\pi$ interaction still remains open. An attempt has been made [310] to solve it by relating it to the basicity of model compounds of the type $Me_3MNMe_2$ and $(Me_3M)_3N$ (where M = Sn, Ge, or Si).

The relative basicities of the above aminostannanes were investigated in the reactions with $CHCl_3$ and $CDCl_3$, which were regarded as pseudoacids. The shifts $\Delta\nu$(C–D) and $\Delta\nu$(C–H) of the frequencies in the infrared spectra of free $CHCl_3$ and $CDCl_3$ and of their complexes with aminostannanes were correlated with the basicities. It was shown that the basicity decreases in the sequence Sn > Ge > Si and for $Me_3SnNMe_2$ it proved to be equivalent to the basicity of the usual aliphatic amines [310]. On this basis, it was concluded that the lone electron pair of nitrogen is fully localised in aminostannanes. It has been noted [31] that the delocalisation of the electron pair of nitrogen in $Me_3MN(GeMe_3)Me$ (M = Si, Ge, Sn, or Pb), investigated by NMR, decreases in the sequence Si > Ge > Sn > Pb. The same sequence of decreasing basicities of aminostannanes has been found by Mack and Yoder [311]. The number of parameters correlated with the basicities has been extended, but unambiguous results have not been obtained [312,313]. This led to the conclusion that the experimental data fail to confirm the occurrence of $d_\pi$–$p_\pi$ conjugation in organotin amines [313]. However, the considerable polarity of the Sn–N bond has been explained by the delocalisation of the lone electron pair of nitrogen on the basis of measurements of the dipole moments ($\mu$ = 1.7) of the Sn–N bond in a large series of compounds having the general formula $R_{4-n}Sn(NR'_2)_n$ (R = $CH_3$, $C_2H_5$, $C_4H_9$, or $C_6H_5$; R′ = $CH_3$ or $C_2H_5$; $n$ = 1–4). [314] It has been shown that this effect makes a significant contribution to the energy of the Sn–N bond [315]. An appreciable shift of the lone electron pair of nitrogen has also been observed in aromatic fluoro-derivatives of aminostannanes [316].

The thermal stability of aminostannanes decreases in the sequence $R_3SnNR'_2 > RSn(NR'_2)_3 \simeq Sn(NR'_2)_4 > R_2Sn.(NR'_2)_2$. [244] The heat of combustion $-\Delta H^\circ_c$, L = 1883 ± 1 kcal mole$^{-1}$ of liquid $(C_2H_5)_3SnN(C_2H_5)_2$ permitted the calculation of the standard heat of formation of this compound ($-\Delta H^\circ_{f,L}$ = 50 kcal mole$^{-1}$) and the average dissociation energy of the Sn–N bond [$\bar{D}$(Sn–N) = 62 kcal mole$^{-1}$] [317]. The last value is somewhat higher than those of $E$(Sn–N) obtained previously for $(CH_3)_3SnN(CH_3)_2$, $[(CH_3)_3Sn]_2NCH_3$, and $[(CH_3)_3Sn]_3N$, which are 43.5, 48.7, and 40.0 kcal mole$^{-1}$ respectively [11,18]. According to Zhuravlev et al. [318], the energies of the Sn–N bond in tributylstannyl isocyanate and *NN′*-bis(tributylstannyl)carbodi-imide are much greater, amounting to 102 ± 5 and 100 ± 5 kcal respectively, which indicates a differenee in the nature of these bonds in organotin isocyanates and carbodi-imides compared with aminostannanes. The dissociation energy of the M–N bond (M = Si, Ge, or Sn) decreases from Si to Sn [317] (79.9 kcal mole$^{-1}$, [319] 63.4 kcal mole$^{-1}$, [18] and 40 kcal mole$^{-1}$ [18]) which indicates a relatively weak Sn–N bond in aminostannanes.

The successful employment of infrared spectroscopy for the determination of the molecular structures of Sn–N derivatives [33,43,44,116,146,148] and for the investigation of the rates of reactions involving Sn–N bonds [111] has been noted. The absorption bands in spectra of compounds of the type $R_3SnNR'_2$, $(R_3Sn)_2NR'$, and $R_2Sn(NR'_2)_2$ have been calculated and assigned [320]. Nevertheless, it has still not been fully decided whether the stretching vibrations of the Sn–N bonds are characteristic and their bands have not been fully assigned. The frequency $\nu_{asym}$ for $(R_3Sn)_3N$ has been found in the range 712–728 cm$^{-1}$; $\nu_{sym}$ is believed to be below 400 cm$^{-1}$. [33] The 510 cm$^{-1}$ band in the spectrum of $Me_3SnN(Ph)CONMe_2$ has been assigned to $\nu$(Sn–N). [146] In the infrared spectra of $(CH_3)_3SnNH(C_6H_5)$ containing the $^{14}N$ and $^{15}N$ isotopes, the 843 and 835 cm$^{-1}$ bands correspond to $\nu$(Sn–$^{14}$N) and $\nu$(Sn–$^{15}$N) respectively; the 535 and 508 cm$^{-1}$ bands are believed to be due to the $\nu_{sym}$ and $\nu_{asym}$ vibrations of the $SnC_3$ skeleton [321]. Analysis of the infrared and Raman spectra showed in its turn that the skeleton has $C_{3v}$ pyramidal symmetry and not $D_{3h}$ [$C_{3h}$] symmetry [103]. The highly polarised band in the Raman spectrum at 514 cm$^{-1}$ has been assigned to $\nu_{sym}(Sn_3–N)$ and the 672 cm$^{-1}$ band has been assigned to $\nu_{asym}(Sn_3–N)$.

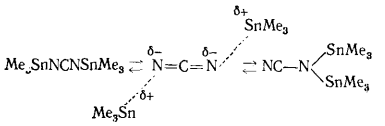
Other examples of the assignment of the bands to the stretching vibrations of the Sn–N bond are as follows: 596 and 592 cm$^{-1}$ for $Ph_3SnN(Ph)P(=NPh)Ph_2$ and $[Ph_3Sn.SnN(Ph)]_2P(=NPh)Ph$ [157]; 880 cm$^{-1}$ for $\nu_{asym}(Sn–N_2)$ in the spectra of $R_2Sn(NR'_2)_2$ [322]; 479, 480, and 472 cm$^{-1}$ for $Me_3SnN(SiMe_3)(CMe_3)$, $R_3SnN[CMe_2(SiMe_3)]$ and $Me_3C.(Me_3Si)NSnMe_2Cl$ respectively [32]; 480 cm$^{-1}$ for $Me_3Sn.NCO$ [323]; $\nu_{asym}$ = 690 cm$^{-1}$ and $\nu_{sym}$ = 602 cm$^{-1}$ in the spectra of $Bu_2Sn(NR_2)_2$ (where R = Me, Et, or Bu). [320] Similar information has also been published elsewhere [33,43,69,86,92,103,313]. One should note the virtually complete absence of publications devoted to studies of the band intensities in the vibrational spectra of nitrogen-containing organotin compounds.

Studies have been made on the NMR spectra of the compounds investigated [31,32,40,57–59,60,61,95,97,98,210,309,312,313,324–326] and on the Mössbauer effect [46,323,327–329]. In all cases, the interpretation of the spectra is consistent with

the proposed molecular structures. Data have also been published for $J_{119}Sn-H$ and $J_{117}Sn-H$ in the Sn–N–C–H systems [30,95,198,309]. For $R_nSn(NEt_2)_{4-n}$ (R = Ph or Me), such interaction was not observed in the range $0 \leq n \leq 3$ [198,309] and band splitting was not observed even at −50°C. [95] However, band splitting in the spectrum of $Et_3SnNMe_2$ was noted at low temperatures, disappearing at 150°C. [324]

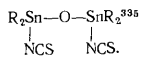
The physicochemical characteristics of nitrogen-containing organotin pseudohalides have been studied much less than the corresponding quantities for aminostannanes. Analysis of the Mössbauer spectra of alkyltin isocyanates has shown that the Sn–N bond is covalent, the tin atom is in the four-coordinated state, and the compounds have the iso-structure [323]. However, $Ph_3SnNCO$ is associated via bridging NCO groups and the tin atom is in the five-coordinated state [327].

Intermolecular coordination has also been suggested for *NN'*-bis(trimethylstannyl)carbodi-imide [330]. According to the authors [88,330], this compound has a structure intermediate between the carbodi-imide, cyanamide, and ionic forms:



However, the study of infrared spectra and dipole moments of organotin ethyl– and butyl-carbodi-imides indicates unambiguously a carbodi-imide structure of such products [90,308].

Investigation of the structures of organotin isothiocyanates by infrared and Mössbauer spectroscopy has shown that the compounds exist in the isocyanate form and that the tin atom is in the five-coordinated state [68,69,331–333]. The occurrence of intermolecular donor–acceptor interactions has been noted also for dimethyltin di-isocyanate, which is a polymer with chains of weakly linked molecules [334], for bis(dicyanamido)dimethylstannane, which has the carbodi-imide structure [86,87], for [polymeric] dibutyltin-carbodi-imidostannane [92], and for distannoxanes of the type



## VI. APPLICATIONS OF NITROGEN-CONTAINING ORGANOTIN COMPOUNDS

The use of nitrogen-containing organotin compounds is in many respects traditional for organotin derivatives, which are widely used in practice as herbicides, disinfectants, polymer stabilisers, and catalysts.

It has been suggested that triphenylstannyl and tributylstannyl isocyanates [1,336], and *NN'*-bis[trialkyl(aryl)-stannyl]carbodi-imides [337,338] be employed as stabilisers of poly(vinyl chloride). The stabilising effect of mixtures of organic phosphines with trialkyl(aryl)stannyl isocyanates and isothiocyanates in the thermal degradation of poly(vinyl chloride) has been studied in detail [339,340]. Aminostannanes are suitable for the stabilisation of rubbers [2,3] and as fungicides, bactericides, and herbicides [8,9,37], and plasticisers [7]. It has been suggested that organic carbodi-imides be synthesised via amino-derivatives of tin [262]. Numerous data have been obtained on the applications of the compounds under consideration in the catalysis of the reactions of isocyanates with compounds having an active hydrogen atom [4–6,341,342]. It has been shown [343] that, when the reaction of butyl isocyanate with phenol is acted upon jointly by organotin compounds and amines as catalysts, a synergistic effect is observed. The use of tin- and nitrogen-containing compounds as catalysts of the synthesis of urethanes [344] instead of the familiar organotin derivatives of aliphatic acids can be definitely economical in view of the low cost and high availability of initial nitrogen-containing products such as amines, urea, cyanuric acid, and their derivatives, compared with organic acids.

The applications of aminostannanes and their analogues have not been studied widely because convenient preparative methods for their synthesis became available comparatively recently.

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# Reactions of Carbanions and Halogenocarbenes in Two-phase Systems

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The review surveys studies on a new two-phase catalytic method whereby reactions between carbanions and halogenocarbenes can be carried out. Numerous examples of the successful application of this method to various (mainly alkylation) reactions of carbanions and halogenocarbenes are given and the advantages, disadvantages, and limitations of the method compared with the traditional single-phase or pseudo-single-phase methods are discussed. Also considered are possible mechanisms of catalysis by ammonium salts in these systems.
The bibliography includes 261 references.

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## I. INTRODUCTION

The reactions of carbanions and halogenocarbenes with various compounds are widely used to form new C–C bonds, which constitutes one of the most important problems in organic synthesis. In this connection, the development of new highly effective methods for the generation of carbanions and halogenocarbenes is of considerable interest.

The principal method for the generation of carbanions involves the abstraction of a proton from a carbon atom in an organic molecule; this process is also the first stage in the formation of halogenocarbenes in the so called $\alpha$-elimination reaction. Many different bases, the majority of which are very sensitive to moisture and air, require the use of considerable amounts of thoroughly dehydrated organic solvents, are explosive, and expensive, have been used for this purpose. It is therefore desirable to carry out the process in a homophase system, which is by no means always possible. Even when the system is apparently single-phase, it is frequently in essence a pseudo-homogeneous system in which the solution of a base or carbanion is colloidal, the molecular weights of the species amounting to thousands of units.

Many of the difficulties and disadvantages enumerated above are eliminated when the synthesis is carried out in a two-phase catalytic system where a concentrated solution of sodium hydroxide in the presence of catalytic amounts of quaternary ammonium compounds plays the role of the base which abstracts protons from the C–H acid in the organic phase. This method, which was introduced into laboratory practice mainly by the present author[1], proved to be extremely effective for many types of reactions of carbanions and particularly halogenocarbenes. The large-scale application of two-phase systems in the chemistry of carbanions and halogenocarbenes began as late as 1970, but since then more than two hundred original publications and several reviews have appeared[2-7]. This provides a good illustration of the increasing interest in these procedures and their extensive possibilities.

The first example of the known use of a two-phase system in the chemistry of anions is provided by Jarousse's[8] brief communication about the possibility of the benzylation and ethylation of phenylacetonitrile by the corresponding chlorides in the presence of 50% aqueous sodium hydroxide and 20 mole % of benzyltriethylammonium chloride. The catalytic action of certain tetra-alkylammonium salts on the alkylation of acetoacetic and malonic esters in the presence of aqueous potassium hydroxide was subsequently described by Babayan[9,10]. Using these data, the present author developed a catalytic method for the alkylation of phenylacetonitrile and its derivatives[1] and the catalytic system was subsequently applied to other reactions of carbanions and also for the generation of halogenocarbenes.

Brändström and Junggren[11] subsequently demonstrated the considerable possibilities in organic chemistry of the method involving the extraction of ion pairs and applied it to the reaction of enolate anions (mainly alkylation reactions). A distinctive feature of the ion pair extraction method, for example "extractive alkylation", is the use of an equimolar amount of a tetra-alkylammonium compound, which in many cases makes it possible to isolate the tetra-alkylammonium–carbanion pair. In 1971 Starks[12] used the concept of "phase-transfer catalysis", based on the transfer of the regulating species by tetra-alkyl-ammonium or phosphonium cations from one phase to another (usually from the aqueous to the organic phase) in reactions involving inorganic atoms. The above methods are based on the formation of ion pairs comprising the tetra-alkylammonium cation and an organic or inorganic anion, which are soluble in organic non-polar solvents. It has been recently discovered that, apart from tetra-alkylammonium or phosphonium salts, crown ethers, which form very stable endocyclic complexes with potassium or sodium ions, can also play the role of catalysts in the two-phase system considered[13]. Potassium and sodium ions are capable of forming ion pairs, soluble in non-polar solvents, with organic and even inorganic anions[14].

The subject of the present review is reactions of carbanions and halogenocarbenes in liquid two-phase systems. The influence of tetra-alkylammonium salts or crown ethers on the reactions of anions in homophase systems as well as on the reactions of inorganic anions in two-phase systems will not be considered.

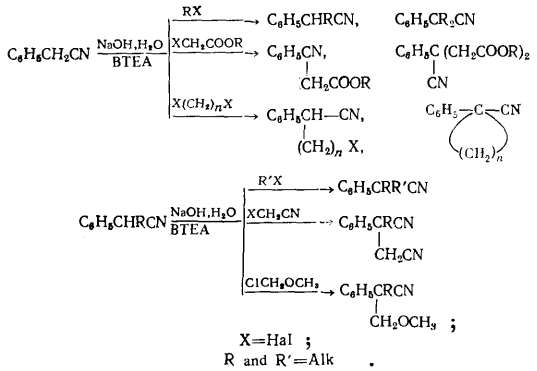
## II. REACTIONS OF CARBANIONS

### 1. Alkylation of Arylacetonitriles

The two-phase catalytic method was first widely used to alkylate phenylacetonitrile and its derivatives. This process is important from the practical point of view, since the structural elements of phenylacetic acid are frequently encountered in drugs, natural products, etc. Compared with previously available procedures, the method is extremely simple[15]: the nitrile, the alkylating agent, and an excess of 50% aqueous sodium hydroxide solutions are stirred vigorously, usually at room temperature, in the presence of ~1 mole % of a quaternary ammonium compound. Benzyltriethylammonium chloride (BTEA) is usually employed, being most readily available and convenient, although it does suffer from a number of disadvantages. In particular, the stability of BTEA is limited in a highly basic medium and it can act as an alkylating agent itself. Alkylation proceeds with a moderate exothermicity, giving high yields of the expected compounds. Despite the fact that the process proceeds in an aqueous solution of alkali, appreciable hydrolysis of phenylacetonitrile begins under these conditions only at temperatures above 90°C; the majority of alkylating agents are also fairly stable under these conditions.

Thus, catalytic alkylation of phenylacetonitrile can be achieved using alkyl and alkenyl halides[16-18], halogenoacetates derived from secondary and tertiary alcohols[19], halogenonitriles[20-21], and certain other substituted halogenoalkanes[17,22]. Even α-chloroalkyl ethers are fairly stable under these conditions and can be used as effective alkylating agents[23]. Alkylation by dihalogenoalkanes makes it possible to obtain ω-halogenoalkyl derivatives, iso- and hetero-cyclic nitriles, dinitriles, etc.[24-26]

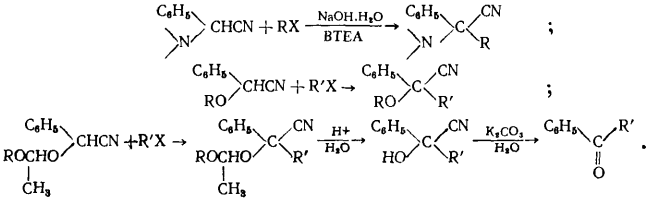
Analogous alkylation reactions proceed successfully in the case of diphenylacetonitrile[23,27-31] and phenylalkylacetonitriles[18,23,28,30,32]. In almost all the instances enumerated above, the results of alkylation (the yield and purity of the products) are much superior to those obtained by traditional methods.



X=Hal ;
R and R′=Alk .

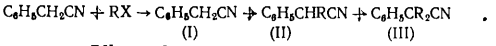
The two-phase method also gave excellent results in the alkylation of phenylacetonitrile derivatives substituted in the aromatic ring[33-35] and of naphthylacetonitrile[36]. Alkylation of phenylacetonitrile by *p*-nitrobenzyl chloride in the presence of dilute alkali (2 *N* NaOH) and a tetraalkylammonium catalyst is believed[37] to proceed via an electron transfer stage as a free-radical process. In the present author's view, typical conditions (50% NaOH) are more suitable for the alkylation of arylacetonitriles by *o*-, *m*-, and *p*-nitrobenzyl chlorides, the electron transfer stage being non-obligatory[38]. Brändström's "extraction of ion pairs"[39] gives very satisfactory results in the alkylation of phenylacetonitrile, but the use of an equimolar amount of expensive tetrabutylammonium hydrogen sulphate makes this method less convenient in practice than the catalytic procedure.

Alkylation of phenylacetonitrile derivatives substituted in the α-position by dialkylamino- or alkoxy-groups, whose properties are similar to those of cyanohydrins, is important for organic synthesis. The alkylation of these compounds in the presence of an aqueous solution of NaOH and BTEA proceeds without difficulty[40,41]. The example of the mixed acetal of benzaldehyde cyanohydrin, which gives rise to aryl ketone cyanohydrins (which are in essence unobtainable by other methods) after alkylation and mild hydrolysis, is particularly interesting[42]. Attempts at the alkylation of aliphatic aldehyde cyanohydrins in a two-phase system led to only moderate yields of cyanohydrin esters: *C*-alkylation was not observed[43]:



Reissert compounds, which are structurally related to α-acylamino-derivatives of phenylacetonitrile, are also readily alkylated in the presence of an aqueous solution of concentrated alkali and BTEA.[44]

Thus the advantages of the two-phase system do not consist solely in the simplicity of the reactions, the use of a cheap base, and the elimination of experimental difficulties associated with the consumption of amides, hydrides, organometallic compounds, etc. A factor which is no less important is the improvement of yields and the high selectivity of the reactions, as a result of which it is possible to avoid difficulties in the synthesis of monoalkylated phenylacetonitrile derivatives which are important in practice. This is clearly illustrated by the following scheme:

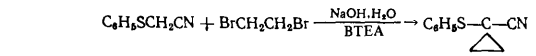


| RX | $CH_3I$ (I) | $C_2H_5Br$ (II) | $C_6H_5CH_2Cl$ (III) |
|---|---|---|---|
| I, % | 21;6 | 15;6 | 31;21 |
| II, % | 50;86 | 70;90 | 33;52 |
| III, % | 19;8 | 15;4 | 30;19 |

In each column, the first set of numbers characterises the composition of the alkylation products obtained in the presence of $NaNH_2$ in liquid ammonia[45,46] and the second set characterises the product compositions in a two-phase catalytic system[46]. The main cause of the high selectivity of alkylation under catalytic conditions is apparently the low concentration of the carbanions present simultaneously in the system, which does not exceed the concentration of the catalyst[46].

Unsubstituted aliphatic nitriles, which are very weak C–H acids, do not form carbanions under these conditions and are naturally incapable of being alkylated. The presence of carbanion-stabilising substituents, such as the arylthio-group in *S*-phenylthioglycolonitrile, permits

the alkylation of these nitriles in the presence of an aqueous solution of NaOH and BTEA [47]:

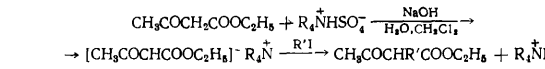


Under analogous conditions, the nitriles of aliphatic 3-chloro-3-nitroacids cyclise to form a three-membered ring [48].

## 2. Alkylation of Carbonyl Compounds

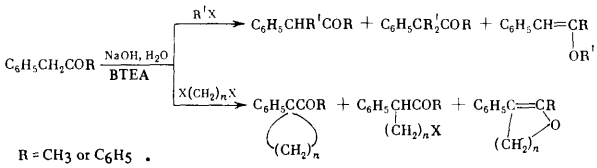
The ester group is usually readily hydrolysed by an aqueous solution of alkali, which hinders the alkylation of malonic, acetoacetic, and cyanoacetic esters. Nevertheless, Babayan succeeded in alkylating these esters in the presence of an aqueous KOH solution [9,10].

The method based on the extraction of ion pairs (the so called extractive alkylation), requiring the use of fairly dilute alkali and equimolar amounts of tetrabutylammonium hydrogen sulphate, gives excellent results in such instances [11,39,49,50]:



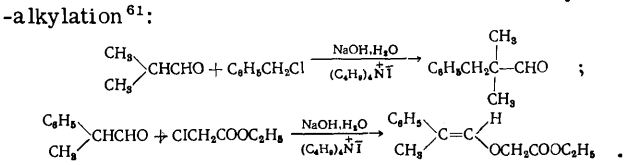
A typical catalytic process requires the use of concentrated alkali, which causes the hydrolysis of methyl or ethyl esters. t-Butyl esters are much more resistant to base hydrolysis and t-butyl malonates, phenylacetates, and diphenylacetates can be alkylated with high yields under these conditions [51].

The two-phase catalytic system is very convenient for the alkylation of $\alpha$-phenylketones, such as desoxybenzoin or phenylacetone [52-54]. A high yield was also obtained when a crown ether was used as the catalyst [55]. The method of the extraction of ion pairs also gives satisfactory yields in such cases [39]. Cyclic $\alpha$-arylketones, acenaphthenone [56], and $\beta$-tetralone [57] usually form dialkylation products under these conditions. The results of the alkylation of ketones by dihalogenalkanes, which leads to the formation of iso- and hetero-cyclic structures, $\omega$-halogenoketones, etc., are particularly interesting [53,54]:

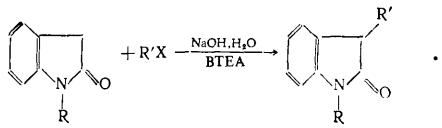


Alkylation by $\alpha$-chloroesters yields mainly *O*-derivatives [58].

Even simple ketones may be successfully alkylated by allyl chlorides in a two-phase catalytic system [59]. Direct alkylation of $\alpha$-substituted aliphatic aldehydes in the presence of concentrated alkali and a tetrabutylammonium salt gives unexpectedly satisfactory results [60]. The use of chloroacetate esters in such cases leads exclusively to *O*-alkylation [61]:



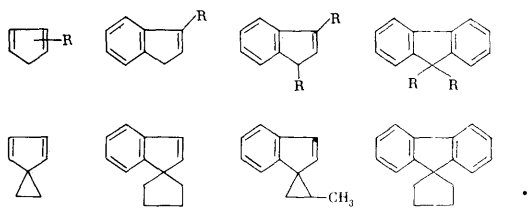
$\beta$-Diketones, which exhibit a high acidity, can be readily converted into tetrabutylammonium derivatives by extraction from aqueous solutions into chloroform or methylene chloride with subsequent alkylation to give a very high yield of the product [62,63]. The same ion pair extraction procedure is the most suitable for the alkylation of $\alpha$-ketosulphones [64,65], benzoylmalonic ester [66], and acetopyruvic acid [67]. The problem of *CO*-alkylation was also thoroughly investigated in the above studies. Certain C–H acid heterocycles, for example 2-hydroxyfuran, 2-hydroxythiophen [68], and derivatives of 2-hydroxybenzothiophen [69], are capable of being alkylated by Brändström's extractive method. Many oxindoles substituted in the 1-position can be alkylated catalytically with excellent yields [70]:



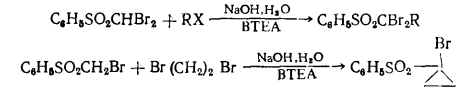
An interesting example of liquid–solid two-phase systems has been described in a study [71] where sodioacetoacetic ester, which is insoluble in the solvents employed, was alkylated in the presence of a tetra-alkylammonium salt. A detailed study has been made of the alkylation of acetoacetic ester by ammonium salts in a two-phase system [72].

## 3. Alkylation of Hydrocarbons and Other Compounds

Hydrocarbons of the cyclopentadienyl series (cyclopentadiene, indene, and fluorene) are sufficiently acid to be converted into carbanions under our conditions. These carbanions may be successfully alkylated by mono-, and di-halogenoalkanes. The alkylation of indene proceeds particularly satisfactorily [73]. Fluorene is alkylated with somewhat more difficulty because of its lower acidity [74]:



The present author found that the C–H acidity of aryl halogenomethyl and aryl dihalogenomethyl sulphones is sufficient for the formation of carbanions when they react with an aqueous solution of sodium hydroxide in the presence of BTEA. These carbanions are fairly stable, so that their alkylation usually takes place with satisfactory yields [75]:



Although the possibilities of these reactions are far from having been elucidated, presumably the alkylation products will serve as useful starting materials in many syntheses.

## 4. Compounds Forming Heteroanions

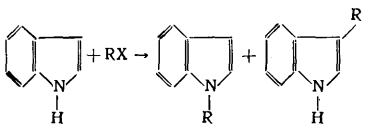
Despite the fact that the subject of the present review is the reactions of carbanions in two-phase systems, it is useful to quote certain examples of the alkylation of heteroanions. In the first place, mention should be made of Babayan's study of the influence of tetra-alkylammonium

salts giving rise to the exclusive *O*-alkylation of phenoxide anions in an aqueous two-phase system[76]. Systematic studies of the alkylation of phenoxide anions in a catalytic two-phase system have been described[78] and the problem of *CO*-alkylation has been discussed[72].

In the presence of a tetra-alkylammonium catalyst, an aqueous solution of sodium hydroxide is a very convenient condensing agent in the synthesis of ethers by Williamson's method[79].

Ammonium catalysts and crown ethers catalyse very effectively the formation of acetates by the alkylation of potassium acetate in benzene or acetonitrile[80,81]. The use of tributylhexadecylphosphonium proved very convenient for the preparation of dialkyl and alkyl aryl sulphides[82].

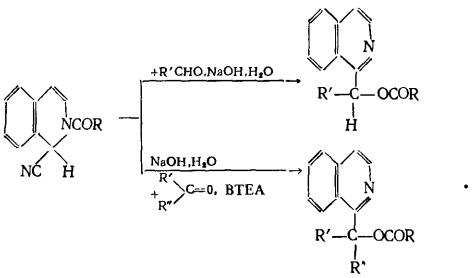
The alkylation of compounds containing N–H acid groups is of considerable practical importance. *N*-Alkylation of phenothiazine, diphenylamine, carbazole, indole, etc. proceeds satisfactorily under two-phase catalytic conditions[83]:



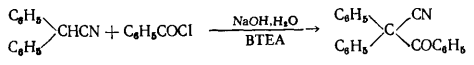
The ambident indole anion forms small amounts of *C*-alkylation products in this reaction. The formation of the aziridine ring by the intramolecular alkylation of *N*-ethoxycarbonyl-β-iodoethylamine has also been described[84].

## 5. The Reactions of Carbanions and Ylids with Polar Double Bonds.

The condensation of Reissert compounds with aldehydes, which results in the formation of isoquinolinyl methyl esters, is carried out mainly in the presence of bases such as butyl-lithium or sodium hydride[85]. This reaction proceeds much more satisfactorily in the presence of concentrated aqueous alkali in a two-phase system even without a quaternary ammonium catalyst, which, however, is necessary for the reaction of a Reissert compound with a ketone[86]:

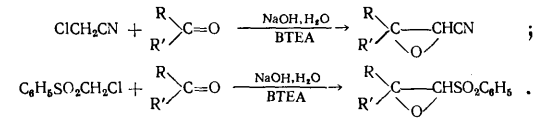


The reaction of the carbanion takes place in the organic phase, as shown by the finding that diphenylacetonitrile is acylated by benzoyl chloride with a high yield[29]:

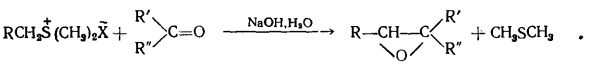


Two-phase catalytic conditions are very convenient for the reaction of α-chloronitriles with aldehydes and ketones (the Darzens reaction). The corresponding nitriles of glycidic acids are usually formed in high yields[87]. The condensation of α-chlorocarbonyl compounds (t-butyl chloroacetate, phenacyl chloride, etc.) proceeds less effectively under these conditions.

Excellent yields of epoxides substituted by an arenesulphonyl group have been obtained by the condensation of α-halogenosulphones with carbonyl compounds[75].

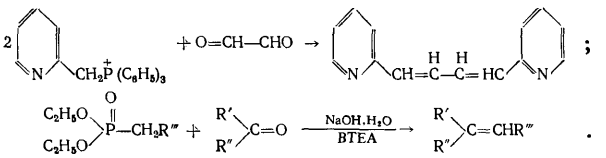


Two-phase systems in which an aqueous solution of sodium hydroxide plays the role of the base are very convenient and effective for the generation of ylids from sulphonium and phosphonium compounds. Since these compounds contain an onium cationic centre, the reactions of ylids in a two-system usually do not require catalysts. Thus Hatch[88] found that dimethylalkylsulphonium chlorides react with benzaldehyde in the presence of concentrated aqueous alkali to form epoxy-compounds. Analogous reactions have been described for many other aldehydes and ketones[89–91]:

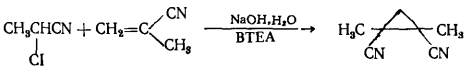


Nevertheless the conversion of trimethylsulphonium or trimethylsulphoxonium salts into ylids requires the use of tetra-alkylammonium salts[92].

Although according to generally accepted views phosphonium ylids are very sensitive to moisture, the benzene–aqueous sodium hydroxide solution system is extremely convenient for carrying out the Wittig reaction with aldehydes[93,94]. The methylene chloride–concentrated aqueous NaOH solution system is particularly suitable for the synthesis of dienes in the reactions of ylids with glyoxal[95] and for the reaction of a stabilised allyl ylid with aldehydes[96]. The use of this system for the Wittig–Horner reaction has also been described[97]:



The α-halogenonitrile carbanions generated in a two-phase system[98] and sulphonium ylids[92] also react with activated double bonds, forming the corresponding cyclopropane derivatives. Particularly satisfactory results were obtained for α-chloropropionitrile:

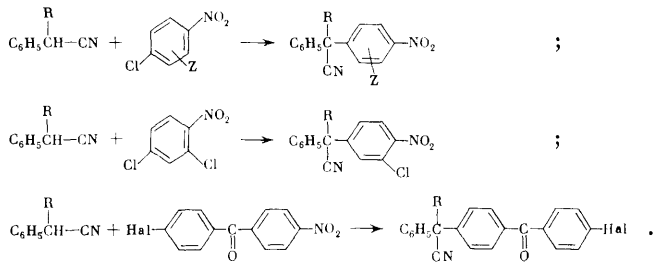


The cyanoethylation of 1-chloronitroethane in a two-phase system can lead directly to a substituted nitrocyclopropane[48].

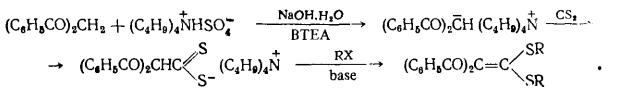
## 6. Reactions of Carbanions with Various Electrophiles

Two-phase catalytic conditions are the most convenient for the nitroarylation of alkylphenyl- and diphenylacetonitriles by *o*- and *p*-halogenonitrobenzenes and their derivatives. The substitution of the halogen atom by the carbanions derived from these nitriles results in the formation of compounds containing *o*- or *p*-nitroaryl

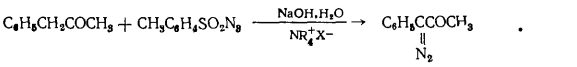
groups, as a rule with high yields. Under other conditions, the yields are small and considerable amounts of tar are formed. The presence of many substituents (halogen, >CO, $CH_3$, $NO_2$, COOR-t, etc.) in *o*- or *p*-halogenonitro-compounds does not interfere with the nitroarylation reaction [13,44,99-102]. Alkylphenylacetonitrile carbanions substitute mainly the chlorine atom in the *p*-position relative to the nitro-group in 2,4-dichloronitrobenzene [102]. Alkylphenylacetonitrile carbanions are capable of substituting not only the halogen atom, but also aromatic nitro-groups in the *o*- or *p*-positions relative to strong electrophilic substituents. For example, their reaction with 4-halogeno-4′-nitrobenzophenones involves exclusively the substitution of the nitro-group [101,103]:



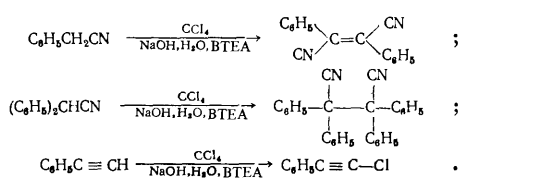
In the reaction of 3,4-dinitrochlorobenzene, the 3-nitro-group is substituted [101]. Sometimes substitution of the halogen or the nitro-group is accompanied by electron transfer, being particularly characteristic of the reaction of the diphenylacetonitrile carbanion, which forms tetraphenylsuccinonitrile [101,103]. Many β-dicarbonyl compounds react with carbon disulphide under the ion pair extraction conditions with formation of salts of the corresponding dithiocarboxylic acids. In the presence of an excess of the base, these salts are converted into dianions whose alkylation leads to the formation of keten mercaptals [104,105]:



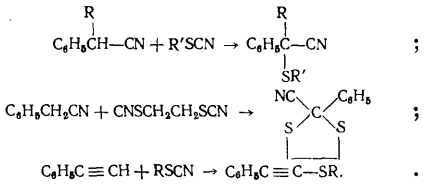
Similar reactions can also be carried out with acetophenone [107]. The use of a two-phase system for the synthesis of aliphatic diazo-compounds is very promising [108]:



Phenylacetonitrile also reacts with carbon tetrachloride, forming *trans*-dicyanostilbene. Under analogous conditions, diphenylacetonitrile is converted into tetraphenylsuccinonitrile [109] and phenylacetylene is converted into phenylchloroactylene [110]:



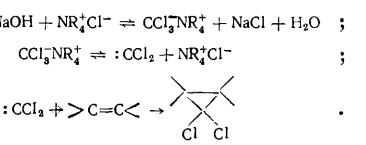
The direct introduction of an alkylthio-group into an organic molecule, usually as a result of the reaction between carbanions and disulphides, has aroused considerable interest in recent years. The present author found that excellent agents for the introduction of alkylthio-groups are the much more readily available thiocyanates, which effectively introduce alkylthio-groups into many C–H acids under two-phase catalytic conditions [110,111]:



## III. REACTIONS OF HALOGENOCARBENES AND POLYHALOGENOCARBANIONS

The use of two-phase catalytic systems in the chemistry of polyhalogenomethyl carbanions and halogenocarbenes gave particularly satisfactory results and has aroused much attention. In 1969 the present author developed a method for the synthesis of dichlorocyclopropanes by the addition to alkenes of dichlorocarbene generated by treating chloroform with concentrated alkali in the presence of benzyltriethylammonium chloride [112].

Despite the fact that this reaction proceeds in an aqueous medium, only an insignificant proportion of the resulting dichlorocarbene is hydrolysed. For example, equimolar amounts of styrene and chloroform give approximately 90% of a substituted dichlorocyclopropane and only 7% of the chloroform is hydrolysed. Dichlorocarbene is formed in the organic phase as a result of the decomposition of the tetra-alkylammonium derivative of the trichloromethyl carbanion as a consequence of the high rate of reaction of dichlorocarbene with hydroxide ions and water. Doering and Hoffman [113], who attempted to obtain the products of the addition of dichlorocarbene to alkenes in the presence of a concentrated aqueous KOH solution, observed mainly hydrolysis. The yield of the desired product did not exceed 0.5%. These fundamental differences are a consequence of the presence of the quaternary ammonium cation, which transports the trichloromethyl anion into the bulk of the organic phase in the form of an ion pair soluble in a non-polar medium. The subsequent formation of dichlorocarbene takes place in the organic medium, as a result of which it is capable of reacting effectively with the alkene:



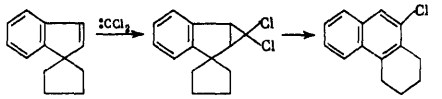
The method immediately found extensive applications in many reactions of halogenocarbenes and is now believed to be one of the most convenient.

### 1. Generation and Reactions of Dichlorocarbene

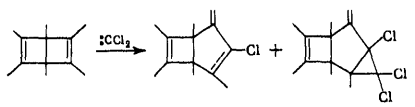
Examples of reactions of dichlorocarbenes in a two-phase system are particularly numerous. In most cases the authors note that the yields of the products of its addition to monoalkenes are usually higher than in cases where other methods were used [12,13,112,114-124]. In some studies it is emphasised that dichlorocarbene, generated by the two-phase catalytic method, is also much more

reactive and gives high yields of adducts, even with alkenes having weakened nucleophilic properties, such as *trans*-stilbene, and with certain acetylenes [114]. These data conflict somewhat with the results of the determination of the relative rates of addition of dichlorocarbene, generated in a catalytic system, to various alkenes, which, according to Starks' study [12], do not differ from the relative rates measured for dichlorocarbene obtained by other methods. These apparent contradictions will be discussed below.

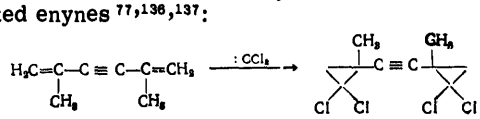
At the end of 1974, Isagawa et al. reported that the addition of dichlorocarbene to alkenes in a two-phase system is very effectively catalysed by trialkylamines [125]. This unexpected catalytic effect is apparently due to the formation of an ammonium ylid at the interface [126]. The addition of dichlorocarbene to cyclopentenes is usually accompanied by a rearrangement with formation of six-membered rings. The addition reaction carried out in a two-phase catalytic system proceeds in the same way [119-121,127-129]. Interesting transformations have been observed in the reactions of dichlorocarbene with indene derivatives [130]:



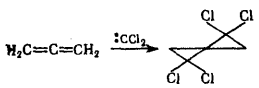
The increased reactivity of dichlorocarbene generated in a two-phase system, noted above, makes it an ideal reagent for the conversion of polyenes into polydichlorocyclopropanes. Bisadducts with divinylbenzene [131], conjugated dienes [114,132], and polyenes [115] have been obtained by single-stage syntheses using this procedure. It also proved possible to obtain a bisadduct with cyclopentadiene [132] and a tetra-adduct with cyclo-octatetrane [133]. By regulating appropriately the reactant ratio and the reaction time, it is possible to obtain mono-, di-, and tri-addition products [133,134]. Hexamethyl Dewar benzene forms under these conditions bisadducts, which undergo further transformations during the reaction [132,135]:



Dichlorocarbene adds exclusively to the double bond of conjugated enynes [77,136,137]:

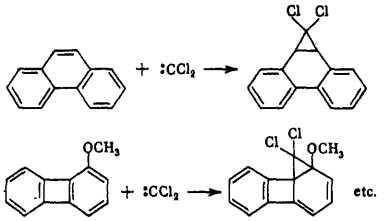


Polyadducts of dichlorocarbene have been obtained in a single stage also as a result of reactions with allenes and other higher cumulenes [114,138-140]:

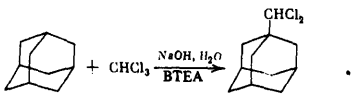


The addition of dichlorocarbenes in a two-phase system to vinyl ethers [141-143] and enol ethers and esters [121,129,144] gives very satisfactory results, although some workers believe that these compounds are insufficiently stable in an aqueous medium [145]. The limitations associated with instability in the presence of aqueous alkali have apparently been overestimated, since, according to Miller, even trimethylsilyl derivatives of alkenes combine with dichlorocarbene in a two-phase system to give excellent yields of products [146].

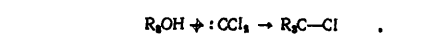
Dichlorocarbene generated in a two-phase system reacts effectively with many aromatic compounds—phenanthrene [115,147-149], alkyl derivatives of benzene and naphthalene [150,151], 1,4,5,8-tetramethoxynaphthalene [152], 1-methoxybiphenylene [153], etc. This results in the formation of both primary dichlorocarbene addition products as well as the products of their subsequent transformations:



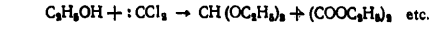
One of the characteristic reactions of dichlorocarbene is insertion in C–H bonds. Usually only thermally generated dichlorocarbene gives acceptable yields of insertion products. In a two-phase system the reactivity of dichlorocarbene is also considerable, as a result of which it is successfully inserted in the C–H bonds in the bridgeheads of adamantane [154,155] and other polycyclic hydrocarbons [156], giving satisfactory yields of the corresponding dichloromethyl derivatives. In the reactions with simpler hydrocarbons (isopropylbenzene, decalin, etc) the yields of dichloromethyl derivatives are moderate, but the reaction may nevertheless be of practical importance, since the unreacted initial compounds are almost completely recovered [157,158]:



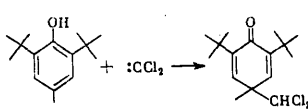
Dichlorocarbene generated in a two-phase system undergoes an unusual reaction with higher alcohols, substituting the hydroxy-group by chlorine with high yields [159]:



Lower aliphatic alcohols give rise to a multiplicity of products. The reaction with ethyl alcohol, where the main product is ethyl orthoformate, is of practical importance [160]:



Various types of transformations have been observed also in the reaction with $\alpha$-diols [161]. Nevertheless many allyl alcohols react with dichlorocarbene under these conditions to form products of addition to the double bond without involving the hydroxy-group [162]. There are as yet no data concerning the influence of tetra-alkylammonium catalysts on the interaction of phenoxide anions with dichlorocarbene (the Reimer–Tiemann reaction). Nozaki and coworkers [163] found that polyalkylphenols form dichloromethyl derivatives of cyclohexadienones:



The reaction of dichlorocarbene with benzaldehyde results in a high yield of mandelic acid [164].

Reactions with nitrogen compounds. On reacting with chloroform in the presence of alkali, primary amines form isonitriles. This reaction, which

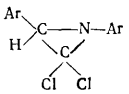
has been known for approximately one hundred years, has not found practical synthetic applications. The use of a catalytic two-phase system greatly improved yields and made it useful in practice [165-168]:

$$RNH_2 + :CCl_2 \rightarrow RNC \quad .$$

Simple formylation of secondary amines by dichlorocarbene in a two-phase system may also find practical applications [169].

Tertiary amines also react with dichlorocarbene under these conditions. The ammonium ylids formed initially rearranges in at least three ways, giving rise to formyl derivatives of secondary amines, carboxylic acid dialkylamides, alkyl chlorides, etc, [170] Polycyclic tertiary $\alpha$-diamines are cleaved by dichlorocarbene to bis-*N*-formyl derivatives [171]. 1-Methyl-1,2-dihydroisoquinoline reacts with dichlorocarbene to form addition and insertion products, but is not cleaved [172]. Despite the fact that enamines and Schiff bases are fairly unstable in the presence of aqueous alkali, their reactions with dichlorocarbene take place successfully under conditions of two-phase catalysis. Depending on the structure of the initial substance, it is possible to isolate the primary addition products—dialkylamino-derivatives of dichlorocyclopropane [173] and dichloroaziridines [174]—or the products of their further transformations:

$$Ar{-}CH{=}N{-}Ar + :CCl_2 \rightarrow$$



.

The enamines derived from certain bicyclic ketones form relatively stable adducts with dichlorocarbene [175].

Dichlorocarbene generated in a two-phase catalytic system may serve as a vigorous dehydrating agent, which converts amides, oximes, and thioamides into nitriles [176,177]:

$$RCONH_2 + :CCl_2 \rightarrow RCN \quad ;$$

$$RCH{=}NOH + :CCl_2 \rightarrow RCN \quad .$$

Webber and coworkers recently used successfully a two-phase system with BTEA or a crown ether in order to obtain diazomethane by treating hydrazine with dichlorocarbene [178]. This method will undoubtedly prove to be of practical importance:

$$N_2H_4 + :CCl_2 \rightarrow CH_2N_2 \quad .$$

The addition of dichlorocarbene to vinyl sulphides proceeds in the usual way with formation of the corresponding dichlorocyclopropane derivatives [179], but certain allyl sulphides rearrange under these conditions with cleavage of the C–S bond, giving rise to monothiocarboxylate esters [180].

The high reactivity of dichlorocarbene generated in a two-phase catalytic system undoubtedly requires explanation. Dichlorocarbene is formed in the organic phase, where its precursor (the trichloromethyl anion) exists in the form of a soluble ion pair with the tetra-alkylammonium cation. Since alkali metal cations are absent from the organic phase, the formation of the corresponding carbenoids is impossible. Despite the fact that the system as a whole is heterogeneous, dichlorocarbene is formed and reacts in a homogeneous medium—the organic phase. An equivalent amount of a tetra-alkylammonium chloride, which is also soluble in the organic phase, is formed simultaneously with dichlorocarbene. As a result of this, the rapid reversible reaction

$$CCl_3^-NR_4^+ \rightleftharpoons NR_4^+Cl^- + :CCl_2$$

ensures the existence of sufficient amounts of dichlorocarbene over a relatively long period, to enable it to react with relatively unreactive compounds. This cannot occur when, for example, dichlorocarbene is generated by treating chloroform with potassium t-butoxide, since the solubility of the potassium derivative of the trichloromethyl anion (and even more so that of potassium chloride) is apparently insignificant in a non-polar medium. This explanation is confirmed by the finding that the overall rate of disappearance of chloroform in a two-phase system is low in the absence of an alkene and depends on its nucleophilic properties.

## 2. Reactions of Trichloromethyl Anions

Trichloromethyl anions are fairly short-lived, but they can be trapped successfully by suitable electrophiles. Catalytic conditions are particularly convenient for these reactions, since both reacting species—the trichloromethyl anion and the organic electrophile—are dissolved in the organic phase. Thus it has been found that two-phase catalytic conditions are the most suitable for the Michael reaction between chloroform and electrophilic alkenes (acrylonitrile, acrylate, esters, vinyl sulphones, vinyl acetate, etc.)[181-183]:

$$CH_2{=}CH{-}Y + CHCl_3 \xrightarrow[\text{BTEA}]{NaOH,H_2O} CCl_3CH_2CH_2Y \quad ;$$

$$Y{=}CN,\ COOR,\ \text{or}\ SO_2R \quad .$$

The yields of the corresponding trichloromethyl derivatives are usually high, greatly exceeding the yields of the same compounds obtained by other methods. When the acceptors Y are moderately electrophilic, the simultaneous addition of trichloromethyl anions or dichlorocarbenes is observed. The mode of these competing reactions depends mainly on the structure of the acceptor and to some extent also on the way in which the reaction is performed. Thus, on diluting the organic phase with an inert solvent (for example, methylene chloride), the reaction may be driven towards the addition of dichlorocarbene. In a detailed study of this reaction, Dehmlow and Höfle observed further interesting transformations of the compounds formed initially [184]:



.

Polymethylated vinyl ketones combine exclusively with dichlorocarbene and not with the trichloromethyl anion [185].

Organic thiocyanates are very effective electrophiles, trapping trichloromethyl anions. Their CN group is substituted and trichloromethyl sulphides are formed in satisfactory yields [111]:

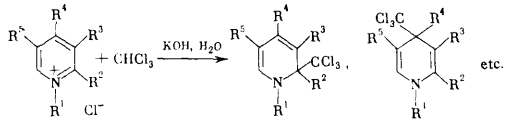
$$CHCl_3 + RSCN \xrightarrow[\text{BTEA}]{NaOH,H_2O} RSCCl_3 \quad .$$

However, standard two-phase conditions proved to be unsuitable for the synthesis of trichloromethylphenylmercury—an important source of dichlorocarbene under neutral conditions. The difficulties in the application of the two-phase method in this synthesis were overcome by replacing the concentrated solution of alkali by a mixed

solution of sodium hydroxide and potassium fluoride in water [186]:

$$C_6H_5HgCl + CHCl_3 \xrightarrow[BTEA]{NaOH,KF,H_2O} C_6H_5HgCCl_3 \quad .$$

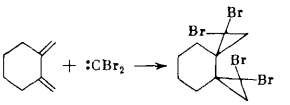
Krőhnke and coworkers [187] found recently that certain *N*-benzylpyridinium chlorides combine with the trichloromethyl anion, forming 2- and 4-trichloromethyldihydropyridine derivatives:



A more detailed study of this reaction showed that it proceeds at the interface [188].

### 3. The Formation and Reactions of Other Carbenes

Two-phase catalytic conditions proved to be very convenient for the conversion into carbanions and then into carbenes of all the remaining trihalogenomethyl derivatives of methane with the exception of fluoroform, which is too weak a C–H acid. The yields of dibromocyclopropane derivatives, obtained from bromoform and alkenes under standard two-phase catalytic conditions, are usually moderate [114,189,190]. Nevertheless, this method has been frequently used for the addition of dibromocarbene to dienes and polyenes [133,136,191]:



The yields increase in the presence of a considerable excess of bromoform [192,193] or when 1–2 mole % of lower alcohols is added to the reaction mixture [194–196].

The reaction with dibromocarbene has been used to substitute the hydroxy-group by bromine in hydroxyadamantanes [197]. Two-phase conditions have been used successfully to achieve the addition of tribromomethyl anions to electrophilic alkenes and, after some modification of the conditions (aqueous NaOH solution with addition of potassium fluoride instead of concentrated alkali), for the synthesis of tribromomethylphenylmercury [186]. A certain degree of stabilisation of tribromomethyl anions by small amounts of alcohols, mentioned above, makes it possible to achieve their alkylation by reactive alkylating agents, but the yields are low [198]:

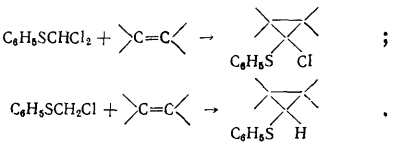
$$CHBr_3 + C_6H_5CH_2Cl \xrightarrow[BTEA]{NaOH,H_2O} C_6H_5CH_2CBr_3 \quad .$$

The formation of derivatives of chlorofluoro-, bromofluoro-, [199] and fluoroiodo-cyclopropanes [200] as a result of the reaction of the corresponding trihalogenomethanes and alkenes in the presence of aqueous sodium hydroxide and BTEA has also been described. Chlorofluorocarbene has been used successfully to synthesise chlorofluorocyclopropyl alcohols [201] and enamines [175] from the corresponding unsaturated compounds:

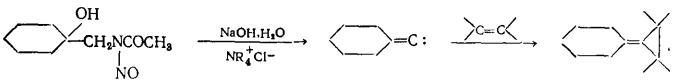
$$H_2C{=}CHCH_2OH + CHCl_2F \xrightarrow[BTEA]{NaOH,H_2O} H_2C(Cl,F)CHCH_2OH \quad .$$

Even di-iodocarbene can be obtained by treating iodoform with an aqueous solution of alkali and BTEA in the presence of alkenes [202].

Dichloromethyl sulphides are relatively close analogues of haloforms, since the 3*d* orbital effect of bivalent sulphur presumably stabilises the carbanions similarly to the influence of chlorine or bromine. Thus, on treatment with a concentrated aqueous solution of alkali in the presence of BTEA, dichloromethyl phenyl sulphide forms the corresponding carbanion and then phenylthiochlorocarbene, which reacts with alkenes to form phenylthiochlorocyclopropane derivatives [203]. The same has also been found for dichloromethyl methyl sulphide [204]. It must be emphasised that even chloromethyl phenyl sulphide is capable of abstracting a proton under these conditions and of converting alkenes into phenylthiocyclopropane derivatives [205]:

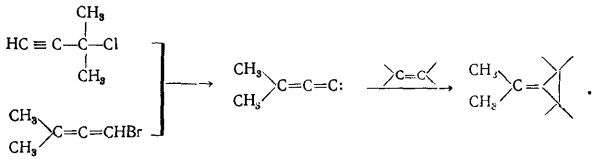


This result is to some extent unexpected, because it indicates a greater ability of the phenylthio-group to stabilise carbanions than that of chlorine, since methylene chloride is incapable of forming a carbanion and monochlorocarbene under these conditions [2]. Unfortunately, the problem of trapping the corresponding carbanions—precursors of alkyl(aryl)thiocarbenes—was not considered by the authors. The two-phase catalytic method gave very satisfactory results in the generation of unsaturated carbenes. Newman and coworkers used this method to convert *N*-(β-hydroxyalkyl)-*N*-nitrosoacetamides into alkylidenecarbenes and found that under these conditions the yields of the products of addition to alkenes or inorganic anions are considerably higher than those of any other products [206,207]:



The alkylidenecarbenes generated in this way also react with carbonyl compounds [208].

The successful addition of vinylidenecarbenes under these conditions to dienes (cyclopentadiene, norbornadiene) [209] and enol ethers [210] has been described. Dimethylvinylidenecarbene has been obtained by the same procedure from methylallenes [211] and butynes [212,213]:



## IV. CONCLUSION

### 1. Applications of the Method

Numerous examples of the use of two-phase catalytic systems and of the ion pair extraction method in many reactions of carbanions and halogenocarbenes constitute a good illustration of the scope and importance of these methods for organic synthesis. However, the two-phase method has many serious limitations. The most important one is that only relatively strong C–H acids may be converted into anions by treatment with aqueous sodium

hydroxide. Naturally, owing to the presence of two phases and catalysts, the acid–base equilibrium is displaced towards the formation of organic anions, but the methods are nevertheless inapplicable to C–H acids whose $pK_a$ is greater than 22. For example, fluorene can be alkylated, while acetonitrile cannot.

The second limitation is a consequence of the instability of certain C–H acids or electrophiles in the presence of an aqueous solution of alkali (for example, the hydrolysis of esters or other functional groups). This limitation can be frequently eliminated by employing more stable t-butyl esters and a less concentrated solution of sodium hydroxide or by increasing the amount of the tetra-alkylammonium salt up to an equimolar proportion. Compounds reacting with carbanions or halogenocarbenes should also be stable in the presence of aqueous alkali. On the other hand, one must not overestimate these limitations, since many readily hydrolysable compounds have been used successfully in the reaction under these conditions.

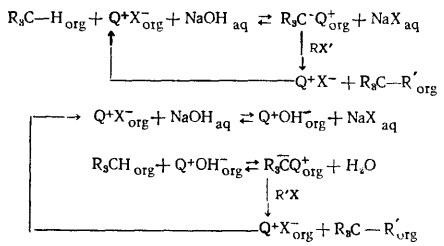
An important limitation of the use of the two-phase catalytic method is that the reaction product cannot be more acid than the initial compound. Otherwise it is converted into the anion more readily than the initial compound and forms a relatively unreactive ion pair with the ammonium cation, whereupon the catalytic reaction stops. Under these conditions and even in the presence of relatively strong C–H acids, the use of equimolar amounts of quaternary ammonium salts, recommended in the ion pair extraction method, appears to be more convenient. Catalytic reactions are frequently inhibited by inorganic anions with a low charge density and poorly solvated by water ($I^-$, $ClO_4^-$, etc.), which restricts the application of iodides as alkylating agents. This is a consequence of the high solubility of the corresponding tetra-alkylammonium salts in organic solvents. Nevertheless, this inhibiting effect is not always observed. It is unimportant when the extraction of ion pairs is employed.

## 2. The Possible Mechanisms of Catalysis in Two-Phase Systems

All the reactions discussed above consist of at least two stages. The first stage involves the formation of a carbanion by the abstraction of a proton from the C–H acid, and the second involves subsequent transformations of the carbanion (reaction with electrophiles, conversion into a carbene, etc.). One of the most important problems is that of the site where the processes occur: in the aqueous phase, in the organic phase, or at the interface. There is no doubt that the second and subsequent stages take place in the organic phase, where the carbanions exist as ion pairs with tetra-alkylammonium cations. This is frequently observed and in fact constitutes the essential feature of catalytic and extractive two-phase methods. The behaviour of these ion pairs in non-polar solvents has been discussed in detail by Brändström[6].

It is much more difficult to determine where the proton is abstracted from the C–H acid and the ion pair is formed. The majority of workers do not consider this problem and refer to all catalytic reactions of carbanions in two-phase systems as "phase-transfer catalysis"[2], a term which was introduced by Starks[12,215]. It arises from the following considerations: two reactants present in two immiscible liquid phases and insoluble in the other phase are unable to react with one another, since they cannot come into direct contact. A third component, capable of transferring one of the reactants from one phase to the other, and thereby enabling the reaction to occur, acts as the catalyst (the "phase-transfer agent"). This approach is well illustrated by the cyanation of alkyl halides in hydrocarbons by an aqueous solution of sodium cyanide. Vigorous stirring of this two-phase system does not lead to the exchange reaction even at an elevated temperature. On the other hand, the addition of catalytic amounts of a quaternary ammonium or phosphonium compound, capable of transporting $CN^-$ ions in the form of the ion pairs $NR_4^+CN^-$ into the organic phase, gives rise to a vigorous reaction. In the reactions of halogenocarbenes or carbanions (derivatives of relatively weak C–H acids) in the presence of a concentrated aqueous sodium hydroxide solution the role of phase transfer catalysis reduces to the transfer of hydroxide anions in the form of tetra-alkylammonium or phosphonium hydroxides from the aqueous to the organic phase.

Thus, according to the mechanism involving transfer from one phase to the other, the abstraction of a proton from C–H acids, and the formation of the carbanion–tetra-alkylammonium cation ion pair should occur in the organic phase. This hypothesis concerning the generation of trichloromethyl anions and dichlorocarbene in a two-phase catalytic system via the formation of a quaternary ammonium base, which then reacts in the organic phase, was put forward by the present author in 1969[1,12]. However, many observations and the results of careful analysis agree better with the hypothesis that the first stage of the carbanionic reaction—the abstraction of a proton and the formation of ion pairs in the two-phase systems under consideration—takes place at the interface. The ion pairs then diffuse into the bulk of the organic phase, where all further transformations, involving the simultaneous liberation of the ammonium cation, take place. These two alternative mechanisms are represented schematically as follows:

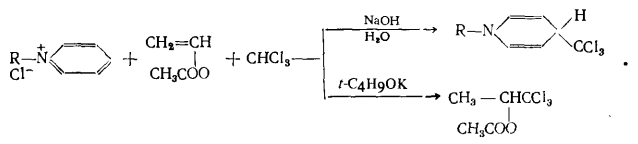



Evidently in the case of relatively strong C–H acids, which are capable of forming anions to a significant extent in the presence of a dilute aqueous NaOH solution, the quaternary ammonium compound acts mainly as a phase-transfer agent, transferring organic anions from the aqueous to the organic phase. However, the most important application of two-phase catalytic systems involves the reaction of weak C–H acids, which do not form water-soluble sodium derivatives. In such cases we are dealing with a distinct immiscibility of the two phases. For example, in the phenylacetonitrile–50% aqueous NaOH solution system the concentration of the first component in the aqueous phase is less than 2 p.p.m., while that of sodium hydroxide in terms of $Na^+$ ions is less than 5 p.p.m. in the organic phase. These values rule out the extraction of carbanions from the aqueous phase, of the kind that can occur in the case of more acid compounds and a dilute NaOH solution.

Thus two possibilities remain: the abstraction of a proton in the organic phase, into which $NR_4^+OH^-$ is transferred as the base, or at the interface. Numerous experiments on the extraction of ion pairs with inorganic anions have shown that in an organic solvent (for example, benzene or acetonitrile)–50% aqueous NaOH solution two-phase system more than 99% of benzyltriethylammonium chloride remains in the organic phase as the chloride and that each anion in the series $SO_4^{2-}$, $F^-$, $OH^-$, $Cl^-$, $Br^-$, and $I^-$ is almost quantitatively displaced from the organic phase by its right-hand neighbour. In view of the small amounts of catalysts used in preparative experiments and the formation of considerable amounts of the $Cl^-$ and $Br^-$ anions in the reaction, the concentration of $OH^-$ anions (i.e. $NR_4^+OH^-$) in the organic phase is presumably negligible. Nevertheless, the rate of attainment of the acid–base equilibrium is usually high compared with other reactions, so that one cannot fully rule out the possibility of the formation of carbanions by the extraction of $NR_4^+OH^-$, although it is unlikely. On the other hand, the possibility of the attainment of the acid–base equilibrium and the formation of carbanions at the interface has been satisfactorily demonstrated by the present author's experiments, in which many reactions of carbanions in a two-phase system without catalysts were observed.

Numerous weak C–H acid exchange hydrogen for deuterium as a result of stirring with a concentrated solution of sodium hydroxide in $D_2O$. Owing to the almost complete immiscibility of the phases, the formation of the carbanion and its reaction with $D_2O$ presumably take place at the interface. The present author found that certain synthetically impotrant reactions of carbanions occur in a two-phase system without catalysts. Bearing in mind the above miscibility data, one may conclude that the reactions occur at the interface. They include mainly those actions of Reissert's compounds with aldehydes [86], Darzens-type condensations of aldehydes with $\alpha$-halogenosulphones [75] and $\alpha$-halogenonitriles, and the addition of $CCl_3^-$ anions to *N*-alkylpyridinium salts [187,188]. The latter reaction is particularly interesting, since pyridinium salts resemble to a considerable degree the catalysts used in the reactions of carbanions.

The formation of adducts of the trichloromethyl anion is not accompanied by the formation of tar. This is evidence against the extraction of $OH^-$ anions into the organic phase, since the products of their addition to pyridinium salts are very unstable. However, the main evidence that the adducts of the trichloromethyl anion are formed at the interface was obtained in competition experiments, where vinyl acetate competed with pyridinium salts for addition to trichloromethyl anions. In a two-phase system, trichloromethyl anions add exclusively to the pyridine ring, while in a homogeneous or pseudohomogeneous system in the presence of potassium t-butoxide, trichloromethylethyl acetate is formed exclusively (when there is competition with styrene, a substituted dichlorocyclopropane is formed) [188]:



Thus it may be regarded as proved that the addition of the $CCl_3^-$ anion to pyridinium salts takes place at the interface, by-passing the ion pair formation stage. Presumably the recently described reactions of dichlorocarbene catalysed by tertiary amines are to some extent associated with the formation of this anion at the interface, where the reaction with the tertiary amine results in the formation of an ammonium ylid. The latter is capable of diffusing into the organic phase, where further transformations occur.

The above observations and considerations permit the conclusion that in a two-phase system comprising a relatively weak C–H acid (in an organic solvent or without it) and a concentrated sodium hydroxide solution, a proton is abstracted with formation of a carbanion even in the absence of a catalyst. However, these carbanions are incapable of leaving the interface, since the sodium cations accompanying them are highly solvated in the aqueous phase and only very slightly in the organic phase; they are therefore incapable of passing to the latter. In this to some extent adsorbed state, carbanions are very unreactive, and react only with strong or positively charged electrophiles. Quaternary ammonium cations react with these carbanions, forming ion pairs soluble in the organic phase. After their migration into the bulk of the organic phase, the ion pairs undergo further transformations. This mechanism is naturally highly simplified. Tetra-alkylammonium cations are in all probability directly involved in the stage where carbanions are formed, lowering the energy of the transition state in the proton abstraction reaction, as a result of the influence of the positive charge from the opposite side of the reaction centre. Not only tetra-alkylammonium and phosphonium compounds but also alkali metal cations, which are highly solvated by certain organic solvents [dimethylformamide (DMF), hexamethylphosphoramide (HMP), etc.], can serve as catalysts in two-phase systems. These solvents in fact catalyse the formation of carbanions in two-phase systems:

$$(C_6H_5)_2CHCN_{org} + NaOH_{aq} \rightleftarrows [(C_6H_5)_2\bar{C}CNNa^+_{solv.}]_{org} + H_2O_{aq}$$

| Solvent | $C_6H_6$ | $CH_3CN$ | DME | THF | Pyridine | DMF | HMP |
|---|---|---|---|---|---|---|---|
| Concn. of carbanion, % | 0 | 1 | 3 | 3 | 12.5 | 88 | 94 |

Crown ethers proved to be very powerful neutral ligands, binding alkali metal cations [14,215]. The stable crown . $Na^+$ complex behaves as an organic cation, forming with many anions ion pairs which are soluble in non-polar organic solvents. This remarkable property of crown ethers has found an interesting application in many reactions involving inorganic anions in non-polar solvents (reactions of "naked" anions) [80,216-218]. In most cases crown ethers were partly converted into a solid sodium or potassium salt in a benzene or acetonitrile solution. The present author showed that crown ethers are very effective catalysts of the reactions of carbanions in a two-phase system. They are no less active than quaternary ammonium salts, but are more stable than the latter [13,55]. The use of diazapolyoxamacrobicyclic compounds as catalysts in liquid–liquid or liquid–solid two-phase systems is also very promising, because their activity in binding cations into complexes with formation of the so called cryptates is much higher than that of crown ethers [219,220].

Summarising the foregoing, it is possible to distinguish three different types of catalytic action of quaternary ammonium salts in two-phase systems, each of which is based on the formation of ion pairs soluble in the organic phase.

1. Extraction of inorganic anions from the aqueous phase into the organic phase—true-phase transfer catalysis, which is observed mainly in reactions of inorganic anions ($CN^-$, $SCN^-$, $MnO_4^-$, etc.) with organic compounds (alkyl and alkenyl halides, etc.).

2. Extraction (into the organic phase) of the carbanions of relatively strong C–H acids formed on treatment with dilute aqueous solutions of sodium hydroxide or water-soluble sodium derivatives of these acids. There is no doubt that such extraction displaces the acid–base equilibrium in the direction of the formation of the carbanion. This corresponds either to phase-transfer catalysis or to the extraction of ion pairs as a function of the amount of quaternary ammonium salt consumed (catalytic or equimolar).

3. The formation of ion pairs soluble in the organic phase and incorporating carbanions located at the interface, with a more or less active involvement of the proton abstraction stage. This pathway is the main one in the carbanionic reactions of relatively weak C–H acids, regardless of whether catalytic or equimolar amounts of tetra-alkylammonium salts are used.

It is impossible to separate clearly these three versions; each plays the main role in individual instances. Some workers include the two-phase reaction considered here with those occurring in cationic micelles ("cages")[4]. Despite the apparent similarity of the systems considered to micellar systems, the essential feature of the catalytic action of onium compounds is different from that of micellar catalysis and their catalytic activity does not vary in parallel with surface activity. Nevertheless one cannot completely reject the possibility of the involvement of phenomena similar to those in micellar catalysis, particularly in reactions occurring at the interface.

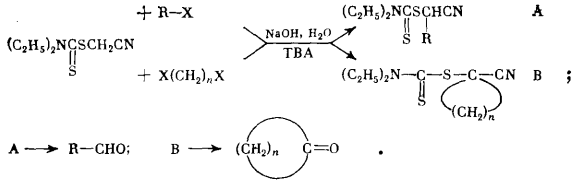
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Two-phase catalytic systems have been used in reactions of carbanions and halogenocarbenes for only about ten years, and they have become more common only in the last five years. The present author's views concerning the potential possibilities of the applications of these methods are therefore by no means exhaustive. In almost all the examples described, both two-phase catalytic methods and methods based on the extraction of ion pairs proved to be better than all other known procedures as regards simplicity, selectivity, yields, etc. Presumably they will be widely used in the immediate future as methods of organic synthesis.

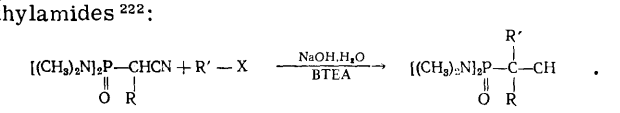
## ADDENDUM

Numerous studies have been published recently, in which the two-phase method of generating carbanions and halogenocarbenes was developed further. The most important results are presented below.

2.1. *S*-Cyanomethyl *NN*-diethyldithiocarbamate can be alkylated with excellent yields in the presence of aqueous alkali and an ammonium catalyst. Since both functional groups are readily split off on hydrolysis, the reaction can be used to synthesise aldehydes and ketones[221]:

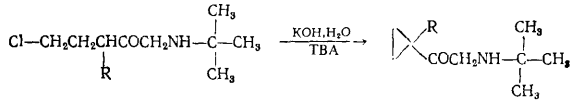


A two-phase catalytic system has been used successfully in the alkylation of cyanoalkylphosphonic tetramethylamides[222]:



Reeves and Hilbrich reported that the alkylation of phenylacetonitrile and phenylacetone in a two-phase system is catalysed by tertiary amines, which are capable of forming quaternary salts under the reaction conditions[223].

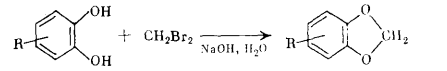
2.2. Using an equimolar amount of BTEA, Singh and Danishefsky[224] alkylated diethyl malonate with ethylene bromide in the presence of concentrated aqueous alkali and obtained directly cyclopropane-1,1-dicarboxylic acid. The application of a two-phase catalytic system in the synthesis of cyclopropyl ketones has been described[225]:



2.3. A two-phase catalytic system proved to be very effective in the alkylation of compounds containing the isonitrile group[226], for example toluene-*p*-sulphonylmethyl isocyanide[227]:

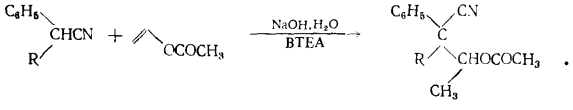


This method gave excellent results in the reaction of methylene bromide with phenols[228,229]:

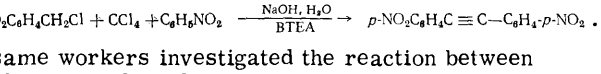


A detailed study of the synthesis of ethers under two-phase conditions has been described[230]. This method has been used in the synthesis of the ethers and acetals of certain sugars[231]. Studies dealing with two-phase *N*-alkylation of indole[232,233], amides[234], phenylhydrazones[235], and aziridine[236] have been published.

2.4. Using aqueous alkali, it was possible to carry out the Wittig reaction with formaldehyde[237]. Among many examples of the Wittig–Horner reaction[238], carried out under two-phase conditions, processes apparently occurring at the interface without catalysts have been discussed[240]. A two-phase catalytic system is very effective in the synthesis of unsaturated compounds by the condensation of aryl methyl sulphones[241], 2-methylbenzothiazoles[242], and similar carbon acids with aromatic aldehydes. Certain carbanions add to vinyl acetate under these conditions[243]:



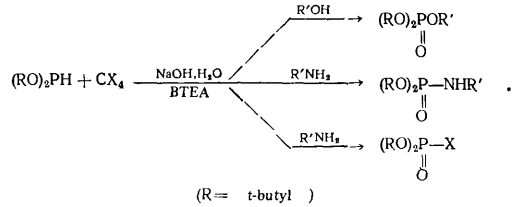
2.5. Using a two-phase system, a direct synthesis of di-(*p*-nitrophenyl)acetylene was achieved[244]:



The same workers investigated the reaction between phenylacetonitrile and nitrobenzene in the presence of aqueous NaOH and BTEA.[245]

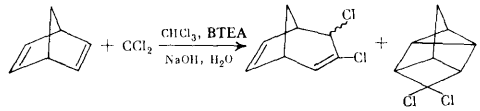
Excellent results were obtained when the Atherton–Todd reaction was carried out under catalytic two-phase conditions. Alcohols, phenols[246], and amines[247] are

phosphorylated with a yield of about 90% and the products do not require additional purification. When t-butyl phosphite is used, it is also possible to obtain the corresponding acid halide[248]:



(R= t-butyl )

3. Dichlorocarbene generated under two-phase catalytic conditions gives rise to products of 1,4-homoaddition to polycyclic hydrocarbons[249,250]:



The high reactivity of dichlorocarbene in a two-phase system can be modified by employing as the catalyst an ammonium salt containing a hydroxy-group[251], which makes the reaction with polyalkenes more selective. Dichloroethane generated under two-phase catalytic conditions is capable of eliminating oxygen from epoxy alkanes[252] and the resulting alkene then combines with dichlorocarbene.

Apart from the studies indicated above, many others have been published in which a two-phase system was used for the synthesis of dihalogenocyclopropanes[253,254].

4. The fact that methyl phenyl sulphone and even dimethyl sulphone[255] react with benzaldehyde in the presence of aqueous NaOH and BTEA demonstrates the considerable ability of this system to abstract a proton. On the other hand, these compounds react only with aromatic aldehydes, so that the existence of carbanions in the organic phase is doubtful. The reactions apparently take place at the interface. New evidence has been obtained for the formation of carbanions at the interface. It has been shown that alkyl iodides are capable of alkylating phenylacetonitrile without a catalyst and that the process takes place at the interface.

The possibility of inducing optical activity by means of an optically active ammonium catalyst has aroused interest. Nazaki's report of a high degree of induced activity in the synthesis of phenyloxiran (styrene oxide) from benzaldehyde and sulphoxonium imide[257] proved to be erroneous. The induction of optical activity in the reaction of dichlorocarbene with styrene is also doubtful[258]. A moderate stereospecificity has been observed in the alkylation of 2-ethoxycarbonylcyclohexanone[259]. Quaternary ephedrinium salts were used as the chiral catalysts in all cases.

Finally, the use as catalysts of quaternary ammonium salts[260] as well as crown ethers[261] attached to solid polymers has been reported. The term three-phase catalysis has actually been proposed[260].

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# Organosilicon Carbonates and Chlorocarbonates

V.D.Sheludyakov and V.F.Mironov

A systematic account is given for the first time of the methods of synthesis, properties, and practical applications of silicon-containing derivatives of carbonic acid—carbonates and chlorocarbonates (chloroformates). Together with monomeric compounds, oligomeric and polymeric products are discussed as well as other compositions from which new organosilicon articles with valuable practical properties, for example with a highly effective gas-separating capacity, have been made.
The bibliography includes 426 references.

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## I. INTRODUCTION

New organic and organosilicon polymeric materials and intermediates in their synthesis are now attracting an increased amount of attention [1-12]. This review is part of a series of previously published reviews dealing with carbonic acid derivatives: organosilicon isocyanates [13], ureas [14], and urethanes [15].

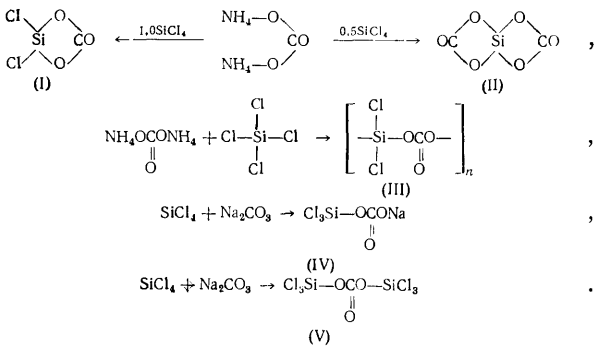
The chemistry of organic chlorocarbonates and carbonates has frequently been the subject of special and general reviews [16-21], but they were all published before studies on the synthesis of the corresponding silicon-containing derivatives were made and therefore naturally do not describe them or anticipate the possibility of their formation. Furthermore, in the last published review [22], the already available extensive data on this problem were not described. A fairly considerable amount of attention has been devoted to silicon-containing carbonic and chlorocarbonic acid esters in a number of studies [23-32], but the latter were incomplete, since they were devoted to specific problems. Carbonates are esters of carbonic acid which does not exist in a free state. Chloroformates may be regarded as esters of chloroformic or more correctly chlorocarbonic acid, because from the chemical point of view the transition from carbonic to its acid chloride is more apt than the transition from formic acid to chloroformic acid.

Depending on the relative positions of the ester $-OC(O)O-$ and silyl groups, silicon-containing carbonates (silyl carbonates) can be divided into two independent classes—compounds in which the above groups are linked directly (*O*-silyl carbonates) and organosilicon carbonates with carbofunctional substituents in which these fragments are separated by a carbon or similar bridge (*C*-silyl carbonates).

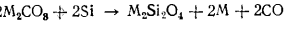
## II. COMPOUNDS WITH THE CARBONATE GROUP AT THE SILICON ATOM

### 1. Methods of Synthesis

When $SiCl_4$ reacts with ammonium and alkali metal carbonates, the products are trichlorosilanol and chlorosiloxanes and not *O*-silyl carbonates [33], for example, compounds (I)-(V):



Nor were silyl esters of carbonic acid isolated in the interaction of inorganic carbonates $M_2CO_3$ (M = Li, Na, K, Rb, or Cs) with reactive finely divided silicon [34], since the process proceeded via the following mechanism:



and was accompanied by oxidation-reduction side reactions:

$$2CO \rightarrow CO_2 + C \quad ,$$
$$2M + CO \rightarrow M_2O + C \quad ,$$
$$Si + 2CO \rightarrow SiO_2 + 2C \quad .$$

The formation of $(Me_3SiO)_2CO$ as a result of an electrochemical reaction was observed by Butts and Rainey [35] by chromatographic and mass-spectrometric and analytical methods. However, the product was not isolated in a pure state.

At the end of 1971, Yamamoto and Tarbell [36] were the first to synthesise mixed alkyl trimethylsilyl carbonates [36]:

$$RONa \xrightarrow{CO_2} ROC(O)ONa \xrightarrow{Me_3SiCl} \underset{(VI)}{ROC(O)OSiMe_3} \quad ;$$

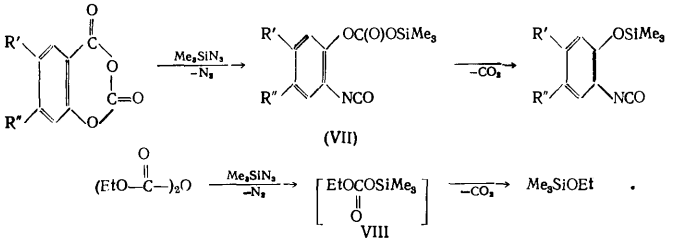
R = Et, iso-Pr, n-Bu, t-Bu, or iso-$Pr_2CH$.

Thio-analogues of the carbonates (VI) as well as the corresponding derivatives of other Group IVB elements, for example germanium, tin, and lead, are formed when alkyl thiocarbonates of alkali metals are acted upon by $R'_3MX$: [36,37]

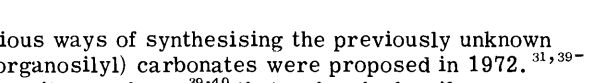
$$ROC(O)SM' + R'_3M{-}X \rightarrow ROC(O)SMR'_3 + M'X \quad ;$$

R = Et or t-Bu; M = Si, Ge, Sn, or Pb; M′ = K or Na; R′ = alkyl.

The asymmetric carbonates (VII) and (VIII) are unstable intermediates in the reaction of $Me_3SiN_3$ with carboxylic acid anhydrides [38]:

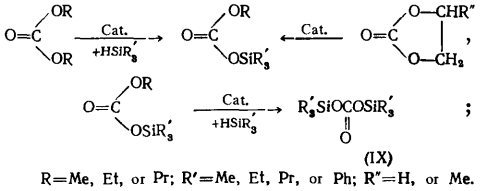


(VII)



VIII

Various ways of synthesising the previously unknown bis(triorganosilyl) carbonates were proposed in 1972. [31,39-42]. Thus it was shown [39,40] that, when hydrosilanes are made to react with dialkyl or alkylene carbonates in the presence of the Ni/$Et_2S$ (or $NiCl_2$/$Me_3SiSiMe_3$) catalyst [43], stepwise displacement of the organic groups by triorganosilyl groups is observed, for example:



(IX)

R=Me, Et, or Pr; R′=Me, Et, Pr, or Ph; R″=H, or Me.

Compounds of type (IX) have been synthesised [31,41,42] by combining reactions involving treatment with phosgene, carboxylation, and protection by silyl groups:

$$R_3SiOH + COCl_2 \xrightarrow[-HCl]{Et_3N} \underset{(IX)}{R_3SiOC(O)OSiR_3} \leftarrow R_3SiONa + COCl_2 \quad ,$$

$$R_3SiONa \xrightarrow{CO_2} R_3SiOCONa \xrightarrow[-NaCl]{R_3SiCl} R_3SiOC(O)OSiR_3 \quad .$$

The last reaction served as the basis of the synthesis of *O*-silyl carbonates with different organosilyl groups [44]:

$$Et_3SiOH \xrightarrow[20°C]{NaH/THF} Et_3SiONa \xrightarrow[2.\ Me_3SiCl]{1.\ CO_2} \underset{(X)}{Et_3SiOCOSiMe_3} \quad .$$

A mixed anhydride of carbonic acid and triorganosilylcarbonic acid (XI) was obtained in the same investigation by treating $Et_3SiOC(O)ONa$ with phosgene:

$$Et_3SiOC(O)ONa + COCl_2 \rightarrow \underset{(XI)}{Et_3SiOCOCOSiEt_3} \quad .$$

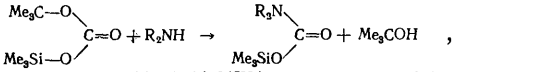
## 2. Physical Properties

The organosilicon carbonates $R_3SiOC(O)OR'$, $R_3SiOC(O)OSiR_3$, and $R_3SiOC(O)OSiR'_3$ (where R, R′, and R″ are alkyl groups) are colourless, transparent liquids or low-melting crystalline substances which can be vacuum-distilled without decomposition. Exceptions are $(Ph_3SiO)_2CO$, which melts at 160°C, $Me_3SiOC(O)OBu$-n, which decomposes with evolution of $CO_2$, and n-$BuOSiMe_3$, which decomposes even at room temperature [31,36,39-42,44]. The infrared spectra of the carbonates $R_3SiOC(O)OR'$ have $\nu$(CO) bands in the ranges 1755–1760 and 1720–1730 $cm^{-1}$. The bands in the spectra of the compounds $R_2SiOC(O)OSiR_3$ are somewhat closer together and are located at 1705 to 1707 and 1740 $cm^{-1}$. The $(Ph_3SiO)_2CO$ spectrum has only a singlet at 1765 $cm^{-1}$. The calculated and observed molecular refractions are similar [39].

The $^1H$ NMR and mass spectra of silyl carbonates have been described [31,36,39,41,44].

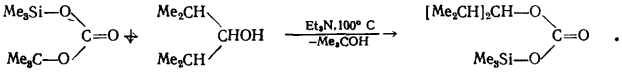
## 4. Chemical Properties

It has been shown [36] that, on treatment with primary and secondary amines, the carbonate $Me_3SiOC(O)OCMe$ is converted into the corresponding silyl carbamate esters†:



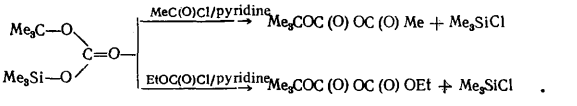
$R_2$=$(CH_2)_4$; $(CH_2)_5$; $(CH_2)_2O(CH_2)_2$; Ph and H; or Ph and Me.

while on reaction with a high-boiling alcohol it is transesterified:



This is evidence for a greater lability of the CO–C bond compared with SiO–C.

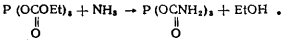
On the other hand, treatment with MeC(O)Cl and EtOC(O)Cl results in the cleavage of the Si–O bond:



Pyrolysis of the *O*-silyl carbonates (VI) and (IX) leads to alkoxysilanes and disiloxanes respectively [44]:

$$(VI) \xrightarrow{t_1} R_3SiOR' + CO_2 \quad ,$$
$$(IX) \xrightarrow{t_2>t_1} R_3SiOSiR_3 + CO_2 \quad .$$

† Phosphorus-containing carbonates behave similarly: the C–(O)OEt bond is cleaved by ammonia in preference to the C–(O)OP bond [45]:

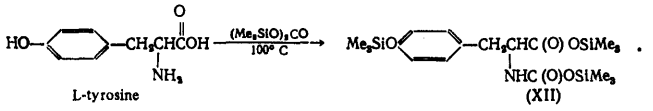


Hydrolysis of the carbonates (IX) in a neutral medium takes place at a moderate rate with formation of $R_3SiOH$ and $CO_2$. In the presence of inorganic acids, the process is sharply accelerated [31,39,41]:

$$(R_3SiO)_2CO + H_2O \xrightarrow[pH<7]{Me_2CO} R_3SiOH + CO_2 \quad .$$

The Grignard reaction with silyl carbonates proceeds via exactly the same mechanism as in the case of organic carbonates [46].

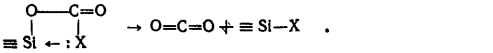
Bis(trimethylsilyl) carbonate behaves as a siloxycarbonylating and silylating agent on interaction with aminoacids [44]. For example, the reaction with L-tyrosine gave the tris(trimethylsiloxy)-derivative (XII):




L-tyrosine (XII)

## 4. β-Elimination Reactions

The products of the reaction of $R_3SiH$ with dialkyl or alkylene carbonates contain alkoxysilanes and disiloxanes, which are apparently formed as a result of the β-decomposition of the intermediate and final organosilicon carbonates. The decomposition of the molecules is the final result of the electron redistribution in the system of σ bonds in the structural fragment $\equiv Si-O-C(O)-X$ (where X = OR or $OSiR_3$) as a consequence of the intramolecular coordination O: $\rightarrow Si\equiv$ in the four-membered transition complex:



$$\rightarrow O=C=O + \equiv Si-X \quad .$$

In this respect organosilicon carbonates show similarities with stannyl carbonates [47-50]:

$$Bu_3Sn-OC(O)-OMe \xrightarrow{60-80° C} Bu_3Sn-OMe + O=C=O \quad ,$$
$$R_3Sn-OC(O)-OSnR_3 \xrightarrow{\sim 90° C} R_3SnOSnR_3 + O=C=O \quad ,$$

and plumbyl carbonates [48]:

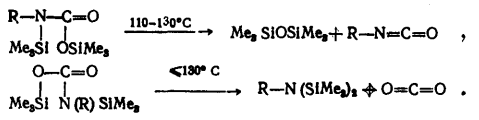
$$Ph_3Pb-OC(O)-OMe \xrightarrow{<110° C} Ph_3PbOMe + O=C=O.$$

The available data already permit the conclusion that the thermal stability of the compounds $R_3EOC(O)OR'$ and $(R_3EO)_2CO$ diminishes in series of similar compounds in the following sequence: C > Si > Sn > Pb. On the other hand, as for the compounds $\equiv Si-N(R)-C(O)-X$ (X = Cl, OR, or $OSiR_3$), [51] the thermal and chemical stability of the $R_3E-OC(O)-X$ (E = C, Si, Sn, or Pb) groups falls sharply with increasing electronegativity of X. A striking example of this is provided by the compound $Me_3C-OC(O)Cl$, which does not exist at room temperature [52-54], and by its silicon [28,31,55,56] and tin analogues, which are undoubtedly formed in the course of the following chemical reactions:

$$R_3SiCH_2CH_2OC(O)Cl \xrightarrow{C_2H_4} R_3SiOC(O)Cl \xrightarrow{-CO_2} R_3SiCl \quad ,$$
$$(R_3Sn)_2O + COCl_2 \xrightarrow{-R_3SnCl} R_3SnOC(O)Cl \xrightarrow{-CO_2} R_3SnCl \quad .$$

Qualitative observations [57-66] have also shown that the replacement of the carbonyl group in the $\equiv Si-O-C(O)-X$ unit by $CH_2$, $C(CF_3)_2$, $SO_2$, or $PO_2$‡ stabilises the molecule as a whole (for example in relation to heating). Subsequent experiments showed that $Me_3SiOC(O)OBu\text{-}n$, $Me_3SiOC(O)OEt$, and $2\text{-}NCOC_6H_4OC(O)OSiMe_3$ [38] evolve $CO_2$ close to room temperature; $Et_3SiOC(O)OAlk$ and $(Et_3SiO)_2CO$ are slowly decarboxylated during synthesis (105–130°C) and more rapidly at 150–200°C. [39] This implies that silyl carbonates are thermally less stable than silyl *NN*-dialkylcarbamates. For example, $Me_3SiOC(O)NEt_2$ can be boiled for a long time without decomposition at 177–178°C. [68]

It is striking that, on passing from $Me_3SiOC(O)NEt_2$ to $Me_3SiOC(O)N(Et)SiMe_3$, [69] the tendency towards thermal decomposition increases and, of the two systems of conjugated bonds present simultaneously in the latter compound, namely $\equiv Si-OC(O)-X$ [X = $-N(Et)SiMe_3$] and $\equiv Si-N(Et)C(O)-Y$ (Y = $OSiMe_3$), the latter is the more labile:



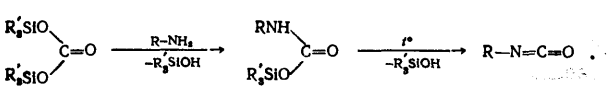
$$R-N(SiMe_3)-C(=O)-OSiMe_3 \xrightarrow{110-130°C} Me_3SiOSiMe_3 + R-N=C=O \quad ,$$
$$R-N(SiMe_3)-C(=O)-N(R)SiMe_3 \xrightarrow{\leqslant 130° C} R-N(SiMe_3)_2 + O=C=O \quad .$$

Thus compounds with the $\equiv Si-OC(O)-X$ and $\equiv Si-NC(O)-X$ bond systems and in a more general form with $\equiv Si-O-E-X$ and $\equiv Si-N-E-X$ (where X is an electronegative group and E a Group II–VIII element) extend Nesmeyanov's classical concept concerning the unusual properties of organoelemental compounds with β-carbofunctional groups and their tendency to undergo β-elimination reactions. These properties are probably characteristic in general of organoelemental compounds with β-functional groups having the general formula $R_{n-1}M^n-E_1-E_2-X$ (where *n* is the valence of the element M and $E_1$ and $E_2$ are group II–VIII elements).

## 5. Practical Applications

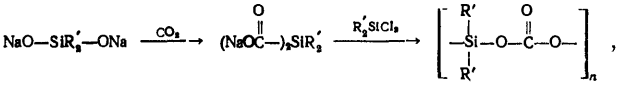
As already mentioned, the silyl carbonates (VI) and (IX) can be used in the synthesis of silyl carbamate esters, aminoacid derivatives, mixed anhydrides of carboxylic and siloxy(alkoxy)carbonic acids, etc. [36] and as mild silylating agents [44], which is extremely important in the study of natural products.

In view of the simplicity with which *O*-silyl carbonates can be obtained, they may serve as a basis for a method of synthesising lower aliphatic isocyanates by a fully phosgene-free method with recycling of the silanol:



$$R'_3SiO-C(=O)-OSiR'_3 \xrightarrow[-R'_3SiOH]{R-NH_2} RNH-C(=O)-OSiR'_3 \xrightarrow[-R'_3SiOH]{t°} R-N=C=O \quad .$$

The synthesis of poly-(*O*-silyl carbonates) by the phosgene-free method,



$$NaO-SiR'_2-ONa \xrightarrow{CO_2} (NaOC(=O)-O)_2SiR'_2 \xrightarrow{R'_2SiCl_2} \left[-Si(R')_2-O-C(=O)-O-\right]_n \quad ,$$

is of theoretical interest because, owing to the ease of decarboxylation on acidification, they can be used in the manufacture of polysiloxane foam materials.

‡ The compound $Me_3SiOSeO_2Cl$ may be unstable owing to its insufficient purity. On the other hand, the stability at a high temperature of $Me_3SiOAlCl_3$ (b.p. 226–236°C) [67] and similar derivatives can be accounted for by their existence in an associated form.

## III. ORGANOSILICON CHLOROCARBONATES AND CARBONATES WITH CARBOFUNCTIONAL GROUPS

Organosilicon chlorocarbonates with carbofunctional groups are intermediates in the synthesis of silicon-containing mono-, oligo-, and poly-urethanes, a wide variety of carbonates, carbazinic acid derivatives, etc. and for this reason will be considered before carbonates.

### 1. Methods of Synthesis of Chlorocarbonates

The hydrosilylation reaction of alkenyl (alkenylaryl) chlorocarbonates is remarkable in that it makes it possible to obtain organosilicon chlorocarbonates with one, two, and three carbofunctional groups at the silicon atom, which are important for subsequent chemical reactions [28,29,31,42,70-75]

$$X_nR_{3-n}SiH + >C{=}C< — Q — OC(O)Cl \xrightarrow{Cat.} X_nR_{3-n}Si — \underset{H}{\overset{|}{C}} — \underset{|}{C} — Q — OC(O)Cl ;$$

X = Cl, OAlk, OSi≡; R = Alk, Ar; Q = alkylene or arylene; $n \leqslant 3$.

Peroxides or Speier's compounds are used as catalysts of the reaction [76]. Its disadvantage is that, in the case of the most readily available compound AllOC(O)Cl§, the addition of hydrosilanes is accompanied by vigorous evolution of $CO_2$ and propene [77-79] (see also Refs. 76, 80, 81)¶ and the greater part of the initial silane is converted into a more highly chlorinated compound.

The data on the hydrosilylation of AllOC(O)X (where X = H, Cl, OMe, or OAll) [28,29,31,42,70-75] have shown that $CO_2$ and $C_3H_6$ are not formed by the reduction of the initial or final chlorocarbonates to unstable formates [82-85] or by the addition of H—Si≡ to the C=O group of the chlorocarbonate with subsequent elimination of siloxy-derivatives via the β-decomposition mechanism. They are produced as a result of double β-decomposition of β-chlorocarbonatopropylsilanes—the products of the addition of H—Si≡ to AllOC(O)Cl in accordance with the Markovnikov rule:

$$\equiv Si — CH(Me)CH_2 — OC(O)Cl \xrightarrow[-C_3H_6]{} \equiv Si — OC(O) — Cl \xrightarrow[-CO_2]{} \equiv Si — Cl .$$

Furthermore, it has been noted that the hydrosilylation of AllOC(O)Cl is sensitive to the conditions of synthesis [31]. For example, when Speier's catalyst [t-butyl peroxide] is added to the entire reaction mass (A), the yield of the desired chlorocarbonate is low. It increases appreciably when the catalyst and a portion of the mixture of reactants is kept in contact until gas evolution ceases and then the remaining portion of the mixture (B) is added. A mixture (C) of t-butyl and dicumenyl peroxides acts even more selectively in the required direction (see Table).

The reaction of phosgene with organosilicon alcohols and phenols containing carbofunctional groups has been studied in detail since 1965. [24,29-31,42,74,75,86-96]. The reactions with alcohols and glycols proceed vigorously regardless of the position of the hydroxy-group relative to the silicon atom [29,31,42,75,87,89,92] via the mechanism

$$O\left[-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-R'-OH\right]_2 \xrightarrow{COCl_2} O\left[-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-R'-OC(O)Cl\right]_2 +$$

(XIII) (XIV)

$$+ Cl-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-R'-OC(O)Cl + Cl-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-R'-Cl ,$$

(XV) (XVI)

(a) R′=$CH_2$; (b) R′=$(CH_2)_3$; (c) R′=$(CH_2)_4$; (d) R′=$CH_2O(CH_2)_2$.

Hydrosilylation of allyl chlorocarbonate [31].

| Hydrosilane | Method of synthesis and yields of carbonates, % | | |
|---|---|---|---|
| | A | B | C |
| $Cl_2SiH$ | 23 | 62 | 60 |
| $Cl_2MeSiH$ | 24 | 46 | 51 |
| $ClMe_2SiH$ | 22 | 37 | 45 |

The appearance of products (XV) and (XVI) is due to the presence of HCl in the reaction mixture, whose removal by flushing with nitrogen or with the aid of a tertiary amine sharply suppresses side reactions and increases the yield of the required bischlorocarbonates (XIV).

In contrast to alcohols, silicon-containing phenols are inert at moderate temperatures in relation to phosgene. In order to avoid their thermal rearrangement, to phenoxysilanes [30,97] as well as other similar reactions involving the bonds formed by the silicon atom, chlorocarbonates are therefore synthesised in the presence of organic bases, for example [29-31,42,91]:

$$HMe_2SiC_6H_4OH + COCl_2 \xrightarrow[-HCl]{EtN} HMe_2SiC_6H_4OC(O)Cl ,$$

(XVII)

$$\left[X-C_6H_3(OH)-R-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-\right]_2O \xrightarrow[-R_3N\cdot HCl]{COCl_2/R_3N} \left[X-C_6H_3(OC(O)Cl)-R-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-\right]_2O ;$$

(XVIII) (XIX)

(a) R = single bond and X = H; (b) R = $CH_2O$ and X = Cl; (c) R = $(CH_2)_3$ and X = H.

Treatment of silyl ethers derived from silicon-containing alcohols and phenols with phosgene is in many cases preferable on a preparative scale to the direct reactions of phosgene with the alcohols and phenols discussed above.

Firstly, when the reaction comes to an end, the reaction mixture does not contain the corrosive HCl, instead of which $Me_3SiCl$, which can be readily removed and which does not cleave the ≡Si—O—Si≡ and ≡Si—O—C≡ bonds, is formed, for example [29-31,86,88,90,91,94,95]:

$$O\left[-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-(CH_2)_nOSiMe_3\right]_2 \xrightarrow[20-25^\circ C]{COCl_2} O\left[-\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{Si}}}}-(CH_2)_nOC(O)Cl\right]_2$$

(XIV)

$n$=1,3.

Secondly, the advantage of this method compared with the treatment of phenols with phosgene in the presence of HCl acceptors is that the formation of both carbonates and

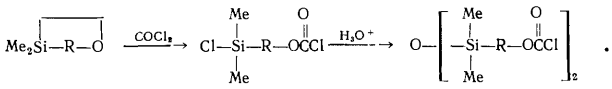
§ Here and henceforth All = allyl.

¶ The evolution of propene during the addition of hydrosilanes to various allyloxy-derivatives was frequently noted also in earlier studies [77-79] and has been described in reviews of the hydrosilylation reaction [76,80,81].

alkylchlorosilanes under the influence of tertiary amines is fully ruled out.

Thirdly, the reaction of $COCl_2$ with alkoxy(alkenoxy, alkynoxy)silanes makes it possible to obtain purely organic chlorocarbonates without HCl, which must usually be removed by special procedures.

The complex (owing to the reversibility of the reaction at high temperatures) stage involving the isolation of organosilicon glycols with carbofunctional substituents (XIII, a–c), (XVIII, b and c), etc. (which are diffiult to obtain in a pure state) during their synthesis from the corresponding silyl ethers (XXI)–(XXIV)†, namely $[-(CH_2)_mOSiMe_2-]_n$ [XXI: (a) $m = 3$, $n = 1$; (b) $m = 4$, $n = 1$; (c) $m = 5$, $n = 1$; (d) $m = 3$, $n \simeq 7-9$; (e) $m = 1$, $n = 2$], $o$-$C_6H_4OCH_2SiMeO$ (XIII), $o$-$C_6H_4(CH_2)_3SiMe_2O$ (XXIII), $o$-$C_6H_4(CH_2)_3SiPh_2O$ (XXIV), etc. is frequently eliminated, because bischloroformates of the disiloxane series can be obtained on a preparative scale by a simpler method involving a combination of the treatment of silyl ethers with phosgene with subsequent hydrolysis of the intermediate monochloroformates:



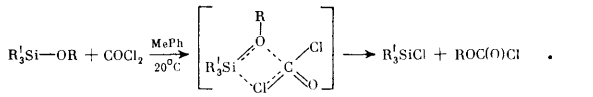
In this connection, it became necessary to investigate in detail the reactivity of the Si–O bonds in various silyl ethers—potential sources of mono- and bis-chloroformates in reactions with phosgene and chloroformates. The reactivity of Si–O bonds in reactions with phosgene depends on many factors and varies within wide limits [31,94]. Thus $Me_3Si$ derivatives of aliphatic alcohols demonstrate a decrease of reactivity: (a) in parallel with the increase in the bulk of the alkyl group: $Me_3SiOMe > Me_3SiOEt \gg Me_3SiOPr\text{-}n > Me_3SiOBu\text{-}n$; (b) on passing to alcohols with a branched structure and to a greater extent the closer the branched site to the reaction centre and the greater the degree of branching: $Me_3SiOPr\text{-}n > Me_3SiOPr\text{-}iso > Me_3SiOcyclohexyl$; $Me_3SiOBu\text{-}n > Me_3SiOBu\text{-}iso > Me_3SiOBu\text{-}s > Me_3SiOBu\text{-}t$.

In the series of trimethylsilyl ether of unsaturated alcohols, the rate of reaction is lower the greater the degree of unsaturation (a): $Me_3SiOPr\text{-}n > Me_3SiOCH_2CH{=}CH_2 > Me_3SiOCH_2C{\equiv}CH$, $Me_3SiOcyclohexyl > Me_3SiOPh$, and the greater the length and degree of branching of the group (b): $Me_3SiOCH_2CH{=}CH_2 > Me_3SiOCH_2CH{=}CHPh > Me_3SiOCH_2C(CH_3){=}CH_2$.

By varying the substituents at the silicon atom, the reactivity of the molecule can also be altered: $CH_2{=}CHCH_2OSiMe_3 > CH_2{=}CH_2CH_2OSiMe_2H$, $MeOSiMe_3 > MeOSiMe_2CH_2Cl$, $Me_3SiOMe > Et_3SiOMe$. Despite the bulky substituents attached to the metal atom, the methoxy-derivatives $Et_3GeOMe$ and $n\text{-}Bu_3SnOMe$ react exothermically with $COCl_2$ and much faster than $Me_3SiOMe$. Conversely, $Me_3SiOCMe_3$ and $Me_3SiOSiMe_3$, as well as certain other disiloxanes vigorously absorb and retain $COCl_2$, but remain unchanged even on heating [31,94,135]. $Me_3SiOMe$ and $Me_3SiOPh$ are resistant to the action of $COF_2$ (at 20°C). [55]

† The principal methods for the synthesis of organosilicon alcohols, phenols, silaoxacycloalkanes, etc. can be found in the following publications (including the attached bibliographies): (a) alcohols [26,27,29–31,98–114]; (b) phenols [29–31,110,114]; (c) silaoxacycloalkanes [29–31,113–115].

The nucleophilic substitution of the alkoxy-group in the silanes $R^1_3SiOR$ in a non-polar medium evidently proceeds via an $S_Ni\text{–}Si$ mechanism with formation of a quasi-cyclic transition complex [136]:



Other conditions being equal, the rate of reaction is therefore determined by the nucleophilic properties of $ROSiR^1_3$, which are in this case determined by the overall influence of the inductive and steric effects of the substituents R and R′ and the effect of the ($p$-$d$) $\pi$-dative interaction via the Si–O bond [137]. Acyloxytrimethylsilanes, where, in contrast to $AlkOSiMe_3$, the lone $p$ electrons of the oxygen atom are involved also in the reverse coordination to the carbonyl oxygen atom: $\equiv Si \leftarrow O\text{—}C(O)R$, therefore exhibit a reduced reactivity. Furthermore, the introduction of electronegative substituents at the silicon atom or the carbonyl group reduces the reactivity of the molecule towards phosgene to an even greater extent [31,94]. For example, acetoxytrimethylsilane reacts faster than $ClCH_2Me_2SiOC(O)Me$, which is in its turn more reactive than $Me_3SiOC(O)CF_3$.

The retardation of the reaction with phosgene on passing from alkoxy- to acyloxy-derivatives can also be followed for germanium and tin compounds, while for acetates of the type $R_3EOC(O)Me$ the rate decreases in the following sequence as a function of E: Sn > Ge > Si [31,94].

The above regularities hold also on treating with phosgene compounds having endocyclic Si–O bonds, although the reaction as a whole acquires a number of new specific features [31]. The main characteristic of such a reaction is that the product of the insertion of $COCl_2$ accompanied by ring opening is formed. The rate of reaction is determined by the size of the heterocycle and the nature of its constituent structural elements. For example [28–31], in the series of silaoxacycloalkanes $Me_2Si(CH_2)_nO$ the rate of ring opening decreases sharply with increase of $n$: compound (XXIa) ($n = 3$) reacts vigorously even in the cold; although the ring of silaoxacyclohexane (XXIa) ($n = 4$) opens spontaneously, the rate of this process at room temperature is low:

$$Me_2Si(CH_2)_nO + COCl_2 \rightarrow ClMe_2Si(CH_2)_nOC(O)Cl \quad ; \quad n \geqslant 3 \ .$$

The oligomeric macrocyclic product (XXId) ($m = 3$, $n \simeq 7-9$) does not react with $COCl_2$ even at 150°C and only in the presence of catalytic amounts of $ZnCl_2$, $AlCl_3$, $FeCl_3$, etc. is it possible to convert it at 100–130°C into the corresponding chlorocarbonate (XVb), but in a low yield (18%). On the other hand, treatment of the products of the thermal depolymerisation of the oligomer (XXId) with phosgene in the presence of $ZnCl_2$ made it possible to increase the yield of the chlorocarbonate to 60%.

However, catalysts of the type of Lewis acids also have a side effect—they initiate the decomposition of the desired chlorocarbonates to alkyl chlorides. Another group of initiators, whose action is based on the cleavage of the Si–O bonds with formation of a free HO group, was therefore proposed [31,88]: treatment of the HO group with phosgene is accompanied by the evolution of HCl, which maintains the reaction. Inorganic acids or hydroxylated organic compounds are used as initiators of this kind.

The decrease of the reactivity of silaoxacycloalkanes in the sequence (XXId) > (XXIa) > (XXIII) ≫ (XXII) > (XXIII) is caused, as in the case of linear silyl ethers, by the reduced nucleophilic properties of the O atom in the siloxy-group. This happens, for example, on passing from compound (XXIe) to (XXIa), eliminating the influence of the *p* electrons of the second oxygen atom, which competes with the conversion of the Si—O linkage into a double bond. For compounds (XXIII) and (XXIV), the cause is different—the involvement of the *p* electrons of the oxygen atom in conjugation with the aromatic ring. The simultaneous presence in the molecule of compound (XXII) of the epoxy- and siloxyaryl groups or the combination in compound (XXIV) of the $SiOC_{Ar}$ fragment with the bulky phenyl substituents at the silicon atom retard sharply the reactions with $COCl_2$.

Thus the reaction of phosgene with silyl ethers, which are intermediates in the synthesis of glycols and bisphenols of the siloxane series, is of preparative value for derivatives of alcohol and is of limited value in the case of a compound with a $Si-OC_{Ar}$ linkage.

The reaction of phosgene with epoxysilanes is of interest as an independent method for the synthesis of organosilicon chlorocarbonates[71]:

$$\equiv Si(CH_2)_3OCH\!-\!CH_2 + COCl_2 \rightarrow \equiv Si(CH_2)_3OCH(Cl)CH_2OC(O)Cl \quad ,$$

a distinctive feature of which is the complete absence of side products.

## 2. Methods of Synthesis of Carbonates

The hydrosilylation of alkenyl carbonates is used to obtain monomeric, oligomeric, and polymeric products containing simultaneously the carbonate and organosilyl groups[29,31,138–145]. The reaction was described for the first time by Haluska in 1976:[138,141,143,144]

$$ROC(O)OA \xrightarrow[H_2PtCl_6]{} \begin{cases} \xrightarrow{HSiR'_nX_{3-n}} ROC(O)OR''SiR'_nX_{3-n} \\ \xrightarrow{HSi(R'_n)O_{(3-n)/2}} ROC(O)OR''Si(R'_n)O_{(3-n)/2} \end{cases} ;$$

R = Alk or Ar; A = alkenyl, $n$ = 1-3; X=OC(O)Me, $NMe_2$, ON=$CMe_2$ etc.

However, since the course of the reaction is treated as unambiguous even in those cases where the initial compounds contain functional groups chemically reactive relative to one another, for example:

$$\equiv Si-H + HOSi \equiv \rightarrow H_2 + \equiv SiOSi \equiv \quad ,$$
$$\equiv Si-H + CH_2=CHSi \equiv \rightarrow \equiv SiCH_2CH_2Si \equiv \quad .$$

the above scheme cannot be regarded as correct. It has been shown[31,145] that the formation of equimolar amounts of $CO_2$, $C_3H_6$, and the corresponding methoxysilanes in addition to $\gamma$-adducts (40–60%) is observed in the hydrosilylation of AllOC(O)OMe. Such proportions of the products of the accompanying reactions have been interpreted as evidence for the formation of unstable $\beta$-adducts, which decompose via a double $\beta$-decomposition mechanism:

$$\begin{matrix} O\!-\!Me \\ | \\ O\!=\!C \\ | \\ O\!-\!All \end{matrix} \xrightarrow[H_2PtCl_6]{R_nCl_{3-n}SiH} \begin{cases} \longrightarrow MeOC(O)OCH_2CH_2(Me)Si \equiv \xrightarrow[2.\ -CO_2]{1.\ -C_3H_6} MeOSi \equiv \\ \longrightarrow MeOC(O)O(CH_2)_3Si \equiv \end{cases}$$

R=Me, Et, or Ph; $n$ = 0 — 3.

Tetramethyldisiloxane and AllOC(O)X (where X = OMe or H) react stepwise via both Si—H bonds, the main and side reactions leading respectively to symetrically and asymmetrically substituted disiloxanes:

$$O\!-\!\left[\begin{matrix} Me \\ | \\ -Si(CH_2)_3OC(O)X \\ | \\ Me \end{matrix}\right]_2 \qquad \begin{matrix} Me\ Me \\ | \quad | \\ X\!-\!SiOSi(CH_2)_3OC(O)X \\ | \quad | \\ Me\ Me \end{matrix} .$$

A general feature of the hydrosilylation of the allyl ethers AllOC(O)X (where X = H, OMe, OAll, or Cl) by hydrosilanes of the same type is a decrease of the fraction of side products as a function of the nature of the group X in the sequence Cl > OMe > H > OAll. For example, diallyl carbonate reacts with hydrosilanes like AllOC(O)OMe, but the liberation of gaseous products in side reactions is observed to a lesser extent, the yield of product (XXV) increasing with increase of $n$ from 56 to 76%:[31,145]

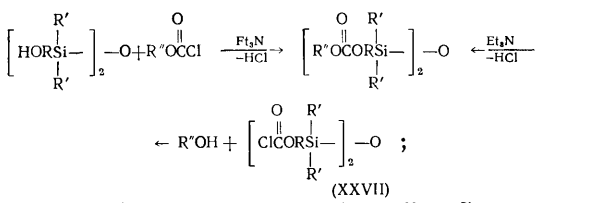
$$Cl_nMe_{3-n}SiH + (AllO)_2CO \rightarrow [Cl_nMe_{3-n}Si(CH_2)_3O]_2CO \quad ; \quad n=1-3 \ .$$
(XXV)

On the other hand, the yield of reaction products diminishes for each AllOC(O)X on passing from $Cl_3SiH$ ($n$ = 3) to less chlorinated hydrosilanes. The tendency towards a decrease of the yield of silyl carbonates with accumulation of alkyl radicals in the initial silane is manifested most clearly by $Et_3SiH$: approximately 14% of the hydrosilane is consumed in the formation of the main product, while the remainder is involved in side reactions with formation of $\beta$-adducts, detected as the products of their $\beta$-decomposition, for example, $Et_3SiOSiEt_3$ and $Et_3Si(CH_2)_3OSiEt_3$.[31,145] Theoretically, these compounds might be formed together with $CO_2$ and propene via the mechanism of the reaction of hydrosilanes and organic carbonates discussed above[39,40]. However, experiments failed to confirm this hypothesis, because the reaction products do not contain $Et_3SiPr$-n and $Et_2SiPr$-iso, which should have been inevitably formed together with the main products.

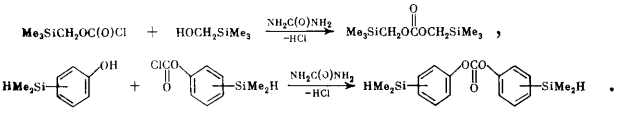
Treatment of organosilicon alcohols and phenols with phosgene leads to symmetrical carbonates if the process does not stop at the stage involving the formation of chlorocarbonates (see Section III, 1). In view of the difficulty of replacing the second chlorine atom in phosgene by an ester group, the reaction is carried out in the presence of organic bases[29–31,42,92,146], for example:

$$HMe_2SiC_6H_4OH + COCl_2 \xrightarrow{Et_3N} (HMe_2SiC_6H_4O)_2C=O \quad .$$
(XXVI)

The reactions of chloroformates with alcohols and phenols lead to symmetrical and asymmetric carbonates with the silicon atom in one or both organic groups [34,138,141,143,144,147-150], for example:



$R=(CH_2)_3$, $(CH_2)_4$, or $(CH_2)_3OCH_2CH(Me)$; $R'=Me$ or Ph; $R''=Me$, n-Bu, $Cl_3C$, or All.



The heterofunctional condensation reaction with participation of siloxy-derivatives and chlorocarbonates makes it possible to obtain organic and organosilicon carbonates and polycarbonates [31,42,55,95]. Compared with phosgene, aliphatic and aromatic chlorocarbonates are less reactive in relation to silyl ethers derived from alcohols and phenols. The reaction proceeds at an appreciable rate only at a temperature of the order of 120–220°C even for alkoxytrimethylsilanes which are most readily cleaved by phosgene:

$$\equiv Si{-}OR + ClC(O)OR' \xrightarrow{t} \equiv Si{-}Cl + ROC(O)OR' .$$

As in the case of $COCl_2$, the $\equiv Si{-}OC_{Ar}$ bond is less reactive than $\equiv Si{-}OC_{Alk}$. On the other hand, the surprising inertness of 1,3-bis(trimethylsiloxymethyl)-1,1,3,3-tetramethyldisiloxane in relation to the bischlorocarbonates (XIVa) and (XIVb) may be a consequence of the steric effect of the $Me_3Si$ group and the stronger $(p\text{-}d)$ $\pi$-interaction via the linkage

$$Me_3Si\overset{\curvearrowleft}{-}O,$$

due to the influence of the second organosilyl group, which usually increases the electron density at the heteroatom in the $\alpha$-position [114].

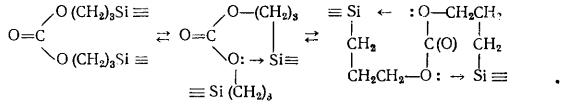
It is of interest that fluorocarbonates are more reactive than chlorocarbonates [55]: ROC(O)F (R = Et, n-Pr, or n-Bu) reacts with $Me_nSi(OR)_{4-n}$ ($n$ = 2, 3) even at 0–20°C with formation of the corresponding carbonates [55].

## 3. The Properties of Organosilicon Chlorocarbonates and Carbonates with Carbofunctional Groups

The available data on the chemical reactions of organosilicon chlorocarbonates and carbonates with carbofunctional groups and their physicochemical properties are fairly extensive and have already been partly surveyed [31]. They make it possible to isolate a number of properties distinguishing this group of compounds from their purely organic analogues.

(a) Infrared spectra. The $\nu(CO)$ band in the infrared spectra of chlorocarbonates and acetates is located respectively in the ranges 1775–1783 and 1739–1786 $cm^{-1}$. The absorption by the carbonyl group in the formates $R_2Si(CH_2)_3OC(O)H$, where $R_3Si$ = $Cl_3Si$, $Cl_2MeSi$, $ClMe_2Si$, $Et_3Si$, $PhCl_2Si$, $(EtO)_3Si$, or $HC(O)OSiMe_3-OSiMe_2$, and in the carbonates $R_3Si(CH_2)_3OC(O)OMe$ and $R_3Si(CH_2)_3OC(O)O(CH_2)_3SiR_3$, where $R_3Si$ = $Cl_3Si$, $Cl_2MeSi$, $ClMe_2Si$, $Et_3Si$, $Cl_2PhSi$, $(EtO)_3Si$, $Me_2(MeO)Si$, or $Ph(EtO)_2Si$, is constant for each series and almost independent of the substituents at the silicon atom: the absorption band in the spectra of the formates is located in the range 1720–1722 $cm^{-1}$ and that in the spectra of the carbonates is in the range 1748–1752 $cm^{-1}$. Comparison showed that, in the series of compounds $\equiv Si(CH_2)_3OC(O)H$, $\equiv Si(CH_2)_3OC(O)OMe$, and $\equiv Si(CH_2)_3OC(O)Cl$, the absorption band is displaced towards shorter wavelengths with increasing electronegativity of the substituent at the carbonyl carbon atom (Cl > OMe > H).

The appearance of a doublet in the region of the $\nu(CO)$ absorption in the spectra of the dicarbonates may be caused by reversible intramolecular coordination:



(b) $^1H$ NMR spectra. Analysis of the integrated spectra for the stable forms of organosilicon chlorocarbonates, carbonates, formates, and intermediate acetates having the general formula $Cl_nMe_{3-n}SiC_3H_6OC(O)X$ (X = H, Cl, OR, or Me), synthesised in different ways, confirms the structure with the trimethylene bridge between the silicon atom and the functional group [28,31,72,73,145].

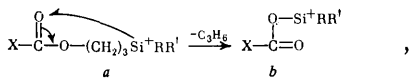
The deshielding influence of the silyl group is a maximum for Si-methylene protons, decreasing with increase of the number of alkyl groups at the silicon atom and decaying rapidly along the chain. The influence of the nature of the substituent X on the $\equiv SiCH_2$ group varies unambiguously both on passing from formates to carbonates and chlorocarbonates for the same silyl substituent and when the silyl group $ClMe_2Si$ is replaced by $Cl_2MeSi$ and $Cl_3Si$ keeping X unchanged. For the protons of the $\beta$- and $\gamma$-methylene groups, the influence of the silyl and X groups is more complex.

Comparison of the chemical shifts of the protons in the $(CH_2)_3$ group in the series of carbonates $(Cl_nMe_{3-n}SiCH_2CH_2O)_2CO$ shows that, on passing from asymmetric to symmetrical carbonates, the deshielding influence of similar silyl groups on the protons in the $\alpha$- and $\beta$-positions relative to the silicon atom diminishes. A decrease is also observed in the degree of deshielding of the $\beta$-protons, the deshielding differing appreciably from the approximately constant value for mono-, di-, and tri-chlorosilyl derivatives of asymmetric carbonates. On the other hand, the tendency towards a decrease of the degree of partial dissociation of $\gamma$-protons in the series of $ClMe_2Si$-, $Cl_2MeSi$-, and $Cl_3Si$-substituted asymmetric carbonates is replaced by the opposite tendency for the symmetrical analogues.

(c) Mass spectra‡. The following features were observed in the study of the mass spectra of the organosilicon formates $R'R_2SiCH_2CH_2CH_2OC(O)H$ [where $R'R_2Si$ = $Me_2ClSi$, $MeCl_2Si$, $Cl_3Si$, $PhCl_2Si$, $(EtO)_3Si$, $Et_3Si$, etc.]

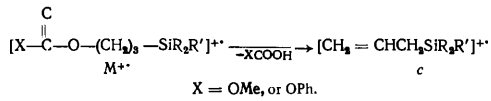
‡ For a comparison of the mass spectra of organic carbonates, see Brown and Gunther [152].

and methylorganosilyl carbonates of the type $R'R_2Si(CH_2)_3.OC(O)OMe$ [where $R'R_2Si = Cl_3Si$, $MeCl_2Si$, $Me_2ClSi$, $(EtO)_3Si$, $Et_3Si$, $MeOMe_2Si$, etc.][31,151]: (a) there are no molecular ion peaks; (b) the peak of the $Si^+R_2R'$ ion has the maximum intensity in all cases, except for the formate with the $(EtO)_3Si$ substituent. The intensities of the $a(M-R)^+$ and $a'(M-R')^+$ ions are low. These ions are sometimes altogether absent. However, the $b(a-C_3H_6)$ and $b'(a'-C_3H_6)$ ions formed via the mechanism



were always observed. This is the mechanism of the rearrangement of trimethylsilylcarboxylic acid esters and chlorides[153,154].

A second characteristic pathway in the decomposition of organosilylcarbonates under the influence of electron impact involves the loss of X–COOH molecules and the formation of the ions c:

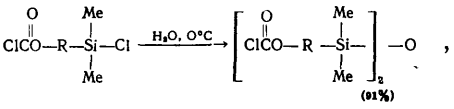


X = OMe, or OPh.

The relative contribution of the decomposition to the ion b or the ion c depends on the nature of the substituents at the silicon atom: with increase of the number of Cl atoms, the contribution of the pathway leading to the ion a increases.

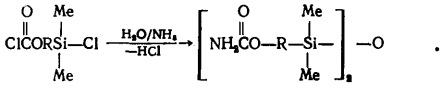
The mass spectrum of $(Me_3SiCH_2O)_2CO$ contains peaks due to the molecular ion with $m/e$ 234 and the $(M-CH_3)$ ion typical for $Me_2Si$ derivatives with $m/e$ 219.

(d) Chemical properties. Organosilicon chlorocarbonates and carbonates may react via the C- and Si-functional centres both separately and simultaneously. Thus hydrolysis of the chlorocarbonates $ClMe_2SiROC(O)Cl$ by ice water leads to the corresponding bischlorocarbonates[28,31,42,86]:

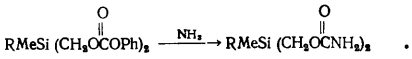


(91%)

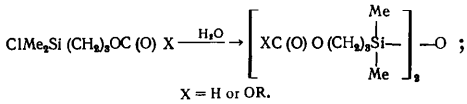
while treatment with aqueous ammonia converts them into the corresponding biscarbamates[28,31,42,75,86,89]:



The latter reaction actually constitutes the specific synthesis of organosilicon carbamates and biscarbamates, which Fessenden and Coon[148,149] obtained by the ammonolysis of the corresponding carbonates and biscarbonates:

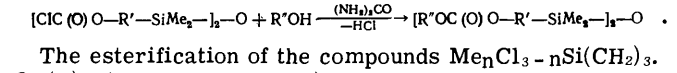


Formates and carbonates are hydrolysed similarly to chlorocarbonates[31,72,145]:

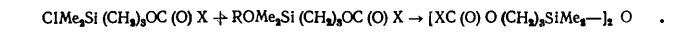


X = H or OR.

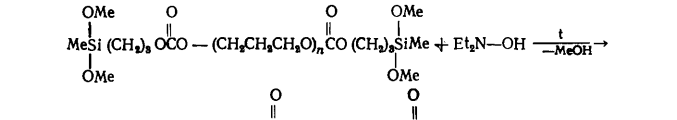
Chlorocarbonates and bischlorocarbonates react with alcohols and phenols to form carbonates and biscarbonates[29–31,91]:



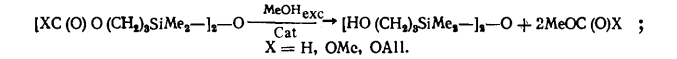
The esterification of the compounds $Me_nCl_{3-n}Si(CH_2)_3.OC(O)X$ (X = H, Cl, or OR) is accompanied by heterofunctional condensation[31,145] via Si–Cl and Si–OR bonds, for example§:



When $Me(MeO)_2Si$-substituted polyoxyalkylene dicarbonates are treated with *NN*-dialkylhydroxylamines, methanol is displaced[140]:

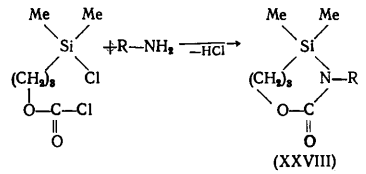


In the presence of toluene-*p*-sulphonic acid or acid ion-exchange resins, organosilicon carbonates are transesterified by the excess methanol, like the acetates and formates[31,72], for example:



X = H, OMe, OAll.

Mono- and bis-chlorocarbonates react with ammonia and organic amines to form carbamates, for example:[28,30,42,89,92,155]

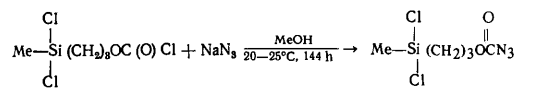


(XXVIII)

Bischlorocarbonates react with hydrazine, aliphatic dihydrazines, acylhydrazines, and diamines in the presence of HCl acceptors to form oligourethanes[31,32,156–160]. It is more convenient to *N*-silylate polyamines in this reaction¶, since the necessity for the removal of corrosive hydrogen chloride and ammonium salts is then obviated[31,32,157].

A similar principle holds in the synthesis of carbonates and polycarbonates, where it proved more convenient to use the silyl ethers derived from alcohols and phenols (rather than the latter themselves) in the reaction with chloroformates[31,96,164] (see below) and in the synthesis of oligosiloxanes with terminal anhydride groups[27], for example from trimellitic acid chloride.

Chlorocarbonates react with alkali metal azides to form the corresponding azidocarbonates[70,71]:



§ Disiloxane may also be formed owing to the presence of $H_2O$ formed by the reaction MOH + HCl → MCl + $H_2O$.

¶ The reactivity of the Si–N bonds in various aminosilanes in relation to organic chlorocarbonates has been studied[161,162].

In the presence of an organic base, t-BuOOH esterifies chlorocarbonates like alcohols [165]:

$$(MeO)_3Si(CH_2)_3OC(O)Cl + HOOBu\text{-}t \xrightarrow[0°,\ 3\ h]{Py,\ Et_2O} (MeO)_3Si(CH_2)_3OC(O)OOBu\text{-}t.$$

The specific synthesis of this peroxide consists in the hydrosilylation of AllOC(O)OOBu-t in the presence of Speier's catalyst [165]:

$$(MeO)_3SiH + CH_2=CHCH_2OC(O)OOBu\text{-}t \xrightarrow[3\ h]{50°C} (MeO)_3Si(CH_2)_3OC(O)OOBu\text{-}t.$$

Bis(organosilylalkyl)-substituted percarbonates have been synthesised from organosilicon chlorocarbonates and hydrogen peroxide [166]:

$$(MeO)_3Si(CH_2)_3OCCl + HOOH \xrightarrow[10°C]{Py} (MeO)_3Si(CH_2)_3OC(O)OO(O)C(CH_2)_3Si(OMe)_3 .$$

The chlorocarbonate $Me_3Si(CH_2)_3OC(O)Cl$ and its organic analogues [167] can be converted into the corresponding aldehydes [31,95]:

$$Me_3Si(CH_2)_3OCCl \xrightarrow{DMSO} \left[Me_3Si(CH_2)_2CH_2-O-C(=O)-S(Me)(Me)\right]Cl^- \xrightarrow[CO_2]{Et_3N} Me_3Si(CH_2)_2C(O)H.$$

However, the sulphoxonium salt derived from $Me_3SiCH_2OC(O)Cl$ forms $ClCH_2SiMe_3$, which is probably due to the enhanced basicity of the oxygen atom in the $\alpha$-position relative to the $Me_3Si$ group:

$$\left[Me_3SiCH_2-O-C(=O)-S(Me)(Me)\right]Cl^- \xrightarrow[-CO_2]{Et_3N} [Me_3SiCH_2OSMe_2]Cl^- \xrightarrow[-Me_2SO]{} Me_3SiCH_2Cl .$$

It is also extremely significant that the steric effect of the $Me_3Si$ group prevents the abstraction of a proton under the influence of $Et_3N$.

(e) Practical importance. It is seen from the foregoing that chlorocarbonates are used to synthesise mono- and bis-carbonates, mono- and bis-carbamates, mono- and bischlorocarbonates, azidocarbonates, organosilicon peroxides, alcohols, diols, aldehydes, heterocyclic compounds, etc. Bischlorocarbonates serve as the basis for the synthesis of silicon-containing polyurethanes and polycarbonates. Positive results have been obtained when carbonates and formates were used as vulcanising agents in the cold hardening of silicon rubbers [31]. Polysiloxanes with carbonatoalkyl(aryl) substituents in the side chains, at the ends of the chains, or in the main polymer chain are obtained from mono- and bis-carbonates with hydrolysable groups at the silicon atom.

All these examples of the practical employment of carbonates are considered in detail in Sections IV and V.

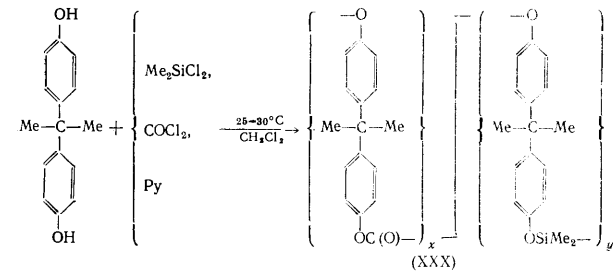
## IV. SILICON-CONTAINING POLYCARBONATES

The overall group of silicon-containing polycarbonates (SCPC) includes statistical copolymers, block copolymers, and other compositions.

### 1. Methods of Synthesis

The SCPC are obtained by treatment with phosgene, transesterification, hydrosilylation, radical polymerisation, and other methods.

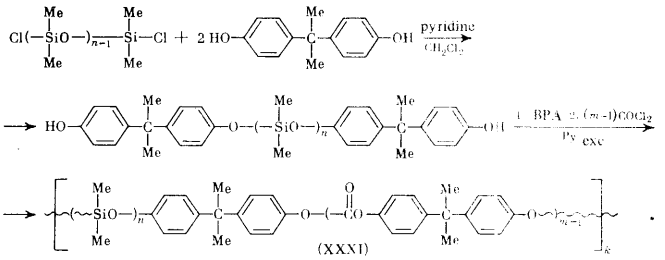
(a) Treatment with phosgene. Two procedures have been proposed for the synthesis of SCPC: firstly, by replacing parts of the phosgene in the treatment of bisphenol A (BPA) with the latter in pyridine by dichlorodimethylsilane (DCDMS), copolymers (CPL) containing bisphenol-carbonate and bisphenol-siloxy-groups were obtained [168-170] (Goldberg's method):



(XXX)

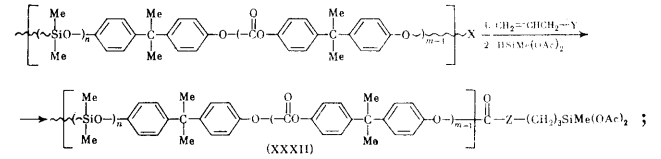
In the second version of the synthesis, an oligocarbonate with $\alpha\omega$-hydroxy-groups is obtained and made to react with DCDMS in the presence of pyridine [168]. When $Me_3SiCl$ is present in the reaction mixture, organic polycarbonates with terminal $Me_3SiO$ groups are obtained [171].

However, these procedures have found only limited applications [172-175] and were subsequently modified [176-203]. Siloxane-carbonate block copolymers, used to make gas-separating membranes, have now been synthesised by the modified method. The modification involves the replacement of DCDMS by an oligosiloxane with terminal Si–Cl bonds (Vaughn's method), which makes it possible to obtain a copolymer with a predetermined content of siloxane blocks whose size is known beforehand [176,180,188,195]:



(XXXI)

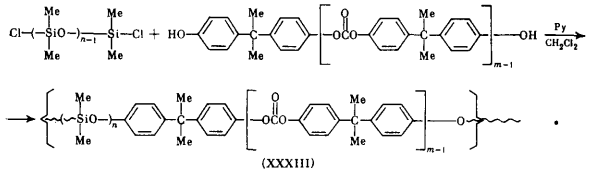
A logical development of this research was a method for the synthesis of block copolymers of type (XXXI) with terminal hydroxy (in the presence of an excess of BPA) or chlorocarbonate (in the presence of an excess of $COCl_2$) groups. After treatment with AllNCO in the former case and with AllOH or allylphenol in the latter, the products are forepolymers capable respectively of being hardened either directly or after hydrosilylation, for example with diacetoxymethylsilane [177,178,184,185,187]:



(XXXII)

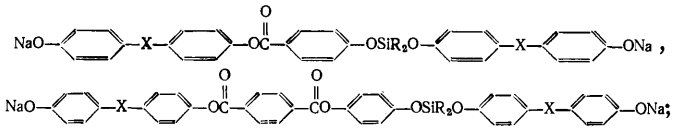
(a) X = OH, Y = NCO, Z = NH; (b) X = C(O)Cl, Y = OH, Z = O .

A variety of this method consists in the copolycondensation of a $\alpha\omega$-dichloropolydimethylsiloxane oligomer with a BPA-carbonate oligomer[197]:



(XXXIII)

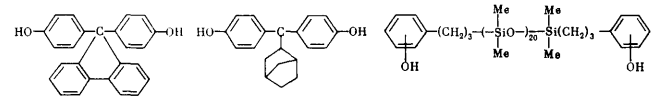
The synthesis of SCPC by treating aryloxysilanes of the type



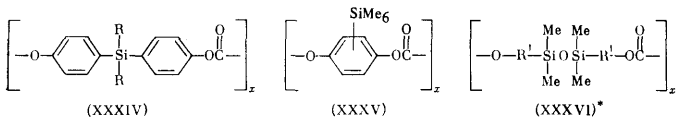
R = Alk or Ar; X=S, O, SO, $SO_2$ etc.

with phosgene has been reported[204].

In the vast majority of studies, BPA or tetrachloro-BPA is used as the bisphenol in the synthesis of SCPC by the above method, while hydrogen chloride is bound by pyridine. The compounds

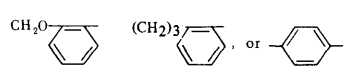


etc. have been recently proposed[186,205] as the dihydroxy-compounds and pyridine has been replaced by $NH_3$ [182] or alkali metal hydroxides[181]. Dichloromethane is a generally used solvent in the stage involving treatment with phosgene. The copolymers are obtained in a pure form by precipitation from solutions with lower alcohols. In all the studies enumerated, polymers were obtained with an Si–OAr bond susceptible to hydrolysis. In order to eliminate this disadvantage, a study was made of the treatment with phosgene of organosilicon diols and bisphenols containing carbofunctional groups and a fundamentally new set of SCPC [(XXXIV),[206,207] (XXXV),[208] and (XXXVI)[31,96,116,209]] was obtained:



(XXXIV) (XXXV) (XXXVI)*

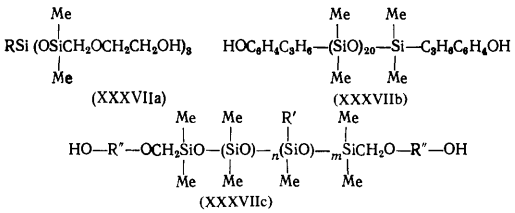
R = Me or Et; R' = $(CH_2)$, $(CH_2)_3$, $CH_2O(CH_2)_2$, $CH_2S(CH_2)_3$,



Apart from the direct treatment of dihydroxy-derivatives with phosgene, modified syntheses of SCPC have been carried out: (a) with partial replacement of the silicon-containing diol or bisphenol by BPA or 1,1-bis-(4-hydroxyphenyl)-cyclohexane (BHPC),[31,96] (b) with partial replacement of $COCl_2$ by silicon-containing bischlorocarbonates with carbofunctional groups[31,96], and finally (c) with complete replacement of $COCl_2$ by a mixture of organic and organosilicon bischlorocarbonates† [164,210].

† Dihydroxy-derivatives with R = $CH_2O(CH_2)_2$, $CH_2S(CH_2)_3$, $CH_2O-C_6H_4$, etc. are considered in this section in view of the similarity of their properties with organosilicon diols and bisphenols containing other carbofunctional groups.

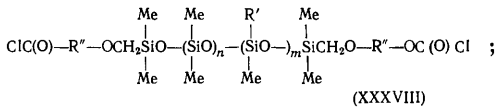
In many cases, oligosiloxanes containing hydroxyalkyl and hydroxyaryl substituents at the silicon atom are used in order to increase the content of siloxy-units in the SCPC:[23-27,164,187,205,211]



(XXXVIIa) (XXXVIIb)

(XXXVIIc)

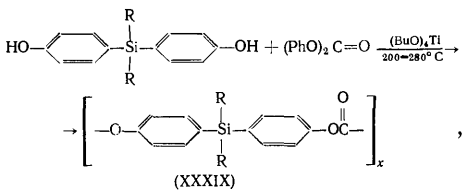
or the corresponding bischlorocarbonates (XXXVIII) are employed, for example[164,210]:



(XXXVIII)

a) R=Me, $m = 0$, $n = 10$; (b) R = vinyl, $n = 6$, $m = 2$;
(c) R=Me, $n = 56$, $m = 0$; (R'' = $-CH_2OCH_2CH_2-$) throughout.

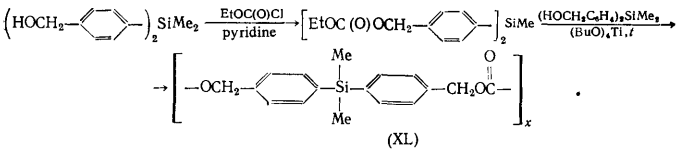
(b) Esterification, hydrolytic, etc. reactions. SCPC are obtained by the transesterification of organic carbonates[206,207] by organosilicon dihydroxy-compounds:



(XXXIX)

where R = Me or Et.

It has been shown[150] that silicon may be present in both initial reactants:



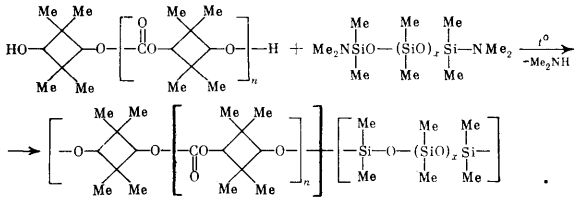
(XL)

It is of interest that compounds of the type $Ph_4Si$ and $Ph_2(EtO)SiH$ are used as catalysts of the reaction of carbonic acid esters with aromatic dihydroxy-compounds both separately, in combination with one another, or in mixtures with alkali metal fluoroborates[212-214]. Presumably they are involved in dehydrocondensation, esterification, and transesterification reactions and probably form part to some extent of the composition of the final polymer in a chemically combined form.

Block copolymers based on a polycarbonate (PC) with terminal $\alpha\omega$-hydroxy-groups and an organopolysiloxane (PS) with 2–4% of Si–OH groups are obtained by heating the initial components in tetrahydronaphthalene at its boiling point. The initial mixture can also include a polyester based on a mixture of tris(hydroxymethyl)propane with ethylene glycol and dimethyl terephthalate. In the latter case, tolylene di-isocyanate or its adduct with tris(hydroxymethyl)propane is added in order to harden varnish compositions, for example[215,216].

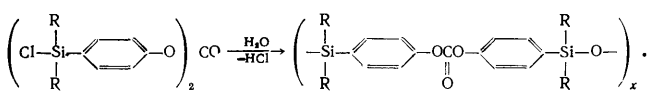
Polyoxyalkylene (POA) with a terminal carbonate group and PS blocks may be linked chemically in the presence of the corresponding combinations of functional groups in pairs (≡Si–H/alkenyl, ≡Si–H/HOC–, and ≡Si–OAlk/HO–C≡) by hydrosilylation, dehydrocondensation, and transesterification reactions[217-222]. It has been reported that αω-$(HO)_2$-PC esterify αω-$Cl_2$-PS in the presence of a tertiary amine, after which the copolymer is made to undergo heterofunctional polycondensation with $MeSi(OAc)_3$ via the ≡Si–Cl groups introduced in excess[223,224].

However, the method of synthesis of SCPC based on the interaction of αω-$(Me_2N)_2$-PS and αω-$(HO)_2$-PC, carried out in a homogeneous medium with formation of the readily removed volatile dimethylamine, has attracted more attention[218,220,221]:



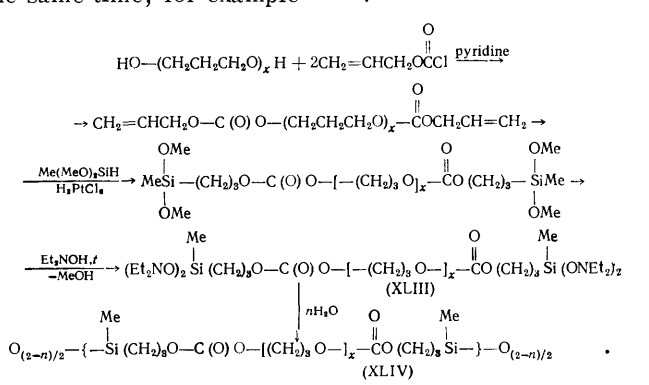
(XLI)

Hydrolysis of organosilicon carbonates containing carbofunctional substituents with participation of the functional groups at the silicon atom is a general method for the synthesis of organopolysiloxanes containing carbonate groups in the polymer side chain, for example[138,143,144,146,216,225]:



(XLII)

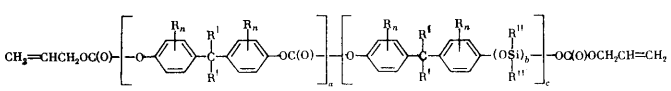
(c) The hydrosilylation reaction. This reaction has a wide scope in the synthesis of SCPC.[139,140,142,177,178,185,218,219,225-231] Its main purpose is to link together the organic and organosilicon components of the polymer. However, the no less important problem of imparting to the adduct the capacity for being vulcanised via the simplest possible scheme is frequently solved at the same time, for example[142,230]:



(XLIII)

(XLIV)

(d) Radical polymerisation. Copolymeric organopolysiloxane-polycarbonates with terminal allyl carbonate groups[139,140,142,177,178,185,228-231]



are mixed with an organosilicon dithiol selected from a group of compounds of the type $[HS(CH_2)_3]_2SiMe_2$, $[HS(CH_2)_n]_2SiMeEt$, and $[HS(CH_2)_3SiMe_2]_2O$, a suitable solvent is added (ethyl methyl ketone, $CH_2Cl_2$), and the system is hardened by irradiation with light in the range 100–20 000 Å at 0–50°C. Vulcanisation takes place as a result of the addition of HS groups to the double bonds[232].

The introduction of a polysiloxane containing vinyl groups has a favourable effect on the properties of the copolymer of diallyldiglycol carbonate and methyl methacrylate. The copolymerisation is carried out in the presence of peroxide catalysts or under the influence of ultraviolet light[233]. The possibility of the copolymerisation of a BPA-based polycarbonate with an unvulcanised silicon rubber in the presence of kaolin (filler), a naphthalene plasticiser, hydroquinone, and a mixture of benzoyl and t-butyl peroxides has been demonstrated[234]. For example, organosiloxane elastomers are obtained by the interaction of the mixture obtained on copolymerising $(Me_2SiO)_4$ and $(MeVinSiO)_4$, $SiO_2$, $Ph_2Si(OH)_2$, and the ester $[BuOCH_2CH_2OC(O)OCH_2CH_2]_2O$ containing a carbonate group in the presence of benzoyl peroxide or on heating[235].

Organic percarbonates and organosilicon percarbonates with carbofunctional groups are used for the vulcanisation of polysiloxane materials[165,236-240].

(a) Other compositions based on silicon-containing polycarbonates. Complex compositions incorporating a wide variety of components and containing both a carbonate group and a silicon atom are known. The effective operational characteristics of these compositions are sometimes retained for a long time, although chemical bonding between the components is either not evident or absent altogether. For example, in order to increase the ultimate strength of plastic lubricants, the latter are thickened with finely dispersed amorphous $SiO_2$ and $C_2$–$C_{18}$ alkylene carbonate is added as the dispersing agent. The resulting lubricant has a penetrability of 251 and can be used successfully at high temperatures[241]. $(SiO)_n$ ($n$ = 1, 2) can form part of the composition based on a high-molecular-weight linear polycarbonate[242].

Polycarbonate-siloxane compositions, which do not adhere to the mould during compression moulding or casting, are obtained by combining an aromatic polycarbonate with solid crystalline phenylcyclosiloxanes[243]. The introduction of a polysiloxane into a polycarbonate is carried out in mixers of the usual type, for example, in a screw-conveyor granulator[243]. The introduction of a polysiloxane into a polycarbonate lowers the viscosity of the melt, increases its resistance to the action of moisture, and reduces its adhesion to the surfaces with which it is in contact and thereby facilitates its processing by pressing, casting under pressure, extrusion, and other methods[235,243-248]. The addition of a polysiloxane and 0.1–2.0% of an alkali or alkaline earth metal carbonate to a polycarbonate also ensures a high resistance of the composition to the action of light at an elevated temperature[249].

The intermediate formation of silyl carbonates is possible during the hardening of αω-$Cl_2$-PS with the aid of a mixture of $CaCO_3$, $SiO_2$ of type U-333, $(EtO)_4Si$, and ethanolamine[250,251] and also in the preparation of moulded foam silicate articles with the composition thickened before foaming (when liquid sodium glass is treated with organic chlorocarbonates as the gel-forming agents)[252].

Silicon may be introduced into the composition of carbonate-containing articles by employing organosilicon compounds as surface-strengthening agents or binders [253-257]. It is also introduced into polycarbonate compositions together with glass fibre (frequently employed for reinforcement [10,11,230,258-261]), silicon carbide [230], and magnesium silicate [262]. In order to modify their surface properties, polycarbonate articles are coated by a solution of an organopolysiloxane with functional substituents [263].

SCPC compositions have been developed in which one of the components is a polycarbonate or poly(vinyl chloride), while the second component is a polycarbonate containing at least one organic substituent with an imide group [264]. Silicon compounds are effective stabilisers of the properties of polycarbonates. For example, the addition of 0.002–0.005% of a high-molecular-weight linear polysiloxane to a polycarbonate makes it possible to obtain homogeneous transparent films. The fibre-forming properties of polycarbonates are improved at the same time [245]. The introduction of 0.1–25.0% of organosilicon halogen-containing compounds into polycarbonate compositions imparts to the latter thermal stability, capacity for internal plasticisation, and self-quenching properties [265].

In order to stabilise the colour of the polycarbonate during its processing, ultramarine and triphenyl or trihexyl-silane are added in amounts of 0.1 and 0.01% respectively [266]. Instead of compounds of the type $R_3SiH$, it is possible to use for this purpose a polysiloxane, for example, methylphenylpolysiloxane, or $SiO_2$ with a hydrophobic coating [267]. Polycarbonates stabilised in this way are resistant to the action of atmospheric moisture, heat, solvents, and wear.

It is believed that the hardening of $\alpha\omega$-$Cl_2$-PS is accelerated in the presence of ammonium carbonate and bicarbonate [268], guanidinium carbonate [269], $(HOCH_2CH_2.NMe_3)_2CO_3$, [236] and Group I, II, and VIII metal carbonates [140,178,205,217,229,230,249-251,271-279].

## 2. Physicochemical Properties of SCPC

The physicochemical properties of SCPC must be considered separately for polysiloxane-polycarbonate block copolymers and similar compounds, SCPC based on organosilicon monomers with carbofunctional groups, and other types of mixed compositions.

(a) Properties of polycarbonates with ≡SiOCAr linkages. Conditions have been found for the preparation of polycarbonates with ≡SiOCAr linkages in the form of single crystals and their physical properties have been investigated [170-175,193-204,260,279-285]. It has been established that the single crystals of SCPC block copolymers have a hexagonal unit cell [197,199], in contrast to BPA-PC and PDMS, which crystallise with a helical structure containing unit cells of the orthorhombic and monoclinic types respectively [281,282].

The changes in the mechanical, optical, and dielectric characteristics of the block copolymers have been studied in detail as a function of the size and the relative contents of the polycarbonate and polysiloxane blocks in the macromolecule [170-175,193-204,260,279,280]. The study of the equilibrium swelling of SCPC specimens having different compositions, swelling as a function of the deforming stress and deformation frequency, small- and large-angle X-Ray scattering, double refraction, and optical dichroism for block copolymers in the swollen and solvent-free states established that there is a distinct tendency towards the association of the polycarbonate blocks into discrete randomly distributed domains. According to X-ray diffraction and electron microscope data, the average distances between the domains are 50–500 Å. [196,201] It has been established that the dielectric losses of the copolymers with short blocks are greater than for those with large blocks [285]. At the same time, the strength of the block copolymer films increases with increasing content of polycarbonate units and the elongation coefficient diminishes correspondingly [195]. With increase of the content of siloxy-groups in copolymers, the softening temperature falls and the intrinsic viscosity decreases [170,172-175].

The thermal decomposition of SCPC begins to develop at an appreciable rate at 350°C owing to the rupture of the ≡Si–O–C≡ linkages. The ultimate tensile strength of the polymer at 100°C is lower by a factor of two than at 20°C. Cooling to −150°C is accompanied by the brittle rupture of the film specimens [174,175]. At the air–water interface, the block copolymers form a monolayer comprising polysiloxane blocks, while the polycarbonate blocks protrude above the interface [193,198]. The surface activity of mixtures of BPA-based polycarbonates and block copolymers deposited in the form of thin, strong films on glass was studied by determining the wetting angles by means of a telescope having a low resolving power and fitted with a goniometer eyepiece [200]. The wetting angles for water on certain copolymer films are in the range between 90 and 100°, which is analogous to the values for PDMS films adsorbed on surfactants [286].

It has been established that the wetting effect depends strongly on the copolymer concentration, the polysiloxane content, and the length of the blocks. After the removal of the films from the surface of glass, the wettability of the latter resembled that of the homopolymer. Consequently the copolymer is absorbed on the glass–polymer interface during the casting process and remains on the surface after the removal of the film. This is confirmed by the finding that a copolymer film with a high polysiloxane content can be removed from the glass by heating or by treatment with a solvent.

For a comparative analysis, one should bear in mind the study [287] of monomolecular films of polymethyl(n-alkyl)siloxanes on organic liquids, including propylene carbonate.

(b) The properties of SCPC based on organosilicon bischlorocarbonates. SCPC in which the silicon atoms are combined exclusively with carbon apart from being involved in SiOSi linkages have been obtained by interfacial condensation at the boundaries between phases based on the organosilicon diols (XIIIa), (XIIIb), (XIIId), (XXVIIa), and (XXXVIIc) and the bisphenols (XVIIIb), (XVIIIc), and (XXXVIIb) with partial or complete replacement of $COCl_2$ by the corresponding bischlorocarbonates (XIVa), (XIVb), (XIVd), (XXXVIIIa), (XXXVIIIb), (XXXVIIIc), (XIXb), and (XIXc). [31,96,116,164,201,206,207,209,210,288,289] 1,1-Bis-(4-hydroxyphenyl)cyclohexane (BHPC) [31,96,288] and BPA [164,201,289] were used as the aromatic dihydroxy-compounds (DHC).

A characteristic property of the SCPC obtained from BHPC and the bischlorocarbonates (XIVa), (XIVd), (XIXb), and (XIXd) in a mixture with $COCl_2$ is a tendency towards a decrease of the intrinsic viscosity, the softening temperature, and the yield with increasing mole fraction of the bischlorocarbonate in the initial mixture of acid chlorides.

Turbidimetric titration data indicate the formation of copolymers with a fairly narrow molecular weight distribution. X-Ray diffraction analysis of the copolymers [31] reveals a low degree of order in their structure regardless of the nature of the bischlorocarbonate employed, which has been explained by the steric effect of the cyclohexyl group of BHPC, which prevents the crystallisation of the macromolecules.

Thermomechanical curves [31] show that the introduction of ≡Si–O–Si≡ groups into the macromolecule of a BHPC-based homopolycarbonate causes a monotonic decrease of $t_g$ and $t_{flow}$, which confirms the determinations of $t_{soft}$ in a capillary. A characteristic feature of these curves is the presence of small regions corresponding to the viscoelastic state.

Data for the thermo-oxidative degradation (thermogravimetric analytical method) [31] of copolymers based on BHPC and the bischlorocarbonate (XIVa) show that both the initial rate of gas evolution and the total amount of gaseous products increase. Methane, ethylene, etc. were detected in the decomposition products, which indicates the elimination of the $Si-CH_3$ groups together with CO, $CO_2$, etc., whose liberation is associated with the degradation of the $-OC(O)O-$ groups.

The amount of water absorbed by the film ($E$, %) [31] decreases from 0.2% for homopolycarbonate obtained from BHPC to 0.01% for the copolymer based on the bischlorocarbonates (XIVa) and (XIVb), while for the bischlorocarbonates (XIXa) and (XIXb) it is in general close to zero. Furthermore, the copolymers exhibit a higher resistance to the action of aqueous alkali compared to organic polycarbonates. Among the series of specimens investigated, the copolymers with 30% of organosilicon fragments showed the greatest resistance to hydrolysis [31]. An important property of the copolymers obtained is their effective adhesion to glass [31].

Protective films made of the copolymers deposited on silicate glass by immersion in 3–5% solutions in chloroform do not impair the optical properties of the glass but at the same time increase its resistance to impact and wear by erosion under dynamic conditions.

The study of the dielectric characteristics of the copolymer based on BHPC and its analogues modified with the bischlorocarbonates (XIVa) and (XIVb) showed [31] that the volume resistivities $\rho_V$ of both copolymers are in the range $(3.0-4.0) \times 10^{15}$ Ω cm; when the frequency increases from 100 to $1 \times 10^6$ Hz, tanδ for SCPC modified by the bischlorocarbonate (XIVa) rises from $4 \times 10^{-3}$ to $9.7 \times 10^{-3}$, while that of the specimen modified with the bischlorocarbonate (XIVb) rises from $2.7 \times 10^{-3}$ to $7.6 \times 10^{-3}$. The dielectric constant remains virtually unchanged (2.3) in the same frequency range. At 50 Hz, the dielectric strengths of the copolymers are 300 and 210 kV $mm^{-1}$ respectively for the SCPC incorporating the $O[SiMe_2CH_2-]_2$ and $O[SiMe_2CH_2OCH_2CH_2-]_2$ groups.

The copolymers are formed in the form of viscous transparent liquids (which can be drawn into filaments), waxy masses, or colourless powders soluble in benzene, toluene, chlorohydrocarbons, etc. Depending on the method of synthesis and the type and ratio of the organic and organosilicon components of the initial mixture, the softening temperature varies from 25° to 175°C and is lower the greater the number of siloxy-units in the copolymer. The copolymers are resistant to hydrolysis.

The transparency of films 40–50 μm thick, cast from solution, to light in the visible region reaches 80–85%. An increase of transparency with increasing content of siloxane groups has been noted.

It is noteworthy that both elastic [31] and brittle [164] SCPC have been obtained from the bischlorocarbonate (XIVa). Elastic and at the same time strong films have been made from bischlorocarbonates with a higher silicon content.

Furthermore, in contrast to the SCPC with $\equiv SiOC_{Ar}$ fragments where an increase of the number of ≡Si–O linkages leads to a decrease of thermal stability [173], the copolymers based on organosilicon bischlorocarbonates containing carbofunctional substituents lose weight starting from 300°C and decompose vigorously at 400–450°C.

Consequently, the introduction of siloxane-containing fragments into the macromolecules of rigid-chain polycarbonates increases to some extent the elasticity of the copolymer and reduces $t_{soft}$ and $t_{flow}$, which is of great practical importance, when the thermal stability is maintained, since it simplifies the conditions necessary for the processing of the polycarbonates by casting under pressure. The capacity of the copolymer for adhesion combined with effective optical characteristics, impact strength, and erosion resistance suggests that they may prove to be valuable constructional materials. The decrease of the amount of water absorbed by the films due to the hydrophobic organosilicon components can probably be used to reduce the hygroscopicity of the polycarbonate when it is stored in granular or powder form.

## V. PRACTICAL APPLICATIONS OF SILICON-CONTAINING POLYCARBONATES AND RELATED COMPOUNDS

By virtue of the successful combination of the practically useful properties characteristics of polysiloxanes and polycarbonates, the SCPC and related compounds, mixtures, and compositions may find and are already finding extensive applications in various branches of science and engineering.

Silicon-containing polycarbonate resins possess effective mechanical [31,96,138,143,164,170,175,176,179,181–185,188,194,196,197,201–204,220,221,285,290,291,294], optical [31,64,96,170,172,175,181,182,201,206,210,216,288,292], and dielectric [31,96,164,168,172,221] properties, exhibit thermal stability and resistance to thermal oxidation [10,11,31,96,164,168,172–174,179,180,184,185,199,204,218,220,261,294,295], are fire- [204,262,295] dirt-, oil-, petrol-, and water-resistant [31,96,257,263], etc. which, considered as a whole, makes it possible to regard them as a new independent group of silicone materials [6,12,26,27,96,142,144,150,164,169,170,173–177,181–185,187,188,190,191,195,205,210,218,220,221,223,226,246,255,256,291,294,296].

The SCPC specimens investigated have molecular weights up to 150 000 [96,164,175,196,199,201] and can be readily converted into fibres, films, and other articles. For example, the film-forming properties of the SCPC [31,144,164,168,176,177,180–185,188,192,193,197–200,206,207,216,220,221,297] are used nowadays to obtain protective coatings on wood, paper, metals, glass, textiles, plastics, etc. [31,96,142,164,184,185,188,216,218,230,254,298–301], which can be soft or hard depending on the type and composition of the polymer [31,204,292,293], may be resistant to light and chemical and thermal effects, and may exhibit viscoelastic properties. Even in a thin layer, they are distinguished by impact strength [31,96,138,143,204,292–294], resistance to erosion [31,96], capacity for adhesion to the support [31,96,172,188,225,228], and a unique gas separating capacity [9,31,302–318]. The Dupont and Owens Companies (USA) developed new coatings of the "Glas resins", "Absite", "Sierracin 311", and "Sierracin 900" types, which serve to protect the glass in aeroplane navigation lights, the coating being resistant to scratching

and friction and the action of solvents, fuels, and sea-water [299,300]. Non-misting coatings with satisfactory adhesion to glass and a high transparency [319], hardness, thermal stability, resistance to the action of acetone and dirt [259,263], and capacity to increase the resistance of glass to the frontal pressure of a shock wave [301] are known.

SCPC are used as foam stabilisers in the manufacture of foam polyurethanes [139,217,219,228,229,231], in the manufacture of electrical insulators, dielectric solutions for condensers (KUS 13°), etc. [168,169,177,320], as finishing compositions for sewing thread [321], packing materials, varnishes, binders, hermetically sealing compounds, moulding materials, cements [165,168,177,215,230,233,255-257,322], hair-treatment agents [222], and water-repellent filamental additives to granulated polycarbonates [248]. By virtue of the combination of transparency, softness, wettability, and permeability to oxygen, SCPC are used as materials for optical lenses correcting astigmatism [292].

The presence of silicon in SCPC in a chemically bound form or as an additive to the polycarbonate facilitates the conditions required for their processing, since it lowers the softening temperature and the viscosity, increases the thermal stability, homogeneity, transparency, and moisture resistance, improves the fibre-forming properties, imparts to the material the capacity for internal plasticisation and self-quenching properties, and stabilises the fundamental technical operational characteristics with respect to time [170,171,212-214,235,243-247,261,262,265-267,275,295,323]. Ammonium, substituted ammonium, guanidinium, and alkaline earth metal carbonates facilitates the hardening of polyorganosiloxanes and at the same time play the role of fillers [178,219,229,236,250,251,268-276,278,324]. There is then a possibility of the formation of low-modulus specimens of silicone rubber and of elastic polymeric materials with a low contraction coefficient, improved thermal stability, and adhesion, and other useful properties [276]. Silicon oxides mixed with aluminium and magnesium oxides or separately, silicon carbide, fibreglass, and alkali metal chlorides and bromides are introduced into polycarbonate compositions to promote structure formation, for their reinforcement, to make them fire-resistant, etc. [10,11,142,235,242,258-261,295,325]. Organic and organosilicon percarbonates are used as initiators of the polymerisation of PDMS and their copolymerisation with other monomers, for example styrene and acrylonitrile [165,166,237-240]. After structure formation and hardening, SCPC can be used as moulded articles [218,224,251,252]. The main practical application of SCPC, which has led to a vigorous search for ways of synthesising these polymers and to a comprehensive investigation of their properties, is for the separation of mixtures of gases and vapours. The employment of the gas-separating capacity of SCPC in medicine has been considered in a review [312]. It remains to add that, according to the advertising leaflets of the General Electric Company (USA), the films and capillaries made of block copolymers based on polysiloxanes and polycarbonates of type "MEM-213" combine permeability to gases close to that of the most permeable silicone rubbers [326-347] with a high gas-separating selectivity, which led to the inclusion of these copolymers among the 100 most important industrial products in 1969. [311] They proved to be suitable for use not only in medicine but also in space, under water, etc. [305-310] It has been shown that, when nitriles, vinyl monomers, or aromatic hydrocarbons are deposited by the plasma method on these copolymers in the form of ultrathin coatings with a thickness $\leq 0.5$ μm, the ratio of the permeabilities to $H_2$ and $CH_4$ increase appreciably (from 0.87 to 33 for PhCN). [305]

A method has been developed for the preparation of ultrathin gas-permeable membranes with a thickness of ~1 μm. [303] It is known that "MEM-213" can form part of more complex polymeric compositions for the same purpose [353]. On the other hand, the search for improved copolymers has continued using other dihydroxy-compounds, including silicon-containing ones [186]. It has been shown that polysiloxanes mixed with hydrated polycarbonates are suitable for the removal of carcinogenic polycyclic hydrocarbons from tobacco smoke [302].

During the preparation of the manuscript for the press, additional studies on the subject of this review were published [354-425].

There are new examples of the synthesis of SCPC [355-358,368-374,405,406,421-423,425] and methods have been described for the preparation of a wide variety of compositions with various properties [373-387,389,399,401,402,413,418-424].

The structure of SCPC has been investigated by X-ray diffraction [360,417], light absorption, light scattering in the presence of various types of deformations [360], and $^1H$ NMR. [362] Studies have also been made on the chemical, physicomechanical, and dielectric properties of SCPC, the phenomena at interfaces [358,359,361,364,367,388,400,407,410,413,415], and permeability to gases [354,366,412,416].

SCPC have been used in articles required for membrane techniques [354,363,366,407-409,411,412] in electrophotography [389], in medicine in the oxygenation of blood, and in astronautics and aquonautics [354,363,365]. Data have been published on the preparation of SCPC-based film coatings on articles [367,398]; SCPC have also been used to prevent the dyeing of polycarbonates [373] and to stick together the components of various materials [388,396-399,410].

It has been shown that BPA-based polycarbonates are adsorbed from solutions on aerosil [394] and that alkali metal carbonates can serve as fillers for polysiloxanes and as catalysts of their hardening [387], while $Ph_3SiCl$ and $Me_3SiCl$ have been recommended for the regulation of the molecular weights and thermal stabilisation of polycarbonates [424]. Oligomeric bischlorocarbonates have been used in the synthesis of silicon-containing polyurethanes [403,404]. The practical properties of SCPC have been examined in detail in a review [426].

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# Photoelectric Phenomena in Polymeric Selenium Structures

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In order to clarify the phenomenon of non-photoactive absorption in molecular solids we have analysed the relationship between the spectra of photoelectric phenomena in selenium and the molecular (and supermolecular) structures of selenium. Non-photoactive absorption is shown to arise from the photo-generation of charge carriers through the state of bound electron-hole pairs (excitons), which is structure-sensitive and dependent on quantum energy, temperature, and applied field intensity. 109 references.

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## I. INTRODUCTION (THE PROBLEM OF NON-PHOTOACTIVE ABSORPTION IN MOLECULAR SOLIDS)

Photoelectric phenomena are among the most important manifestations of the interaction between light and matter, underlying many biological processes (photosynthesis, colour vision) as well as the fixation of optical images (photographic processes). Recent systematic studies of the absolute quantum yield of photoelectric phenomena in molecular (polymeric) photoconductors have led to the hypothesis of non-photoactive edge absorption in these materials, in contrast to the classical crystalline semiconductors such as germanium and silicon. Non-photoactive absorption, extending partly into the depth of the absorption band, has been observed in molecular photoconductors of various classes, including organic (anthracene) and inorganic (selenium) crystalline photoconductors, amorphous inorganic photoconductors (amorphous selenium structures and selenium structures with tellurium, arsenic, and germanium hetero-atoms), organic poly-conjugated polymeric photoconductors (polyacetylenes), organic saturated polymeric photoconductors (vinyl polymers), and also dye-sensitised organic polymers[1-5]. The basic factor which determines the appearance of non-photoactive absorption in these photoconductors is the photo-generation of charge carriers through the state of a bound hole–electron pair (exciton), depending on the quantum energy, the temperature, and the strength of the applied electric field. The effect is found to be structure-sensitive: some selenium structures (both crystalline and amorphous) do not show non-photoactive absorption over a wide range of quantum energy, giving an internal photo-effect with a very high quantum yield (approaching 100%) over the whole visible region of the spectrum.

In this review we shall analyse the relationship between the molecular (and supermolecular) selenium structures and the spectra of the photoelectric phenomena in selenium. Amorphous, amorphous–crystalline, and crystalline selenium structures will be considered, with special emphasis on the photoelectric phenomena in the presence of external electric fields: photoconductivity (electrophotographic sensitivity) in strong fields, which collect all the light-generated carriers and allow us to measure one of the most important characteristics of the interaction of light with matter (the quantum yield of the internal photo-effect, equal to the number of hole–electron pairs created by each quantum of light absorbed), and photoconductivity in weak electric fields, in particular at very high frequencies, which allows us to minimise the influence of contacts and to study photoconduction with very small "displacements" of the charge carriers. We shall also discuss photoelectric phenomena in the absence of applied electric fields, and in particular the diffusion of photocarriers along a concentration gradient (capacitive photo-e.m.f. and contact potential difference).

The modern view of the structure of selenium is of an inorganic polymer which can easily change its molecular and supermolecular structure[6]. A clear understanding of the correlation between the structure and the properties of such an inorganic polymer, which is highly photosensitive over a wide spectral region, should help us to formulate methods of controlling the physical properties of polymers in general, and in particular it should suggest ways of improving the photosensitivity of organic polymers.

## II. CRYSTAL STRUCTURES OF SELENIUM

### 1. Structure of the Molecule and Allotropic Forms

Selenium forms complex molecules easily altered under the influence of various factors. This feature of selenium is responsible for the existence of several allotropic forms of selenium in the solid state, able to coexist over a wide range of temperature[7]. The state of the outer electrons in an isolated selenium atom corresponds to the $4s^2 4p^4$ configuration. Of the six outer electrons, two (paired) are in the $s$-state, and two (paired) in the $p$-state, and do not take part in bond formation. The bond between atoms is created by the two unpaired electrons. The electron clouds of the unpaired $p$-electrons of each atom overlap the $p$-clouds of the neighbouring atoms to give filled $p$-orbitals. The bond angle (105.5°) causes the atoms to adopt a helix configuration in the molecular chain, or alternatively to form eight-membered rings. We note that selenium can have a valence of 4 or 6 as a result of the transition of two or four unpaired electrons from $p$ (or $s$ and $p$) orbitals into a $d$-orbital[8]. The interatomic bonding within

the molecule is strong and covalent, though the nature of the intermolecular bonds is still controversial. Some workers[9,10] argue, in view of the low melting point and of the easy cleavage of the crystal along planes parallel to the molecular chains, that the intermolecular forces must be of the Van der Waals type. Others[11] stress that the distance between chains in selenium is too short for Van der Waals interactions and that the coordination number is greater than the maximum possible number of $p$-bonds, and conclude that rotary resonance of the chemical bonds is present in selenium crystals. Bond hybridisation is postulated, extending over four atoms of the second coordination sphere of different molecular chains. Hybrid orbitals have a greater bond energy than non-hybridised orbitals, and therefore their stability is higher[12]. Furthermore we expect intermolecular energy barriers to be lowered by the presence of hybridised bonds[12].

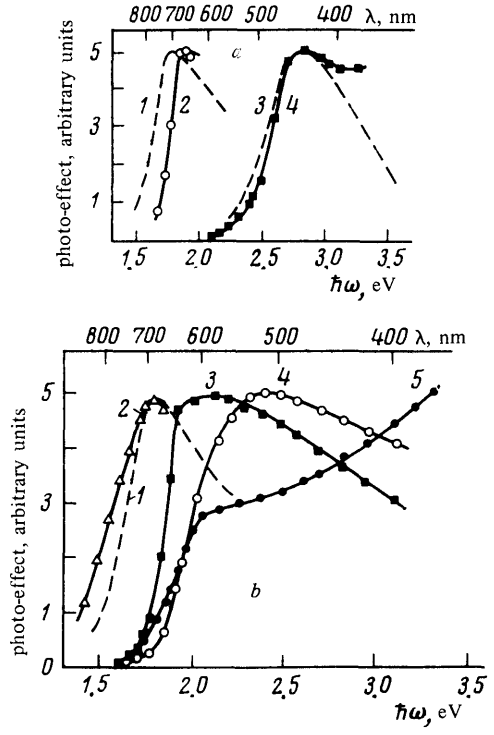



**Figure 1.** Photo-effect spectra of the crystalline selenium structures and of the corresponding amorphous analogues: (*a*) *1*) trigonal selenium, *2*) its amorphous analogue, *3*) monoclinic selenium, *4*) its amorphous analogue; *1*) and *3*) d.c. photoconductivity, *2*) and *4*) electrophotographic sensitivity[23]; (*b*) trigonal selenium; *1*) d.c. photoconductivity[24], *2*) and *3*) electrophotographic sensitivity of a polycrystalline sample[1] and of microcrystals dispersed in an organic matrix[23] respectively, *4*) photo-e.m.f., *5*) contact potential difference.

The most stable crystalline form of selenium is the trigonal modification. The monoclinic ($\alpha$ and $\beta$) and the cubic ($\alpha$ and $\beta$) modifications, with different elementary cells in different space groups, are also true crystalline phases[7]. The structural features of the crystalline forms are largely determined by the molecular structure of selenium[13]. The basic structural element of trigonal selenium is a polymeric helical molecular chain with an interatomic distance of 2.32 Å and a bond angle of 105.5°. A parallel orientation of such chains, with an axial separation of 3.48 Å, creates a hexagonal lattice with parameters $a = 4.35$ and $c = 4.94$ Å.[14] Another crystal form ($\alpha$ and $\beta$ monoclinic selenium) is formed from eight-membered, puckered selenium molecules (closed rings in the $\alpha$ modification, open rings in the $\beta$ modification) with an interatomic distance of 2.3 Å,[15] a spacing of 2.9 Å between rings, and lattice parameters $a = 9.1$, $b = 9.1$, $c = 11.6$ Å, $\varphi = 90°16'$ for $\alpha$-monoclinic selenium[16-18]. Both modifications are molecular crystals. For the cubic modifications[19,20] we have $a = 2.97$ Å (for the $\alpha$-cubic lattice) and a bond length of 2.97 Å.

## 2. Photoelectric Phenomena

The photoelectric properties of crystalline selenium have been studied by various methods, including photoconductivity in strong electric fields (electrophotographic (EP) sensitivity)[21], photoconductivity at ultra-high ($10^{10}$ Hz) frequency[22], capacitive photo-e.m.f., influence of light on the contact potential difference, etc.[23-26]. Spectral curves for the photo-effects observed by the above methods in monoclinic and trigonal selenium are shown in Fig. 1. The EP sensitivity spectrum (curves *2* and *3* of Fig. 1*b*) extends over the whole visible region of the spectrum up to 800 nm. Its long-wavelength edge is close to the edge of the photoconductivity spectrum of polycrystalline layers of trigonal selenium (curve *1* of Fig. 1*b*). We should note that the EP sensitivity (curve *3* of Fig. 1*b*) is discussed in terms of a model consisting of a dispersion of trigonal selenium microcrystals (of micrometre dimensions) in an organic matrix based on styrene copolymers[21]. Single crystals of trigonal selenium have zero EP sensitivity because their resistance is too low to give an acceptably long relaxation time. Transverse current can be obtained in these heterogeneous layers in fields of $10^4$–$(2 \times 10^5)$ V cm$^{-1}$ if the gaps between crystallites are not too great (a few nanometers).

The photo-e.m.f. and contact potential difference spectra (curves *4* and *5* of Fig. 1*b*) are displaced towards shorter wavelengths, as are the corresponding spectra of organic photoconductors[27]. On the other hand, the EP sensitivity curve of polycrystalline trigonal selenium (curve *2* of Fig. 1*b*) has a maximum at 700 nm, characteristic of the single crystals and coinciding with the photoconductivity maximum of the individual microcrystals measured at a frequency of $10^{10}$ Hz.[22] In these measurements the red edge of the photoconductivity lies at longer wavelengths than the red edge of other photoelectric effects. By comparing the EP sensitivity and the photoconductivity curves we conclude that the low EP sensitivity in the long-wavelength part of the spectrum arises from the specific structure of the heterogeneous (amorphous–crystalline) system, resulting in a particular field distribution. Because of the short Debye screening length, the electric field penetrates into the selenium microcrystals to a depth of only 0.1 μm, and only the surface regions of the crystals are able to contribute to the EP sensitivity of the system. Generation of hole–electrons pairs in the depth of the crystals cannot contribute to the EP sensitivity if the applied electric field is excluded from these regions. The range of quantum energy in which the EP sensitivity is

found to fall corresponds to a decrease in the absorption coefficient from $10^5$ $cm^{-1}$ (for 2.1 eV) to $10^4$ $cm^{-1}$ (for 1.8 eV). Exciton effects associated with non-photoactive absorption cannot be excluded, but while the results do not contradict this interpretation they do not positively confirm it.

In contrast to trigonal selenium, with the monoclinic form of selenium the spectra of the photoelectric effects are shifted (curves *3* and *4* of Fig. 1*a*) towards the centre of the absorption band (curve *7* of Fig. 5*a*).

The crystal structure of selenium consisting of long helical molecules (trigonal selenium) differs from that consisting of closed eight-membered rings (monoclinic selenium) in having an internal photo-effect with a quantum yield close to 100% over a wide region of the spectrum (see curve *1* of Fig. 6*a*).[28] This is the only known example of a molecular crystal in which the yield of the internal photo-effect is maximal over a wide spectral range.

## III. AMORPHOUS AND AMORPHOUS–CRYSTALLINE SELENIUM STRUCTURES (MICROCRYSTALLINE PHASE AND PHASE BOUNDARY)

### 1. Amorphous–Crystalline Structures

The essential feature of the structure of matter in an amorphous state is the absence of long-range order in the arrangement of its atoms or molecules. The term order (long-range or short-range) denotes the correlation in the mutual disposition of atoms or molecules in the solid: a correlation at a distance of the same order as the mean interatomic spacing is termed short-range order, whereas a correlation without limit as to distance is termed long-range order. Amorphous and amorphous–crystalline selenium structures can be prepared both from the gas phase (by thermal evaporation in a vacuum) and from the liquid phase (by quenching)[6,29].

*a*) Molecular composition of the melt. As we have already pointed out, the crystal lattices of all the known modifications of selenium are built up from different structural units. Hence these structural units must be present as equilibrium forms[7] when selenium is crystallised (from the vapour, the liquid, or the amorphous state) to give one or other of the crystalline modifications of the element. However we do not clearly understand the conditions of formation of these structural units, their stability, or their mutual interconversion. The main difficulty is the presence of molecules of different structure and size in selenium samples at any temperature below the melting point (220°C). Several workers have found that the liquid phase consists of closed rings and molecular chains of different size, whereas selenium vapour (up to 1000°C) consists of a mixture of molecules (containing eight, six, four, or two atoms) and single atoms. Liquid selenium retains all the attributes of a molecular liquid down to 200°C,[29-32] and is reported[33] to be associated.

Existing information on the form and relative amount of the different molecules in liquid selenium is contradictory. Some workers[34] state that liquid selenium consists of helical molecular chains, while others[35,36] suggest that parallel orientation of the chains persists up to 300°C. X-ray diffraction studies[32,35] have shown that six- and eight-membered rings are present in liquid selenium. More recent work[37,38] has led to the suggestion that eight-membered rings are in equilibrium with polymeric chains in liquid selenium. The formation of long polymeric chains begins at a critical temperature (83°C) well below the melting point of selenium, the rate of formation increasing with temperature. It is reported[38,39] that at the melting point the chains contain at least $10^2$–$10^4$ atoms of selenium. Other workers[40] find that at 220°C the mean chain length in pure selenium is $2 \times 10^5$ atoms. The high-polymer nature of liquid selenium has been demonstrated by viscosity measurements[41], according to which the polymeric chains contain up to 500 atoms at temperatures up to 220°C.

Contradictory information has been published also on the temperature dependence of the melt composition. Measurements of magnetic susceptibility[35,36,42] suggest that the dissociation of the selenium molecules is insignificant in the region of 230–650°C. On the other hand, substantial structural changes in liquid selenium have been observed[33,43] over the range 300–320°C, but the nature of these changes is unknown. Thus practically all the structural units of the crystalline forms are present in liquid selenium, including[32,35] small regions of normal hexagonal lattice. Selenium samples prepared from the liquid or the vapour phase are believed to include equilibrium structural units of the different crystalline modifications, which can subsequently undergo crystallisation or formation of an amorphous state[7].

In spite of the apparent simplicity of the vacuum evaporation method, the deposition of thin films of amorphous selenium gives poorly reproducible results, and the relationship between the deposition conditions and the structure and physical properties of the films is still not clear. A great deal of information has been published on metallic films[44,45], but the deposition of a material like selenium in the form of thin films differs radically from the deposition of metal films, because the beam of evaporating material is molecular in the former case and atomic in the latter[45]. The structure of films resulting from the condensation of vapour produced by vacuum evaporation depends on the physicochemical properties of the solid source and on the evaporation conditions: residual pressure in the vacuum chamber, rate of deposition, temperature and structure of the substrate, etc.[44] The molecular composition of the vapour is by no means the least important condition[46].

*b*) Effect of the molecular composition of the vapour on film structure. The molecular structure of selenium vapour depends on its temperature. Above 1500°C selenium molecules dissociate into atoms: the selenium–selenium bond energy of diatomic molecules, determined from spectroscopic data and from the heat of dissociation[6], is 2.9 ± 0.2 eV. When the temperature is lowered to 1000°C the vapour phase includes molecules of all degrees of complexity between monatomic and eight-atomic, the relative amounts depending on temperature. Molecular complexes and quasi-crystalline formations apparently exist in the vapour phase at not too high temperatures. The evaporation of selenium as molecular complexes, which persist in the vapour phase up to 680°C, enables the molecular and super-molecular forms present in the source material to be transported to the condensing layer[43,47]. Nesmeyanov[48] critically reviewed published work on the temperature dependence of the pressure and composition of selenium vapour, and concluded that insufficient information is available on vapour composition at temperatures close to the melting point. Two papers[49,50] are selected[48] as the most reliable. One of these[49] treats the evaporation of selenium as the formation of an equilibrium mixture of diatomic and six-atomic molecules, the

proportion of diatomic molecules increasing with temperature from 12% (at 185°C) to 25% (at 684°C, the boiling point of selenium). According to the second paper[50] selenium vapour at 550–900°C contains tetra-atomic and eight-atomic molecules in addition to diatomic and six-atomic, the relative amount of each species being a function of temperature. Molecules containing eight atoms have been shown to be present in small amounts at temperatures below 500°C by a vapour density method, and the formation of a small amount of atomic selenium at temperatures near 1000°C has been confirmed by the same method[51,52]. Electron-diffraction studies[53] have shown that selenium vapour at ~ 450°C consists mainly of six-membered molecular rings in the "chair" configuration, with a smaller number of diatomic molecules.

Thus at the evaporation temperatures (300–500°C) normally used for the deposition of thin films of amorphous selenium the vapour consists mainly of six-atomic molecules. Diatomic molecules are also present, at lower concentration. The structural, electrical, and photoelectric properties of amorphous selenium layers are reported[46] to be very sensitive to the temperature of the selenium vapour (in the range 200–900°C) from which the layers are deposited. The phenomenon is ascribed partly to the role of the thermal velocity of the molecules, and partly to the degree of dissociation of the molecules. Unfortunately these two factors could not be separated in the experiments described.

*c*) Effect of residual gas pressure on film structure. Another important parameter influencing the structure of amorphous selenium layers is the pressure of residual gases in the chamber[54]. Thus, with a residual air pressure $> 6 \times 10^{-2}$ mmHg we obtain sooty, rough layers of low average density with a fibrous surface structure. Other gases (e.g. oxygen and argon) have a similar effect on the macro-structure of the layer when present at pressures $> 6 \times 10^{-2}$ mmHg. At pressures $< 2 \times 10^{-2}$ mmHg, where the mean free path of the evaporating molecules becomes comparable to the distance between the evaporator and the target, the residual gas molecules cease to affect the condensation of selenium, and dense layers with a mirror-smooth surface are obtained by vacuum evaporation. However the properties of these layers are still strongly dependent on the nature of the residual gas.

It has been suggested[54] that molecules or atoms of the residual gas can be incorporated in the condensing layers, thus influencing their microstructure or acting as electrically active impurities (which influence the electrical and photoelectric properties of the layers). Unfortunately no systematic study of the effect of residual gas pressure on the microstructure of amorphous selenium layers appears to have been reported. Electron-microscopic measurements[55] failed to show any structural difference between layers deposited at different residual gas pressures in the range from $10^{-3}$ to $10^{-6}$ mmHg. Furthermore, if the residual gas in the chamber has a high affinity for selenium we can expect compound formation at high substrate temperatures and high background pressures. Hence the preparation of dense and pure films of amorphous selenium should only be attempted in a vacuum of $10^{-5}$ mmHg or better.

*d*) Effect of rate of deposition on film structure. The rates of condensation used in the preparation of amorphous selenium films are quite high and usually in excess of 1 $\mu$m min$^{-1}$ (i.e. about 100 atomic layers per second). These high rates of condensation lead to the evolution of substantial amounts of latent heat, and because of the low thermal conductivity of amorphous selenium ($\sim 3 \times 10^{-4}$ cal cm$^{-1}$ s$^{-1}$ K$^{-1}$) this effect gives the molecules of condensate a high surface mobility and assists structural rearrangements within the layer[46]. However experiments[46] at rates of condensation between 0.5 and 2.5 $\mu$m min$^{-1}$ failed to reveal any difference in the electrical and photoelectric properties of amorphous selenium films. This suggests that the structure of amorphous selenium becomes insensitive to deposition rate at these high rates of deposition.

*e*) Effect of substrate temperature on the structure. The structure of the selenium layers is affected most markedly by the temperature of the substrate during deposition[8,15,56–62] and by the subsequent annealing conditions[8,37,38,63–65]. The effect of substrate temperature (in the range 0–100°C) on the structure of the selenium layers has been studied[57] by electron microscopy and by X-ray and electron diffraction. Layers prepared at substrate temperatures between 0 and 10°C had a pale grey surface, changing to red when the substrate temperature was raised to 35–40°C. The surface of layers prepared at low substrate temperatures is covered with hillocks. At higher substrate temperatures the layers develop a dark red colour and a mirror-smooth surface. X-ray and electron diffraction studies[57] and optical studies in polarised light[8,15,57] have confirmed that the structure of these layers is amorphous immediately after preparation. The proportion of crystalline phase in samples prepared at a substrate temperature of 90–100°C is only 7–8%.

## 2. Amorphous Forms of Selenium

Nabitovich and coworkers point out[57] that layers prepared at low (20–30°C) and intermediate (50–60°C) substrate temperatures have different amorphous structures: both the height and the width of the diffraction peaks are different in the X-ray and the electron diffraction patterns. The presence of different amorphous structures in selenium has been reported also by other workers[29,32,58,61,63]. Electron diffraction studies of the structure of thin layers of amorphous selenium deposited on cellulose nitrate substrates at 20°C have shown[63] the presence of two forms of amorphous selenium, characterised by different coordination numbers and different radii of the coordination sphere. The first is formed at substrate temperatures around 20°C, the second becomes predominant at substrate temperatures of 60–70°C. A gradual transition from one form to the other can be achieved at intermediate temperatures without going through a crystalline form. At 30–40°C the deposited layer is a mixture of approximately equal amounts of the two forms. Nabitovich and coworkers[15,16] evaluated the short-range order parameter in different forms of amorphous selenium and determined their molecular structure. Condensation on substrates at 20°C produces the first form of amorphous selenium, consisting mainly of eight-membered molecular rings; the second form, consisting mainly of long molecular chains of selenium, is obtained at substrate temperatures of 50–55°C. The crystallisation processes of these two forms of amorphous selenium are also quite different[15].

Some earlier workers[29,58] also reported two different forms of amorphous selenium, detected by X-ray diffraction, but differing in structure from those reported in Refs. 15 and 63. Thus selenium deposited on substrates

cooled to −180°C was found[29] to have an amorphous "packet" structure consisting of six-membered molecular rings. This report was later confirmed[56]. The authors[29] were led to the hypothesis of a packet structure of six-membered rings by an analysis of the diffraction patterns of films obtained under different condensation conditions (in particular, the molecular composition of the vapour and the substrate temperature during deposition). The second form of amorphous selenium is observed[58] when selenium is evaporated on to substrates at 20°C, and consists mainly of molecular chains similar in structure to those of trigonal selenium. Furthermore, selenium samples prepared at room temperature often contain micro-crystals of trigonal selenium[29,58]. The presence of molecular chains in the layers was confirmed by neutron diffraction and X-ray diffraction studies of amorphous selenium structures[67].

In contrast to these findings, Richter and Herre[29] report that selenium layers formed at 20°C consist of a mixed phase of molecular chains, six-membered rings, and elements of the normal hexagonal selenium lattice. Richter later showed by X-ray structural analysis[68] that selenium layers are predominantly in one of three amorphous forms, depending on the method of preparation: all three forms have the chain structure characteristic of trigonal selenium but the interatomic distance within the chain is different in the three cases. In an earlier investigation[69] the X-ray data obtained from similar samples had been interpreted as evidence for an amorphous selenium structure composed of eight-membered rings (characteristic of monoclinic selenium).

## 3. Crystallisation of Amorphous Selenium

The vapour deposition of selenium at substrate temperatures above 60°C invariably produces layers containing some crystalline phase[8,59,70]: on raising the temperature of the substrate the concentration of the crystalline phase increases[8,59], and at substrate temperature of 80–90°C a continuous layer of trigonal selenium is formed on the substrate surface[8,60,62]. We should note that amorphous selenium crystallises spontaneously to an appreciable extent even at room temperature[8,59,70,71]. Crystallisation is fastest in amorphous layers prepared on substrates at temperatures below 20°C: such layers are fully crystalline after a few months.

It is well established that the crystallisation of amorphous selenium occurs in two steps: nucleation and crystal growth. The optimum nucleation temperature is 130°C, whereas the best temperature for crystal growth is 210°C. According to Krebs[30,41] crystallisation begins at specific sites in the amorphous selenium, where small ordered regions of parallel chains (micelles) are formed. On raising the temperature the micelles can grow at the expense of the amorphous selenium. On the other hand, selenium often forms spherulites[30,41]—a special type of rounded, textured polycrystalline formation growing from a single centre, often encountered in the crystallisation of polymers. The temperature range of spherulitic crystallisation for amorphous selenium is 70–150°C.

The rate of crystallisation of selenium is strongly influenced by the annealing schedule, by the purity of the starting material, and by some external conditions. Increase of temperature produces a sharp increase in the rate of crystallisation, the time for complete crystallisation varying from several hours at 70°C to 2–3 min at 217°C. Impurities such as thallium, antimony, indium, alkali metals, oxygen, and halogens catalyse the conversion of amorphous into trigonal selenium.

The action of light, electrons, positive ions, $\gamma$-rays, electric fields, and various organic or inorganic solvents also favours the conversion of amorphous selenium into a thermodynamically more stable crystalline state[6].

Selenium layers prepared under uncontrolled or special conditions may contain all the known amorphous and crystalline phases. Thus layers prepared by the sublimation method[72–76] are evaporated on to the substrate from another surface held at 185°C, the substrate temperature is then raised to 83°C and the layer is held at this temperature for approximately 15 min to stabilise the structure. Films prepared in this way contain a layer of trigonal selenium (adjacent to the surface of the substrate), and a layer of glassy selenium consisting of the amorphous forms. It has been shown[62,77,78] that vacuum evaporation of selenium on a substrate at ~ 85°C produces small islands of crystalline selenium[77] which merge into a continuous sublayer of trigonal selenium at a higher substrate temperature (98°C). The thickness of the crystalline sublayer depends on the temperature of the substrate[78,81]: ~ 0.1 μm at 70°C and 0.8 μm at 90°C. At a substrate temperature of 70–80°C the crystalline layer is fairly smooth, but at higher temperatures we observe dendritic growth to a diameter of 1 μm (at 90°C) and to a depth of 1–2 μm into the layer. At 70–80°C we find, between the trigonal and the amorphous layer, a layer 0.1–0.4 μm thick consisting of a mixture of the monoclinic and the trigonal modification, which is gradually converted into the trigonal modification at room temperature.[80] At 50–60°C the continuous crystalline layer is not formed, but separate crystalline inclusions up to several hundred $\mu m^2$ in area are produced. Crystallisation can be retarded by depositing a sublayer of arsenic triselenide 0.2–0.5 μm thick[79]. Evidently, the same result is obtained using a layer of cellulose nitrate[82,83], which stabilises the properties of layers prepared at 65°C.

Following Nabitovich[7] we can summarise our understanding of the selenium structures as follows. It is now well established that the structure of selenium films is determined first and foremost by the technological conditions used in their preparation. When the films are prepared by vacuum condensation of a molecular vapour on an isotropic substrate the structure is determined by the temperature of the melt, the condensation time, the substrate temperature, and the post-deposition annealing conditions. Immediately after deposition these layers can be in three states: crystalline, supercooled, or amorphous. Condensation of selenium on a substrate at 97–100°C invariably yields crystalline layers, irrespective of the rate of condensation. Selenium layers condensed on substrates at 60–100°C and rapidly cooled to room temperature are always in a supercooled metastable state.

## 4. Photo-electric Phenomena in Amorphous Selenium Structures

Amorphous selenium structures show photosensitivity in the region of $\lambda < 600$ nm (Fig. 2). The photosensitivity spectrum in the visible region has two more or less sharply defined maxima[1] at 370 and 470 nm (curves *1* and *2* of Fig. 2*b*). The photosensitivity increases as the wave length decreases to 140 nm (Fig. 2*a*). This increase arises from the multiplication of the photo-generated

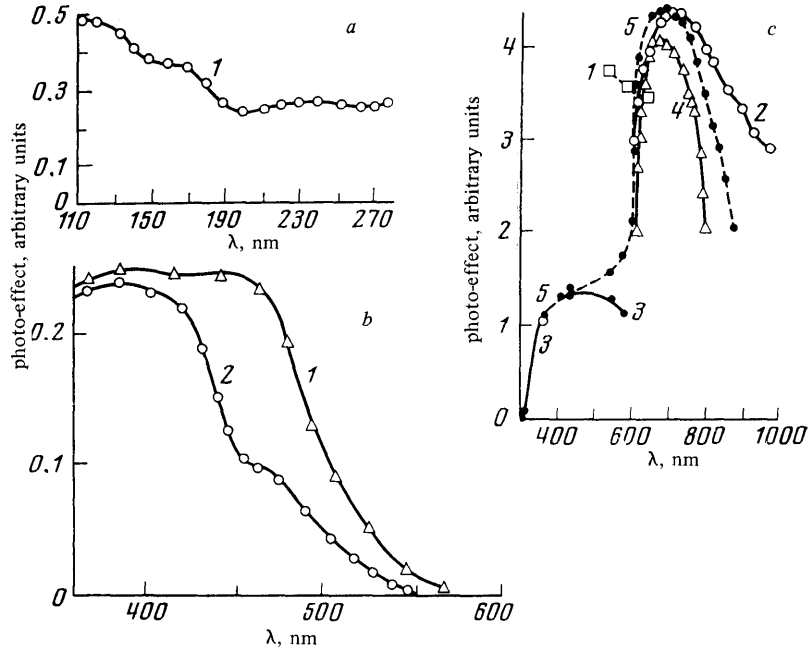



**Figure 2.** Photo-effect spectra of the amorphous and amorphous–crystalline selenium structures: (*a*) and (*b*) d.c. photoconductivity (electrophotographic sensitivity) of amorphous selenium[91]; (*b*) *1*) layer prepared at 300 K, *2*) 120 K; (*c*) photoconductivity at $10^{10}$ Hz[22]: *1*) amorphous selenium (second amorphous form), *2*) amorphous selenium containing 30% of trigonal selenium, steady illumination, *3*)–*5*) modulated illumination, amorphous selenium with different amounts of crystalline phase (*3*) 1–2%, *4*) > 10%, *5*) 30%). The curves for steady (*2*) and modulated (*5*) illumination are normalised to the same peak value; a logarithmic scale is used for the photo-effect.

current carriers at photon energies greater than the forbidden energy gap of selenium in the absence of concentration-dependent recombination. Lowering the substrate temperature during deposition to −150°C lowers the photosensitivity in the spectral region above 400 nm (curve *2* of Fig. 2*b*). Conversely, heat treatment of the amorphous selenium layer, leading to the appearance of a crystalline phase, increases the photosensitivity in the long-wavelength region of the spectrum (Fig. 2*c*). Heat treatment of the layers in air at 60°C for 24 h extends the region of photosensitivity to 880 nm.

The sensitivity spectra of the amorphous and the crystalline phase in heterogeneous selenium layers have been studied by photoconductivity measurements at ultra-high frequencies[22] with steady illumination[85] and with light modulated at 200 Hz.[86] These measurements make clear the relationship between the bulk photoconducting properties and the molecular and supermolecular structure of the selenium sample under conditions which minimise the effect of contacts and allow the photoconductivity to be studied with small "displacements" of the carriers. The basic characteristics of the photoconductivity, i.e. its magnitude, spectral distribution, and temperature dependence, are a function of the amount of crystalline phase in the amorphous selenium. Thus, with 1–2% of crystalline phase photoconductivity (with positive photo-carriers) is observed in the region of 300–600 nm (curve *3* of Fig. 2*c*). The photoconductivity limits of the layers are different for a frequency of $10^{10}$ Hz ($\Delta\sigma_{\sim}$) and for direct current ($\Delta\sigma_{=}$). With direct current $\lambda_{\frac{1}{2}} \simeq 500$ nm,[25,87] i.e. well within the optical absorption band (absorption edge ~ 600 nm). The $\Delta\sigma_{\sim}$ limit, as shown in curve *5* of Fig. 2*c*, occurs at the wavelength $\lambda_{\frac{1}{2}} \simeq 750$ nm, i.e. beyond the absorption edge. Increasing the amount of crystalline phase to 10–30% produces a large (approximately 1000-fold) increase of $\Delta\sigma_{\sim}$ in the red region of the spectrum as well as extending the photoconductivity to even longer wavelengths (up to 1100 nm) with a maximum at 690 nm (modulated illumination, curve *5*) or at 710 nm (steady illumination, curve *2*). The photosensitivity in the spectral region beyond 700 nm is higher with steady than with modulated illumination, showing that the contribution to $\Delta\sigma_{\sim}$ from slow processes is considerable in this region. The maximum of $\Delta\sigma_{\sim}$ coincides with the maximum of $\Delta\sigma_{=}$ of trigonal selenium crystals[88], and is shifted far into the long-wavelength region as compared with the $\Delta\sigma_{=}$ maximum of polycrystalline layers (630 nm).[25]

On lowering the temperature $\Delta\sigma_{\sim}$ is found to decrease, unlike $\Delta\sigma_{\sim}$ for layers with a low content of crystalline phase. The temperature dependence of $\Delta\sigma_{\sim}$ is described by the expression $\Delta\sigma_{\sim} = \Delta\sigma^{0} \exp(-\Delta E/kT)$, where the thermal activation energy $\Delta E = 0.03$ eV is the same for carriers photo-generated in the bulk ($\lambda = 600$ nm) or at the surface ($\lambda = 436$ nm) of the layer. The activation energy is needed, apparently, for the photo-carriers to overcome intermolecular (but not intercrystalline) energy barriers. In practice the displacement of the carriers at a frequency of $10^{10}$ Hz in a field of $10^{2}$ V cm$^{-1}$ is less than 50 Å (the

carrier mobility in amorphous selenium is much less than 50 $cm^2 V^{-1} s^{-1}$). Thus the carrier displacement is much smaller than the size of the micro-crystals, which are usually several thousands of Ångstroms in diameter.

Many of the phenomena which we have discussed can be interpreted by the exciton model of photo-generation in selenium, as we shall show below. Here we only need to point out that the changes in the "structure–property" relationship observed at ultra-high frequency have provided a solution to the opposite problem: the use of photoconductivity at ultra-high frequency as a method of studying the degree of heterogeneity of glassy selenium[90].

## IV. AMORPHOUS ANALOGUES OF SELENIUM CRYSTAL STRUCTURES

### 1. Structure

It may be assumed that if a molecular solid can exist in several crystalline modifications, with different types of short-range order, the solid should also exist in several amorphous structures with different types of short-range order (and therefore with different energy spectra). Among the possible examples of substances (or, indeed, elements) showing several amorphous structures selenium is a particularly good choice, because it can also exist in several crystalline modifications differing in molecular structure and therefore in short-range order.

Selenium layers prepared from a molecular vapour at a given temperature, at a given rate of condensation and substrate temperature, and homogenised under prescribed conditions, can form an amorphous state with two different amorphous structures (the amorphous forms of selenium) or consisting of a mixture of these two amorphous structures[7]. In contrast to the supercooled state, the short-range order in amorphous selenium manifests itself as a constant interatomic distance and also as an arrangement of atoms in definite configurations, leading to a diffraction pattern with several sharp maxima.

The first amorphous form of selenium is formed by evaporating the element from a melt at 220–270°C, condensing the vapour on a substrate at 18–40°C, and annealing the layer in a vacuum at room temperature for 30 h. This structure has a definite diffraction pattern. Its structural units are distorted structural units of the crystal lattice of the monoclinic $\alpha$ and $\beta$ modifications: molecular rings consisting of eight atoms. During the formation of the structure these rings polymerise into agglomerates responsible for the "cobble-stone" outline of the sample surface.

The second amorphous form of selenium is formed by evaporation from a melt at a temperature above 350°C, condensation of the vapour on a substrate at 50–80°C, and subsequent annealing of the layers at 50°C in a vacuum for 20–30 min. This structure also gives a well defined diffraction pattern. The structural units of the second amorphous form are distorted structural units of the crystal lattice of trigonal selenium: short molecular chains. During the formation of the structure, the predominant process is polymerisation of the short molecular chains into long polymeric chains, randomly interweaved and looped.

The intermediate amorphous state of selenium is formed at moderate rates of evaporation on a substrate at 40–60°C, with slow cooling of the layer to room temperature. The diffraction pattern of this structure depends on the relative numbers of units of the first and of the second amorphous form. Using electron-diffraction results on the radii of the coordination spheres and on the coordination numbers, and making allowance for the presence of atomic selenium in the intermediate state, Nabitovich[7] concluded that the intermediate amorphous state includes not only ring and chain molecules of different size but also a significant number of selenium atoms, which tend to attach themselves to other atoms or to the ends of other molecules in a tetrahedral configuration. The first and the second amorphous form contain ~ 10% of these atoms, which join together the distorted ring or chain molecules and allow them to polymerise. Hence the main difference between the amorphous structures and the crystalline lattices is that the structural units in the former lack the parallel arrangement of the latter.

### 2. Photoelectric Phenomena in the Amorphous Analogues of the Selenium Crystal Structures

The first study[23] of the photoelectric properties of the amorphous analogues of selenium crystal structures aimed to explain the influence of short-range order on the photoelectric properties of various amorphous structures and to compare them with the properties of the corresponding crystalline structures. The measurements were made on layers of amorphous selenium with two types of molecular structure, prepared by vacuum evaporation of selenium of $B_4$ grade (99.9999% Se) with controlled melt and vapour temperature (230–250°C), deposition rate ($\leqslant 30$ Å $s^{-1}$), residual gas pressure ($10^{-6}$ mmHg), and substrate temperature (20°C for the first type of structure, consisting mainly of ring molecules, and 55°C followed by vacuum annealing for the second type of structure, consisting mainly of chain molecules). Great care was taken to ensure the absence of crystalline phase in the layers. The structure of the surface of the layer, and of that of the sub-layer adjacent to the substrate, was investigated by the carbon replica method in an EM-5 electron microscope (20 000 × magnification). Fig. 3 shows some micrographs of amorphous selenium layers obtained by this method (*e*, *f*) and by scanning electron microscopy (*a*, *b*, *c*, *d*). The layer surface, the cross-section of the layer, and the substrate surface are clearly visible in the SEM pictures (*a*, *b*, *c*, *d*). With amorphous selenium films the surface of the layer and that of the sub-layer on the side of the substrate are smooth, specular, and free from microscopic inclusions of crystalline selenium, and the electron diffraction patterns (Fig. 3*g* and 3*h*) are typical of amorphous structures, with two or three diffuse rings (clearly visible in the microdensitometer traces of Fig. 3*j* and 3*k*). After heat treatment of these layers at 70°C microscopic inclusions of crystalline selenium appear in the amorphous selenium. These are clearly visible in the micrographs, and they are accompanied by the formation of spots on the diffraction pattern (Fig. 3*i*).

We should note that these methods of structural analysis can detect crystalline inclusions in the amorphous selenium layers only a few tens of Ångstroms in diameter. The reflection electron diffraction method is the most "non-destructive" method of studying amorphous selenium structures, and is therefore preferable to the simpler transmission method. By varying the thickness of the layers and by examining structurally both the free surface and the surface in contact with the substrate (after removing the layer from the substrate), and also by studying both surfaces and the cross-section of the layer with an electron

microscope, using shadowed carbon replicas, we have obtained reliable information on the amorphous forms of selenium[23,104] confirming the results of the leading workers on the amorphous selenium structures (Nabitovich, Richter, Herre, and others)[7,29,68].

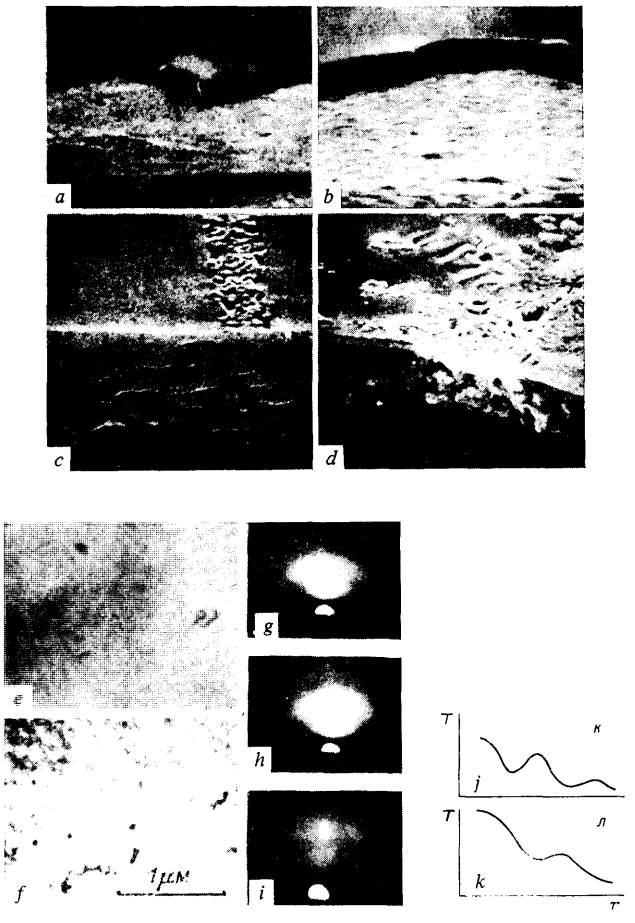



**Figure 3.** Electron diffraction patterns and micrographs of amorphous selenium structures[21,104]: *a*) and *e*) amorphous analogue of monoclinic selenium (free surface and substrate interface respectively), magnification × 14 000; *b*) and *f*) amorphous analogue of trigonal selenium; *c*) and *d*) for comparison, amorphous selenium containing some crystalline phase; *g*), *h*), and *i*) electron diffraction patterns for *a*), *b*), and *c*) respectively; *j*) and *k*) microdensitometer traces of the diffraction patterns of the amorphous analogues of monoclinic (*g*) and trigonal (*h*) selenium.

Studies of the spectral distribution of photoconductivity in strong electric fields (electrophotographic sensitivity), of photoconductivity at ultra-high frequency ($10^{10}$ Hz), of the capacitive photo-e.m.f., and of the effect of light on the contact potential difference, made on the same samples over the spectral region 360–800 nm, have shown substantial differences in photoelectric properties between the two amorphous structures of selenium (Fig. 4). Firstly, the photo-effect spectra for selenium in one of the amorphous structures (curves *1*(*2*), *2*(*2*), *3*(*2*) of Fig. 4) show a marked shift towards the long wavelength region in comparison with the other amorphous structure (curves *1*(*1*), *2*(*1*), *3*(*1*), *4*(*1*) of Fig. 4). Secondly, the amorphous selenium structures have different photoconductivity types: one of the amorphous structures conducts mainly by positive holes, the other mainly by electrons. Thirdly, one of the amorphous structures has a fairly high photoconductivity at $10^{10}$ Hz (curve *2*(*2*) of Fig. 4).

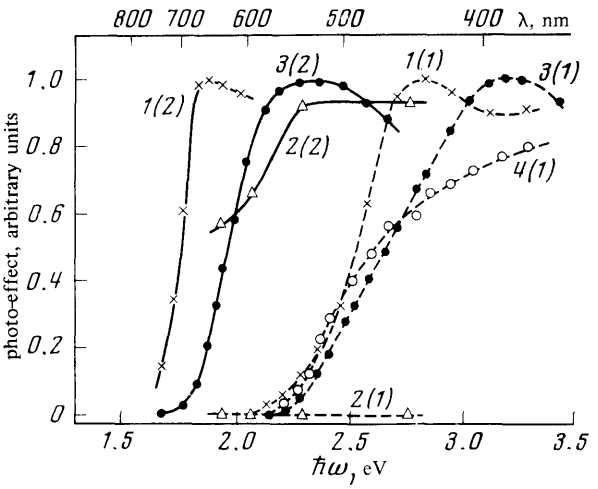



**Figure 4.** Isoenergetic spectra for the photo-effect in the amorphous analogues of the crystalline selenium structures[23]: *1*) d.c. photoconductivity (electrophotographic sensitivity), *2*) photoconductivity at $10^{10}$ Hz, *3*) photo-e.m.f., *4*) contact potential difference; in all curves (*1*) denotes the amorphous analogue of monoclinic selenium and (*2*) the amorphous analogue of trigonal selenium.

Comparison of the photo-properties of the amorphous and the crystalline structures has shown[23,92,104] that the two amorphous selenium structures with different short-range order are the amorphous analogues of the known crystalline structures of selenium (monoclinic and trigonal). The transition from crystal to amorphous analogue shows the theoretically predicted shift of the absorption edge towards longer wavelengths (Fig. 4).

The work described above has confirmed the crucial importance of short-range order in determining the properties of materials, and it has shown that short-range order in disordered materials can be controlled by varying the molecular structure: the survival of the molecular structure of molecular (polymeric) solids during the crystal–glass transition enables the glass to "remember" the short-range order (and the properties) of the crystal and to "forget" the long-range order.

To conclude this section we shall consider to what extent the photoelectric properties of amorphous selenium could be due to an undetected crystalline phase.

Existing methods of analysis by electron microscopy and electron diffraction methods, coupled with solid-state photoelectric spectroscopy, offer a fairly extensive and sensitive check on the phase composition and the molecular

state of selenium samples. As stated above, the following non-crystalline selenium structures (with different properties) have been recognised: amorphous (glassy) selenium, amorphous–crystalline selenium (amorphous selenium containing some crystalline phase), amorphous–crystalline selenium with a phase boundary (an amorphous layer with a crystalline sub-layer), and amorphous analogues of the crystalline selenium structures (monoclinic and trigonal). The role of the crystalline phase in the amorphous and amorphous–crystalline selenium structures has been discussed above. The existence of amorphous forms of selenium with structural units of crystalline selenium, demonstrated by Richter, Nabitovich, and others, is no longer in doubt. Recent work has shown[23] that the amorphous forms of selenium are true analogues of the corresponding crystalline structures, and that the crystal–glass transition in the appropriate pairs is accompanied by the theoretically predicted changes in optical and photoelectric properties.

Hence the properties of the amorphous analogues differ from those of amorphous selenium with crystalline inclusions or with a crystalline sub-layer in the following respects: the photoconductivity spectra at $10^{10}$ Hz, the spectra of the light-induced changes in contact potential difference and in capacitive photo-e.m.f., the photosensitivity spectra in the EP regime, the photoluminescence spectra (many lines in trigonal selenium[84] and a broad band in the amorphous analogue), the temperature dependence of the optical absorption edge[3], and the shape of the thermally stimulated conduction spectra[93].

## V. PHOTOSENSITIVITY AND THE STRUCTURAL SENSITISATION OF THE PHOTO-EFFECT

Studies of non-photoactive absorption in molecular (polymeric) solids have led to the discovery of the phenomenon which we have termed structural sensitisation of the photo-effect[91]: a dependence of the spectral distribution and magnitude of the quantum yield for the internal photo-effect of molecular photoconductors upon the molecular and super-molecular structure of the solid. The phenomenon stems essentially from the photogeneration of current carriers in molecular photoconductors (in contrast to the photogeneration in classical semiconductors of the germanium and silicon type) through the state of a bound hole–electron pair (or exciton) over a wide spectral region. The features of the molecular and super-molecular structure determine the probability of generating free charge carriers from the bound state[28].

Let us consider in greater detail the photogeneration of free carriers in the amorphous analogues of the crystalline selenium structures. The theory of excitons in disordered semiconductors has been developed by Bonch-Bruevich[94] in recent years. We know at least three reasons for the lack of sharp absorption lines when excitons are present in disordered semiconductors. Firstly we have small-scale fluctuations in the electric field, which broaden the exciton lines; there is also strong scattering of the electrons, resulting in non-conservation of the quasi-momentum; lastly, the absorption coefficients are not additive, so that if an additional spectrally dependent absorption mechanism is present (in parallel with the exciton mechanism) the exciton structure of the absorption spectrum becomes blurred. However, the coulombic field must be acting on the electron and the hole as it does in crystals, and it must lead to the formation of bound states. Furthermore many disordered structures have relatively small dielectric constants, and if the effective mass of the carriers is not too small this should result in a large binding energy.

The presence of excitons had been previously suggested by various workers (Hartke, Regensburger, Siemsem, Fenten, Stuke, Davis, Boon) to account for various properties of amorphous selenium[84,95,96,100,101]. Our more recent investigation[92] differed from the earlier work on amorphous selenium in combining measurements of optical properties and of the quantum yield of the internal photo-effect as a function of quantum energy, temperature, and applied field on the same samples in order to reveal exciton effects. Layers of amorphous selenium were prepared by the molecular beam method in a vacuum[23] as analogues of monoclinic (first amorphous form, I AF) and trigonal (II AF) selenium, with different molecular structures (eight-membered rings and linear molecules up to several hundreds of atoms in length).[23] The thickness of the layers was varied between 0.1 and 10 $\mu$m. Tests for the absence of crystalline phases were made by electron microscopy and electron diffraction: this combination of methods could detect crystalline inclusions a few tens of Ångstroms in diameter within the amorphous layers. The quantum yield of the internal photo-effect ($\eta$) was measured in the electrophotographic regime; the low-field photoconductivity was measured with extremely small displacements of the charge carriers (a few Ångstroms) using a frequency of $10^{10}$ Hz with both steady and modulated illumination. The diffuse reflectance and the transparency of the layers were measured with and without an applied electric field of $2 \times 10^5$ V cm$^{-1}$; the kinetics of photo-discharge (in the EP regime) and of luminescence were studied at quantum energies in the range 1.5–3.3 eV and temperatures in the range 4.2–300 K, using SF-4 and SF-8 spectrophotometers and a cryostat designed to allow all the measurements to be done on the same sample.

The temperature shift of the absorption edge of the amorphous forms of selenium (Fig. 5*a* for I AF, curves *1* and *2* of Fig. 5*b* for II AF), unlike the temperature shift for crystalline selenium (curves *3* and *4* of Fig. 5*b*), depends on the quantum energy, falling to zero as the energy of the quantum increases[3]. The application of an electrostatic field of up to $2 \times 10^5$ V cm$^{-1}$ shifts the absorption towards smaller quantum energies (Franz–Keldysh effect), but the change in transparency of the film due to this effect is less than 1%. Toyazawa's theory of localised excitons was used to analyse the temperature shift of the absorption edge. Transition probabilities for non-photoactive absorption, which can be compared with theory, were calculated by the method of Hartke and Regensburger[95], which is convenient for the case of several independent mechanisms of optical absorption. The experimentally determined transition probabilities $\epsilon_2^H \cdot (\hbar\omega)^2$, where $\epsilon_2^H$ is the imaginary part of the dielectric constant $\epsilon$, corresponding to the non-photoactive absorption process (indicated points in curves *4–6*), agree quite well with theoretical predictions (solid curves *4–6* of Fig. 5*a*). The calculation is correct for the edge region of the non-photoactive absorption, for which the quantum yield of the internal photo-effect is $\eta \simeq 0$, and it explains the temperature dependence of the position of the absorption edge and its Urbach behaviour in terms of localised excitons.

When $\hbar\omega$ increases the excitons (of the Wannier–Mott type) dissociate in a strong field to give free charge carriers, and $\eta$ becomes a function of quantum energy, electric field, and temperature. The $\eta$ spectra (Fig. 6*a*)

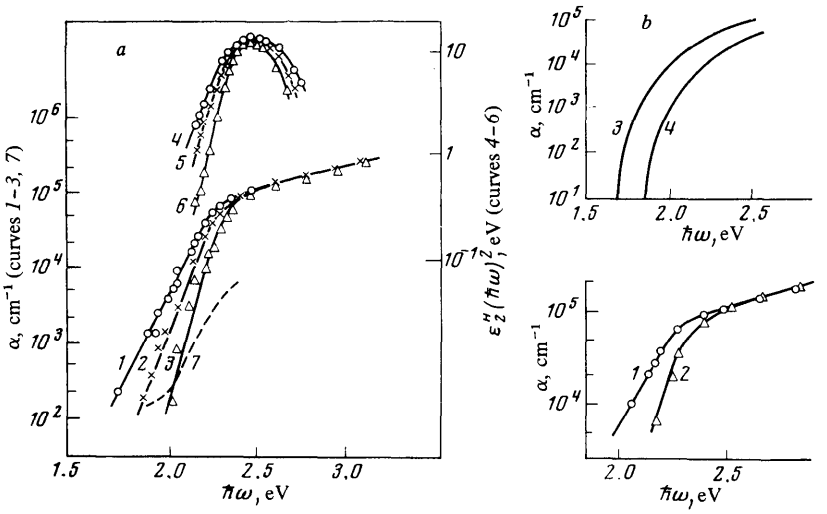



**Figure 5.** Optical properties of the amorphous analogues of crystalline selenium structures[103]: (*a*) absorption coefficient $\alpha$ of the amorphous analogue of monoclinic selenium: *1*) 300, *2*) 200, *3*) 95 K; *4*)–*6*) are the probabilities of the photoconducting transitions (*4*) 300, *5*) 200, *6*) 95 K, field $2 \times 10^5$ V cm$^{-1}$); *7*) absorption coefficient $\alpha$ of monoclinic selenium[24]; (*b*) absorption coefficient $\alpha$ of the amorphous analogue of trigonal selenium: *1*) 300, *2*) 95 K. The $\alpha$ values of trigonal selenium[109] are also shown for comparison: *3*) 300, *4*) 93 K.

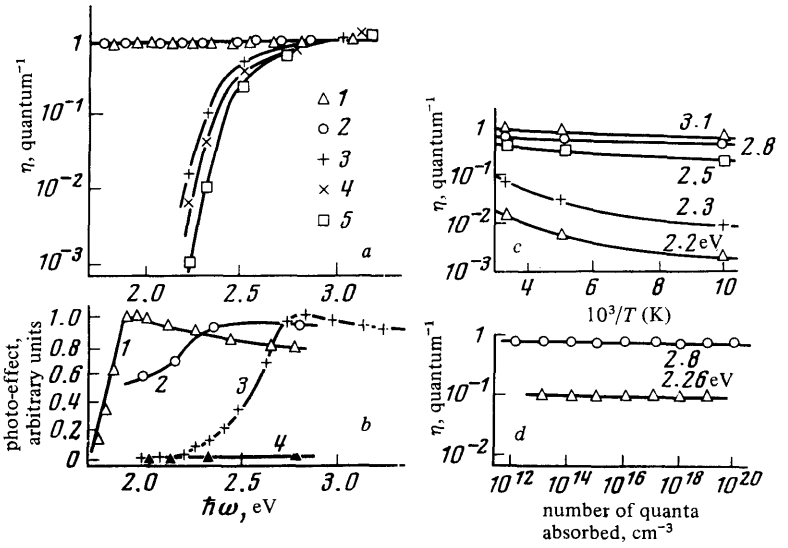



**Figure 6.** Quantum yield (*a*) of the internal photo-effect (*b*) and its temperature (*c*) and concentration (*d*) dependence[92]: (*a*) *1*) trigonal selenium and *2*) its amorphous analogue, field $2 \times 10^5$ V cm$^{-1}$, $T = 300$ K; *3*)–*5*) amorphous analogue of monoclinic selenium: *3*) 300, *4*) 200, *5*) 95 K, field $2 \times 10^5$ V cm$^{-1}$; (*b*) photo-effect in the highest possible (*1*, *3*) and in low (*2*, *4*) fields for the amorphous analogues of trigonal (*1*, *2*) and monoclinic (*3*, *4*) selenium; *c*) and *d*) refer to the amorphous analogue of monoclinic selenium.

and their dependence on temperature (Fig. 6*c*) and on field (Fig. 6*d*) are quite different for the two amorphous forms of selenium. For II AF (curve *1* of Fig. 6*a*), as for trigonal selenium (curve *2* of Fig. 6*a*), the $\eta$ value is close to unity and practically constant in the region of 1.7–3.1 eV, i.e. up to the absorption edge, the carriers being generated in pairs. Conversely, for I AF (curves *3–5* of Fig. 6*a*) $\eta$ decreases as the quantum energy, the temperature, and the field decrease, reaching zero at fields of the order of $10^2$ V cm$^{-1}$ (curve *4* of Fig. 6*b*), while the spectrum is shifted into the centre of the absorption band (the "red anomaly" according to Moss). Under these conditions, with a field of $2 \times 10^5$ V cm$^{-1}$ and quantum energies between 2.8 and 2.26 eV, $\eta$ is independent of the number of quanta absorbed over a range of eight orders of magnitude up to $10^{20}$ cm$^{-3}$ (Fig. 6*d*), showing that concentration-dependent recombination is absent and that the carriers are generated in pairs.

The features observed for the I AF form of selenium, including carrier generation in pairs, independence of $\eta$ upon ionisation density, increase of $\eta$ with quantum energy, and variation of the activation energy of $\eta$ (Fig. 6*c*) with quantum energy (falling to zero at the higher quantum energies), all suggest an exciton mechanism of photogeneration through the state of a coulombically bound pair. The results[92] are consistent with the theory of photogeneration in selenium developed by Pai[97,108], Ing[97], Tabak[98], Warter[98,99], Davis[100], and Vishchakas and Montrimas[102].

For the amorphous analogue of trigonal selenium we may again assume that carrier generation occurs through an exciton stage, but in this case the excitons are effectively dissociated by a small electric field in accordance with the theory of Bonch-Bruevich. In this model the quantum yield should not be lowered substantially by a decrease in the applied field: as shown in curve *2* of Fig. 6*b*, the quantum yield does not fall to zero (in contrast to the case of the analogue of monoclinic selenium).

Both amorphous structures give luminescence bands at 4.2 K, but the luminescence is quenched by increase of temperature[103]: in both cases the width of the band is 0.23 eV. However the position of the band relative to the forbidden gap $E_{opt}$ and the spectral distribution of the luminescence yield are very different in the two cases. For I AF (Fig. 7*a*) the quantum energy corresponding to the peak of the luminescence band is 1.80 eV, and $E_{opt}$ = 1.88 eV[104] (see Table); the quantum yield of the luminescence $\varphi_{lum}$ depends on the energy of the quantum, falling to zero as the quantum increases, as well as varying in a sense opposite to that of $\eta$. We must stress three facts. Firstly, at low values of $\hbar\omega$ and at low fields $\eta \simeq 0$, and $\varphi_{lum} = 0$, showing that the luminescence arises from annihilation of bound pairs rather than from recombination of free carriers. Secondly, increasing $\hbar\omega$ leads to $\eta \simeq 1$, but in this case $\varphi_{lum} = 0$, i.e. the free carriers do not contribute to the luminescence. Lastly, the changes in opposite sense of the $\eta$ and $\varphi$ spectra follow unambiguously from the alternative mechanisms: annihilation of the exciton, with luminescence, or dissociation with formation of free current carriers.

Optical and photoelectric forbidden gap ($E$) of selenium with different molecular structures.

| $E$, eV | Eight-membered ring | | Polymeric chain | |
|---|---|---|---|---|
| | crystal | glass | crystal | glass |
| $E_{phot}$ | 2.48 | 2.53 | 1.78 | 1.79 |
| $E_{opt}$ | 2.0 | 1.88 | 1.78 | 1.81 |

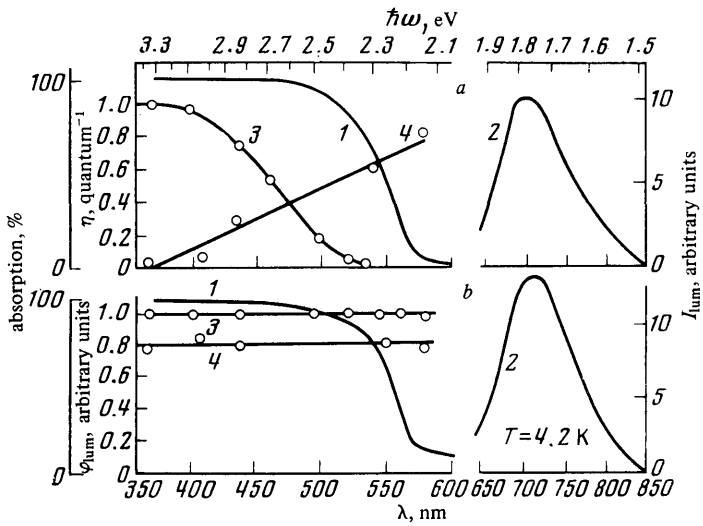



**Figure 7.** Spectra of the photo-processes in the amorphous analogues of the crystalline selenium structures (*a*) monoclinic, *b*) trigonal)[103]: *1*) absorption, *2*) photoluminescence ($I$), *3*) quantum yield of the internal photo-effect $\eta$ (extrapolated from 30 K), *4*) quantum yield of the photoluminescence $\varphi$.

The observed luminescence cannot be due to impurities, which could not explain the specific effects discussed above, and would also be inconsistent with the fact that Urbach's rule is found to apply up to absorption coefficients greater than $10^4$ cm$^{-1}$.[96] However participation of impurities or defects in the luminescence of amorphous selenium is possible in principle, but only if we retain the assumption of interaction via excitons: in this way the luminescence can be interpreted as exciton luminescence. The ground state of the exciton, measured[92] from the luminescence spectrum ($E_{exc}$ = 1.80 eV), lies 0.08 eV below the bottom of the conduction band ($E_{opt}$ = 1.88 eV). We note that $E_{opt}$ was determined according to Sturge's criterion for $\alpha$, corresponding to the mobility threshold ($\sim 10^3$ cm$^{-1}$), whereas $E_{phot}$ was determined by the Moss criterion[104]. The photon energy corresponding to $E_{exc}$ according to Toyazawa's theory and measured from the photoconductivity spectrum was 2.44 eV,[3] i.e. 0.09 eV lower than $E_{phot}$ = 2.53 eV. It may be assumed that the difference between the $E_{exc}$ values measured in absorption and in emission is due to energy dissipation by the excited pair.

In amorphous selenium with a molecular chain structure the quantum energy at the luminescence maximum (1.75 eV) is close to $E_{opt}$ = 1.78 eV, and the $\varphi_{lum}$ spectrum is correlated to the $\eta$ spectrum and does not depend on $\hbar\omega$. This behaviour, and also the very high quantum yield $\eta$ of unity, allow us to interpret the luminescence as recombination-induced, of a type previously observed in amorphous chalcogenide semiconductors[105-107]. As Fig. 7 shows, no exciton absorption peak is observed in either amorphous structure at temperatures down to 4.2 K.

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The optical and photoelectric properties of amorphous selenium structures discussed above indicate the existence of exciton effects in disordered polymeric semiconductors.

By comparing the roles of exciton effects in the photogeneration of charge carriers in organic and in inorganic polymeric photoconductors[28] we conclude that these effects are weaker in inorganic photoconductors because the coulombic interaction of the hole–electron pair created by the absorption of a light quantum is more effectively screened in these materials.

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# Gas-chromatographic Analysis of Products of the Decomposition of Proteins and Nucleic Acids

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Various gas-chromatographic methods for analysing amino-acids, nucleic acid bases, nucleosides, and nucleotides, and also the use of pyrolytic gas chromatography to determine the composition of proteins and nucleic acids, are surveyed critically. A comparison is made of the best analytical results for mixtures of the above compounds by the use of gas-liquid chromatography and high-pressure liquid chromatography. A list of 243 references is included.

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## I. INTRODUCTION

Molecular biology and kindred disciplines are unable to develop if the structures of proteins and nucleic acids, i.e. the sequences of monomeric units (amino-acids and nucleotides) in their molecules, are not established. Such a procedure is extremely laborious because of the high molecular weight of biopolymers. Therefore automation and acceleration of such determinations are highly significant.

Methods of liquid chromatography are widely used in separating mixtures of proteins and nucleic acids and in the qualitative and quantitative analysis of their decomposition products. However, the classic forms of such methods are laborious and insensitive, so that, immediately following the discovery of gas-liquid chromatography[1], research workers became interested in the possibility of using it to separate mixtures of amino-acids[2]. But the need to convert the latter into relatively unstable volatile derivatives presented considerable difficulties in the application of gas-liquid chromatography to their analysis.

In 1958 an automatic method was developed for analysing mixtures of $\alpha$-amino-acids by ion-exchange chromatography[3-6] with a photocolorimeter to detect the amino-acid derivatives; the time required for a complete analysis was a few hours, when the sensitivity of a determination reached $10^{-7}$ mole. By the end of the 1960s the first models of high-pressure liquid chromatographs were manufactured with an ultraviolet-absorption detector, which shortened to 1 h the time required to analyse a mixture of $\alpha$-amino-acids and improved the sensitivity to $10^{-9}$ mole. A limitation of these instruments is the need to obtain aromatic derivatives of amino-acids for detection by their ultraviolet spectra. It might appear that they would displace gas-liquid chromatography completely from laboratory research on biopolymers. However, this method possesses certain advantages over the high-pressure chromatographs—sensitivity enhanced by factors of $10^2$–$10^3$, incomparably greater separating power, and cheaper apparatus (Table)—which explains the development of research on its application to the analysis of breakdown products of biopolymers and its widespread use together with high-pressure liquid chromatographs in practical biochemical investigations.

Comparison of optimum characteristics of gas-liquid chromatography and high-pressure liquid chromatographs in the analysis of degradation products from proteins and nucleic acids.

| Characteristic | Gas-liquid chromatography | High-pressure liquid chromatograph |
|---|---|---|
| Separation of amino-acid mixtures: | | |
| time of separation of 20 protein amino-acids | 15 min | 70 min |
| detection limit—average | $10^{-8}$ g* | $10^{-7}$ g |
| minimum | $10^{-12}$ g** | $10^{-8}$ g |
| stability of derivatives for analysis | moderate | high |
| resolution of optical isomers | possible | impossible |
| total duration of one determination | < 1 h | ~1 h |
| Analysis of amino-acid phenylthiohydantoins: | | |
| time of separation or identification | 50 min | |
| limit of detection | $10^{-10}$ g*** | $10^{-7}$ g |
| Analysis of amino-acid methylthiohydantoins: | | |
| time of separation or identification | 50 min | not used |
| Analysis of peptides: | | |
| possible number of amino-acids in 1 mol. | 4 (12****) | unlimited |
| establishment of structure | possible | impossible |
| Nucleic-acid bases: | | |
| time of separation | 24 min | |
| limit of detection | $10^{-9}$ g | $10^{-7}$ g |
| Cost of complete equipment, $1000 | 10 | 50 |

*Flame-ionisation detector.
**Electron-capture detector.
***Photometric flame detector.
****Theoretically possible number.

Aspects of the gas-chromatographic analysis of amino-acids and nucleic-acid bases (here and subsequently the Reviewer uses the term "nucleic-acid bases" for brevity to cover purine and pyrimidine bases, major and minor,

present in nucleic acids and their fragments—nucleotides and nucleosides) have been considered in > 500 papers. However, reviews on this topic either have become out of date[6-14] or deal with individual aspects[15-17]: relatively complete reviews of the gas–liquid chromatographic analysis of amino-acids have appeared only recently[18-20]. One of these[19] is concerned mainly with quantitative aspects of the analysis of amino-acids, and hardly mentions pyrolytic gas–liquid chromatography and the separation of hydantoin derivatives of the acids. Furthermore, several fundamentally new methods for the analysis of amino-acids and nucleic-acid bases have appeared during the past one or two years.

The present Review surveys critically methods for the gas-chromatographic analysis of amino-acids, nucleic-acid bases, nucleosides, nucleotides, peptides, proteins, and nucleic acids, and compares the best gas-chromatographic methods with results obtained by other chromatographic methods. Most of the above compounds cannot be determined directly by gas chromatography because they are non-volatile, so that attention is directed mainly to quantitative methods for obtaining volatile decomposition products of biopolymers†.

## II. PREPARATION AND SEPARATION OF VOLATILE DERIVATIVES OF AMINO-ACIDS

Twenty α-amino-acids—termed "protein amino-acids"—may be present in proteins. Several other amino-acids are also met in Nature, and some derivatives are hormones. Amino-acids can be classified according to reactivity, which depends on the radical R attached to the amino-acid grouping $H_2N.CH.COOH$; the different groups are characterised by differences in the difficulty of obtaining volatile derivatives and of their gas-chromatographic separation. The first group—glycine, alanine, valine, leucine, isoleucine, methionine, phenylalanine, and proline—exhibit minimal reactivity. A second group comprises threonine, serine, lysine, tyrosine, asparagine, and glutamine. The most active amino-acids—arginine, cysteine, tryptophan, and histidine—form the third group. In addition, several other amino-acids are encountered, e.g. norvaline, α-aminobutyric acid, norleucine, and cystine. Some amino-acids contain iodine (tyrosines); many contain sulphur.

When heated, amino-acids undergo decarboxylation to the corresponding amines. Over the temperature range 180–240°C members of the first group other than isoleucine are converted into amines containing one carbon atom fewer than in the original amino-acid; this applies also to threonine, serine, and norvaline[10]. Raising the temperature to 300°C forms complexes of ammonia with amines containing 1–5 carbon atoms[10]. Complete thermal decomposition of amino-acids results in the evolution of nitrogen, which was used earlier[10] for the qualitative identification of amino-acids. It is now more advisable to employ for this purpose thermionic detectors that are selective for nitrogen[21].

Deamination yields finally aldehydes, which are comparatively easy to determine by gas–liquid chromatography. The oxidation of amino-acids by sodium hypochlorite was examined[10] with α-aminobutyric acid, norvaline, valine, norleucine as examples, the resulting aldehydes being separated on a dinonyl phthalate column at 92°C. However, sodium hydrochlorite proved to be too strong an oxidant, causing degradation of the carbon skeleton, so that the yield of aldehyde from an amino-acid was not quantitative.

Ninhydrin was used to convert leucine and isoleucine into aldehydes, which were then separated on silicone oil at 69°C. Alanine, valine, isoleucine, leucine, norleucine, methionine, threonine, and α-aminobutyric acid were converted quantitatively into aldehydes after reaction for 15–30 min; glycine and phenylalanine were also converted into aldehydes. The amino-acids were oxidised by ninhydrin in a reaction vessel[10-22] comprising a column filled with a solid carrier impregnated with ninhydrin. Alanine, valine, norvaline, leucine, isoleucine, and norleucine were converted[10] into aldehydes with the reaction vessel at 125°C; the aldehydes were then separated on a glycerol–silicone oil column at 65°C.

Although the aldehyde method has not been successful with all protein amino-acids, it is extremely attractive in regard to the ease of separation of volatile derivatives. A recent paper[23] has reported the conversion of amino-acids into aldehydes by means of aqueous silver picolinate for analysis of a mixture of alanine, valine, leucine, isoleucine, proline, glycine, and norleucine, the aldehydes being separated on a polyethylene glycol 4000 column. A suggestion[10] that aldehydes obtained from amino-acids should be oxidised with permanganate to acids and then determined on a polypropylene glycol column at 150°C is hardly advisable, since acids are considerably more difficult than aldehydes to determine chromatographically. Attempts to use ninhydrin to obtain aldehydes from the second and third groups of amino-acids have proved unsuccessful.

Deamination occurs also on the addition of sodium nitrite in acetic acid; the resulting acid is esterified with diazomethane, and the methyl esters are separated on a silicone-oil column with temperature programming[18]. Examination of a mixture of glycine, alanine, valine, leucine, asparagine, and glutamine has shown[24] that the reaction is not quantitative, although the systematic error is constant within the range 2–10%. Esters of isoleucine, threonine, methionine, phenylalanine, histidine, and arginine have been obtained by the same method. The methyl esters from five amino-acids of the first group were separated on a capillary column with Apiezon L at 130°C.[18]

Decarboxylation of amino-acids by *N*-bromosuccinimide has been used to analyse derivatives of alanine, valine, leucine, phenylalanine, and norvaline[18]; the ratio of nitriles and aldehydes obtainable by this reaction varies within wide limits, but the former predominate. The products from alanine, valine, leucine, isoleucine, norleucine, norvaline, and α-aminobutyric acid were separated on a silicone-oil column. Nitriles of amino-acids are formed also by treating them with iodosobenzene; the reaction products were separated on polyethylene glycol and 1,2,3-tris-(2-cyanoethoxy)propane.[18]

The carboxy-group of an amino-acid is reduced to hydroxyl by lithium tetrahydroaluminate with formation of the corresponding aminoalcohol. Reduction products from the first group of amino-acids (other than proline) were separated on a column with 20% of SE-96 or SE-52 silicone oil over the range 155–200°C.[10] Under these conditions the aminoalcohol obtained from tryptophan does not emerge from the column, while the corresponding glycine derivative is masked by the solvent peak. A polar

†Because of limitations of space some of the references to original papers (mostly examples of applications) are quoted from published reviews.

stationary phase—polyethylene glycol 3000—has also been used to separate these products. This method has been employed to establish the composition of the hydrolysate from peptides [18].

Treatment of the first group of amino-acids with a mixture of hydrochloric and nitric acids yields α-chloro-derivatives, whose methyl esters are separated on a mixture of polyethylene glycol with silicone oil and stearic acid [18], a method used to detect norleucine and norvaline in natural products and to establish the structure of dipeptides [18]. Derivatives corresponding to phenylalanine and methionine are not recorded on the chromatogram when the amino-acids are converted into the methyl esters of α-chloro-acids, and treatment of serine gives two peaks. *N*-Thiocarbonyl derivatives have been obtained from the n-propyl esters of amino-acids; tryptophan does not undergo this reaction, while cystine and cysteine form only thiocarbamates [25].

Even the latter comparatively mild methods for obtaining volatile derivatives of amino-acids by removing active groups have not found application in practical analysis, owing to the difficulty of quantitative conversion of the second and third groups of amino-acids.

In the preparation of methyl esters of amino-acids in the presence of hydrogen chloride as catalyst the hydrochlorides of the esters are usually obtained. The free esters are formed by shaking the methanolic solution of the salt with an ion-exchange resin: the resulting solutions remained unchanged for 1–24 h. [10] Methyl esters containing a free amino-group were separated on a column of 2% of poly(neopentyl glycol succinate) on Fluoropak-80; diatomaceous carriers proved to be active for these systems. Great difficulties arose in the chromatographing of the methyl esters of tyrosine, histidine, and tryptophan. Attempts to convert the hydrochlorides into the free esters by thermal dissociation in the heated injector of the chromatograph have proved unsuccessful. Columns with the above sorbent have been used to separate derivatives of isomeric hydroxyprolines. Esters of amino-acids with $C_{2-4}$ alcohols are relatively non-volatile and therefore less suitable for gas–liquid chromatography. Mass-spectrometric investigation of the structure of the ethyl esters of several amino-acids has shown [18] that all these derivatives are indeed ethyl esters, with the exception of ornithine, which cyclises into a lactam.

The most common method for obtaining esters is to treat the amino-acid with the anhydrous alcohol in the presence of hydrogen chloride; sometimes hydrogen bromide and sulphuric acid are used as catalyst. Alcohols can be replaced by derivatives of diazo-compounds. Moisture must be absent from reagents and from initial specimen for quantitative esterification. Small quantities of aqueous amino-acids can be dried by means of an electrically heated platinum spiral [26] in an atmosphere of an inert gas. Esterification is quantitative at 70°C after 30 min [23], although other régimes have been reported: 1.25 *N* methanolic hydrogen chloride at 20°C required 30 min [27]; the n-propyl ester of an amino-acid is formed by treatment with 8 *N* propanolic hydrogen chloride at 100°C for 20 min [28]. Acetyl chloride with methanol and an orthoformate in methanolic hydrogen chloride are also used as esterification catalysts. Another process for obtaining esters is to reflux an amino-acid and an alcohol in the presence of an ion-exchange resin [18]. Methylation by refluxing with dimethyl sulphite in methanolic hydrogen chloride is quantitative and rapid [18,29]; it can be effected also by thionyl chloride with methanol [30].

The sparing solubility of amino-acids in high alcohols complicates their esterification, and this applies especially to cysteine, lysine, and histidine. It has been proposed [18] to overcome such difficulties by initially obtaining the methyl esters and then transesterifying (e.g. with 1.25 *N* n-butanolic hydrogen chloride at 100°C for 150 min [23]). In practical analysis a more common method for dispersing amino-acids in $C_{3-5}$ alcohols is the use of ultrasound: a suspension of the amino-acid in n-butanol was subjected to ultrasonic treatment for 15 s. [31] Recently, however, it has been found [32] that only 50% of the total quantity of amino-acid is esterified under these conditions, and therefore treatment of the suspension for 5 min is recommended, but more complete dissolution of the amino-acid can be effected by adding dichloromethane (10% on the total quantity). Esterification with n-butanol is accomplished in 3.5 *N* hydrogen chloride at 150°C for 15 min [32]; isoleucine is the most difficult to esterify (by 85%), but tryptophan is 15% decomposed; when esterification is prolonged to 2.5 h, isoleucine is completely esterified, but then tryptophan is also completely decomposed [31-36]. The dissolution of amino-acids in alcohols can be improved by adding trifluoroacetic acid; lysine hydrochloride is then completely esterified in a stream of dry hydrogen chloride at 108°C. [37] Amino-acids can be esterified also by means of isodobutane in the presence of methanolic phenyltrimethyl- or tetramethyl-ammonium hydroxide; this reaction takes place in dimethylformamide at room temperature within 10 min. [38]

Thus almost all derivatives of the protein amino-acids can be obtained quantitatively by esterifying the carboxy-group. However, such esters are either hydrochlorides or free esters of the amino-acids with free amino-groups: i.e. they contain at least one active group, which lowers the volatility of the derivative and causes appreciable adsorption on diatomaceous carriers of the compounds to be separated.

Formic acid in acetic anhydride has been used to acylate the second active group [10]. The resulting derivatives were separated on a column with 25% of a high-vacuum oil at 194°C, when conversion into the *N*-formylated methyl esters was at least 95%. The latter compounds contain no hydrogen atoms capable of forming a hydrogen bond, but such esters are highly polar, which prevents their effective chromatographic separation. Indeed, the molecule of an α-amino-acid comprises a radical and an amino-acid group, and such acids differ only in the nature of the radical, so that their successful separation by gas–liquid chromatography requires that the effect of the amino-acid group (free or esterified and acylated) on the retention of the compound should be minimal. This requirement is satisfied only when the amino-acid group is attached to the stationary phase merely by dispersion forces, i.e. with complete shielding of polar bonds by alkyl radicals. A methyl group usually shields polar bonds only to a slight extent. These considerations were confirmed by experiment: comparison of the gas-chromatographic behaviour of *N*-formyl and *N*-acetyl esters revealed [39] comparable retention times, but separation of the latter esters was incomparably better than that of the former, so that use of the *N*-formyl esters to analyse mixtures of amino-acids had to be rejected. The logarithm of the retention time of an ester of a $C_{2-5}$ alcohol with an *N*-acetylated amino-acid is proportional to the molecular weight of the alcohol, whether the stationary phase used is polar or non polar [40]; this indicates fairly complete shielding of polar groups by the ethyl radical.

Acetic anhydride must be used to obtain acetyl derivatives, but its acylating power is not strong enough to acylate quantitatively the hydrochloride of an arginine ester even at 150°C. It is therefore proposed[28] to pass this ester through an ion-exchange resin or to neutralise the salt with an alkali-metal carbonate; it is also possible to convert arginine enzymatically into ornithine, and histidine by ozonolysis into asparagine[18], but such methods are too laborious to be recommended. It is more advisable to acylate amino-acid esters with a mixed reagent comprising acetone, triethylamine, and acetic anhydride in the proportions 5 : 2 : 1 [41] at 60°C for 30 s; arginine then undergoes 78% acylation reproducibly.

The gas-chromatographic behaviour has been studied of methyl and ethyl esters of *N*-acetylated amino-acids[10,39], propyl and isopropyl esters [10,28,41-44], butyl and isobutyl esters [10,44], and pentyl and isopentyl esters [10,45].

The best results for the separation of a mixture of protein amino-acids have been obtained[42] by esterifying the acids in 8 *N* n-propanolic solution at 110°C for 20 min, and acylating with a 5 : 2 : 1 mixture of acetone, triethylamine, and acetic anhydride at 60°C for 30 s. At room temperature the resulting esters do not decompose for several days, and at 4°C they can be kept for several months. The injector unit and the detector were respectively at 250 and 300°C, and the temperature of the column was programmed to rise from 125 to 180°C at 8 deg $min^{-1}$, and from 180 to 250°C at 32 deg $min^{-1}$. A column 90 cm in length and 3 mm in diameter was filled with a sorbent comprising a mixed stationary phase (0.31% Carbowax 20 M + 0.28% Silar 5CP + 0.06% Lexan) deposited on Chromosorb W. Before application of the stationary phase the carrier was heated at 400°C for 1 h. The efficiency of the column was 2250–2400 theoretical plates with respect to a tryptophan derivative, with norleucine as standard. The sample was introduced by means of a Perkin–Elmer automatic capsule injector. Under these conditions derivatives of all three groups of protein amino-acids were separated, as well as ornithine and hydroxyproline, with a detection threshold of $10^{-12}$ mole; the reproducibility of a quantitative analysis was 2–5%. Certain difficulties arose in the analysis of cystine, which have been overcome[46] by first converting cystine and cysteine into their *S*-methoxycarbonyl derivatives, when the sum of these amino-acids is determined. Similar mixtures had been separated in earlier work[43,44], but with poorer results. Separation of amino-acids as *N*-acetylated n-propyl esters has only recently been made possible by the appearance of new equipment and the development of new forms of high-temperature chromatography; in the early stages of the development of gas–liquid chromatography efforts were directed mainly at preparing more volatile derivatives of amino-acids, such as esters of the perfluorinated acids. The emergence of these derivatives from the column is more rapid than that of their non-fluorinated analogues by factors of 3–6, which is why amino-acids were analysed for a long time as such perfluorinated derivatives. The preparation and the gas-chromatographic properties of methyl esters of *N*-trifluoroacetylated amino-acids have been reported[18,35,47-56]; although derivatives of all 20 proteins amino-acids could not be separated in a single analysis, these investigations enriched significantly the experience of working with derivatives of perfluorinated esters. It was observed in particular that *O*- and *S*-trifluoroacetylated amino-acids decompose on polar stationary phases such as polyethers and cyano-derivatives.

Acylated amino-acid esters can in principle be obtained in two ways: (*a*) the ester is obtained initially, and then acylated; or (*b*) initial acylation is followed by esterification. In the latter case esters of hydroxy-acids are not formed, and arginine and histidine do not give volatile products; hence the first method is used for quantitative analysis. Hydrochloride salts of methyl esters of amino-acids are acylated quantitatively with trifluoroacetic anhydride at 120°C in 20 min[10]. It has been recommended[33,34,36] that the dry ester be acylated with a 50-fold excess of the anhydride at 180°C for 5 min; the most difficult to acylate are the arginine and histidine esters, while derivatives of cysteine and of a hydroxylated amino-acid are most liable to hydrolysis. It must be borne in mind that trifluoroacetylated esters are extremely sensitive to moisture, so that it is advisable to introduce the reaction mixture into the chromatograph injector without preliminary vaporisation of the reagents and the solvent. Evaporation of the solvent may involve an indeterminate loss of the most volatile esters of alanine, glycine, and valine, so that the temperature of the mixture should not exceed 0°C during removal of the solvent. Since the histidine derivative is the least stable, it is recommended[57] that it be converted into the *N*-ethoxycarbonyl-*N*-trifluoroacetylated n-butyl ester, which greatly improves its detection. Several authors[58-60] advise that, to prevent hydrolysis of the histidine derivative, excess of the acylating agent should be added before the sample is introduced, since its partial vaporisation from the reaction medium is responsible for the appearance on the chromatogram of a peak due to the mono-acylated histidine derivative[61]. At room temperature all protein amino-acids other than arginine and histidine are acylated within a short time.

In the temperature-programmed analysis of *N*-trifluoroacetylated methyl esters of the 20 protein amino-acids on a column with neopentyl glycol succinate, glycine and leucine remained unresolved, as well as glutamine and phenylalanine; furthermore, the arginine derivative gave three peaks, and considerable difficulties were experienced in the analysis of cysteine and histidine[18]. The best separation of *N*-trifluoroacetylated methyl esters of amino-acids is obtained with a column 3.25 m long full of Diatoport S with 1.5% of a mixed stationary phase (silicone oils XE-60, QF-1, and MS-200 in the proportions 46 : 27 : 27), the temperature being programmed from 90 to 231°C; under these conditions the histidine derivative does not emerge from the column. The time of separation is 85 min.

Widespread use of methyl esters is typical of the first stages in the application of perfluorinated derivatives of amino-acids, but their high polarity impairs separation, while the great volatility diminishes the accuracy of quantitative analysis, especially for the alanine, valine, glycine, and leucine derivatives. As a consequence of these disadvantages attention was directed to esters of alcohols having higher boiling points—ethyl[10], isopropyl[10,62,63], n-propyl[18,44], s-butyl[18,19,64,65], n-butyl[18,31,33,34,58,66-71], n-pentyl and isopentyl[18,37,72-74], and benzyl—as well as to vinyl esters[18].

The n-butanol derivatives have been most widely used for gas-chromatographic analysis, largely because of the work of the Gehrke school. The quite large alkyl radical shields the polar ester group well, and the derivatives possess moderate volatility. Such amino-acid derivatives have been completely separated[33,34] on two columns both 1.5 m long, one filled with Supelcoport impregnated with 2% of silicone oil OV-17 and 1% of silicone oil OV-210,

and the other filled with Chromosorb W impregnated with 0.65% of polyethylene glycol adipate, with temperature programming of the columns from 60 to 225°C. Histidine, arginine, and cysteine do not emerge from the latter column: the former column serves for their determination. Furthermore, hydroxyproline and ornithine are also separated, as well as all the protein amino-acids. With chromatograms from the two columns recorded in parallel the total time for separation does not exceed 30 min. The life of the columns is 2–6 months. Other workers have somewhat varied the quantities of stationary phases on these carriers [75], with 1% of polyethylene glycol adipate and 4.5% of silicone oil OV-17.

In the chromatographic analysis special attention is paid to absence of contact between vapours of the amino-acid derivatives and heated metal surfaces: the injector, the column, and the inlet to the detector should be made of glass. The carrier gas is dried with molecular sieves (the glutamine and asparagine derivatives are the first to be hydrolysed). All glass surfaces in contact with vapours of amino-acid derivatives, including the glass wool used to seal the columns, should be silylated with a 10% solution of dimethyldichlorosilane in toluene at room temperature for 10–12 h, then washed with methanol and toluene, and subsequently dried at 200°C. When not in use, the apparatus should be purged with the carrier gas at 200°C.

The above methods involve the use of small quantities of the stationary phase on a carrier. Under such conditions, however, the form of the retention volume is especially strongly influenced by the various adsorption effects due to the presence of active interfaces in the chromatographic column. The influence of interfacial adsorption on the retention volume of amino-acid derivatives is so great that variation in the quantity of stationary phase on the carrier over the range 0.5–2% changes the sequence in which the methionine, hydroxyproline, and phenylalanine derivatives emerge, as well as the leucine–isoleucine pair [76]. Such effects are extremely undesirable in establishing reliable reproducible methods for commercial analyses. The chief active interface in the separation of amino-acid derivatives is that between the solid carrier and the stationary phase, so that special care is required in the choice of carrier. When polyethylene glycol is used as stationary phase, the inertness of the carrier towards the derivatives increases in the sequence—Chromosorb W AW, Chromosorb W AW DMCS, Gasochrome Q, Chromosorb W HP or G HP [28,77]—but sometimes by no means the most inert carriers, e.g. Chromosorb W AW, [78] have proved quite unexpectedly to be the best. The arginine derivative emerges from a column with OV-17 deposited on Chromosorb W HP, but does not separate when a sorbent based on Chromosorb G HP is used.

A two-column scheme of analysis is not the optimum arrangement, for in particular two pen-recorders are required. The amino-acid derivatives could have been analysed successively on each column, and recorded on a single instrument, but this would lengthen to 50 min the time required for an analysis. The use of switches to transfer the recording from one column to the other and some staggering of the time of introduction of the sample into each column enables this time to be shortened to 35 min.[79]

The chief obstacle to a single-column analysis of protein amino-acids is the poor selectivity of stationary phases having little or no polarity; polyether stationary phases possess good selectivity for the separation of these compounds, but they react with *O*- and *S*-trifluoroacetylated amino-acids. A mixture could be separated only by increasing the quantity of stationary phase (Apiezon M) in the column to 10% on the weight of Chromosorb W.[80] Such quantities of stationary phase lower adsorption effects, which makes the method more reproducible. Eighteen derivatives of protein amino-acids, including cystine and hydroxyproline, have been separated in 35 min on a 2.5 m column with such a sorbent and the temperature programmed to rise from 90 to 260°C. A proportion of the derivatives (14% of methionine, 37% of histidine, and 54% of cysteine) does not emerge from the column, but these quantities are reproducible and do not diminish the value of the quantitative method. The relative error of a determination is 5%.

The use of simple devices to remove excess of reagent and solvent [62] enables down to $10^{-9}$ g of amino-acid to be determined by means of a flame-ionisation detector, and down to $10^{-12}$ g with an electron-capture detector. A thermal ionisation detector with rubidium salts, which detects nitrogen-containing compounds, is intermediate in sensitivity [81]. This last detector is extremely convenient for numerical calculations, since its signal is proportional to the number of nitrogen atoms in the molecule of the test compound, so that preliminary calibration is unnecessary; the sensitivity of such a detector exceeds that of a flame-ionisation detector by factors of 3–20. The sensitivity of the determination of amino-acids can be enhanced by acylation with a chlorophosphate in diethyl ether or in acetonitrile in the presence of triethylamine; the reaction takes 30 min at room temperature, although not all amino-acids give a quantitative yield of products. These derivatives are detected by means of a thermal ionisation detector having a threshold of $10^{-12}$ g.[82] Such derivatives of the first group of amino-acids, asparagine, glycine, and $\beta$-alanine are separated on a 2-m column containing 6% of silicone oil OV-17 on Chromosorb G HP with the temperature programmed from 210 to 250°C. This method has been used to establish the amino-acid sequence in the proteins of gramicidin S.

The extremely high sensitivity of gas chromatography has enabled amino-acids to be determined in specimens of the moon's surface brought back by the crews of Apollo 11 and 12.[83]

The time consumed in preparing volatile amino-acid derivatives is comparable with that required to separate these compounds: a series of papers therefore appeared on accelerating the preparation of samples. For example, three separately heated aluminium blocks can be used having depressions for ampoules, in which all operations to prepare derivatives are conducted [84]. The most radical solution to the problem was suggested to obtain methyl esters of *N*-heptafluorobutyrylated amino-acids [85] using an MS-41 (Perkin–Elmer) automatic capsule injector. The specimen and the methylating reagents were placed in a gold capsule, which was then closed; the process was conducted at 80°C for 10 min. The capsule was then opened, and moisture was removed by azeotropic distillation with dichloromethane. Hydrochlorides of methyl esters of amino-acids can be kept in a desiccator for a long time. Before an analysis an acylating agent was added to the capsule, and reaction occurred in the closed capsule at an elevated temperature; the cooled capsule was placed in the carrier of the automatic injector. Subsequent analytical operations and calculation of the results were effected automatically.

The search for amino-acid derivatives suitable for gas–liquid chromatography was not confined to the trifluoroacetyl compounds: acylation with pentafluoropropionic[59,86-89] and with heptafluorobutyric[59,61,85,86,90,91] acids was tried. The use of derivatives containing a large number of fluorine atoms enhances the sensitivity of an electron-capture detector, and enlarging the non-polar radical has a favourable influence on the selectivity of columns. The diminished polarity of the heptafluorobutyryl derivatives tends to shorten the retention time by 35% in comparison with the trifluoroacetyl compounds. The former are not so sensitive to moisture as the latter, and can be washed with organic solvents without danger of hydrolysis, while removal of the excess of reagent and solvent from the reaction mixture presents no difficulties[91]. For example, solutions of n-propyl esters of heptafluorobutyrylated amino-acids can be evaporated without risk of a change in quantitative composition of the amino-acid derivatives; at the same time the tendency of the solvent peak to mask the most volatile components of the amino-acid mixture becomes less marked. Among the disadvantages of heptafluorobutyric anhydride are its high cost, its toxicity, and its persistent unpleasant odour.

n-Propyl esters of heptafluorobutyryl derivatives of 19 protein amino-acids have been separated in 35 min on a glass capillary column with chemically bound polydimethylsiloxane and the temperature programmed from 70 to 230°C[159]; isoleucine forms two peaks, one due to isoleucine itself, and the other to alloisoleucine. Such esters from 18 amino-acids, including hydroxyproline and cystine, have been separated in 43 min on a 3.6-m glass column with 3% of silicone oil OV-1 and the temperature programmed from 100 to 250°C.[185] Determination of histidine is improved by introducing into the column, after addition of the sample, a small quantity of acetic anhydride; methionine and asparagine are not completely separated.

Eighteen protein amino-acids, pipecolic acid, ornithine, kynurenine, and cystine have been separated in 35 min as the isopentyl esters of the heptafluorobutyryl derivatives on a 3.5-m glass column with 3% of silicone rubber SE-30 and the temperature programmed from 70 to 240°C [18]; the sensitivity of the determination by means of a flame-ionisation detector is $10^{-10}$ g of the amino-acid. Large quantities of glutamine in the mixture impair its separation with lysine and tyrosine. Somewhat poorer results in separating the same amino-acid derivatives have been obtained[91] on a glass column 2.4 m long full of a carrier with 15% of Dexsil-300 and the temperature programmed from 140 to 270°C; serine and valine are not separated, but hydroxyproline gives two peaks, one of which corresponds to its allo-isomer. Isopentyl esters of heptafluorobutyryl derivatives have been regarded[61] as most suitable for the analysis of amino-acids, because preparation of the samples involves no loss of ester by vaporisation.

Perfluoroacyl derivatives esterified with various alcohols are widely used in the analysis of mixtures of non-protein amino-acids—those of peat[92], metabolites of tyrosine and tryptophan[93], iodinated[94] and cyanoethylated[18] amino-acids, mixtures of hydroxyproline and proline[18], and mixtures containing β-alanine[95]—and several publications[96-99] have dealt with the separation of acylated esters in the determination of amino-acids in various biological materials and individual aspects of such analyses. Thus esterification and acylation enable volatile derivatives to be obtained quantitatively from all protein and many non-protein amino-acids. Although a large proportion of the investigations have been concerned with separating volatile esters of perfluorinated acids, the most rapid determinations have been made by separating n-propyl esters of *N*-acetyl derivatives.

Because the use of acylated esters has the important disadvantage of involving two stages, efforts have been made to develop a single-stage process for obtaining volatile compounds, primarily trimethylsilyl derivatives of amino-acids. Silylating agents react both with the carbonyl and with amino- and hydroxy-groups, which makes it possible to conduct the whole treatment in a single stage. The amino-group is most difficult to silylate, which limits the overall rate. The first report on trimethylsilyl derivatives of amino-acids appeared in 1959,[100] almost simultaneously with the start of investigations on the separation of acylated esters. Trimethylchlorosilane was used as silylating agent for the first group of amino-acids, when the process was quantitative. All these derivatives, other than the methionine and proline esters, were separated on a column with silicone oil at 165°C; the cysteine, lysine, and histidine derivatives underwent partial decomposition in the column.

All silyl derivatives of amino-acids are extremely sensitive to moisture and to oxygen[15,101]: even a fresh rubber washer for the injector must be conditioned two or three times before an analysis to remove moisture. The great lability of trimethylsilyl derivatives of amino-acids and the difficulties of quantitative silanisation of all protein amino-acids led to a prolonged interruption of research on their application in gas–liquid chromatography. To increase the stability of the trimethylsilyl derivatives the starting materials must be carefully purified and the diethylamine that is formed must be removed from the reaction zone. Because of the inadequate silylating power of trimethylchlorosilane a search was begun for optimal silanising agents. A mixture of trimethylchlorosilane with hexamethyldisilazane has been used[15]. Leucine, serine, and asparagine are then the most difficult to silanise; their silanisation is improved by the use of trimethylsilyldiethylamine in the presence of aluminium and silicon oxides as catalysts. Detailed investigation showed that derivatives containing different numbers of trimethylsilyl groups are formed, those with more groups being less volatile, so that it is advisable to arrest the process in the early stages[102]. Various compounds—trimethylsilyldiethylamine, trimethylsilylamine, bistrimethylsilylacetamide, bistrimethylsilyltrifluoroacetamide, and *N*-methyl-*N*-trimethylsilylacetamide—have been proposed as silanising agents.

Amines proved the best agents when non-polar solvents were used[103]. *N*-Trimethylsilylimidazole and trifluoro-*N*-methyl-*N*-trimethylsilylacetamide have also been tried[15]. When polar solvents have been used, the best results have been obtained with amides[104], especially bistrimethylsilylacetamide. In separation on silicone stationary phases, however, the peaks of the glycine and alanine derivatives are masked by the solvent peak, so that the use of bistrimethylsilyltrifluoroacetamide is preferable[105,106]. A mixture of such derivatives of all protein amino-acids has been separated in 42 min on a 2-m column full of Supelcoport with 10% of silicone oil OV-11 and the temperature programmed from 80 to 210°C.[107-109]; ornithine and arginine are not separated. Lengthening the column to 6 m enables good separation to be obtained for all the mixture components and ornithine. Polyether stationary phases are not used in the separation of trimethylsilyl derivatives of amino-acids, since they

cause decomposition[110]. The separation of such derivatives of 18 protein amino-acids on a 3.7-m glass column with 3% of silicone oil DC-550 and the temperature programmed from 60 to 280°C required 24 min [111-113]; proline and glutamine were not separated.

Careful choice of esterification parameters is necessary in obtaining trimethylsilyl derivatives of amino-acids. The principal difficulties in quantitative esterification lie in the need for control at the stages of mono- and di-substitution in the amino-group; this is especially important with glycine, tryptophan, and lysine. If a non-polar solvent is used for silylation, glycine gives only the mono-substituted product, but arginine does not react; addition of 1% of trimethylchlorosilane to bistrimethylsilyltrifluoroacetamide enables arginine to be silanised, but disubstituted products of other amino-acids appear. In a polar solvent (acetonitrile) addition of trimethylchlorosilane can be avoided, but the time required for complete silanisation at 150°C is 2.5 h. With a polar solvent under optimum conditions the reaction is conducted for 1.5 h, which sharply diminishes the content of disubstituted products, with some incompleteness of reaction.

Several non-protein amino-acids undergo structural changes during silanisation. Thus cyclic products are formed from glutamic and $\alpha\gamma$-diaminobutyric acids[114]; derivatives of $\omega$- and $\alpha\omega$-amino-acids emerge from the column as two peaks with different numbers of trimethylsilyl groups in the molecule.

Like the acylated ester derivatives, the trimethylsilyl compounds can be prepared in hermetically sealed gold capsules, which are then introduced into the chromatograph by means of an automatic injector.

The time required for the separation of protein amino-acids as their trimethylsilyl derivatives is double that required for the acylated esters. An undoubted advantage of the former is that they can be obtained in a single stage, but the duration of silanisation is far longer than for esterification and acylation. Furthermore, trimethylsilyl derivatives are rather less stable than the acylated esters; arginine is difficult to silanise, but histidine and tryptophan do not readily yield acylated esters; and the composition of a mixture of amino-acids can be determined more reliably by combining these two methods. Flame-ionisation and thermoionic detectors with a threshold of $\sim 10^{-9}$ g are usually employed for trimethylsilyl derivatives of amino-acids.

Trimethylsilyl derivatives of the amino-acids containing sulphur and selenium that are necessary for the efficient nutrition of animals can be separated by means of columns with silicone elastomer SE-30: at 117°C derivatives of cysteine, methionine, and their sulphur and selenium analogues are separated[115]. Selenium-containing amino-acids decompose when heated with bistrimethylsilylacetamide, and therefore the reagent "trisil" is used for their silanisation. With cysteine, cystine, homocystine, cysteic acid, and *L*-2-thiohistidine dark-coloured oxidation products appear on silanisation.

Trimethylsilyl derivatives of amino-acid esters have also been investigated[15]: silanised n-butyl esters of the 20 protein amino-acids have been separated in 32 min on a glass column containing glass beads with 0.2% of OV-17 at from 90 to 225°C; cysteine emerges together with hydroxyproline. However, the involvement of yet another stage, esterification, cannot be regarded as desirable for analytical work.

The difficulty of obtaining trimethylsilyl derivatives and their instability have resulted in continuous search for mild new methods of obtaining amino-acid derivatives. It has been proposed[116] that treatment of the hydrochlorides of the methyl esters with sodium carbonate, isobutyraldehyde, and a hydrogen sulphite should be followed by reduction to give stable esters resistant to hydrolysis. Another suggestion[117,118] is to introduce trifluoroacetylated amino-acids directly into the heated zone of the chromatograph injector, when volatile oxazolin-5-ones are formed. Eleven oxazolines of the first and second groups of amino-acids have been separated on a column with polyethylene glycol adipate deposited on Chromosorb W HP with the temperature programmed from 40 to 140°C. Cyanoethyl and cyanobutyl esters of amino-acids have been examined[119]. A mixture of dimethylformamide with a dialkyl acetal and 1,3-dichlorotetrafluoroacetone has been used to obtain volatile derivatives of amino-acids in a single stage[120]. This reagent alkylates the carboxyl and condenses with the amino-group; however, hydroxy-groups do not react, and additionally require acylation. The total time of the reaction is ~1 h, and the greatest difficulties are encountered in obtaining the asparagine derivative.

Halogenated acetones provide an extremely promising method for obtaining volatile derivatives of amino-acids. A rapid procedure developed recently[121] involves condensation with dichlorotetrafluoroacetone in weakly alkaline medium at room temperature to give a cyclic structure within a few minutes; both hydroxy-groups and also $\omega$-amino-groups must be acylated. These derivatives are stable for several months, but the acylated derivatives for only a week (when kept at 4°C). A column 1.8 m long with 5% of silicone elastomer SE-30 and the temperature programmed from 150 to 230°C has been used; satisfactory separation is achieved also by means of silicone oil OV-17.[122] Amino-acids containing iodine have been determined by these methods.

It has been proposed[123] to determine tryptophan as the trimethylsilyl derivative of 2,3,4,5-tetrahydro-*S*-carboline-4-carboxylic acid on silicone elastomer SE-30. Methyl esters of *N*-isobutoxycarbonylated amino-acids (protein amino-acids other than arginine) have been separated on a column containing 0.7% of a mixed stationary phase (Poly-A-101A, Poly-A-103, and FFAP in the proportions 3 : 3 : 1).[124]

The above survey of various methods for obtaining volatile derivatives of amino-acids has shown that a convenient single-stage method is not yet available. However, the development of several methods, e.g. cyclisation, will probably enable stable volatile derivatives to be obtained in the near future.

## III. SEPARATION OF OPTICAL ISOMERS OF AMINO-ACIDS

Optical isomers are resolved mainly by two methods: (1) derivatives of amino-acids with optically active reagents are obtained, and are resolved on the usual stationary phases; (2) volatile derivatives obtained without the use of optically active reagents are separated on an optically active stationary phase. A necessary condition for resolution by gas–liquid chromatography was the presence of at least two asymmetric carbon atoms either in the sorbate molecule or in a molecule of the stationary phase. This rule enables derivatives of hydroxy-amino-acids to be separated on the usually stationary phases[18], since the molecules of such amino-acids contain two optically active carbon atoms.

1. Separation of an Optically Inactive Stationary Phase

Any optically active alcohol, e.g. butan-2-ol or a homologue, can be used as reagent. Esterification is accomplished in a 4–8 *N* solution of hydrogen chloride in the alcohol at 100°C for 1 h. Esters of secondary alcohols and amino-acids of the first group, including asparagine, lysine, glutamine, and hydroxyproline, acylated with trifluoroacetic anhydride, were separated on a 50-m capillary column with polypropylene glycol or fluorosilicone oil FS-1265.[125,126] Optical isomers of derivatives of octan-2-ol are separated better than are those of butan-2-ol, but the former are less volatile, and amino-acids are sparingly soluble in the latter alcohol. Optical isomers of s-butyl esters of *N*-trifluoroacetylated protein amino-acids, other than histidine, arginine, and cysteine, were separated on a capillary column with polyethylene glycol or Yukon LB-550X.[127,128] Partial resolution of optical isomers of a mixture of alanine, valine, leucine, threonine, serine, cysteine, phenylalanine, and tyrosine as the s-butyl esters of the *N*-trifluoroacetylated derivatives has been effected on a 1.8-m column full of the carrier with 0.65% of polyethylene glycol adipate and the temperature programmed from 80 to 215°C. All these compounds, together with isoleucine, proline, and methionine, have been separated[129] under the same temperature conditions but with a lower content (0.32%) of polyethylene glycol adipate on the carrier. Splitting of peaks into optically active components was not observed for lysine and ornithine. The total time required to separate isomers of 17 amino-acids was 80 min. The use of sorbents with a small quantity of stationary phase is open to the same objections as in the separation of acylated esters.

Gas-chromatographic separation of optical isomers of amino-acids as s-pentyl and s-butyl esters has been regarded[129-133] as more advisable. The influence of the structure of the alcohols on the resolution of optically isomeric amino-acids has been examined with phenylalanine as example[134]: increasing the length ratio of the radicals attached to the asymmetric atom in the ester improves the resolution; elimination of branching of the carbon chain from the optically active carbon has a similar effect. The best separation has been obtained with the 1,2,2-trimethylpropyl esters, which forms the basis[135] of a method for separating optical isomers of 16 amino-acids (arginine, histidine, and cysteine were not studied). Volatile derivatives of these amino-acids were separated on a 3-m column full of Chromosorb W with 10% of silicone oil OV-17. Esters of other alcohols have also been used—those of pentan-2-ol to resolve valine isomers, methyl esters[2], and t-butoxycarbonyl derivatives treated with (*D*)-1,3-dimethylbutylamides.[18]

Esters of $C_{5-8}$ secondary alcohols and acyl derivatives from trifluoroacetic, pentafluoropropionic, and heptafluorobutyric anhydrides have been examined[130] to determine optimum conditions for the gas-chromatographic separation of isomeric amino-acids. Optical isomers of asparagine (*N*-trifluoroacetylated 1,2,2-trimethylpropyl and *N*-perfluorobenzoylated s-butyl esters) have been resolved on a capillary column 50 m long with Yukon LB-550X [136-141] and with polyethylene glycol.[128]

An alternative method for obtaining optically active volatile derivatives of amino-acids is acylation with optically active agents. The carbonyl chlorides—α-chloropropionyl,[136,142,143] α-bromopropionyl,[144] α-chloroacetyl,[142,143] *N*-trifluoroacetylthiazolin-4-ylcarbonyl,[145] and *N*-trifluoroacetylprolyl [146-152]—have been used for this purpose. The applicability of the chlorides of various α-chloro-carboxylic acids for acylating amino-acids has been studied[143-153], and use of a polar stationary phase shown to give the best separation of isomers. α-Bromopropionic derivatives gave the best resolution of optical isomers of phenylalanine on a capillary column 46 m long with polypropylene glycol or silicone oil XE-60 [154]; however, difficulties were noted in preparing the optically pure reagent. Acylation of methyl esters of amino-acids with *N*-trifluoroacetyl-*L*(or *D*)-prolyl chloride is most widely used in practical analysis; this reagent is prepared by treating the *L*-proline with thionyl chloride[146]. Although the preparation is made under very mild conditions, racemisation of the product is not excluded[147]. Measures have been suggested[147] to control individual stages in the preparation with the aim of preventing racemisation.

Hence either esterification with optically active alcohols or acylation with optically active agents can be used to obtain optically active volatile derivatives of amino-acids for their subsequent separation by gas–liquid chromatography. Only capillary columns are normally employed in the former method, because of the small differences in the retention of optical isomers. Differences in the retention times of derivatives are larger in the latter case, and their separation is usually accomplished on packed columns.

2. Separation on Optically Active Stationary Phases

Optically active stationary phases can be divided into three groups—(*a*) ureides, (*b*) ethers, and (*c*) dipeptides—among which the last group find the greatest analytical use.

The separation of optically active isomers of amino-acids was first accomplished as their *N*-trifluoroacetyl-*L*-prolyl derivatives on an optically active stationary phase[146,154,155]; it was later shown that the best stationary phase is the cyclohexyl ester of *N*-trifluoroacetyl-*L*-valyl-*L*-valine.[156-158] The upper temperature limit at which this stationary phase can be used is 110°C, which rises by 10 deg when the same ester of *N*-trifluoroacetyl-*L*-phenylalanyl-*L*-leucine is employed[159,160]. Some results[161-165] indicate that the latter stationary phase retains its effectiveness up to 140°C, when the use of perfluoropropionylated isopropyl derivatives of amino-acids enables retention times to be shortened considerably. Mixtures of optical isomers of 17 amino-acids have been separated on short and long capillary columns (30 and 120 m) under isothermal conditions at temperatures of 110–125°C.[156-160]

The separation of derivatives of optical isomers of amino-acids on an optically active stationary phase has been attributed to the formation of triple hydrogen bonds between the interacting molecules, steric hindrance to hydrogen bonding being minimal if sorbate and sorbent belong to the same optical class. The selectivity of stationary phases is increased by using esters of alcohols having branched chains. Comparison of the separating properties of cyclohexyl esters of *N*-trifluoroacetyl-*L*-valyl-*L*-valine and *N*-trifluoroacetyl-*L*-valyl-*DL*-valine showed that better results are obtained when the latter stationary phase is used[168].

An appreciable disadvantage of optically active stationary phases is their low thermal stability: the maximum temperature at which tripeptides can be used does not exceed 120°C, while solid polypeptides, though stable up to 200°C, are incapable of resolving optically active isomers[18]. If the formula of an amino-acid derivative is

written $CF_3.CO.NH.CHR.COOR'$, the achievement of maximum isomeric selectivity requires that $R > COOR'$.[169,170]

Since differences in the retention of optical isomers are small, it is preferable to use capillary columns. For example, isobutyl esters of *N*-trifluoroacetamido-acids have been separated on a dipeptide optically active stationary phase in a capillary column 120 m long; a time of 70 min did not result in complete separation of the isomers of alanine, valine, threonine, isoleucine, serine, and leucine; and tyrosine and arginine isomers were resolved on a short (12 m) column[159]. Isoproyl esters of *N*-trifluoroacetamido-acids were separated on capillary columns 30–150 m long with the cyclohexyl ester of *N*-trifluoroacetyl-*L*-valyl-*L*-valine [108]; on the cyclohexyl ester of *N*-trifluoroacetyl-*L*-valyl-*L*-leucine at 110°C mixtures of isomers of valine, alanine, threonine, isoleucine, leucine, and proline were separated with a column length of 30 m in 130 min[167]. A mixture of isomeric isopropyl esters of *N*-trifluoroacetylated alanine, valine, threonine, isoleucine, leucine, serine, proline, and glycine has been separated on a column 120 m long with cyclohexyl *N*-trifluoroacetyl-*L*-$\alpha$-aminobutyrate at 100°C.[136] Optical isomers of such ester derivatives of amino-acids have been resolved also on a glass column with the cyclohexyl ester of *N*-trifluoroacetyl-*L*-valyl-valine at 110°C,[171] a procedure that has been used for several applied investigations[18].

Each of the above methods for determining optically active isomers of amino-acids has its advantages. However, the first method requires reagents of high optical purity, and a highly efficient column must be used to separate esters of branched alcohols and amino-acids. The second method does not demand high optical purity of the stationary phase, but its possibilities are restricted by the relatively low limiting temperature at which such stationary phases can be used.

## IV. SEPARATION OF PEPTIDES

The same methods as for amino-acids are used to protect active groups in peptides, while the thermal stability of the derivatives is limited by the temperature of rupture of peptide bonds (200–250°C). The possibility of the gas-chromatographic separation of peptides as volatile derivatives is interesting from the two aspects of (*a*) the extent to which large polymeric molecules possess the required volatility and (*b*) the separating power needed by a chromatographic column to separate all dipeptides (400 are possible for protein amino-acids). The reduction of peptides with lithium tetrahydroaluminate gives polyaminoalcohols, which are separated on a column with 8% of Apiezon L. This procedure has been used to separate mixtures of di-, tri-, and tetra-peptides.[18,160] Methyl esters of *N*-trifluoroacetylated penta- and hexa-peptides have been obtained, and finally volatile derivatives of peptides containing up to 12 amino-acids have been reported[172]. The thermal stability of peptides is largely determined by the nature of the monomer units, so that not all tri- and poly-peptides can be analysed by gas–liquid chromatography. Volatile derivatives of these compounds have been described[173–178].

Methyl esters of *N*-trifluoroacetylated dipeptides have been separated at 180–220°C, and the corresponding derivatives of tripeptides at 250°C.[18] The gas-chromatographic separation of esters of acetylated, trimethoxyacetylated, trifluoroacetylated, and pentafluoropropionylated derivatives of 37 dipeptides has been examined on various stationary phases[179]. Separation of dipeptides as their *N*-trifluoroacetylated esters is usually accomplished by high-temperature gas–liquid chromatography with a small quantity of stationary phase on the carrier and with temperature programming. Peptides containing arginine form volatile derivatives with difficulty. In several cases the inertness of the solid carrier surface plays a decisive part in separating volatile derivatives of dipeptides: the first few samples are chemisorbed, and preliminary introduction of three or four samples into the column is necessary to obtain quantitative information.

A highly promising approach is to combine mass spectrometry with gas chromatography to determine the composition of di- and poly-peptides. In contrast to liquid chromatography, the great efficiency of gas–liquid chromatography enables many isomeric compounds to be separated, and then their structure to be established mass-spectrometrically; moreover, by withdrawing separate portions of the chromatographic zones emerging from the column, it is possible by means of a mass spectrometer to establish the presence of unseparated compounds.

The above results indicate the great possibilities of the gas-chromatographic method for separating peptides containing up to 12 monomer units in the molecule. An especially promising approach to the analysis of peptides is to combine high-pressure liquid chromatographs and gas–liquid chromatography, which in many respects are complementary.

## V. APPLICATION OF PYROLYTIC GAS CHROMATOGRAPHY

The principle of pyrolytic gas chromatography consists in almost instantaneous decomposition of a microsample (0.1–1 mg) at a controlled temperature. Only products of the initial degradation reactions are then observed, so that the composition of the test substance can be determined unambiguously. It is a qualitative method, suitable mainly for identifying a single compound or for establishing its structure.

Studies in which volatile derivatives of amino-acids were obtained by heating to 300°C were mentioned at the beginning of the Review. The use of higher temperatures in pyrolytic gas chromatography enables characteristic spectra of decomposition products (pyrograms) to be obtained[180–182]. With pyrolysis on a platinum spiral heated to redness and use of a squalane separating column, for example, several characteristic peaks were observed[183] for phenylalanine and alanine. In the absence of temperature control of the spiral, however, this method of pyrolysis is not generally applicable: histidine, tryptophan, and tyrosine do not form volatile products, and about half the protein amino-acids do not give characteristic pyrograms. Only the use of pyrolysers with strict temperature control (e.g. with ferromagnetic heaters having a definite Curie point or with electronic temperature control of the spiral) has enabled characteristic pyrograms to be obtained for amino-acids. Pyrolysis of protein amino-acids at 700°C with mass-spectrometric identification of the products will yield characteristic pyrograms, which show that the chief decomposition products from amino-acids are nitriles[184–187].

Lowering the pyrolysis temperature and using a column 2.4 m long with 5% of 1,2,3-tris-(2-cyanoethoxy)propane and temperature programming from −180 to 125°C gave different products[188,189]. The same study showed that the

pyrolysis spectra of ten different dipeptides were combinations of the characteristic pyrograms of their constituent amino-acids.

Investigation of the pyrolysis of equimolecular mixtures of amino-acids in an atmosphere of nitrogen at 850°C indicates [190-192] that the addition of non-aromatic amino-acids to those containing aromatic rings lowers appreciably the quantity of aromatic hydrocarbons among the pyrolysis products. However, this does not prevent qualitative determinations, since only the proportions of the decomposition products change, but the characteristic peaks on the pyrograms do not disappear. Hence the pyrolysis of peptides will provide information on their amino-acid composition; the temperature of pyrolysis may be either low (300°C) or high (about 800°C), and this temperature influences the composition of the products [193-196].

The determination of pyrolysis products is of interest also for study of the mechanism of the thermal breakdown of biopolymers. In several investigations [197-199] the products of pyrolysis at 500°C were identified by means of a mass spectrometer, and separation was effected on the polymeric sorbent Tenax with the temperature programmed from 25 to 285°C. At these temperatures aliphatic amino-acids undergo decarboxylation with the formation of amines and several other compounds; this is accompanied by condensation of the amino-acids with their conversion into dipeptides and subsequent formation of the corresponding dioxopiperazine. While losing ammonia, $\beta$-amino-acids are converted into unsaturated acids, whereas $\gamma$- and $\omega$-amino-acids form on pyrolysis 2-oxopyrrolidines and 2-oxopiperidines respectively. The presence of large quantities of hydrogen cyanide among the pyrolysis products as a consequence of cyclisation reactions provides evidence of such a mechanism [197]. Since dioxopiperazines are quite volatile, it is of interest to use them as derivatives of the dipeptides for gas-chromatographic analysis. Thus products of the pyrolysis of dipeptides at 400°C have been separated on a column with 5% of silicone liquid OV-17 at 240°C. [198] The dioxopiperazine method is restricted by the need for condensation of the amino-acid (in the determination of individual amino-acids). This can be effected e.g. by heating the methyl esters of the amino-acids in molten phenol at 150°C. [192] Silanisation of the pyrolysis products with bistrimethylsilylacetamide at 80°C for 10 min permits the time required for the analysis to be greatly shortened and the symmetry of the peaks to be improved, which removes the difficulties encountered [19] in determining dioxopiperazines.

Pyrolytic gas chromatography has been used to determine the sequence of amino-acids in peptide molecules: pyrolysis of the initial peptide is followed by detachment of the terminal amino-acid and then pyrolysis of the product, when comparison of the two pyrograms enables the terminal amino-acid to be identified [200]. This method has been used to establish the primary structure of the proteins in four actinomycins [198]. Several amino-acid phenylthiohydrantoins have been studied by pyrolytic gas chromatography [201].

Pyrograms of proteins and nucleic acids have been obtained with pyrolysis temperatures of 800°C; although they contain the same numbers of characteristic peaks, the proportions of the latter can be used to identify the macromolecules. Such determination of proteins and nucleic acids is considerably simplified by use of a thermal ionisation detector sensitive to nitrogen; the pyrograms contain a total of six characteristic peaks, the relative heights of which enable the molecule to be identified. Furthermore, pyrolytic gas chromatography has proved an extremely effective procedure for classifying proteins, nucleic acids, individual cells, viruses, etc.; combination with mass spectrometry is widely used to study the nature of biopolymers [18].

## VI. DETERMINATION OF THE SEQUENCE OF AMINO-ACIDS IN PROTEINS

Several methods of successively detaching terminal amino-acids have been developed to establish the primary structure of protein molecules. Pyrolytic gas chromatography can be used to determine the amino-acid composition of proteins, but the amino-acid sequence can be studied only by the application of mild methods. From two to five successively combined amino-acids can be determined in a single procedure: since the molecular weight of proteins may reach several millions, determination of the primary structure of a protein is obviously a most laborious operation.

Among several methods of detachment the most widely used is Edman's [18], in which the starting material is treated with phenyl isothiocyanate, after which the terminal group is split off in hydrochloric-acid medium; the final product is a phenylthiohydantoin, whose bicyclic molecule contains an imino-group, a carbonyl group, and the radical of the original amino-acid. The absence of a carboxy-group enhances the volatility of the derivative, while the presence of the benzene ring is extremely useful for application of a high-pressure liquid chromatograph, with which an ultraviolet detector is used. The phenylthiohydantoin derivative of only one amino-acid is obtained after each unit operation, so that the task of gas–liquid chromatography is to establish the nature of the derivatives from retention data. Demands on the analytical technique are increased when it is necessary to determine in one sample the products of 2–5 detachment stages without elution.

Amino-acids can be divided into three groups according to the volatility of the phenylthiohydantoin derivatives: (*a*) asparagine, glutamine, and cysteine give low volatility, and silanisation is necessary for their gas-chromatographic determination; (*b*) serine, threonine, and histidine give moderate volatility, and silanisation is desirable; and (*c*) silanisation of the remaining amino-acid phenylthiohydantoin derivatives makes no appreciable difference to their volatility. Silanisation is effected in a mixture of bistrimethylsilyltrifluoroacetamide with acetonitrile (1 : 1) and added pyridine [202]. The first separation of phenylthiohydantoin derivatives of amino-acids revealed [176,203] considerable difficulties in analysing the derivatives of serine, threonine, tyrosine, and hydroxylated amino-acids. The separation of 18 such derivatives has been reported [204]; silanisation has been used to increase their volatility [205]. These techniques have been applied to determine the sequence of amino-acids in proteins [18].

The analytical procedure for phenylthiohydantoin derivatives of amino-acids has been described in some detail [206]. As with the esters, contact with heated metal surfaces must be avoided. Silanisation of the derivatives directly in the column by successively injecting the silanising agent is recommended, but under these conditions not all such derivatives react: in particular, it is advisable to silanise those of asparagine, cysteine, and glutamine before introduction of the sample, while those of lysine and *S*-carboxymethylcysteine are extremely

difficult to silanise. The trimethylsilylated phenylthiohydantoin derivatives of asparagine, glutamine, and cysteine are adsorbed appreciably on the carrier, while the phenylthiohydantoin derivatives of tyrosine and tryptophan are not very volatile. A mixture of derivatives can be separated on a mixed stationary phase (11% SP-400 + 8% silicone liquid OV-210 + 1% OV-225) in a 1.2-m column with temperature programming from 165 to 270°C; complete separation is found with 13 derivatives. The sample is analysed twice—the initial mixture and the silanised products—to ensure reliable identification. Although the phenylthiohydantoin derivatives of serine, threonine, histidine, glutamine, asparagine, and lysine are partly decomposed in the column, this is not significant for qualitative analysis. The total time of separation is 40–50 min.

Trimethylsilylated phenylthiohydantoin derivatives of protein amino-acids can be partly separated on a column 3.25 m long containing 5% of silicone liquid OV-17 and 1% of Dexsil-300.[207] Nineteen of the twenty trimethylsilylated amino-acid phenylthiohydantoins have been separated on a capillary column of length 4.5 m and diameter 0.13 mm with a mixture of silicone liquids OV-101 and OV-225; the phenylthiohydantoin of histidine is evolved only at high temperatures, cysteine was converted into cystine, and arginine into ornithine[208]. Special difficulties arise in analysing the trimethylsilylated phenylthiohydantoin of arginine: on no stationary phase could escape of this derivative be achieved. The peak of the arginine phenylthiohydantoin emerges only after the derivative has been acylated with a mixture (4 : 1) of acetic anhydride and pyridine at 100°C for 5 min [209]; acylation can be effected also by introducing the phenylthiohydantoin sample with acetic anhydride directly into the heated injector of the chromatograph. Such derivatives have been used to establish the molecular structure of several proteins[18].

Volatile derivatives of amino-acid phenylthiohydantoins have been obtained also by treating proteins with perfluorophenyl isocyanate[210]. These derivatives of protein amino-acids other than arginine and histidine have been separated on a 1.2-m column full of Chromosorb W with 10% of silicone liquid DC-500 and 2% of OV-25 with temperature programming from 160 to 240°C.

The sensitivity and the selectivity of the gas-chromatographic determination of amino-acid phenylthiohydantoins are considerably enhanced by use of a flame-photometric detector, which records only compounds containing sulphur. This enables the aggregate fractions from removal of terminal amino-acids to be analysed successfully without the need to wash away the products after each stage. The sensitivity of a determination is $10^{-9}$ g of amino-acid phenylthiohydantoin.

Methylthiohydantoins have also been used to determine the amino-acid sequence in proteins; the process of sequencing is then simplified, and the greater volatility of these derivatives compared with the phenylthiohydantoins favours their gas-chromatographic separation. Silanisation is not essential at least for 16 amino-acid methylthiohydantoins, which can be separated on two columns, with silicone elastomer SE-30 and silicone liquid OV-17.[211] Five other methylthiohydantoins—those of asparagine, serine, arginine, and cystine—are determined only after silanisation, which is conducted in the same way as for the phenylthiohydantoins[207,212]. It is recommended[213] that a solution of bistrimethylsilylacetamide in acetonitrile be used at 20°C for 5 min; the yield of the histidine ester is doubled by introducing the sample with excess of the silylating agent. To complete the reaction the temperature is raised to 100°C and the exposure is extended to 10 min.[214,215] Nineteen amino-acid methylthiohydantoins have been separated[208] in 55 min on a capillary glass column 4.5 m long full of a mixed stationary phase (95% of silicone liquid OV-101 and 5% of OV-225) with the temperature programmed from 120 to 280°C. The initial compounds were treated with a mixture of bistrimethylsilyltrifluoroacetamide and 2% of trimethylchlorosilane, when several of the methylthiohydantoins formed disubstituted derivatives; that of arginine could not be determined. Optimum conditions for the separation of methylthiohydantoins of amino-acids (other than arginine) involve[214,215] a column 1.65 m long full of Gasochrome Q with 2% of silicone liquid OV-17 and the temperature programmed from 145 to 230°C, when the time of the determination is 45 min. Further separation of the pair of methylthiohydantoins of asparagine and phenylalanine requires 4.5 min.

The greatest difficulties arise in the silylation of the methylthiohydantoins of arginine and histidine. It is therefore recommended that these derivatives should be extracted with ethyl acetate, and then silanised and separated independently[204].

Another method used to determine the primary structure of proteins is 2,4-dinitrophenylation of the amino-acids[18]. The methyl esters of such derivatives of 13 amino-acids were separated on a 4-m column with 1.5% of silicone elastomer SE-30 and temperature programming from 170 to 230°C [216]; the threonine and serine derivatives were not separated. This method has been used to determine the amino-acid sequences in the proteins of malformin A and gramicidin A.[18]

## VII. SOME APPLICATIONS OF GAS–LIQUID CHROMATOGRAPHY TO THE DETERMINATION OF AMINO-ACIDS IN BIOLOGICAL MATERIALS AND IN GEOLOGY

Difficulties arise in the analysis of biological media in connection with preparation of the sample and removal of interfering impurities. The most convenient procedure[35] for the gas-chromatographic analysis of a protein hydrolysate involves initial ultrasonic removal from the sample of air, which would impede the determination of methionine and cysteine. The protein is hydrolysed in 6 *N* hydrochloric acid at 145°C for 4 h (whereas in the usual process this operation lasts 18–24 h, with tryptophan, theonine, serine, tyrosine, methionine, and cysteine partly decomposing, while the links with valine and leucine are not completely hydrolysed). Inorganic acids are removed from the hydrolysate by means of an ion-exchange resin, and the residue is dried, esterified, and acylated. The amino-acid composition of ribonuclease and the protein of grains and fish has been determined in this way, in good agreement with analytical results obtained by other methods.

Protein hydrolysates have been analysed[217–219] by means of the isopropyl esters of the *N*-acetylated amino-acids, with 2,2-dimethoxypropane added to the initial mixture to diminish hydrolysis. The threshold of detection of amino-acids is $5 \times 10^{-8}$ g. Gas–liquid chromatography has been used to analyse the amino-acid composition of diverse proteins, in particular of fossil animals, soil, and antibiotics.[18]

In addition, free amino-acids in various media can be determined by gas–liquid chromatography. It is recommended[33,34] that 0.1–0.4 ml of plasma be denatured with

4 volumes of saturated aqueous picric acid, the solution centrifuged, and the filtrate passed through a column with an ion-exchange resin (the column is washed first with water and then with aqueous ammonia). The view has been expressed[220,221] that this method is unsuitable for arginine and lysine, and it is therefore proposed that 0.1 ml of plasma be diluted with 10 volumes of 1 *N* acetic acid and passed through the ion-exchange column, whence amino-acids are washed out with water and aqueous ammonia; this involves loss of part of the amino-acids.

Histidine, histamine, *N*-methylhistamine, and *N*-dimethylhistamines have been separated as their trimethylsilyl derivatives and their trifluoroacetylated and heptafluorobutyrylated esters by means of silicone liquid OV-17.[222] The methyl esters of *N*-nitroso-derivatives of proline, sarcosine, and pinacolinic acid have been separated on a diethylene glycol succinate column at 180°C.[223]

Trimethylsilyl derivatives are widely used for analysing hormones and products of vegetable origin[18].

The extraordinarily high sensitivity of the gas-chromatographic method permits use of the component determination of amino-acids in microquantities on various materials, as well as in objects of extraterrestrial origin[224].

## VIII. SEPARATION OF BASES OF NUCLEIC ACIDS, NUCLEOSIDES, AND NUCLEOTIDES

Heterocyclic bases—purines and pyrimidines—are present in nucleic acids. The carbonyl group is readily enolised, which is the reason for strong hydrogen bonding and correspondingly diminished volatility. Volatile derivatives of nucleic-acid bases are obtained mainly by silanisation.

The first studies on the separation of methylated derivatives of adenosine and uridine by gas–liquid chromatography appeared in 1964.[225,226] Better results were obtained with silanised derivatives[227]. Noteworthy attempts were made to separate nucleic-acid bases as triacetates[228]. Separation of trimethylsilyl derivatives of adenosine, cytidine, adenosine 5′-sulphate, 5′-monopropionate, and 2′-, 3′-, and 5′-monophosphates, and nicotinamide–adenine dinucleotide (NAD) has been accomplished[15] on a column with silicone elastomer SE-30 at temperatures from 228 to 249°C; silanisation may yield[229,230] several derivatives with different numbers of trimethylsilyl groups attached to the amino-nitrogen atom. Treatment of five nucleic-acid bases with bistrimethylsilylacetamide at 150°C for 45 min gives quantitative yields of trimethylsilyl derivatives; bistrimethylsilyltrifluoroacetamide reacts under the same conditions, and the reagent peak is more sharply distinguished from the product peaks. Trimethylsilyl derivatives of nucleic acids were separated on a 1-m column with 4% of silicone elastomer SE-30 and temperature programming from 95 to 230°C in 24 min; xanthin, 5-methylinosin, and hypoxanthin were also determined[212]. The minimum detectable quantity of nucleic-acid bases is $3–5 \times 10^{-9}$ g. A mixture of uridin, inosin, adenosine, xanthosin, and cytidine was separated under the same conditions, with an error of 3% in the determination; cytidine gave two peaks, and silylation of adenosine produced small quantities of a tetrakistrimethylsilyl derivative[229].

In the silanisation of thymin it is proposed[231] to deactivate excess of the silylating agent with methanol and remove in a vacuum substances that tend to promote hydrolysis. In the gas-chromatographic determination of trimethylsilyl derivatives of guanosine and adenosine it was recommended[175] first to obtain the methoxy-derivatives, and then to silanise them. Bistrimethylsilyltrifluoroacetamide derivatives of several minor nucleosides were obtained, and separated by gas–liquid chromatography[230]. A comprehensive investigation of the gas-chromatographic behaviour of trimethylsilyl derivatives of 32 nucleosides has used[232] two silicone stationary phases—OV-17 and SE-30.

Gas-chromatographic methods of analysing bases of nucleic acids and nucleosides are widely used in practical analysis[19,233–236].

In a technique[56] for the gas-chromatographic investigation of hydrolysates from ribonucleic and deoxyribonucleic acids at three levels—micro, semimicro, and semiquantitative analysis, with samples respectively of $10^{-3}$, $10^{-4}$, and $5 \times 10^{-7}$ g—the hydrolysate is freed from perchlorates, phosphates, and other inorganic ions on an ion-exchange column, where ribose, which interferes with the determination, is also removed. Results of gas-chromatographic analysis agree well with those obtained by other methods.

Nucleic-acid bases are usually analysed by combining thin-layer chromatography with spectrophotometry, when semiquantitative results are obtained with a detection limit of $10^{-4}$ g, the time taken being considerably longer than in gas-liquid chromatography. Electrophoretic methods enable down to $5 \times 10^{-5}$ g of nucleic-acid bases to be detected[18]. Gas-chromatographic determination of these bases enables the sensitivity of detection to be improved by factors of $10^2$ and separation to be effected in a short time (24 min). An appreciable disadvantage of gas–liquid chromatography is the need to silylate the initial substances and the attendant difficulties.

Phosphorus was determined in nucleotides and nucleic acids[237–242] by silylating salts of phosphates of hexadimethyldisilazane with trimethylchlorosilane in pyridine at high temperatures. Derivatives are obtained also by treating the initial substance with a 10–20-fold excess of bistrimethylsilylacetamide or bistrimethylsilyltrifluoroacetamide, and are determined on a 1.8-m column containing silanised Chromosorb W impregnated with 5% of silicone liquid OV-101 at 155°C.[243]

Recent achievements of gas–liquid chromatography and high-pressure liquid chromatographs in the determination of proteins, nucleic acids, and their breakdown products enable conclusions to be reached on the limits of the application of these methods. With the time required for preparation of the sample taken into account, analysis of the 20 protein amino-acids is quicker by the former method, but derivatives for the latter are obtained more easily and are more stable. However, the separating power of gas–liquid chromatography is incomparably greater, so that this procedure is more advisable for analysing mixtures of protein and non-protein amino-acids; its greater separating power also enables optical isomers of amino-acids to be resolved. Sequencing is appreciably less laborious than with high-pressure liquid chromatographs. The extraordinarily high sensitivity makes gas–liquid chromatography unique in analysing traces of amino-acids, and combination with mass spectroscopy enables the structure of unknown amino-acids and peptides to be established.

The possibilities of gas–liquid and high-pressure liquid chromatography in separating nucleic-acid bases are comparable, but again the former is more sensitive. The Table lists comparative characteristics of the two methods

in analysing degradation products of proteins and nucleic acids. It is evident that these methods are largely complementary, but not mutually exclusive. The choice of method depends on the problems involved, the skill of the investigator, and the availability of the necessary equipment.

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