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ELUCIDATION OF GAS CHROMATOGRAPHIC FRACTIONS IN HYDROGENATION AND OXIDATION REACTIONS

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SUMMARY

Several methods for determining the components of gas chromatographic fractions were developed. The compounds underwent hydrogenolysis in a post-column reactor and only highly volatile reaction products were detected. The method enabled the alkoxyl groups present, their amounts and structure to be determined, and the alkyl chains cleaved by the hydrogenolysis of the carbon–carbon bond to be established.

The hydrogenation, dehydrogenation and hydrogenolysis reactions were applied to the gas chromatographic effluents in argon carrier gas, which contained 5–30 % of hydrogen. The results were recorded in the form of changes in hydrogen concentration. The dependence of reaction kinetics on the nature of the functional group (hydroxyl, carbonyl, ether, unsaturation), its position in the molecule and on the structure of the carbon skeleton was investigated.

The oxidation of hydrocarbons and oxygen-containing compounds was studied by measuring the consumption of oxygen (in the helium stream containing oxygen) in a post-column reactor. The dependence of the oxidation kinetics on the structures of compounds and the nature of catalysts was investigated.

A reaction gas chromatographic method for ultimate oxygen determination is presented, as well as a technique for the determination of the C:O ratio of compounds in gas chromatographic fractions.

INTRODUCTION

Gas chromatography (GC) is presently the most effective technique for separating complicated mixtures of volatile organic compounds. The identification of the separated components, however, has remained a time-consuming and difficult task. For the complete analysis of the components, separation methods are used primarily to provide samples to which specific methods of identification can be applied. The most effective methods of identification are either chemical or spectrometric. For analytical purposes or physicochemical investigations, chemical reactions are frequently used in association with GC. The most suitable reactions are heterogeneous catalytic gas-phase techniques, as they proceed with high velocity and can be performed in a carrier gas stream either before a sample enters or after it emerges from the separating column. This technique was critically reviewed recently[1].

In the field of pre-column hydrogenolysis, the work of BEROZA and co-workers is well known[2,3]: by splitting off functional groups from the hydrocarbon part of a molecule, saturated hydrocarbons are formed. The carbon skeleton of a compound is the simplest starting point for the determination of its structure.

Valuable results on the structural elements and functional groups of components are obtained from reactions after the GC separation. The most used post-column reactions are oxidation of organic vapours eluted from the column into carbon dioxide and water, or their reduction to methane or hydrogen. In the last few years many principles of chemical multiplication techniques have been published[4-9].

In this laboratory, we have been studying the composition of oil produced by the low-temperature carbonization of oil shale. For this purpose, several methods of pre-column and post-column reaction GC have been developed. The results of this work, however, have not been published in the generally available literature, so that some description of our studies would seem to be desirable. In this paper, short descriptions of the methods developed are presented, followed by a discussion of the problems encountered in their practical application.

EXPERIMENTAL

Principles of operation

In the first reaction chromatographic scheme, the effluent emerging from the separating column was passed through a micro-reactor packed with a catalyst or a solid reagent. In this micro-reactor, the separated compounds were submitted to destructive reactions, the nature and extent of which depended on the structures of the compounds. A short adsorption column was attached to the reactor, in which unreacted compounds and high-boiling reaction products were entirely removed. Only highly volatile reaction products entered the detector.

In the second reaction chromatographic scheme, a gas (hydrogen or oxygen) that reacted with the separated compounds was added to the carrier gas. The transformations of fractions that proceeded in the catalyst bed were accompanied by the consumption of hydrogen or oxygen, and in some instances hydrogen was split off from the molecules. Subsequently, all reaction products and unreacted compounds were quantitatively removed. Only the amount of the reactive gas consumed (or split off) by the separated compounds was determined.

Apparatus

A Soviet-made YX-1 chromatograph was used to carry out reaction chromatography according to the scheme column → reactor → column. The apparatus was equipped with a thermal conductivity detector and two columns connected in series. In this work, the second column was substituted for the micro-reactor. For obtaining chromatograms of the original samples, the carrier gas could be passed from the first column directly into the detector. A post-reactor column was located outside the apparatus and was maintained at room temperature. The same arrangement of equipment was used for all the chromatographic methods discussed in this work.

The multicomponent mixtures were separated on the first column mostly consisting of a 4–6 m × 4 mm I.D. copper column containing 10–15 % of Carbowax 20M or Apiezon L on 60–80 mesh Chromosorb W. The flow-rate of the carrier gas was 60 ml/min. Temperature-programming of the column was used for samples having wide boiling ranges. Fractions emerging from the column entered the catalyst assembly, consisting of a glass or quartz reactor tube (4 mm I.D.) containing 1–2 ml of catalyst and a furnace for heating the tube. The post-reactor columns were of various sizes, depending on the substances to be determined. A 5-cm charcoal column was used for methane and ethane. In this column, methane was not retarded and its peaks coincided with those of the corresponding compounds on the original chromatogram. The shape of the peak was not altered, as peak broadening was observed with ethane. Other hydrocarbons were removed. If there was evidence that saturated C_3–C_5 hydrocarbons were formed during hydrogenolysis, a 50-cm silica gel column was used for their separation. In most instances only methane was formed, so that there was no danger of the peaks overlapping.

Occasionally, short columns with liquid phases were used in the investigation of the composition of reaction products. For the removal of all compounds, a 20-cm charcoal column was used.

Catalyst

A commonly used catalyst, 5 % of metal (palladium, platinum, nickel or copper) on 60–80 mesh diatomite or silica gel, was prepared from the corresponding metal salt and raw untreated column support material[10]. The catalyst was reduced in the reaction tube in a stream of hydrogen by gradual increase of the temperature to the operating temperature. We did not neutralize the catalyst, and did not observe any decrease in the strengths of carbon–carbon bonds on this catalyst (hydrocracking reactions) as was noticed by BEROZA and co-workers[2,3]. It is interesting to note that the catalyst support had a remarkable influence on catalytic reactions. The metals on passive, chemically pre-treated supports (Celite 545, Chromosorb W or porous glass beads) did not promote dehydrogenation or hydrogenolysis reactions. In the pre-column work, palladium on Chromosorb W (1 cm^3) was used[11] for the hydrogenation of unsaturated bonds without hydrogenolysis of oxygen-containing groups at up to 300°.

General remarks

For the analysis of oxygen-containing compounds, we have used pre-column carbon skeleton chromatography over a long period of time. The dehydrogenation and hydrogenolysis reactions proceeded at 330–350°, at which temperatures aromatic structures are unaffected while the cyclohexane ring undergoes dehydrogenation. We always attempted to obtain complete dehydrogenation, because polyalkylcyclohexanes exist as numerous *cis* and *trans* isomers, the identification of which is rather complicated.

When working with compounds of high molecular weight, the catalyst was often poisoned. Reactivation of the catalyst was carried out in an air stream at the operating temperature. The activity of the catalyst was checked by ensuring that cyclohexane dehydrogenation proceeded with not less than 80 % conversion to benzene. Usually a palladium catalyst was used, because it is not poisoned as easily as platinum and the hydrogenation of aromatic structures proceeds to a lesser extent than on platinum. In general, however, the difference between the metals is not great enough to prevent the use of platinum.

The pre-column reaction technique has been applied to the hydrogenation and dehydrogenation of hydrocarbons with helium as the carrier gas [12]. The composition of complex mixtures of phenols (naphthols, resorcinols, etc.), boiling at up to 350°, studied by dehydroxylating them to aromatic hydrocarbons, has been discussed in several papers[10,13–17]. Phenols are easily dehydroxylated; the catalyst life usually exceeds several months and several hundreds of analyses can be performed. Carbonyl compounds, especially cyclic ketones, however, poison the catalyst to some extent[18–20].

In comparison with the carbon-skeleton method proposed by BEROZA and co-workers[2,3], we used higher temperatures, higher gas flow-rates, smaller charges of catalyst (but not smaller amounts of metal) and larger samples. In our pre-column reaction, the cracking of carbon–carbon bonds with the formation of the next lower homologues of the carbon skeleton, if primary oxygen groups were present, did not proceed to the same extent as in the reactions described by BEROZA and co-workers[2,3]. This result is due to the shorter reaction time and higher concentration of the sample in the carrier gas.

CLEAVAGE METHODS FOR INVESTIGATING THE STRUCTURES OF FRACTIONS

Aromatic ethers

In the course of the hydrogenolysis of aromatic ethers, a corresponding relatively high-boiling aromatic hydrocarbon and, from the alkoxyl group, a hydrocarbon of low molecular weight are formed:

$$\mathrm{Ar{-}O{-}Alk} + 2\mathrm{H_2} \rightarrow \mathrm{Ar{\cdot}H} + \mathrm{H_2O} + \mathrm{Alk{\cdot}H}$$

The analysis of the chromatograms, on which only the alkyl groups split off from the alkoxylenes are recorded, shows which of the components carry alkoxyl groups. The cleavage of oxygen containing groups proceeds quantitatively at temperatures above 300°, which enables the number and structures of alkoxyl groups to be determined[21].

In analytical work, one of the most important factors is the minimization of secondary reactions. In phenolic ethers, the presence of a hydroxyl group weakens the bond between the alkyl chains and the aromatic nucleus, and at high temperatures these ethers are readily dealkylated. The cleavage of alkyl chains in the *ortho* position to the hydroxyl group proceeds particularly easily. For example, the alkyl group is removed completely from *o*-isopropylphenol at 350°. Dealkylation does not take place at temperatures below 325°. The course of the dealkylation reaction depends on the conditions of hydrogenolysis (concentration of sample): the pre-column dehydroxylation of *o*-isopropylphenol is accompanied by gradual demethylation (ethylbenzene and toluene are formed), but in the post-column reactor only propane is formed.

Hydrogenolysis of carbon–carbon bonds

LEVY AND PAUL[22] used the thermal fragmentation of effluent compounds for their identification. In general, in catalytic reactions proceeding at moderate temperatures, cleavage of chemical bonds occurs in particular more selectively in the dealkylation of alkylaromatic compounds. These fragmentation reactions can be used in the elucidation of the structures of side-chains[23]. When carrying out hydrogenolysis of alkylaromatic compounds ($\mathrm{Ar}\overset{\alpha}{\text{—}}\mathrm{C}\overset{\beta}{\text{—}}\mathrm{C}$) in post-column conditions on platinum and palladium catalysts, it is mainly the α-bond that is cleaved[21,24], but under thermal cracking conditions β-fragmentation proceeds more readily[25]. Nickel promotes the formation of methane from the terminal carbon atoms of chains[26]. By taking into account the particular properties of a catalyst, it is possible to obtain valuable structural information.

The hydrogenolysis of aliphatic ethers and esters produces volatile hydrocarbons but in this instance the rupture of the carbon–carbon bonds can make the study of the carbon skeleton difficult. The oxygen-containing groups, particularly the primary ones, induce weakening of neighbouring C–C bonds. With an oxygen-containing group on a terminal carbon atom (primary alcohols, aldehydes, acids, ethers, esters), this carbon atom may be removed partially or entirely with the oxygen-containing group, and the next lower homologue of the series is formed[2,3]. Ethyl alcohol and acetaldehyde are both completely decomposed to methane, but diethyl ether and ethyl acetate to the extent of 23 % and 28 %, respectively (post-column reaction, 5 % of palladium on diatomite, 300°). With the carbon chain becoming longer, the velocity of the demethanation reaction decreases. Taking into account the experience obtained in the dehydrogenation of oxygen-containing compounds[27,28] and the easy decarbonylation and decarboxylation of aldehydes and acids in catalytic or thermal reactions[26,29,30], we assume that demethanation proceeds with preliminary hydrogenation reactions:

$$\underset{\text{Alcohol}}{\text{R–CH}_2\text{OH}} \xrightarrow{-\text{H}_2} \text{R–CHO} \rightarrow \text{RH} + \text{CO} \xrightarrow{+3\text{H}_2} \text{RH} + \text{CH}_4 + \text{H}_2\text{O}$$

$$\underset{\text{Ester}}{\text{R–COO–R}'} \xrightarrow{+\text{H}_2} \text{R–COOH} + \text{R}'\text{H} \rightarrow \text{RH} + \text{R}'\text{H} + \text{CO}_2 \xrightarrow{+4\text{H}_2} \text{RH} +$$
$$+ \text{R}'\text{H} + \text{CH}_4 + \text{H}_2\text{O}$$

Both moieties of an ether or an ester cannot take part in the decarbonylation (or decarboxylation) reaction at the same time, and the yield of methane from these compounds is therefore smaller.

If the oxygen atom in an ether is bound to different hydrocarbon radicals, the two carbon–oxygen bonds do not have equal strengths, so that one of them will be hydrogenolyzed more radily. In the course of dealkoxylation of aromatic ethers, alkyl groups in spite of the neighbouring oxygen atom are demethylated to the extent of only a few per cent. This may be the result of the formation of an intermediate phenol, which could occur for the same reasons as in the cleavage of phenolic ethers with hydriodic acid: only phenol is formed, with no aliphatic alcohols [26,30].

The formation of methane is a disadvantage in common carbon-skeleton chromatography, but in post-column conditions it can be used for the determination of oxygen-containing groups in terminal positions.

Identification of oxygen-containing compounds with a straight carbon skeleton

Oxygen-containing compounds separated by GC were hydrogenolyzed to hydrocarbons in a micro-reactor. The reactor effluents were passed through a short column of molecular sieve 5A, where all the normal carbon chains were adsorbed and only iso or cyclic hydrogenolysis products reached the detector. The method was used for the determination of normal ketones[31].

Determination of the carbon:oxygen ratio in gas chromatographic fractions

Oxygen was detected either as water or as carbon monoxide. In the first method the components in the hydrogen stream were quantitatively converted on a nickel catalyst (10 mg of nickel on 1 cm^3 of porous glass, 450°) into methane and water. The products from every component were first determined together in one peak (methane + water). Small amounts of water from oxygen-containing compounds arrived quantitatively at the detector only when the carrier-gas was moistened in a preliminary step. In the second reaction–separation, water was removed on a silica gel column, and only methane was detected. The comparison of both reaction chromatograms and the use of an internal reference standard enabled the C:O ratio of components up to a value of 5 to be determined[32]. Owing to the low sensitivity of the thermal conductivity detector towards water vapour, the method has only a limited application.

In the second method the oxygen of the components was converted into carbon monoxide over charcoal (2 cm^3, 900°). In addition to carbon monoxide, hydrogen is also formed, but in the stream of hydrogen or helium it does not interfere with the operation of the detector. The combination of hydrocracking (carbon determination) and pyrolysis (oxygen determination) enables the ratio of carbon to oxygen atoms in compounds up to a value of 10 to be reliably determined[32]. A similar reductive pyrolysis of effluent components was proposed by KOJIMA *et al.*[33] for the selective determination of oxygen-containing compounds.

REACTIONS OF ELUTED COMPOUNDS IN A CARRIER GAS CONSISTING OF TWO CONSTITUENTS

If the hydrogen carrier gas took part in the reaction, the results were recorded as the amount of hydrogen split off by dehydrogenation or consumed in the hydrogenation or hydrogenolysis reaction. The carrier gas used in this work was argon containing 5–30 % of hydrogen. After emerging from the reactor all the components were removed and the detector sensed only increases or decreases in the hydrogen concentration in the form of negative or positive peaks in both directions from zero line, respectively.

Hydrogenation and dehydrogenation of hydrocarbons

In the post-column reactor in a stream of pure argon the derivatives of cyclohexane are dehydrogenated (5 % of platinum on diatomite as catalyst) even at 220° and the dehydrocyclisation of straight hydrocarbon chains proceeds at 300° (ref. 34). The catalyst is easily poisoned. If the carrier gas contains 5 % of hydrogen, the catalyst is active for a long period and the undesirable reactions of normal chains do not proceed. In spite of the low concentration of hydrogen, olefins are saturated quantitatively.

Identification of alcohols in gas chromatographic fractions by dehydrogenating to carbonyl compounds

Primary and secondary alcohols easily split off hydrogen atoms on a dehydrogenation catalyst and form carbonyl compounds (aldehydes and ketones). Under the same conditions, tertiary alcohols are dehydrated and on hydrogenation catalysts the olefins formed are saturated[34]. The peculiarity of the reactions of alcohols depends essentially on the nature of the catalyst and on the temperature. Tertiary alcohols are always dehydrated, but on a copper catalyst (5 % of copper on Chromosorb W) the hydrogenation of olefins does not proceed and hydrogen is not consumed. Secondary alcohols are more active than primary ones in dehydrogenation as well as in dehydration reactions. On an active catalyst (platinum or palladium on diatomite) at 300–320°, secondary alcohols are dehydrated, while on passive catalysts dehydrogenation takes place. At low temperatures (250°), secondary and aromatic alcohols are more readily dehydrogenated than primary ones.

Dehydrogenation is a sensitive reaction to use for the identification of alcohols, and it allows insignificant amounts present to be detected.

Dehydrogenation of other oxygen-containing compounds

In addition to alcohols, other oxygen-containing compounds, *e.g.*, aldehydes, can be dehydrogenated[28]. This reaction was unexpected since it occurred with the dehydrogenation products of primary alcohols. On passing aldehydes over palladium or platinum catalysts at temperatures above 270°, a small amount of hydrogen was split off. This reaction was favoured by higher temperatures. On a copper catalyst, aldehydes were only hydrogenated. The study of the dehydrogenation products revealed the formation of ketones from aldehydes:

$$2\ \mathrm{R{-}CHO} \rightarrow \mathrm{R{-}CO{-}R} + \mathrm{CO} + \mathrm{H_2}$$

When only 5 % of hydrogen is present in the carrier gas, carbon monoxide is not hydrogenated. Aliphatic ethers and esters are also dehydrogenated to some extent.

The formation of ketones is a bimolecular reaction. Owing to the low concentrations of components, especially in the post-column reactor, the conditions are not favourable for the inter- and intramolecular rearrangement of radicals, although some instances have been described (only for pre-column reactions). The thermal cracking of *n*-octane at 385° produced isononanes[35], in the hydrogenolysis of alkoxybenzenes alkylbenzenes were formed[36], and catalytic dehydrogenation of cyclohexane produced toluene[37].

The reactions of oxygen-containing derivatives of cyclohexane may be accompanied by the aromatization of their hydrocarbon skeletons. Hydrogen is then split off from both the alcohol and ketone. The hydroxyl group present favours the dehydrogenation of the ring (phenol formation), and the reaction begins at 250° and proceeds also on the passive catalyst, platinum on Chromosorb W. As a result of aromatization, cyclohexanols split off more hydrogen than aliphatic alcohols. Carbonyl derivatives of cyclohexane differ from cyclohexanols, as they split off hydrogen only on platinum and palladium catalysts at high temperatures (300–350°). By lowering the temperature, the yield of hydrogen rapidly decreases and below 250° hydrogenation of carbonyls takes place.

Hydrogenation of carbonyl compounds

By increasing the concentration of hydrogen in the argon carrier gas up to 30 %, the equilibrium [alcohol $\rightleftarrows$ carbonyl compound + H_2] can easily be shifted towards the formation of alcohols. The influence of some structural factors on the kinetics of the hydrogenation of carbonyl compounds was investigated[38] between 200° and 350°.

It was established that in reaction chromatographic transformations, the position of the carbonyl group in *n*-alkyl ketones does not affect the hydrogenation ratio. Carbonyl groups at the terminal positions have a much different reaction ability — aldehydes are hydrogenated considerably more readily than ketones. The alkyl chains present in the carbon skeleton of ketones have a negligible effect on reaction kinetics if they are situated far enough from the carbonyl group. 3,3-Dimethylbutanone-2 consumed more hydrogen than other ketones as a result of the cleavage of the C–C bond between the carbon atoms in position 2 and 3. A similar phenomenon was observed in the hydrogenation of unsaturated ketones: 4-methylpenten-3-one-2 consumed 1 mole of hydrogen more than did hexen-5-one-2.

Some differences were also observed in the reaction kinetics of cyclic ketones. On a copper catalyst, the rate of hydrogenation of carbonyl compounds decreased in the following sequence: aldehyde > cyclohexanone > cyclopentanone > *n*-alkyl ketone. In the liquid or gas phase, the carbonyl compounds are in tautomeric equilibrium with their enolic forms:

$$-CH_2-CO- \rightleftarrows -CH=C(OH)-$$

The proportion of the enolic form present decreases in the same order. This leads to the conclusion that alcohol formation proceeds via the hydrogenation of the unsaturated bond of the enolic form of the carbonyl compound.

Ultimate determination of oxygen by gas chromatography and two-fold conversion

The oxygen content in organic compounds is usually determined by reductive pyrolysis. The carbon monoxide formed is often determined by GC[39]. To enhance the sensitivity of oxygen detection, a second conversion was performed in this investigation. The pyrolysis reactor (3 cm^3 of activated charcoal, 1100°) and other parts of the system in the gas-line of a chromatograph were continuously purged with argon containing 8 % of hydrogen. Carbon monoxide was separated from the remaining pyrolysis products in a column packed with molecular sieves and then hydrogenated in the next reactor to methane:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Hydrogenation was accomplished on a nickel catalyst at 400–500°. Instead of carbon monoxide, the detector recorded the amount of hydrogen consumed in the hydrogenation. This hydrogenation technique greatly increases the sensitivity of the detector.

A reaction gas chromatographic method for the investigation of oxidation reactions

In this experiment[40], the compounds were separated by using helium containing 4 % of oxygen as the carrier gas, and were subsequently catalytically oxygenated in a post-column reactor. After the products had been completely adsorbed, the results were recorded as changes in oxygen concentration. The catalysts contained 15–60 mg of metal (platinum, copper(II) oxide, vanadium pentoxide) on 1 cm^3 of support. The most selective catalyst was platinum, on which the amount of oxygen consumed by *n*-octane exceeded that by isooctane more than ten-fold between 300° and 350°. The oxygen consumption of other hydrocarbons was also in good accordance with their octane number (an index used to characterize the oxidation stability of motor fuels and their individual constituents[41]).

Experiments with isomeric propyl and butyl alcohols demonstrated the dependence of the oxidation rate on the structures of compounds and the composition of the catalyst. The same phenomenon was observed in the oxidation of alkylaromatic compounds. The small amounts of platinum used in this work were poisoned at temperatures above 400°; attempts to reactivate the catalyst were not successful. This observation has also been described by other investigators[41].

CONCLUSIONS

The above summary of our work has described methods for the determination of some structural elements of compounds separated by GC. Only hydrogenolysis products of low molecular weight are detected. The small amounts of methane formed (less than equimolecular with respect to the initial compound) are derived from the primary functional groups present.

The fact that the catalytic gas-phase transformations used in reaction GC proceed instantaneously does not, however, prevent the formation of intermediate products. The nature of these short-lived compounds exerts an important effect on the composition of the final products.

The kinetics and character of the hydrogenolysis of carbon–carbon bonds (for example, dealkylation of aromatic hydrocarbons) is influenced by the various functional groups present. From compounds that all have the same isopropylbenzene hydrocarbon skeleton, the following amounts of the original hydrocarbon skeleton remain after hydrogenolysis: isopropylbenzene, 93 %; *o*-isopropylphenol, 61 %; and 3-methyl-6-hydroxybenzofuran, 79 % (pre-column reaction, 5 % of palladium on diatomite, 350°)[10,42].

The hydrogenolysis technique can sometimes be used to establish the positions of functional groups in aliphatic compounds, *e.g.*, secondary alcohols and ketones. At high temperatures, these compounds frequently undergo fragmentation at the carbon atom to which an oxygen atom is attached. Of the carbon skeleton of 2,4-dimethylpentanone-3, only 40 % survives, while under the same conditions, of the corresponding hydrocarbon 2,4-dimethylpentane, 65 % remains intact (the reaction conditions being the same as above).

The reaction GC technique in a carrier gas consisting of two constituents (inert gas containing a small amount of hydrogen or oxygen) is distinguished by its simplicity of equipment, operation and interpretation, being a useful technique for studying the reactivities of compounds, reaction kinetics and the qualities of catalysts.

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