Translated from *Uspekhi Khimii*, **55**, 1390-1406 (1986) U.D.C. 543.51

Reaction Chromato-mass Spectrometry

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The principles of the highly effective reaction chromato-mass-spectrometric method, based on the use of chemical reactions of the test specimens directly in the reaction system of a chromato-mass-spectrometer, are examined. The possibilities of the method in the determination of the structures of organic compounds and in the study of the mechanisms of dissociative ionisation, heterogeneous-catalytic reactions, and high-molecular-weight compounds are demonstrated.
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I. INTRODUCTION

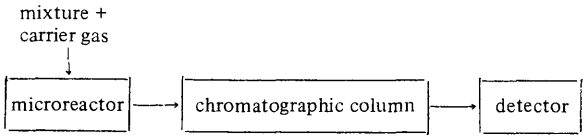
Preliminary chemical transformation of the test specimens is a common methodological procedure in the mass-spectrometric study of organic compounds. Various chemical methods, mainly derivatisation methods, are used in mass spectrometry to increase the volatility and the thermal and catalytic stabilities of the substances analysed, to improve the chromatographic characteristics (in chromato-mass-spectrometric investigations), to obtain additional information about the structure from the mass spectra of the reaction products, and to increase the sensitivity of the method in selective ionic detection.[1,2] The use of degradation methods (hydrolysis, pyrolysis) is extremely effective in mass-spectrometric research.[3,4] The majority of the known chemical modification methods are based on the use of reactions in solution. In such reactions, carried out in separate experiments, much labour and time must be expended on the isolation and separation of the products. In many instances comparatively large (microgramme) amounts of the test specimen are used in the chemical reactions. However, a much more convenient chemical transformation procedure involves gas-phase reactions in a microreaction system incorporated directly into the injection system of the mass spectrometer. Submicrogramme amounts of the test specimens, i.e. amounts sufficient for the mass-spectrometric analysis, can then be transformed. The most important advantage of this method is the possibility of carrying out the reactions directly in the course of the mass-spectrometric study. This creates a basis for the development of high-speed and highly effective research techniques whose possibilities are enhanced still further when chromato-mass spectrometry is employed. This method is called "reaction chromato-mass-spectrometry"[5] because it involves chemical reactions directly in the injection system of the chromato-mass spectrometer.

II. PRINCIPLES OF REACTION CHROMATO-MASS SPECTROMETRY

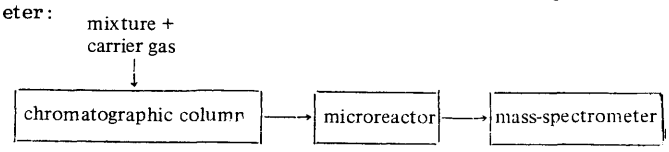
In reaction chromato-mass spectrometry (RCMS) the substances analysed or mixture components are modified chemically directly in the injection system of the chromato-mass spectrometer (in microreactors, in reactions on separating columns). This is done in order to alter the physicochemical properties of the substances analysed, in order to obtain from the mass spectra of the reaction product additional or new information about the structures of the starting materials, to investigate dissociative ionisation mechanisms, to study the modes and mechanisms of gas-phase reactions, etc. The familiar reaction gas-chromatographic (RGC) method may be regarded to some extent as a precursor of RCMS,[6] but distinctive features and advantages are characteristic of the RCMS method.

In the first place the value of the information about the structure which can be obtained by the above methods is not the same. Whereas RGC provides for the preparation of products with known chromatographic characteristics or the creation of simpler mixtures from complex mixtures by "subtracting" individual components, the RCMS method provides for specific modification of substances in order to obtain compounds whose mass spectra yield additional information about the structure of the starting materials. The most important advantage of the RCMS method is the possibility of synthesising compounds labelled with stable isotopes (in particular, deuterium) directly in the course of analysis, which is exceptionally promising in the study of the mechanisms of the dissociative ionisation of organic substances and reaction mechanisms. In RGC there is no such possibility.

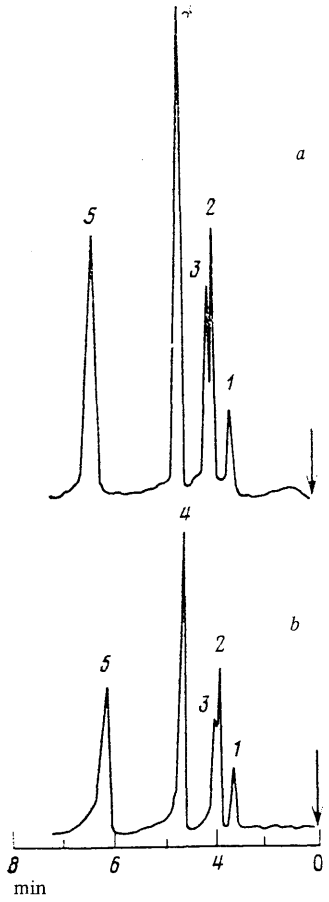
The microreaction system in RGC is usually placed before the separating chromatographic column:



Only when the subtraction method or the procedure is designed to increase the sensitivity of the analysis (if the detector is insensitive to the given component but is sensitive to its derivative) can the microreactor in RGC be placed between the column and the detector. In contrast to this, the microreaction system in RCMS is best located between the chromatographic column and the mass spectrometer:



The fundamental characteristic of this scheme is that each component eluted after chromatographic separation is subjected to chemical action. The chromatogram recorded under these conditions characterises the initial mixture (which ensures the possibility of a quantitative estimation of its composition), while the mass spectra correspond to the reaction products (which are used for structural assignments). This makes it possible to analyse separately even the isomeric compounds which give rise to identical structures on chemical modification and are naturally not susceptible to analysis by the RGC method.



Chromatogram of the initial mixture of alkenes (*a*) and the same mixture after passage through the hydrogenation microreactor placed between the column and the mass spectrometer (*b*): 1) 2,4,4-trimethylpent-1-ene; 2) oct-1-ene; 3) oct-2-ene; 4) non-1-ene; 5) dec-1-ene.[15]

In certain cases, for example, when it is necessary to decrease the polarity by means of a chemical reaction or to investigate the mechanism of a gas-phase process, the microreactor in the RCMS system can be usefully mounted before the separating column. The "subtraction microreactor" is positioned in the same way when there is a need to simplify the mixture for one reason or another.[7] Sometimes, especially in the analysis of individual substances, the separating column can be altogether disconnected and the microreactor is placed between the evaporator of the chromatograph and the mass-spectrometer.

As in RGC, in investigations by the RCMS method it is very important to select correctly the reactions which ensure the rapid, quantitative, and selective transformation of the substances analysed. Admittedly, a high selectivity is not always obligatory in relation to RCMS; it will be shown below that sometimes side reactions can assist in the determination of the structure.

In the RCMS method which provides for the gas-chromatographic injection of the test substances, gas-phase catalytic reactions are used for the chemical transformation of the compound. The amount of the catalyst required for the complete transformation of the compound depends to a large extent on the degree of its dispersion and on the necessary length of the reaction zone. In order to select the correct amount of the catalyst, the microreactor is placed before the chromatographic column and several experiments are performed varying the length of the catalyst bed and the amount of specimen injected. This also makes it possible to determine the process selectivity at different temperatures.

As stated above, the chemical reactions in RCMS can be achieved in microreactors, reaction columns, or directly in the separating column. A convenient wholly metallic microreactor for RCMS has been described.[8] The minimum number of valves whereby the substance in the stream of carrier gas can be passed either around the catalytic zone (by-pass) or through the catalyst bed are used in this reactor. The system is adequately miniaturised and can be placed within the chromatographic thermostat. The catalyst bed of the required height is placed in the microreactor cartridge between glass wool plugs.

The reaction columns employed in RCMS usually consist of metallic or glass tubes placed directly in the chromatograph thermostat. Such columns are filled with a catalytic packing or an active substance attached to a solid carrier, as in the preparation of packed analytic columns.

It is noteworthy that the RCMS method does not eliminate the need for the usual mass- or chromato-mass-spectrometric analysis of the initial compound. On the contrary, only a combined analysis of the mass spectra of the initial substances and their transformation products permits the most complete solution of structural-analytical problems.[9]

III. INVESTIGATION OF THE STRUCTURES OF ORGANIC SUBSTANCES

1. Olefins

For the general case, in the study of the structures of olefins it is necessary to determine the structure of the carbon skeleton and the position and geometry of the double bond. Mass-spectrometry with ionisation by electron impact (EI) yields relatively little information in the solution of these problems owing to the preferential ionisation of unsaturated molecules at the double bond and the "migration" of the latter along the chain.[10,11] Many methods for the chemical "fixation" of double bonds, permitting the determination of their position and sometimes of their geometry from the mass spectra of the products, have been developed.[2,12] However, the majority of these methods are laborious, do not ensure the determination of the structure

of the carbon skeleton, and are unsuitable for the investigation of mixtures. New possibilities for the solution of these problems are provided by the RCMS.

The determination of the structure of the carbon skeleton of olefins is based on the fact that the mass spectra of paraffins, in contrast to those of unsaturated hydrocarbons, have many features from which one can infer the presence and character of branches in their carbon chains. Furthermore, the mass spectra of many alkanes are known and are contained in computer libraries and the structure of alkanes can therefore be sometimes established automatically. Olefins can be successfully hydrogenated in a microreactor placed in the injection system of a chromato-mass spectrometer when hydrogen is used as the carrier gas, serving simultaneously as a reactant. The efficiency of this procedure has been demonstrated in relation to the investigation of mixtures of α-olefins[13] and cyclohexenols.[14] However, the above method was used in these studies only to demonstrate the presence of the double bond and its other structural-analytical possibilities were not discussed. These questions were examined more thoroughly in other investigations.[5,15]

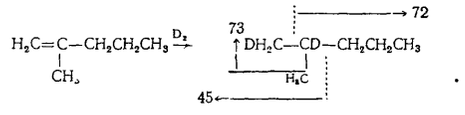
Olefins can be hydrogenated within the framework of the RCMS method using deposited platinum, palladium, or nickel catalysts. The 1-2% Pt/Chromaton and 1% Pd/porous glass catalysts, which ensure quantitative hydrogenation in the temperature range 50–250 °C without inducing undesirable reactions, in particular hydrogenolysis, have been employed for for such purposes.[5,15] The hydrogenation microreactor can be equally successfully placed after both packed and capillary columns and, when the amounts of the catalyst and the reaction temperature have been chosen correctly, an appreciable impairment of the chromatographic separation owing to the possible sorption of hydrocarbons on the catalyst is not observed (Figs. *a* and *b*). Using this method, the molecular weight of each component is established from the mass of the molecular ions (M^+) and the structure of the carbon skeleton can be determined from the mass spectra of the hydrogenation products. However, the problem of the determination of the position of the double bond remains. Its solution by the RCMS method can be achieved by the selective deuteriation of olefins at the double bond using deuterium as the carrier gas and the reactant. This approach has been studied in detail.[5,16]

Table 1. The isotope distribution (%) in the products of the deuteriation of n-octenes on the Pd/porous glass catalyst (100 °C).[16]

Initial n-octene	[D_n]Octane								
	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9
Oct-1-ene	6	34	22	14	10	6	5	3	—
Oct-2-ene	4	20	15	15	12	8	8	6	6
Oct-4-ene	3	20	13	10	9	9	9	8	7

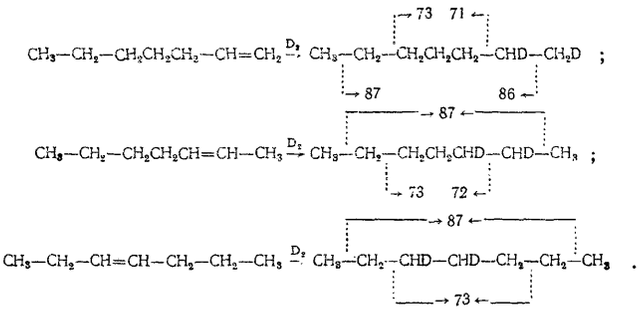
Heterogeneous hydrogenation catalysts based on transition metals are known[17] to ensure the selective deuteriation of olefins because they induce an intense exchange of the substrate hydrogen atoms for deuterium in both liquid-phase and gas-phase processes. However, this exchange proceeds more vigorously at elevated temperatures (>150 °C). It has been shown[5,16] that a decrease of the reaction temperature below 100 °C when the Pt/Chromaton and Pd/porous glass catalysts are used suppresses significantly the deuterium exchange. As an example, Table 1 presents the isotope composition of the products of the deuteriation of isomeric n-octenes. Evidently, in the case of an α-olefin deuterium exchange plays a less important role relative to deuteriation than in the case of olefins with inner double bonds. This finding can be used to differentiate olefins with terminal and inner positions of the double bond.

The deuterium exchange accompanying the addition of deuterium diminishes if the molecule contains a branch at the carbon atom involved in the double bond. This results in an increase of the fraction of vicinal dideuterioalkanes and the determination of the position of the deuterium label and hence of the position of the double bond in the olefin is thereby facilitated. For example, the spectrum of the product of the deuteriation of 2-methylpent-1-ene contains a doublet with equal peaks due to the fragment ions $[M-CH_3]^+$ (m/z 73) and $[M-CH_2D]^+$ (m/z 72) and also an intense peak of the ion with m/z 45, which demonstrates unambiguously the position of the double bond:[5]



The next step in these studies involved the search for a metal complex catalyst which might be used in RCMS for selective deuteriation. Attention was turned to tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst, which is widely used for such purposes under homogeneous liquid-phase conditions.[18] However, the application of this catalyst in RCMS requires that it be made heterogeneous. Heterogeneous packing based on Wilkinson's catalyst had been obtained earlier by impregnating porous carriers with a solution of $(Ph_3P)_3RhCl$ in comparatively high-boiling liquids. These were used for the gas-phase hydrogenation and hydroformylation of lower olefins (ethylene and propene) at 25 °C.[19] However, this type of packing is unsuitable for RCMS, since the solvent evolved enters the mass spectrometer and creates a strong backgound. It was therefore suggested that the catalyst be converted into a heterogeneous form by depositing it, after dispersion in a stationary liquid phase (Carbowax 20 M), on Chromaton.[20] This catalytic system ensured the selective deuteriation of higher alkenes (up to C_{12}) in the gas phase at 50–80 °C under the conditions of heterogeneous catalysis. The column, filled with the catalyst on the carrier, was connected to a mass spectrometer and the substrate in a stream of D_2 was passed through it. It was shown[16,21] that the reaction column with an appropriate length ensures the quantitative deuteriation of mono- and di-substituted olefins with substituents attached at the double bond, mass-spectrometric analysis confirming the high isotopic purity of the vicinal dideuterioalkanes formed (>96%).

It is recommended that, for the mass-spectrometric determination of the position of the label in dideuterioalkanes, one should analyse the ions formed as a result of the elimination of the simplest alkyl radicals from molecular ions at the ends of the chain or at branching points. It is shown below how information about the mass numbers of the characteristic fragment ions from isomeric dideuterioheptanes can be used to determine the position of the double bond:



The method described can be employed also for the determination of the position of the double bond in branched alkenes. In the study of mixtures, the individual units of the apparatus are arranged in the following sequence:

separating column → reaction column → mass spectrometer.

It has been suggested that hydrogenation beyond the column, in the chromato-mass spectrometer, be used to determine the configuration of the centre in the 4-position in the stereoisomeric 4-vinyl-*trans*-4-decahydroquinolinols, obtained by the Norman reaction in the form of mixtures. The feasibility of this approach arises from the fact that the mass spectra of the ethyl analogues show intense peaks due to the ions $[M-C_2H_5]^+$, whose intensity depends on the configuration of the centre in the 4-position (the ease of the elimination of the substituent C_2H_5 is greater when it is in the axial position), whereas the formation of the ions $[M-CH=CH_2]^+$ is not characteristic of the vinyl analogues. It has been shown[22] that, when the 1–2% Pd/porous glass (150–200 °C) catalyst is used in chromatography in a stream of H_2, each component of the mixture of isomeric vinyl alcohols is converted quantitatively into the corresponding ethyl analogue with retention of configuration. The stereospecificity of the fragmentation on electron impact, of the same kind as that observed when the individual stereoisomers of 4-ethyl-substituted alcohols are passed through the direct injection system, is manifested in the mass spectra of the alcohols under these conditions.

Post-column hydrogenation can also be carried out in a tube made of a hydrogen-permeable alloy based on platinum or palladium.[23] After chromatography in a stream of hydrogen, hydrogenation takes place in this case on the walls of the tube and the hydrogen is removed by diffusion through the walls. Such a tube can serve as an effective interface between the chromatograph and the mass spectrometer.

2. Alicyclic Compounds

The necessity for the development of additional methods assisting in the determination of the structures of alicyclic compounds arose because their mass spectra frequently resemble the spectra of the isomeric olefins and do not always contain reliable features whereby one could distinguish condensed, bridged, spiran, and jointed systems and also to differentiate cyclopentane and cyclohexane structures.

Cyclic and olefinic structures can be distinguished by means of post-column hydrogenation, because only the mass spectra of the latter are then altered.[5] Further, this method is not applicable to cyclopropane compounds, which undergo ring opening under hydrogenation conditions with formation of aliphatic products. A special method was therefore developed for cyclopropane compounds which increases the diagnostic possibilities of the procedure.[24] The method is based on the use of the hydrogenolysis reaction, which takes place readily in the gas phase in the presence of the Pt/Chromaton, PtO_2, and Pd/porous glass catalysts.[25]

It has been shown that the hydrogenolysis of monoalkylcyclopropanes leads to the formation, under these conditions, of a mixture of compounds with branched (A) and linear (B) structures, which can be readily distinguished mass-spectrometrically:

$$\text{>}-R \xrightarrow{H_2} \underset{(A)}{(CH_3)_2CHR} + \underset{(B)}{CH_3CH_2CH_2R} ;$$

$$R = n\text{-}C_8H_{17},\ CH_2CH_2COOCH_3,\ CH_2CH_2COOC_2H_5 .$$

Regardless of the reaction temperature (50–200 °C) and the nature of the substituent R, the ratio of the products (A) and (B) is 94:6. This fact is important, because it allows the microreactor to be placed between the chromatographic column and the mass spectrometer. Indeed, although the measured mass spectrum constitutes the sum of the spectra of both products, it is largely determined by the structure (A). However, a new problem of the differentiation of the cyclopropane compounds and the isomeric branched olefins, which give rise to identical products on interaction with hydrogen, arises under these conditions:

$$\text{>}-R \xrightarrow{H_2} (CH_3)_2CHR \xleftarrow{H_2} H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}R .$$

It has been suggested that the problem be solved by employing deuterium as the carrier gas and the reactant, because deuteriation of cyclopropane and unsaturated compounds gives rise to products with different positions of the label, which can be readily determined from the fragment ions in the mass spectra:

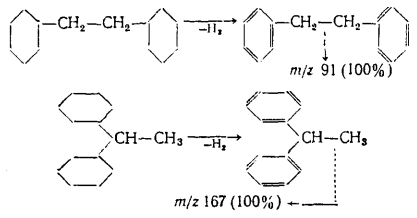
$$\text{>}-R \xrightarrow{D_2} DH_2C-\underset{\displaystyle CH_2D}{\underset{|}{CH}}-R ;$$

$$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-R \xrightarrow{D_2} DH_2C-\underset{\displaystyle CH_3}{\underset{|}{CD}}-R .$$

This method may prove to be exceptionally effective in the determination of the structures of cyclopropane derivatives of biological origin.[26]

It has been suggested that compounds containing five- and six-membered structures be investigated by means of the dehydrogenation reaction (Pt, C; 320 °C) in a microreactor positioned between the chromatographic column and the mass spectrometer.[27] In this case the process is carried out in a stream of carrier gas which consists of a mixture of 95% of helium and 5% of hydrogen. It has been shown for a large number of mono- and bi-cyclic hydrocarbons with known mass-spectrometric characteristics[28] that the cyclohexane derivatives contained in the mixtures, which do not contain quaternary carbon atoms, or compounds containing a six-membered ring which does not form part of the composition of bridged structures, are dehydrogenated with formation of the corresponding aromatic hydrocarbons. Five-membered cyclic derivatives do not react under these conditions. The number of six-membered rings in the initial molecule and also certain elements of the initial structures can be determined from the mass spectra of the aromatic hydrocarbons produced. The presence of intense M^+ peaks in the mass spectra of aromatic hydrocarbons permits a reliable determination of the molecular weight of the parent alicyclic compounds whose spectra do not contain the M^+ peaks. The characteristic decomposition of the aromatic hydrocarbons as a result of the benzil dissociation under electron impact makes it possible to detect branching at the

α-carbon atom of the alkyl substituent. In particular, 1,2- and 1,1-dicyclohexylethanes can be readily distinguished by this method:

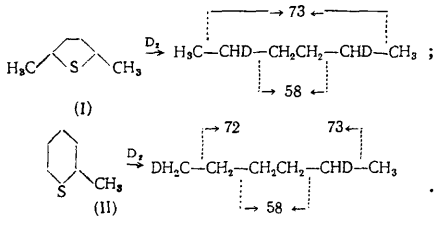


The structure of polycyclic hydrocarbons of the jointed type can also be established from the characteristic mass spectra of the dehydrogenation products.[29,30]

3. Cyclic Sulphides

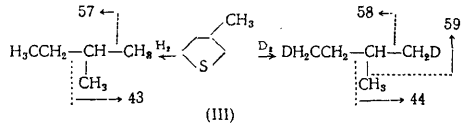
The RCMS method is used to study the structures of cyclic sulphides because EI mass spectrometry yields little information as regards the size of the heterocycle and the positions of its substituents. For a more reliable determination of the structures of monocyclic sulphides in mixtures, it has been suggested that the parallel hydro- and deuteriodesulphurisation of the mixture components in a microreactor placed between the chromatographic column and the mass spectrometer be used.[31] Pd/Al_2O_3 or Raney nickel could be used for the reaction, because both these catalysts give rise to effective hydrodesulphurisation in the presence of hydrogen at 150–250 °C. However, in the presence of deuterium, intense deuterium exchange takes place at these temperatures, while at lower temperatures Pd/Al_2O_3 becomes inactive. On the other hand, Raney nickel fixed on Chromaton by means of Apiezon is active also at 20–80 °C and at the same time ensures the selective formation of dideuteriohydrocarbons (the deuterium atoms are located at the carbon atoms which are linked to sulphur in the initial sulphides). The mass spectra measured under these conditions can be readily interpreted and make it possible to determine the position of the deuterium label and hence the size of the heterocycle. The positions of the substituents can be established in many cases on the basis of these spectra and also the spectra of the alkanes formed on hydrodesulphurisation.

It is easy to distinguish by this procedure, for example, 2,5-dimethylthiolan (I) and 2-methylthiane (II), whose mass spectra are similar. Although both compounds yield n-hexane on hydrodesulphurisation, the replacement of H_2 by D_2 leads to the formation of dideuteriohexanes with different positions of the label, which can be readily established mass-spectrometrically:[31]



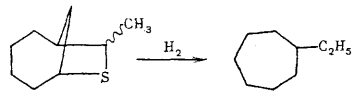
In the study of the structure of 3-methylthiolan (III), the position of the methyl substituent can be demonstrated already in the hydrodesulphurisation stage, since the recorded mass spectrum corresponds to 2-methylbutane.

The spectrum of the dideuteriohydrocarbon contains in its turn a doublet comprising peaks of equal size due to the ions $[M-CH_3]^+$ and $[M-CH_2D]^+$; this demonstrated unambiguously that the reaction product is 1,4-dideuteriomethylbutane and the initial sulphide therefore has the structure (III):

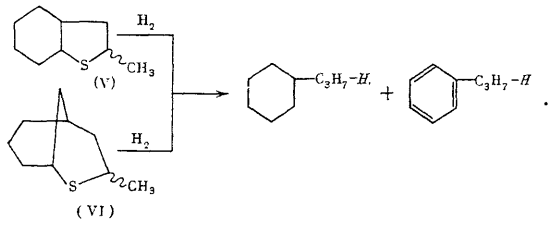


The employment of the deuteriodesulphurisation reaction in the study of polycyclic sulphides is pointless, since the position of the deuterium label in the naphthenic hydrocarbons formed cannot be determined mass-spectrometrically. Nevertheless, even simple hydrodesulphurisation can yield definite information about the structure of polycyclic sulphides. The qualitative composition of a mixture containing structural and geometrical isomers of methylthiabicyclononanes has been studied in this way.[32] The AP-56 catalyst, ensuring the quantitative hydrodesulphurisation of the test mixture at 300–315 °C, was then used. The desulphurisation microreactor was placed between a capillary column and the mass spectrometer. There was in this instance a risk that the separation of the eluted chromatographic zones would disappear even for small sorption effects of the catalyst. However, it was shown that, for an appropriate thickness of the catalyst bed, the impairment of the separation of the components, achieved with the aid of the capillary chromatographic column, is hardly detectable.

The results of the investigation confirmed the presence in the mixture of stereoisomeric 8-methyl-7-thiabicyclo[4.2.1]nonanes (IV), which gave rise to ethylcycloheptane on hydrodesulphurisation:



The mass spectra of the products of the hydrodesulphurisation of 8-methyl-7-thiabicyclo[4.3.0]nonanes (V), which are components of a mixture, consist of the spectra of the expected product (n-propylcyclohexane) and n-propylbenzene



Analogous mass spectra were recorded after the minor components had been passed through the catalytic zone. The structure of the isomeric 7-methyl-6-thiabicyclo[3.3.1]nonanes (VI) was proposed for such components.

Although the aromatisation of the cyclohexane hydrocarbons reduced the process selectivity and complicated the character of the mass spectra,[32] the latter are easy to interpret. Furthermore, this finding can be used to distinguish thiacyclanes with six-membered carbocycles

from the isomeric compounds with five- and seven-membered carbocycles. The characteristic nature of the mass spectra of aromatic hydrocarbons is also important, yielding additional information about the nature and positions of the substituents in the initial sulphides.

The results quoted by Mikaya et al.[32] are a good illustration of the fact that even those isomeric compounds which give rise to identical products in the reaction can be analysed separately by the RCMS method, which cannot be done by the RGC method.

4. Alcohols

Alcohols, especially aliphatic alcohols, are very important products of laboratory and industrial synthesis, frequently obtained in the form of mixtures. A wide variety of alicyclic alcohols (terpene and steroid alcohols) are isolated from biological objects. Thus the complexity of the mixture composition and the limited amount of the biological material available for study suggest that the chromato-mass-spectrometric method is most likely to be useful for their investigation. However, the mass spectra of the alcohols themselves yield insufficient information (or altogether fail to provide it) about their molecular weight and the nature and character of the carbon skeleton.[12] Derivatisation methods, based on liquid-phase reactions, are therefore very widely used for their investigations.[1,2] The RCMS method constitutes a good alternative to these procedures.

The combined RCMS method developed for the study of alcohols is based on the following gas-phase reactions.

1. The dehydrogenation reaction (catalyst—powdered copper; 320 °C)[33,34] carried out in a microreactor using helium as the carrier gas. Under these conditions, primary and secondary alcohols are quantitatively converted into aldehydes and ketones respectively, while tertiary alcohols remain unchanged. The mass spectra of the carbonyl compounds are characterised by the presence of M^+ peaks and also the peaks of the acyl ions RCO^+ and ions appearing as the result of the McLafferty rearrangement.
2. The reaction involving the exchange for deuterium of the enolysable hydrogen atoms in aldehydes and ketones formed on dehydrogenation of primary and secondary alcohols. This reaction takes place at 20–300 °C in a reaction column containing Chromaton on which dispersed KOD in a stationary SE-30 liquid phase is deposited.[35,36] The number of hydrogen atoms adjoining the carbonyl group exchanged for deuterium is determined from the shift of the M^+ peak, the peaks of the acyl ions, and the ions due to the McLafferty rearrangement.
3. The reaction involving the deoxygenation of alcohols to the corresponding hydrocarbons in the presence of a fused iron catalyst (300–320 °C).[37] It takes place in a microreactor in the presence of hydrogen, which serves at the same time as the carrier gas. The structure of the hydrocarbon is established from its mass spectrum by comparison with data in libraries of mass spectra or by analysing the characteristic decomposition under electron impact.

Various systems employed in the analysis of both individual alcohols (*A*–*C*) and their mixtures (*D*–*F*) have been developed on the basis of the reactions indicated:

A—dehydrogenation microreactor;
B—dehydrogenation microreactor → reaction column;
C—deoxygenation microreactor;
D—separating column → dehydrogenation microreactor;
E—separating column → dehydrogenation microreactor → reaction column;
F—separating column → deoxygenation microreactor.

All these systems can be placed in a thermostat of the chromatograph and connected to the inlet of the mass spectrometer.[38]

In the study of mixtures the analysis can be carried out in four stages. The chromatograms and mass spectra of the individual components of the initial mixture bypassing the reactor are recorded initially. The three subsequent stages of the analysis involve chromato-mass-spectrometric study using the *D*, *E*, and *F* systems. At each stage it is possible to obtain the relevant information about the structures of the individual elements of the alcohols investigated, which ultimately makes it possible to reproduce reliably the structure of the latter. Table 2 shows what information can be obtained from the mass spectra of aliphatic alcohols and their reaction products.

Table 2. Information about the structure of the alcohols obtained at different stages of their investigation by the RCMS method.[38]

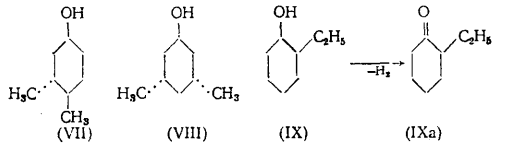
Reaction employed	Product analysed	Information obtained
Without reaction (bypass)	initial alcohol	determination of approximate data on the molecular weight, the nature of the alcohol, and the position of the OH group
Dehydrogenation of alcohol	carbonyl compound	reliable determination of molecular weight; differentiation of primary, secondary, and tertiary alcohols and dialkyl ethers; determination of the position of the OH group; determination of approximate (sometimes accurate) data on the character of the branching at the carbon atoms in the α-position relative to the carbonyl group
Deuterium exchange involving dehydrogenation products	deuterium-labelled carbonyl compound	determination of the nature and character of the substitution at the carbon atoms in the α-position relative to the carbonyl group
Deoxygenation of alcohol	hydrocarbon	determination of the structure of the carbon skeleton of the alcohol

It is noteworthy that in a number of instances there is no need to carry out all the stages of the investigation and it is sufficient to employ only some of them. Thus in the study of industrial alcohols, only the post-column dehydrogenation and pre-column deoxygenation were used.[39]

The RCMS method using the above reactions is very useful for the determination of the structures of alicyclic alcohols, whose mass spectra are relatively non-characteristic. The possibilities of the method have been demonstrated[40] in relation to mono- and bi-cyclic alcohols. In particular, it is possible to differentiate 3,4- and 3,5-dimethylcyclohexanols, compounds (VII) and (VIII) respectively, by this method and also to obtain information about their steric structures. After the deoxygenation, the mass spectra of *trans*-1,2-dimethyl- and *cis*-1,3-dimethyl-cyclohexanes respectively were recorded, which demonstrates a specific steric orientation of the CH_3 groups in the initial molecules.

When the *A* and *B* systems were used for the analysis of both alcohols, the mass spectra of ketones and their tetradeuterio-analogues were recorded respectively, which indicates the absence of substituents in the α-position relative to the OH groups. The fact that the spectrum of the ketone obtained from one alcohol [compound (VII)] contains peaks due to the ions $CH_3CH{=}CH\overset{+}{C}O$ (*m*/*z* 69) and

$CH_2=CHC\equiv\overset{+}{O}$ (m/z 55), which shift when deuterium is used (the *C* system) to m/z 70 and 56 respectively, while the spectrum of the ketone obtained from the other alcohol [compound (VIII)] contains only the peak of the first ion with m/z 69 indicates the positions of the substituents in these cyclohexanols.



(VII) (VIII) (IX) (IXa)

Even simple dehydrogenation of 2-ethylcyclohexanol (IX) shows that it contains the C_2H_5 group in the α-position relative to the carbonyl group, since the maximum peak in the mass-spectrum of the ketone (IXa) is due to the $[M-C_2H_4]^+$ radical-cation, which appears as a result of the McLafferty rearrangement. This is also confirmed by the finding that only three hydrogen atoms in the ketone (IXa) are exchanged for deuterium.

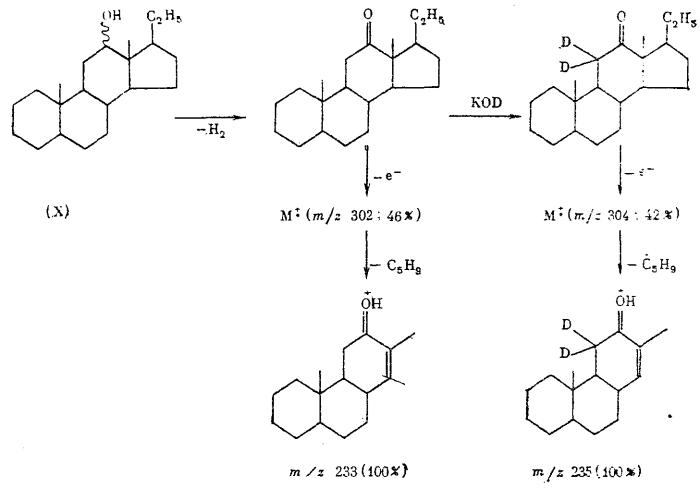
The problem of the mass-spectrometric determination of the position of the OH group is fairly acute in the case of steroid alcohols. The RCMS method gives rise to certain possibilities for the investigation of compounds of this type.[41]

Table 3. Composition of the products of the catalytic reactions of steroid alcohols (Cu, 320 °C, total conversion 100%).[41]

Initial alcohol	Product (content in %)
12α- and 12β-hydroxypregnanes (X)	12-hydroxypregnane (100%)
3β-Hydroxyandrostan-17-one	androstane-3,17-dione (100%)
17β-Hydroxyandrostan-3-one	androstane-3,17-dione (100%)
Cholesterol	cholesta-3,5-diene (20%), cholesta-4,6-dien-3-one (70%), and cholest-4-en-3-one (10%)
6-Methylcholesterol	6-methylcholesta-3,5-diene (18%), 6-methylcholesta-4,6-diene-3-one (72%), and 6-methylcholest-4-en-3-one (10%)
3β-Hydroxypregn-5-en-20-one	pregna-3,5-dien-20-one (15%), pregna-4,6-diene-3,20-dione (78%), and preg-4-ene-3,20-dione (7%)

Table 3 presents the results of the investigation of individual steroid alcohols by the RCMS method using the dehydrogenation microreactor → separating column system. In all cases the alcohols react quantitatively. Saturated alcohols (hydroxypregnanes and hydroxyandrostanones) were only dehydrogenated under these conditions with formation of the corresponding ketones. On the other hand, mixtures were obtained from unsaturated alcohols (cholesterol, 6-methylcholesterol, 3β-hydroxypregn-5-en-20-one) in which the expected ketones constituted only an insignificant proportion and the main bulk of the mixture consisted of the products of their further dehydrogenation and also the alcohol dehydrogenation products.

The formation of a mixture of products, noted for unsaturated alcohols, in a microreactor placed between the separating column and the mass spectrometer is undesirable, because the interpretation of the mass spectra of the unresolved mixture gives rise to difficulties. On the other hand, the method can be used effectively for saturated alcohols. For example, the dehydrogenation of 12α- and 12β-hydroxypregnanes (X), whose mass spectra are exceptionally non-characteristic, results in the formation of the same ketone (Xa), the intense peak with m/z 233 in the mass-spectrum of which characterises the 12-oxo-group. As might have been expected, only two hydrogen atoms in this ketone are exchanged for deuterium:



The application of chromato-mass-spectrometry to the study of mixtures of diols and alkoxyalcohols is limited owing to their low volatility, poor chromatographic properties, and the relatively non-characteristic mass spectra. The RCMS methods described above are also unsuitable in this case. On the other hand, the conversion of such compounds into silyl ethers appears definitely promising. In order to increase the speed of the analysis, it is desirable to obtain the silyl ethers directly in the course of the chromato-mass-spectrometric analysis and not in separate experiments.

The method involving direct silylation in the chromatographic column and subsequent mass-spectrometric analysis has been used successfully in the study of a mixture of the aliphatic diols $HO(CH_2)_nOH$ (n = 4–10) obtained synthetically.[42] *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% of added $(CH_3)_3SiCl$ was used as the silylating agent. It was added directly 5 s after the injection of the reaction mixture. The volume ratio of the specimen and BSTFA, amounting to approximately 1 : 3, ensured the quantitative silylation of the diols. The mass-spectrometric characteristics of the trimethylsilyl ethers of the diols were established, the molecular weights of the diols were determined, and the character of the alcoholic functions (whether they are primary or secondary) was deduced. Unfortunately, the mass spectra of the silyl ethers have no distinctive features which would make it possible to determine the structure of the carbon skeletons of the diols.

An analogous approach has been used in the study of mixtures of the alkoxyalcohols $RO(CH_2)_nOH$ (R = CH_3 or t-C_4H_9).[43] It was shown that the peaks of the $[M - CH_3]^+$ ions can be used to determine the molecular weights of the methoxyalkanols from the mass spectra of the trimethylsilyl

ethers. In the case of t-butoxyalkanols, the peaks of the ions $[M - C_4H_9]^+$ and $[M - C_4H_9O]^+$ can be used for these purposes.

The method of silylation directly in the chromatographic column can be used also for the investigation of other hydroxy-compounds (carbohydrates, steroid and terpene alcohols, lipid diols and triols, and acids).

IV. INVESTIGATION OF DISSOCIATIVE IONISATION MECHANISMS

Deuterium-labelled analogues are used widely in the mass-spectrometric study of the mechanisms of the fragmentation of organic compounds. In all the known instances, preparative methods involving the isolation of the required products are used to obtain such derivatives. However, in certain cases the deuteriated analogues can be obtained directly in the injection system of the mass spectrometer without subsequent isolation. This procedure makes it possible to work with submicrogramme amounts of the test substance and sharply reduces the time of the investigation. Naturally, only those deuteriation methods are then permissible which ensure the selective introduction of the label into specific positions in the molecule. These requirements are satisfied by the above method in which reaction columns containing KOD are employed.

The mechanisms of the fragmentation of certain aliphatic ketones under electron impact have been investigated with the aid of a reaction column containing KOD dispersed in a stationary liquid phase and deposited on a solid carrier.[36] The starting materials were not the ketones themselves but the corresponding alcohols, which were subjected to preliminary dehydrogenation in a microreactor placed before the reaction column.

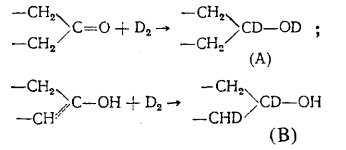
The reaction column, which contained $(Ph_3P)_3RhCl$ dispersed in Carbowax 20M on Chromaton and ensured the selective addition of deuterium to the double bonds of olefins under catalytic conditions, was used to investigate the mechanisms of the fragmentation of cyclobutane hydrocarbons.[44] The initial substrates employed were methylene-, vinyl-, and propylene-cyclobutanes. When these were passed through the above column in a stream of hydrogen or deuterium, the corresponding saturated hydrocarbons and their vicinal dideuterio-analogues were formed according to the mass-spectrometric data. Comparative analysis of the mass spectra permitted the conclusion that the $M^{\ddagger}$ species derived from the alkylcyclobutanes can decompose in both intact cyclic and acyclic forms. The decomposition of the former ensures the characteristic division of the ring "in half" with elimination of the C_2H_4 molecule. On the other hand, the elimination of any alkyl radical takes place after the isomerisation of $M^{\ddagger}$ to the open-chain acyclic form. The results obtained also indicate a low probability of the existence of the cyclobutyl cation in the gas phase.

The fragmentation of 1,1-dimethyl-1-silacyclopentane, 1-ethyl-1-methyl-1-silacyclobutane, and ethyltetraethoxysilane was investigated by an analogous procedure. Together with the corresponding dideuterio-analogues, these compounds had been obtained from 1,1-dimethyl-1-silacyclopent-3-ene, 1-methyl-1-vinyl-1-silacyclobutane, and triethoxyvinylsilane respectively.[45]

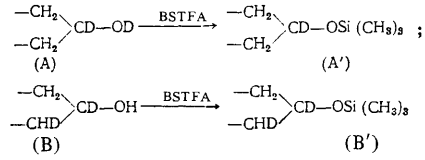
V. INVESTIGATION OF HETEROGENEOUS CATALYTIC REACTIONS

The use of the microreaction technique and chromato-mass-spectrometry opens up wide prospects for the investigation of the pathways and mechanisms in heterogeneous catalytic reactions. In the course of a single experiment, it is possible to record by this method the chromatogram of the mixture of products (used for the quantitative estimation of the composition) and to obtain mass spectra permitting the high speed determination of the structures of the products. Although microreactors have been used for a long time in the study of catalytic reactions in combination with gas chromatography, this approach has not yet been as widely adopted in chromato-mass-spectrometry as it should despite its one significant advantage—it permits investigations using labelled compounds. The possibility of investigating by the RCMS method of reactions such as hydrogenation, dehydrogenation, hydrogenolysis, deoxygenation, etc., using deuterium is of undoubted interest. At present one can point to only one study where this method has been used to determine the mechanism of a heterogeneous-catalytic reaction and where its advantages have been fully manifested. It concerned the investigation of the mechanism of the hydrogenation of alicyclic ketones on a fused iron catalyst in a pulse microreactor → separating column → mass-spectrometer system.[46]

The hydrogenation of carbonyl compounds is known to proceed via the addition of hydrogen either to the carbonyl group (the ketone mechanism) or to the double bond of the corresponding enol (the enol mechanism). If the reaction takes place in a deuterium atmosphere, the isotopic forms of the alcohols (A) and (B) should arise respectively when these mechanisms operate:



In a direct mass-spectrometric study of the alcohols formed, it is not possible to establish reliably their isotope composition owing to the low intensity of the $M^{\ddagger}$ peaks, the presence of the peaks of the $[M-H]^+$ ions, and also the reverse D/H exchange of the active hydrogen atoms in the mass spectrometer. It has therefore been suggested[46] that the alcohols be silylated with the aid of BSTFA directly in the separating column. In this case the silyl ethers (A′) and (B′), with different numbers of D atoms which can be readily determined mass-spectrometrically, are then formed from the alcohols (A) and (B):



A special reactor containing an additional inlet for BSTFA was constructed for studies by the above procedure; in order to avoid the poisoning of the catalyst, the silylating agent was introduced into the gas stream beyond the catalyst layer but before the inlet into the chromatographic column.

Calculation of the isotope composition of the silyl ethers of the alcohols taking into account the isotope composition of the unreacted ketone established that the hydrogenation of cyclopentanone and cyclohexanone in the presence of the above catalyst in the temperature range 50–210 °C proceeds with equal probabilities via the enol and ketone mechanisms.

In carrying out such investigations, one must bear in mind that during chromatography different isotopic forms can be eluted in different ways (the forms enriched in deuterium are eluted more readily), although in the general

case the chromatographic zone is not resolved. In order to determine the true isotope composition, it is in this case necessary to scan repeatedly in the course of the elution of the test substance. The calculation is in this case based on the overall mass spectrum.

VI. PYROLYTIC CHROMATO-MASS-SPECTROMETRY

The combination of pyrolytic methods with chromato-mass-spectrometry (PCMS) can be used for different purposes. In the first place PCMS is an effective procedure for the investigation of the mechanisms of the thermal decomposition of organic compounds.[47,48] From the standpoint of analytic possibilities, the application of the PCMS method to the study of the structures of high-molecular-weight compounds is of greatest interest. For the qualitative analysis of the composition of the pyrolytic reaction mixture, the PCMS method is much more effective than the pyrolytic mass-spectrometric method. However, it is not always suitable for the determination of the quantitative composition, because the volatility of the pyrolysis products may be low and they may not be eluted from the chromatographic column or their molecular weight may exceed the limit of the molecular weights detectable by the mass spectrometer. Nevertheless in some cases it is possible to establish by this method both the qualitative and the quantitative composition of the pyrolytic reaction mixture.[49]

The same pyrolysers (pyrolysers based on the Curie point and filamental and tubular pyrolysers) are used in PCMS as in pyrolytic mass-spectrometry or pyrolytic gas chromatography.[3,4]

In terms of the speed of analysis, PCMS is inferior to pyrolytic mass spectrometry, but the level of structural information obtained in the former case is undoubtedly much greater. The determination of the structures of the pyrolysis products and on that basis also of the structures of high-molecular-weight compounds can be evidently facilitated by using the additional chemical methods discussed above.

The efficiency of the method has been demonstrated in relation to the study of polychloroprene, polyisoprene, a polynitrile, and other industrial elastomers.[50] In the study of the copolymers of acrylonitrile and styrene by this method using a capillary column, the monomers, dimers, and trimers were identified mass-spectrometrically.[51] Analysis of the data obtained made it possible to infer the sequence of units in such polymers.

Very important information, of both theoretical and practical value, has been obtained in the study of coal by the PCMS method.[52] Various saturated and unsaturated hydrocarbons, aromatic hydrocarbons, and phenols were identified among the pyrolysis products.

Although the pyrolytic mass-spectrometric method is used widely in the study of biopolymers, there have been virtually no studies using the PCMS method for this purpose. This is most likely to be due to the high polarity of the pyrolysis products formed, which are poorly eluted in gas-chromatographic separation. Presumably the use of intracolumn derivatisation will render such objects susceptible to analysis also by the PCMS method. In addition, the PCMS method using liquid chromatography may prove to be promising for the investigation of biopolymers.

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