# REACTION GAS CHROMATOGRAPHY–MASS SPECTROMETRY

## VI. USE OF DEUTERIUM AS THE CARRIER AND REAGENT GAS IN REACTION GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

The use of deuterium as the carrier and reagent gas for structural determinations of alkenes, cyclopropane compounds and cyclic sulphides by reaction gas chromatography (GC)–mass spectrometry is described. Catalytic transformation of the compounds was accomplished in an on-line gas-phase microreactor located between the GC column and the mass spectrometer or on the reaction column. Valuable structural information may be extracted from the mass spectra of the products obtained from the addition of deuterium to double bond of alkenes [catalysts: Pd–porous glass or Chromaton W coated with a dispersion of $(Ph_3P)_3RhCl$ in Carbowax 20M] or the sites of ring opening for cyclopropane compounds (catalyst: Pd–porous glass) and cyclic sulphides (catalyst: Raney nickel).

INTRODUCTION

On-line derivatization is widely used in gas chromatography (GC) to improve the chromatographic behaviour of compounds, to convert the compound under study into derivatives having known chromatographic parameters or to increase the sensitivity to the detector employed[1]. The application of a similar approach to gas chromatography–mass spectrometry (GC–MS) can offer new possibilities for improvement of the diagnostic power of mass spectrometry, which led to the development of reaction GC–MS[2,3]. This technique involves on-line derivatization of compounds directly in the inlet system of a gas chromatograph–mass spectrometer. Particular attention is paid to the use of gas-phase microreactors located between the GC column and the mass spectrometer. In some instances, the location of a microreactor between the injection port and the GC column, *i.e.*, in the position that is most frequently used in reaction GC, is also considered useful. The advantages of the former position of a microreactor were shown for the first time by Teeter *et al.*[4], who inserted a micro-hydrogenator between the GC column and mass spectrometer in the study of unsaturated compounds in mixtures. The main advantage is that the

microreactor in such a position allows each effluent to be chemically converted. In this instance, the chromatogram corresponds to that of initial mixture (which permits its quantitative treatment) and the mass spectra correspond to the products of transformation (which assists in structural elucidation). It is very important that such a location of a microreactor permits all the components that give rise to identical compounds after chemical transformation to be investigated separately.

For on-line derivatization in reaction GC–MS (as well as in reaction GC), the hydrogenation and hydrogenolysis reactions (hydrogen is used as the carrier and reagent gas) are of interest as they are fast and proceed quantitatively. Such reactions can lead to derivatives whose mass spectra give additional information on the structure of the initial compounds.

In this paper we report on the possibilities of the use of deuterium as the carrier and reagent gas for performing similar transformations in reactions GC–MS in structural determinations of alkenes, cyclopropane compounds and cyclic sulphides mixtures. The basis of such an approach is to obtain products containing a deuterium label at the position of the initial double bond (for alkenes) or at the sites of ring cleavage (for cyclopropanes and cyclic sulphides) in on-line catalytic hydrogenation or hydrogenolysis. The position of the deuterium label in the deuterated compounds thus obtained can be deduced from the mass spectra and, hence, the structures of initial compounds can be determined more reliably.

EXPERIMENTAL

*Materials*
    All alkenes were commercial analytical-reagent grade materials (Polyscience, U.S.A.). The synthesis of the cyclopropane compounds investigated was described recently[5]. Cyclic sulphides were the same materials as investigated earlier[6]. All the compounds used for the study were at least 99% pure. Tris(triphenylphosphin)rhodium(I) chloride was commercial grade reagent (Fluka, Buchs, Switzerland). Gaseous deuterium was of at least 99% purity.

*Preparation of catalysts*
    The 1–2% Pd–porous glass (100–120 mesh) catalyst, prepared by a standard procedure, was used for the study of alkene and cyclopropane compounds.
    Pre-heterogenization of Wilkinson's catalyst, $(Ph_3P)_3RhCl$, was accomplished as follows. To a solution of 59 mg of $(Ph_3P)_3RhCl$ in 2 ml of methylene chloride, a solution of 180 mg of Carbowax 20M in 5 ml of methylene chloride was added with stirring under an argon atmosphere. To this solution, 1.2 g of Chromaton W (120 mesh) was added. The slurry obtained was stirred for 20 min and evaporated. The catalyst system thus prepared was used in the study of alkenes.
    Raney nickel catalyst supported on Chromaton W (120 mesh) was obtained accordingly to the method of Undeova and Janek[7]. This catalyst was used in the study of cyclic sulphides.

*Reaction gas chromatography–mass spectrometry*
    The work was performed on an LKB-2091 gas chromatograph–mass spectrometer. The mass spectra were obtained at an ionizing energy of 70 eV, an emission

current of 25 $\mu$A and temperatures of the ionization chamber and molecular separator of 200°C.

Three types of chromatographic columns were employed. A stainless-steel capillary column (70 m × 0.25 mm I.D.) containing Apiezon L was used for the study of alkenes (column temperature 100°C; splitting ratio 1:20). A stainless-steel column (3 m × 3 mm I.D.) packed with 5% SE-30 on 120-mesh Chromaton W was used for the study of cyclopropane compounds (column temperature 100°C). A stainless-steel column (3 m × 3 mm I.D.) packed with 10% ethylene glycol adipate on 150-mesh Spherochrom was used for the investigation of cyclic sulphides (column temperature programmed from 50 to 100°C at 3°C/min). In all instances deuterium was used as the carrier and reagent gas at a flow-rate of 20 ml/min.

The microreactor employed was described recently[8]. It included a system allowing the compounds to by-pass the catalyst when the chromatogram and the mass spectra of the initial mixture are being recorded. The catalyst (Pd–porous glass or supported Raney nickel) was placed in the microreactor tube between plugs of glass-wool and the microreactor system was connected between the analytical GC column and the mass spectrometer. Prior to analysis, both catalysts were activated in a flow of deuterium at 200°C for 2 h. A plug of catalyst 2 mm in diameter and 4–5 cm long achieved quantitative conversion of 10–50 $\mu$g of the individual compounds under study at temperatures of 50–200°C.

For the investigation of individual alkenes a glass column (1.5 m × 3 mm I.D.) packed with the catalyst system containing 5% $(Ph_3P)_3RhCl$ and 15% Carbowax 20M on Chromaton W (see above) was used. This reaction column was directly connected to the mass spectrometer. Individual alkenes were passed through the column in a flow of deuterium at a rate of 20 ml/min. This reaction column achieved quantitative deuteration of 50–100 $\mu$g of alkenes (up to $C_{12}$) at temperatures of 50–80°C.

For structural determinations of alkenes, cyclopropane compounds and cyclic sulphides by reaction GC–MS, the microreactor containing a by-pass system was located between the GC column and the mass spectrometer. Analysis by this method may be accomplished as follows. The first stage involves the recording of the chromatogram and the mass spectra for the mixture to be studied with the aid of the by-pass technique. In subsequent stages, the components of a mixture are passed over the catalyst, hydrogen or deuterium being used as the carrier and reagent gases. The mass spectra of the products obtained by using hydrogen provide some additional information regarding the carbon skeleton and substitution pattern of molecules and are also necessary for comparison with the spectra of the deuterated analogues.

It should be noted that for mass spectrometric determination of the position of the label in deuterated alkanes, those ions which are formed from the molecular ions due to the loss of small alkyl radicals from the ends of the chain or from branching points are used, as only such species are eliminated as a result of simple bond cleavage. These data are further used for structural elucidation of the initial compounds.

RESULTS AND DISCUSSION

*Alkenes*

The electron impact mass spectra of alkenes do not provide much useful information for the determination of the carbon skeleton and the position of double bonds. Reaction GC–MS, involving the use of a micro-hydrogenator (for example, 1–2% Pd–porous glass) and hydrogen as the carrier and reagent gas, permits the determination of the carbon skeleton of alkenes in a mixture more reliably, as the mass spectra of saturated alkanes are very sensitive to branching of the aliphatic chain[2,4]. The problem of determining the double bond position in alkenes remained, however, as the electron impact mass spectra of isomeric alkenes are frequently similar. A number of methods devised to obtain this information have relied on the chemical derivatization of alkenes prior to mass spectrometric analysis[9]. All of them, however, involve solution reactions and are mainly applicable to individual alkenes and are time consuming. The use of deuterium offers a new possibility for on-line derivatization. In fact, the mass spectra of vicinal dideuteroalkanes obtained from alkenes by deuteration in the described system should permit the determination of the position of the deuterium label and, hence, the location of the double bond in the alkenes under study[10].

Fig. 1 shows the chromatograms obtained with the by-pass technique and the microreactor (1–2% Pd–porous glass) for a standard mixture of alkenes using deuterium as the carrier and reagent gas. A comparison of the chromatograms shows that there are no essential differences in retention times and peak separation either with or without the microreactor. It should be noted, however, that owing to the adsorption effect, a high dispersion of the solid support or a low temperature of the catalyst employed can lead to increases in retention times and decreases in resolution.

The catalyst used achieved quantitative deuteration of alkenes in the temperature range 50–250°C. No side-reactions, *e.g.*, isomerization or cracking, were observed under such catalytic conditions. At the same time, this catalyst (Pd–porous glass), as well as similar supported catalysts containing transition metals, does not provide the selective addition of deuterium to the double bonds of alkenes owing to extensive isotope scrampling. By using isomeric *n*-heptenes and *n*-octenes, we found that the latter process proceeds particularly extensively at high temperatures (above 150°C). A decrease in temperature (below 150°C), however, gives rise to suppression of isotope scrambling and the addition of deuterium to the double bond predominates over scrambling. Table I shows the deuterium content in the products of the deuteration of 1-, 2- and 4-octenes at 100°C. It can be seen that isotope scrambling occurs less extensively with 1-octene than 2- and 4-octene. A similar difference in deuterium distribution was observed for other isomeric *n*-alkenes. This fact may be used for the differentiation of alkenes with terminal and internal double bonds.

The selectivity of deuterium introduction is particularly increased if an alkene possesses branching at position 2. Fig. 2 shows the mass spectra of 2-methylpentane and the product of deuteration of 2-methyl-1-pentene. The latter shows that the $M^{+\cdot}$ peak ($m/z$ 88) is much more intense than the $m/z$ 89 peak corresponding to deuterium addition plus scrambling. Diagnostically the most characteristic $(M - CH_3)^+$ ($m/z$ 71) peak observed in the mass spectrum of 2-methylpentane (Fig. 2a) is completely shifted and is converted into a doublet at $m/z$ 72 and 73 corre-
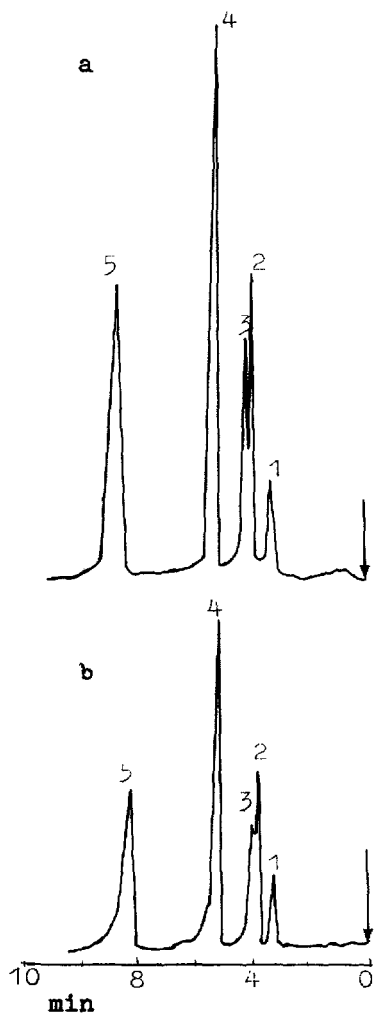
Fig. 1. Chromatograms of mixtures obtained (a) by the by-pass method and (b) by using the microreactor between the GC column and the mass spectrometer. (1) 2,4,4-Trimethyl-1-pentene; (2) 1-octene; (3) 2-octene; (4) 1-nonene; (5) 1-decene.

sponding to the $(M - CH_2{}^2H)^+$ and $(M - CH_3)^+$ ions, respectively. This fact permits an unambiguous determination of the position of the double bond in the initial alkene.

Further efforts were directed to the search for a catalyst giving rise to selective deuterium introduction without contamination by isotopic scrambling. In this connection, we studied the homogeneous Wilkinson's catalyst, $(Ph_3P)_3RhCl$, which is widely used for the selective deuteration of various unsaturated compounds in solution chemistry. We decided to employ this catalyst in reaction GC–MS after its pre-heterogenization. This catalyst was earlier used in the supported form (solid support coated with a solution of Wilkinson's catalyst in various solvents) to achieve

TABLE I

DEUTERIUM CONTENT (%) IN DEUTERATED OCTANES OBTAINED FROM $n$-OCTENES
ON 1–2% Pd–POROUS GLASS (100°C)

| $n$-Octene | $^2H_n$-Octane (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $^2H_1$ | $^2H_2$ | $^2H_3$ | $^2H_4$ | $^2H_5$ | $^2H_6$ | $^2H_7$ | $^2H_8$ | $^2H_9$ |
| 1-Octene | 6 | 34 | 22 | 14 | 10 | 6 | 5 | 3 | — |
| 2-Octene | 4 | 20 | 15 | 15 | 12 | 8 | 8 | 6 | 6 |
| 4-Octene | 3 | 20 | 13 | 10 | 9 | 9 | 9 | 8 | 7 |

hydrogenation and hydroformylation of lower alkenes at 25°C[11]. Such a catalytic system, however, is not suitable for reaction GC–MS as the solvents can be evaporated and admitted into the mass spectrometer even at low temperatures if the reactor is directly connected to the instrument. Hence we carried out the heterogenization of Wilkinson's catalyst by coating the solid support (Chromaton W) with a dispersion of $(Ph_3P)_3RhCl$ in the stationary phase (Carbowax 20M). It was found that the reaction column packed with the catalytic system provided the selective addition of deuterium to the double bonds of alkenes at temperatures of 50–80°C. The mass spectra showed that dideuteroalkanes possess extremely high isotopic purity (about 100%). At higher temperatures, however, pronounced isotope scrambling begins to occur, which is possibly due to decomposition of $(Ph_3P)_3RhCl$.

Fig. 3a–c show the mass spectra of dideuteroheptanes obtained from 1-, 2- and 3-heptenes by using the reaction column. The qualitative differences observed in these
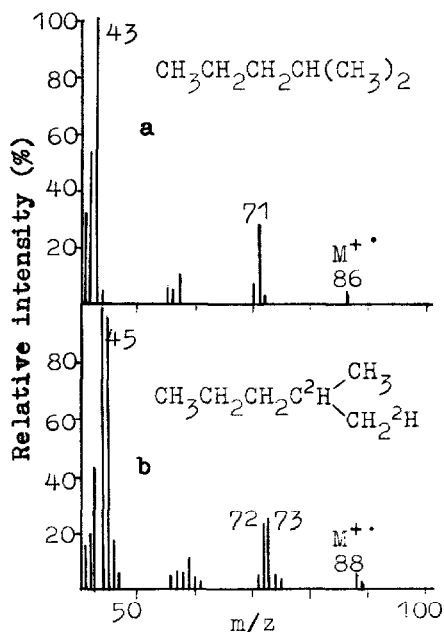


Fig. 2. Mass spectra of (a) 2-methylpentane and (b) 2-methyl-1,2-dideuteropentane.

spectra are easily interpreted and may be used for the determination of the positions of the double bonds in alkenes (Table II). In fact, the doublets both of the $(M-CH_3)^+$ and $(M-CH_2{}^2H)^+$ ions and of the $(M-C_2H_5)^+$ and $(M-C_2H_3{}^2H_2)^+$ ions are characteristic of 1,2-dideuteroalkanes produced from 1-alkenes. For 2,3-dideuteroalkanes (produced from 2-alkenes), diagnostically the most important peaks are due to the single $(M-CH_3)^+$ ion and to a doublet of the
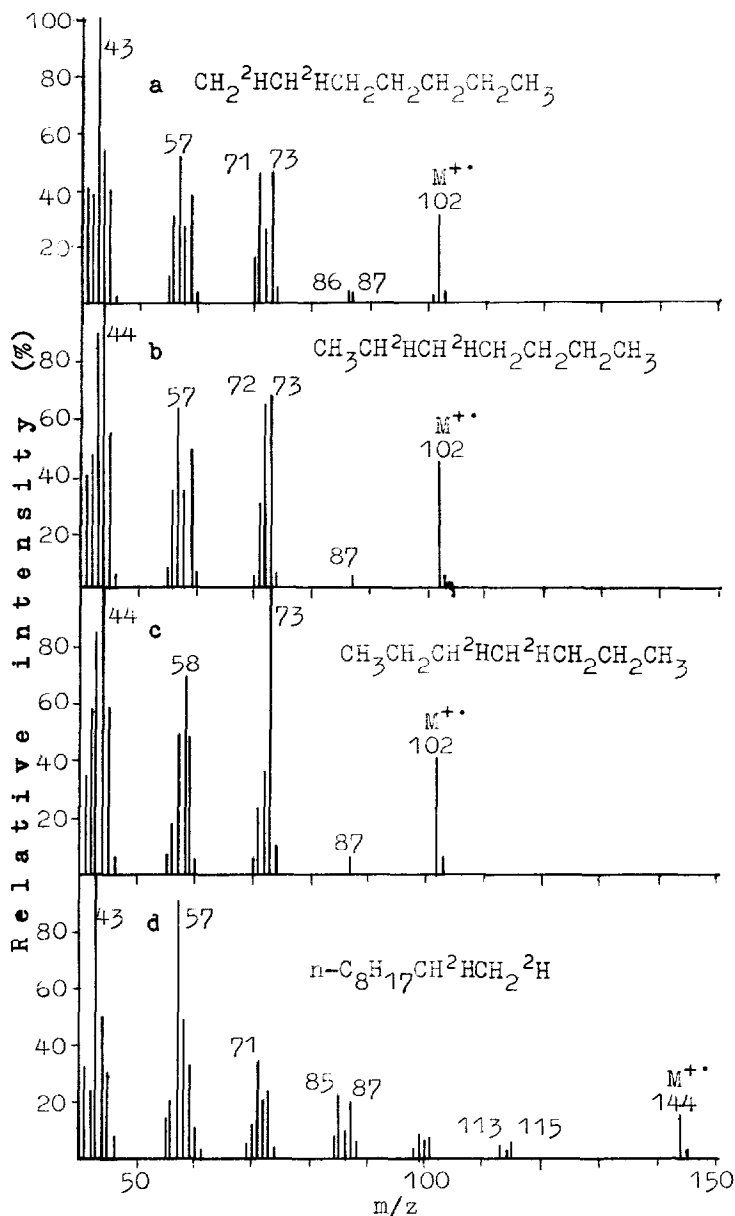


Fig. 3. Mass spectra of (a) 1,2-dideuteroheptane, (b) 2,3-dideuteroheptane, (c) 3,4-dideuteroheptane and (d) 1,2-dideuterodecane.

TABLE II

DIAGNOSTIC IONS IN THE MASS SPECTRA OF DEUTERATED COMPOUNDS

| Initial compound | Deuterated compound | Molecular weight after deuteration | Diagnostic ions (m/z) |
|---|---|---|---|
| 1-Heptene | $^2HH_2CCH^2HC_5H_{11}$ | 102 | $(M-CH_3)^+$ (87), $(M-CH_2{}^2H)^+$ (86), $(M-C_2H_5)^+$ (73), $(M-C_2H_3{}^2H_2)^+$ (71) |
| 2-Heptene | $H_3CCH^2HCH^2HC_4H_9$ | 102 | $(M-CH_3)^+$ (87), $(M-C_2H_5)^+$ (73), $(M-C_2H_4{}^2H)^+$ (72) |
| 3-Heptene | $H_3CCH_2CH^2HCH^2HC_3H_7$ | 102 | $(M-CH_3)^+$ (87), $(M-C_2H_5)^+$ (73) |
| 2-Methyl-1-pentene | $H_7C_3C^2H(CH_3)CH_2{}^2H$ | 88 | $(M-CH_3)^+$ (73), $(M-CH_2{}^2H)^+$ (72), $(C_3H_5{}^2H_2)^+$ (45) |
| 2-Ethyl-1-hexene | $H_9C_4C^2H(C_2H_5)CH_2{}^2H$ | 116 | $(M-CH_2{}^2H)^+$ (100), $(M-C_2H_5)^+$ (87) |
| 1-Decene | $^2HH_2CCH^2HC_8H_{17}$ | 144 | $(M-C_2H_5)^+$ (115), $(M-C_2H_3{}^2H_2)^+$ (113) |
| n-Octylcyclopropane | $H_{17}C_8CH(CH_2{}^2H)_2$ | 158 | $(M-CH_2{}^2H)^+$ (142) |
| Methyl β-cyclopropylpropionate | $(CH_2{}^2H)_2CHCH_2CH_2COOCH_3$ | 132 | $(M-CH_2{}^2H)$ (116) |
| Ethyl β-cyclopropylpropionate | $(CH_2{}^2H)_2CHCH_2CH_2COOC_2H_5$ | 146 | $(M-CH_2{}^2H)^+$ (130) |
| 3-Methyltetrahydrothiophene | $^2HH_2CCH_2CH(CH_3)CH_2{}^2H$ | 74 | $(M-CH_3)^+$ (59), $(M-CH_2{}^2H)^+$ (58) |
| 2,5-Dimethyltetrahydrothiophene | $H_3CCH^2HCH_2CH_2CH^2HCH_3$ | 88 | $(M-CH_3)^+$ (73), $(M-C_2H_4{}^2H)^+$ (58) |
| 2-Methyltetrahydrothiopyran | $^2HH_2CCH_2CH_2CH_2CH^2HCH_3$ | 88 | $(M-CH_3)^+$ (73), $(M-CH_2{}^2H)^+$ (72) |
| 4-Methyltetrahydrothiopyran | $^2HH_2CCH_2CH(CH_3)CH_2CH_2{}^2H$ | 88 | $(M-CH_3)^+$ (83), $(M-C_2H_4{}^2H)^+$ (58) |
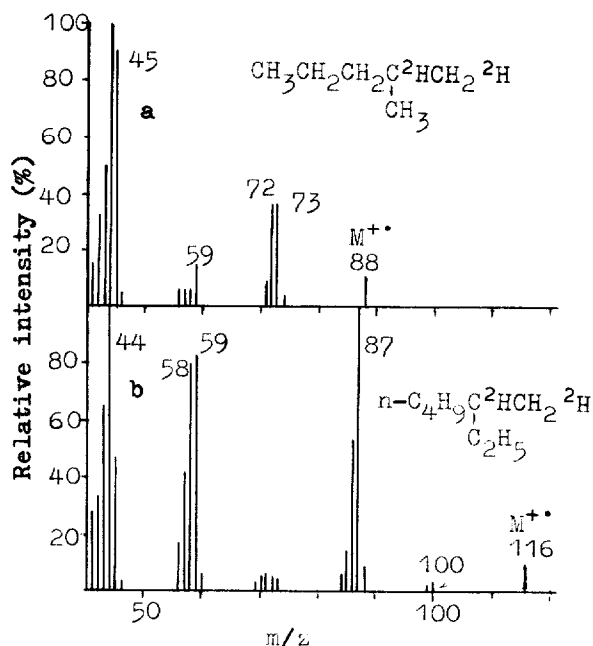
Fig. 4. Mass spectra of (a) 2-methyl-1,2-dideuteropentane and (b) 2-ethyl-1,2-dideuterohexane.

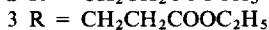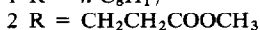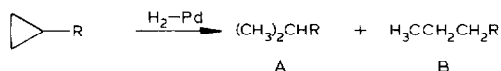$(M - C_2H_5)^+$ and $(M - C_2H_4{}^2H)^+$ ions. The sole $(M - CH_3)^+$ and $(M - C_2H_5)^+$ ions and the doublet of the $(M - C_3H_7)^+$ and $(M - {}_3H_6{}^2H)^+$ ions are considered to be the principal ions for 3,4-dideuteroalkanes obtained from 3-alkenes. Although the formation of the $(M - CH_3)^+$ ions is not peculiar to higher $n$-alkanes, the presence of the $(M - C_2H_5)^+$ and $(M - C_2H_3{}^2H_2)^+$ ions in the mass spectra recorded after the deuteration of higher 1-alkenes with straight chains may serve as unambiguous evidence of a terminal double bond (Fig. 3d).

The efficiency of the method is further examplified by the investigation of branched alkenes. In fact, the mass spectrum of labelled 2-methylpentane (Fig. 4a) obtained from 2-methyl-1-pentene permits an unambiguous determination of the position of the double bond (see above). The location of the double bond in 2-ethyl-1-hexene is readily recognized from the mass spectrum of the corresponding dideutero analogue (Fig. 4b), which reveals the $(M - CH_2{}^2H)^+$ and $(M - C_2H_5)^+$ ions resulting from the loss of alkyl radicals from the branching point.

Although the scope of the method involving the use of Wilkinson's catalyst was demonstrated with the aid of individual alkenes, it may apparently be applied to the investigation of mixtures. In this instance the system analytical GC column → reaction column → mass spectrometer could be used. The only problem is that the reaction column employed has to be operated at relatively low temperatures (up to 80°C), which requires the analytical GC column to be operated at similar temperatures. In this respect, high-performance capillary columns containing liquid-crystalline stationary phases[12] are of considerable interest as they permit the separation not only of positional but also of geometric isomers of alkenes (up to $C_{13}$) at temperatures of 70–90°C.
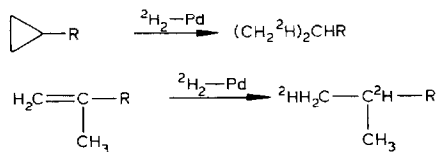
*Cyclopropane compounds*

The electron impact mass spectra of organic compounds containing a cyclo-propane ring frequently provide limited information regarding not only the location of the three-membered ring but also its detection. The main reason for this is that the cyclopropane ring is capable of opening and isomerization into alkenes under electron impact which makes the mass spectra of cyclopropanes closely similar to those of isomeric alkenes[13]. To differentiate cyclopropane and unsaturated compounds in mixtures, we decided to use hydrogenolysis, which may be carried out in the microreactor (1–2% Pd–porous glass) located between the GC column and the mass spectrometer. Monosubstituted cyclopropanes (1–3) were studied. Preliminary results obtained with the microreactor located before the column showed that the hydrogenolysis of these compounds (carrier and reagent gas, hydrogen; temperature of catalyst, 50–200°C) gives rise to the mixtures of open-chain structures (A and B) in a ratio of 94:6:

$$\triangleright\!\!-R \xrightarrow{\text{H}_2-\text{Pd}} (CH_3)_2CHR \quad + \quad H_3CCH_2CH_2R$$
$$\qquad\qquad\qquad\qquad\qquad A \qquad\qquad\qquad B$$

1  R = $n$-C$_8$H$_{17}$
2  R = CH$_2$CH$_2$COOCH$_3$
3  R = CH$_2$CH$_2$COOC$_2$H$_5$
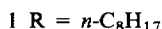
This important fact allows the microreactor to be located after the GC column, as the mass spectrum thus recorded for the mixture of the products A and B should be essentially identical with that of the product A. At the same time, such a position of the microreactor does not permit a distinction to be made between cyclopropane compounds and some branched alkenes if hydrogen is used as the carrier and reagent gas. If fact, hydrogenolysis of cyclopropane compounds and hydrogenation of iso-meric branched alkenes (which proceeds under the same catalytic conditions) could lead to identical compounds:

$$\triangleright\!\!-R \xrightarrow{\text{H}_2-\text{Pd}} (CH_3)_2CHR \xleftarrow{\text{H}_2-\text{Pd}} H_2C\!=\!\underset{\underset{CH_3}{|}}{C}\!-R$$
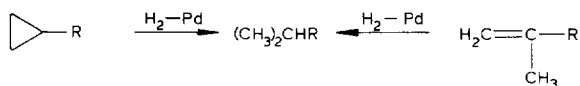
For the differentiation of similar types of cyclopropane and unsaturated compounds, we propose the use of deuterium as the carrier and reagent gas. It was expected that both types of compounds would give rise to dideutero products with different positions of the label that could be easily determined mass spectrometrically:

$$\triangleright\!\!-R \xrightarrow{^2\text{H}_2-\text{Pd}} (CH_2{}^2H)_2CHR$$

$$H_2C\!=\!\underset{\underset{CH_3}{|}}{C}\!-R \xrightarrow{^2\text{H}_2-\text{Pd}} {}^2HH_2C\!-\!\underset{\underset{CH_3}{|}}{C^2H}\!-R$$

Deuteration of cyclopropanes over the 1–2% Pd–porous glass catalyst involves not only the addition of deuterium to the sites of ring cleavage but also considerable
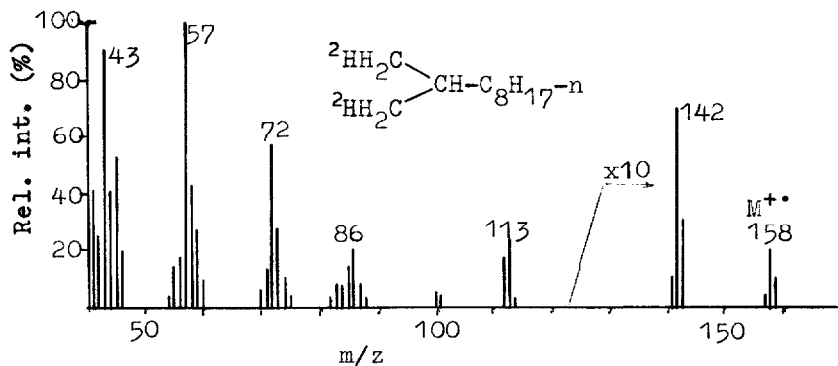
Fig. 5. Mass spectrum of 2-deuteromethyl-1-deuterodecane.

isotope scrambling. At 40–80°C, however, isotope scrambling is strongly supressed and dideutero analogues are formed preferentially. Fig. 5 shows the mass spectrum of the product obtained from $n$-octylcyclopropane after deuteration. It contains only the $(M - CH_2{}^2H)^+$ ion formed by bond scission at the branching point and, as was expected, it is essentially free of the $(M - CH_3)^+$ ion. A similar picture is observed in the mass spectra of the products obtained from esters (2 and 3) after deuteration (Table II). In contrast, the spectrum of the product derived from deuteration of 2-methyl-1-pentene under the same conditions (Fig. 2b) reveals a doublet of the $(M - CH_3)^+$ and $(M - CH_2{}^2H)^+$ ions.

*Cyclic sulphides*

The electron impact mass spectra of cyclic sulphides also are not very informative with respect to the determination both of the size of the heterocycle and of the positions of substituents[6]. We therefore decided to use the catalytic hydrodesulphurization of thiacyclanes into saturated hydrocarbons, the structures of which are indicative of the substitution pattern of the initial molecules. This reaction can be performed in a microreactor located between the GC column and the mass spectrometer. Similar catalytic conversions have often been employed in reaction GC using Raney nickel or Pd–Al$_2$O$_3$ catalysts[7,14]. This latter method (the microreactor is usually located before the GC column) frequently does not permit the determination of the structures of thiacyclanes mixtures or the distinction of those compounds which are converted into identical hydrocarbons after hydrodesulphurization. The application of deuterium as a carrier and reagent gas in reaction GC also confers no advantages. In contrast, the use of deuterium as the carrier and reagent gas when performing on-line desulphurization in reaction GC–MS could afford much useful information regarding the structure of each component of a mixture eluted after chromatographic separation. In this connection, we sought a catalyst and optimal reaction conditions for obtaining hydrocarbons containing a deuterium label at carbon atoms connected with the sulphur atom in sulphides. We found that both Raney nickel and Pd–Al$_2$O$_3$ catalysts gave undesirable isotope scrambling at temperatures of 150–200°C, the latter catalyst losing its activity at lower temperatures. The use of Raney nickel, at 20–80°C, however, allows the production of labelled hydrocarbons with relatively high contents of dideutero analogues whose mass spec-
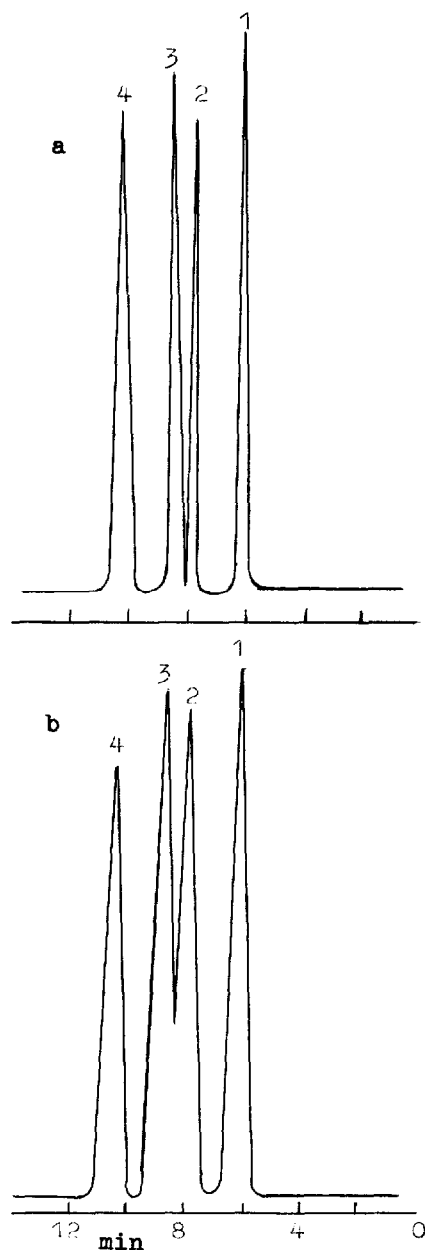
Fig. 6. Chromatograms of mixtures obtained (a) by the by-pass method and (b) by using the microreactor between the GC column and the mass spectrometer. (1) 2,5-Dimethyltetrahydrothiophene; (2) 3-methyltetrahydrothiophene; (3) 2-methyltetrahydrothiopyran; (4) 4-methyltetrahydrothiopyran.

tra are interpretable. Such low temperatures naturally lead to a decrease in the separation of the chromatographic peaks even for low-molecular-weight compounds. This is demonstrated, for example, by comparison of Fig. 6a and b, which represent
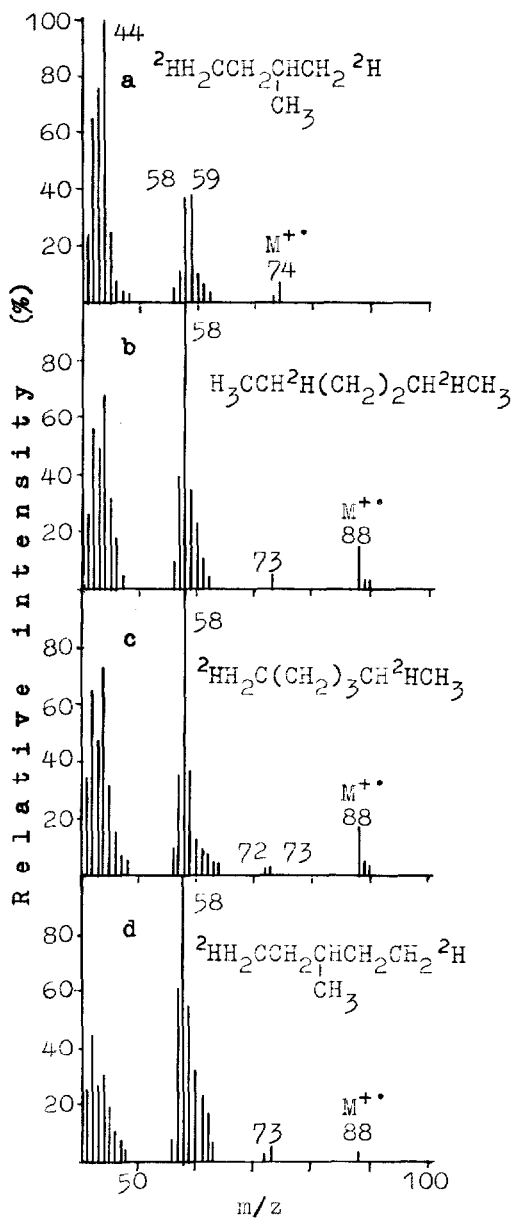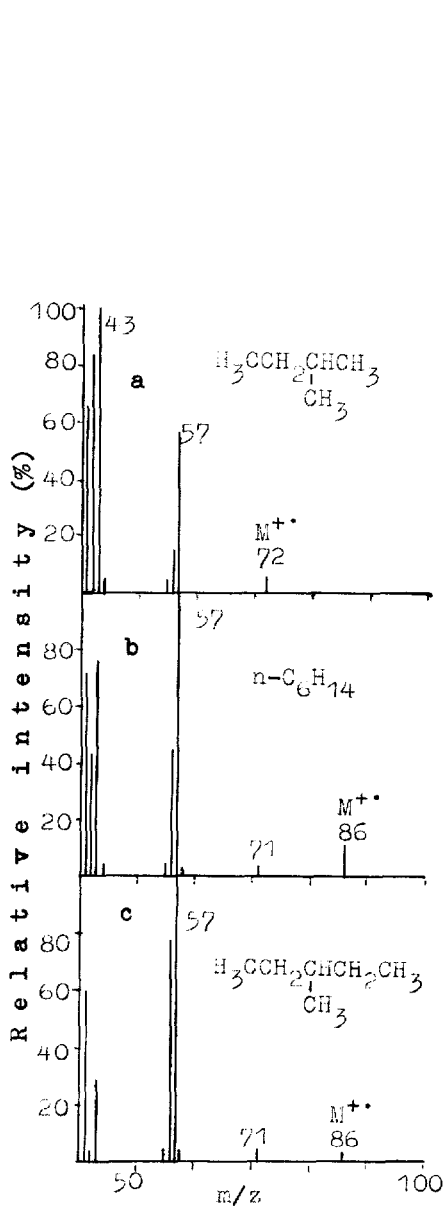
Fig. 7. Mass spectra of (a) 2-methylbutane, (b) *n*-hexane and (c) 3-methylpentane.

Fig. 8. Mass spectra of (a) 2-methyl-1,4-dideuterobutane, (b) 2,5-dideuterohexane, (c) 1,5-dideuterohexane and (d) 3-methyl-1,5-dideuteropentane.

the chromatograms of artificial mixtures obtained by using the by-pass techniques and the microreactor (Raney nickel) located between the GC column and the mass spectrometer, respectively. Nevertheless, the suggested method can be applied with success to a number of lower cyclic sulphides (Table II).
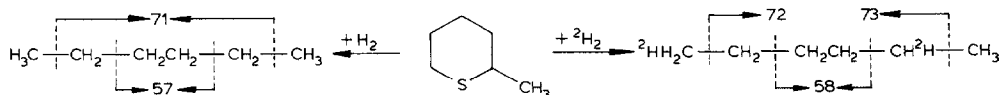
Hydrodesulphurization of 3-methyltetrahydrothiophene in the presence of hydrogen gives rise to 2-methylbutene (Fig. 7a), the main electron impact-induced fragmentation of which occurs due to bond scissions at the branching point [the $(M-CH_3)^+$ and $(M-C_2H_5)^+$ ions]. The mass spectrum of the corresponding dideutero analogue (Fig. 8a), obtained by using deuterium as the carrier and reagent gas, shows a distinct doublet for the $(M-CH_3)^+$ and $(M-CH_2{}^2H)^+$ ions in addition to the sole $(M-C_2H_4{}^2H)^+$ ion. This proves unambiguously the structure of 2-methyl-1,4-dideuterobutane and, hence, the structure of 3-methyltetrahydrothiophene.
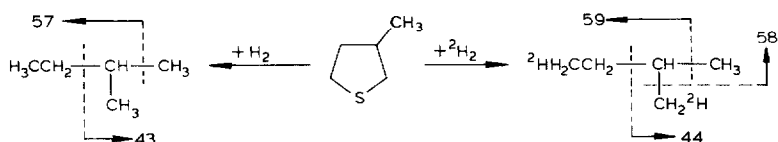


Differentiation of 2,5-dimethyltetrahydrothiophene and 2-methyltetrahydrothiopyran represents another demonstration of the possibilities of the method. Their mass spectra cannot be distinguished if the spectra of authentic compounds are not available. In both instances, hydrodesulphurization leads to n-hexane (Fig. 7b). At the same time, the use of deuterium as the carrier and reagent gas gives rise to dideuterohexanes with different positions of the label which may be readily determined mass spectrometrically. In fact, the mass spectrum of the product derived from 2,5-dimethyltetrahydrothiophene (Fig. 8b) shows the sole $(M-CH_3)^+$ and $(M-C_2H_4{}^2H)^+$ ions, which prove that the labelled hydrocarbon is 2,5-dideuterohexane:
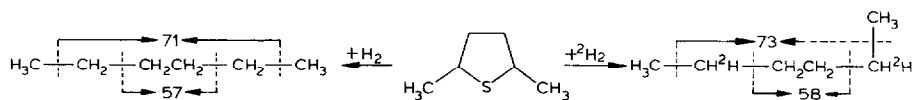


The mass spectrum of the product derived from 2-methyltetrahydrothiopyran (Fig. 8c) exhibits a doublet for the $(M-CH_3)^+$ and $(M-CH_2{}^2H)^+$ ions and the sole $(M-C_2H_4{}^2H)^+$ ion, which proves the structure of 1,5-dideuterohexane:



The structure of 4-methyltetrahydrothiopyran was established less distinctly by the described method. Diagnostically the most important peaks in the spectrum of its hydrodesulphurization product, 3-methylpentane (Fig. 7c) correspond to the $(M-CH_3)^+$ and $(M-C_2H_5)^+$ ions (scissions at branching points). The mass spectrum of the product obtained after deuterodesulphurization (Fig. 8d) demonstrates the $(M-CH_3)^+$ and $(M-C_2H_4{}^2H)^+$ ions, which could arise from both 3-methyl-1,5- and 3-methyl-1,4-dideuteropentanes. Hence, on the basis of these data only, 4-methyltetrahydrothiopyran and 2,3-dimethyltetrahydrothiophene could not be distinguished.
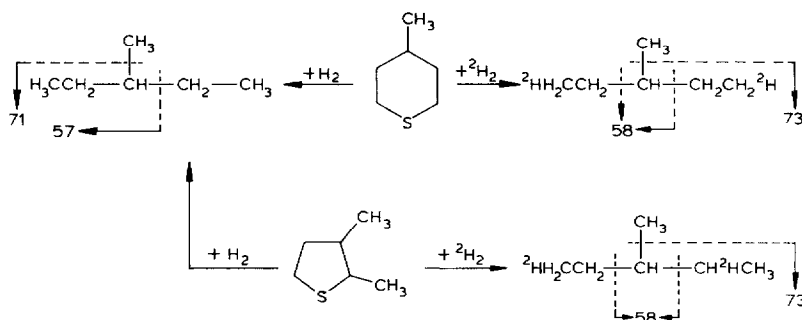
It should be mentioned that the use of deuterium as the carrier and reagent gas may not always be efficient for the investigation of polycyclic sulphides, as the mass spectra of alkyl(cycloalkyl)cycloalkanes usually do not permit the determination of the position of the deuterium label.

CONCLUSION

The use of deuterium in reaction GC–MS offers a new methodological approach to structural elucidations of organic compounds mixtures. The only problem is the need to search for catalytic systems that permit the selective introduction of deuterium without contamination by isotope scrambling at higher temperatures.

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