Tableau IV. Volumes de rétention spécifique (en ml) d divers alcanes à 80 °C

Phases / Solutés	n-dotriacontane	n-dioxa-15, 17 hentriacontane	n-dioxa-15, 18 lotriacontane
Hexane	59	58,8	58,9
Heptane	138,1	137,9	136,1
Octane	321,8	321,7	316,8
Cyclohexane	103,2	104,7	103,3

vérifier sur quelques unes de nos phases la cons nce des volumes de rétention spécifique de plusieurs lcanes de référence. Les résultats obtenus figurent dans tableau IV.

3. Conclusion

Les grandeurs de rétention de tous les alcanes étudiés sont indépendantes du nombre et de la position des atomes d'oxygène disséminés dans la molécule de phase stationnaire, tant que ce nombre reste faible. Par conséquent, du point de vue de la chromatographie un atome d'oxygène inclus dans un hydrocarbure l néaire se comporte vis à vis des alcanes comme un grou pe méthylène. Le système des indices de Kovats co stitue dans ces conditions une grille de référence utilis le au même titre que les volumes de rétention spécifi e.

La démarche suivie devrait permettre une prévi n plus aisée des grandeurs de rétention à partir des car téristiques de la phase stationnaire dans la mesure où nt éliminés les paramètres de structure habituellen t confondus dans le terme «polarité» [6 à 10]. Po des solutés autres que les alcanes les indices de réte ion devraient dépendre du nombre et de la position es atomes d'oxygène présents dans la molécule de nase stationnaire, et ce d'autant plus que le soluté es plus polaire.

Des travaux en cours nous permettront d'étendr cette étude à un plus grand nombre de phases stationn aires et à des solutés appartenant à différentes familles c imiques.

4. Partie Expérimentale

Les éthers-oxydes et les polyéthers-oxydes synt étisés en vue de notre étude résultent de la condensat n d'alcoolates alcalins sur des halogénures d'alkyl elon la méthode de Williamson.

utilisé Varian-Aerograph 1200 équipé d'un détecteur à ionisation de flamme et d'un régulateur différentiel de débit. Le gaz vecteur est de l'azote sous un débit de 25 ml par minute. Injecteur et détecteur sont maintenus à 150 °C. La température du four est régulée à 0,1 °C.

Les phases stationnaires étudiées ont été déposées sur du Chromosorb T 30 à 60 mesh à un taux d'imprégnation de 10 %. Les colonnes utilisées sont en acier inoxydable de 1/8 de pouce de diamètre et 1,70 m de longueur et comportent trois spires.

Les quantités de soluté injecté ont toujours été aussi faibles que possible (1 à 50 μl de la vapeur surmontant le liquide). Les temps de rétention ont été mesurés au chronomètre au 1/10 de seconde. La position du pic de l'air a été déterminée par des injections de méthane.

La mesure des volumes de rétention spécifique a été réalisée sur un appareil* comportant un détecteur à catharomètre avec de l'hydrogène comme gaz vecteur. Injecteur et détecteur ont été utilisés à température ambiante. Les colonnes sont en verre de diamètre 4 mm et de longueur 1,50 m, elles ont la forme d'un U. La masse de phase stationnaire est de l'ordre de 5 à 600 mg.

* Nous remercions Monsieur *Serpinet* pour avoir bien voulu mettre à notre disposition le matériel correspondant aux mesures des volumes de rétention spécifique.

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Gas Chromatographic Analysis of the Pr ucts from the Gamma-Induced Reaction Between H_2 and CCl_4

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Summary

To obtain an adequate separation of the produ ts of this reaction, which consisted of a mixture of chlor derivatives in solution in CCl_4, with concentrations less th n 0.1 %, the method of programmed temperature (100- 160 °C) gas chromatography was applied. A column co taining 30 % DC-11 silicone on Chromosorb W, and io zation detectors were used. Five products (CH_2Cl_2, C Cl_3, C_2Cl_4, C_2HCl_5 and C_2Cl_6) were identified. Q ntitative determination of two of them ($CHCl_3$ and C_2 ,) was made, using calibration curves.

Introduction

As part of a line of work on hydrogenation reactions induced by gamma radiation [1] a method of analysis of the products from the gas phase reaction betw en CCl_4 and H_2 induced by gamma radiation, was developed.

These products, after separation in a vacuum l ne of HCl and excess H_2, consisted of a solution in the r maining CCl_4 of a small amount (approximately 0.1 % of totally or partially chlorinated derivatives of methan and ethane. A previous separation of these products was c nsidered not convenient and as their boiling points diff in a wide range, after several attempts with other meth , programmed temperature gas chromatography w adopted as most suitable for a complete analysis in on peration.

Experimental

A Varian Aerograph Model 1520 gas chromat raph, equiped with a stainless steel column (1/8″ di neter, 2.54 m length) filled with 30 % DC-11 silicon on Chromosorb W, 80–100 mesh and flame ioni tion detector, was used. The temperature was cont olled with a matrix programmer.

Fig. 1, shows a typical chromatogram of one of the samples. The conditions of operation were: ca rier gas: nitrogen, 25 ml/min; column temperature: in tial: 100 °C, isotherm for 4 min, then linear increase at 30 °C/min for 2 min, and finally isotherm at 160 °C; sample 1 µl; injector and detector: 200 °C; chart speed: 0.5 n./min. range: 1 mV.

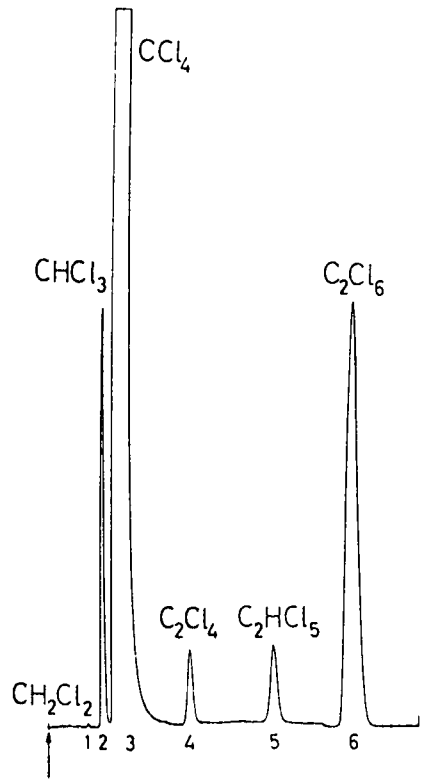

Fig. 1

• Typical chromatogram of analysed samples.

The identification and quantitative analysis of the components was made by injection of measured amounts of the different compounds, as discussed below.

Results and Discussion

A flame ionization detector was used after several attempts with a thermal conductivity detector proved that it had not enough sensitivity to detect some of the components.

The detector had to be cleaned periodically, when considerable increase in noise level was noticed. This was attributed to contamination of the detector due to the chemical nature of the compounds involved.

Several assays at constant temperature indicated the impossibility of a good separation of all the components. Finally a temperature program was adopted with an

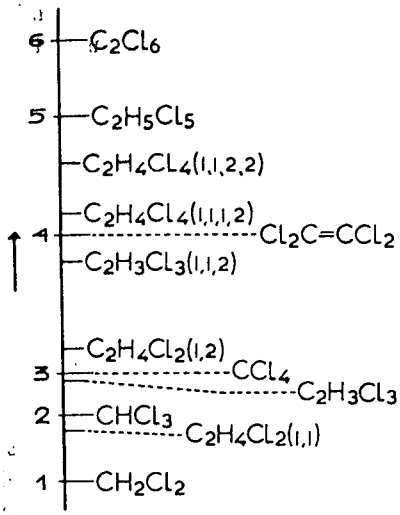

Fig. 2

● Possible products arranged on a scale of increasing boi g points. Numbers identify the compound actually present (refe ed to Fig. 1).

initial temperature of 100 °C. Some of the possible lower boiling components (CH_3Cl, C_2H_5Cl, CH_4, C_2H_6), would elute as a single peak, but in some experiments at lower temperature it was shown that they were not present in significant amounts. The first important compound (CH_2Cl_2) was separated sufficiently from the next one ($CHCl_3$) and the inconvenients of the large difference in magnitude between the CCl_4 and neighbour peaks was overcame. The final temperature of 160 °C, was adequate for the determination of C_2Cl_6, which is the heaviest compound analysed. The operation in dual mode was not necessary as the temperature differential used only small base line shifts which did not interfere with the analysis. The total elution time was about 8 minutes.

A preliminary identification of the peaks was made from the retention times of $CHCl_3$, CCl_4 and C_2Cl_6 which were obtained with pure samples, and considering the boiling points of the other components. Fig. 2 shows all the possible compounds in increasing order of boiling points, starting with CH_2Cl_2. Even accepting this sequence as valid for retention times, as the chromatograms have less peaks, the identification was not possible, without using authentic samples of all the compounds involved. As some of them were not available at the moment, a mixture of known composition was obtained by irradiating pure $CHCl_3$ [2] (gamma radiation, dosis 1.7×10^{18} eV/g). Its composition [3] is shown in Table 1 (HCl is also produced, but it was not included as it is eliminated before the gas chromatographic analysis).

From the retention times, peak 1 was identified as CH_2Cl_2, peak 4 as C_2Cl_4 and peak 5 as C_2HCl_5. This was later confirmed by injection of known samples of C_2Cl_4 and C_2HCl_5.

Table 1. Radiolysis products of pure $CHCl_3$

Retention times, min.	Compound	Yield G = mol/100 eV	Peak number in Fig. 1
1.1	CH_2Cl_2	0.9	1
3.1	$C_2H_3Cl_3$ (1,1,2)	0.57	–
3.6	$Cl_2C=CCl_2$	0.15	4
5.3	$C_2H_2Cl_4$ (1,1,2,2)	1.1	–
5.8	C_2HCl_5	1.2	5
7.7	C_2Cl_6	3.1	6

The absence of 1,1,2-$C_2H_3Cl_3$ which should appear between peaks 3 and 4 and 1,1,2,2-$C_2H_2Cl_4$, which should appear between peaks 4 and 5, was also ascertained.

The quantitative determination of peaks 2 and 6 was based on the use of calibration solutions of $CHCl_3$ and C_2Cl_6 in pure CCl_4 injected after the sample. Two examples of calibration curves are shown in Fig. 3. They were obtained from solutions of 0.5 % $CHCl_3$ and 2.5 % C_2Cl_6 in pure CCl_4, with injection volumes ranging between 0.5 and 1.0 µl. Peak heights were used as a good linearity is observed within this short range, although it does not extend to wider ranges.

The relative molar response data for $CHCl_3$ and C_2Cl_6 listed in Table 2 are valid between 5–20 µg approximately.

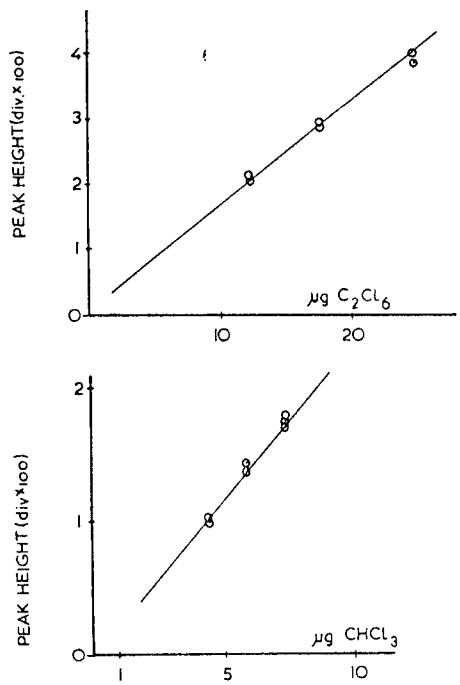

Fig. 3

● Calibration plots for $CHCl_3$ and C_2Cl_6 peaks.

Table 2. Gas chromatographic data of samples

Peak No.	Retention time		Relative molar response	compound
	min	relative		
1	1.1	0.78	–	CH_2Cl_2
2	1.4	1.00	1.00	$CHCl_3$
3	1.7	1.21	–	CCl_4
4	3.6	2.57	1.45	C_2Cl_4
5	5.8	4.15	1.27	C_2HCl_5
6	7.7	5.50	1.47	C_2Cl_6

Conclusion

The method described was found convenient to analyse CH_2Cl_2, $CHCl_3$, C_2Cl_4, C_2HCl_5 and C_2Cl_6 in solution of CCl_4 as obtained by radiolysis of mixtures of CCl_4 and H_2.

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