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IDENTIFICATION OF SUBSTANCES CONTAINING CARBON–CARBON SINGLE BONDS BY USE OF REACTION GAS CHROMATOGRAPHY

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SUMMARY

A procedure has been developed for the chromatographic detection of substances containing alkyl groups bound to aromatic rings and of substances with C–C bonds. The method is based on destructive hydrogenation on a platinum gauze of substances leaving the gas chromatograph. The C–C bond yields methane. Other decomposition products are absorbed.

INTRODUCTION

Colorations formed by suitable detection reactions can be used in addition to R_F values for the identification of organic substances separated by paper or thin-layer chromatography. In gas chromatography (GC), where information other than the elution times is rarely available, methods of identification employ selective detectors, *e.g.*, for sulphur, phosphorus or halogens, selective absorption or combination techniques with spectral methods or with chemical modifications[1,2]. Most of these methods place high demands on instrumentation, and only selective absorption and chemical modification can be employed without extensive adaptations and costly instrumentation.

One of the problems of identifying substances in mixtures is the determination of an alkyl group on an aromatic ring. For pure substances, alkyls can be detected using our method described earlier[3]. However, there is no simple method of identification of alkyls on a chromatogram. During the development of a method for the determination of the carbon-to-sulphur ratio in substances leaving a chromatographic column[4], we found that, when passed in a hydrogen stream over a heated platinum gauze, alkyls dissociate in the form of methane from substances with an aromatic ring, the aromatic ring remaining intact. Pyridine derivatives behave analogously. We utilized this fact for the detection of alkyls on aromatic rings and also for the detection of substances with aliphatic carbon chains, as aliphatic carbon chains also undergo destructive hydrogenation.

The detection of alkyl groups in substances leaving a gas chromatograph involves GC separation, destructive hydrogenation and introduction of the methane formed, after separation of water or ammonia which may also be formed, into a GC

detector. The chromatogram thus obtained is compared with a chromatogram obtained under identical conditions, but omitting destructive hydrogenation; the comparison of the appropriate peaks indicates which of the chromatographed substances contain an alkyl group on an aromatic ring or, generally, which contain a C–C bond.

EXPERIMENTAL

A normal gas chromatograph was used, enabling placement of a catalytic oven with a platinum gauze and absorption vessels for water and ammonia between the chromatographic column and the detector (see Fig. 1). A cylinder of the carrier gas (1) was connected to a gas purifier (2), a manostat (3) and a manometer (4). The chromatographic column (6), provided with an injection block (5) and oven (7) for destructive hydrogenation, was connected, through the reference cell of the thermal conductivity detector (9), to the manometer (4). An absorber (8) containing active charcoal and 4% palladium was inserted between the hydrogenation oven (7) and the measurement cell of the thermal conductivity detector (9). The detector (9) was connected to a recorder (11) and a flow-meter (10).

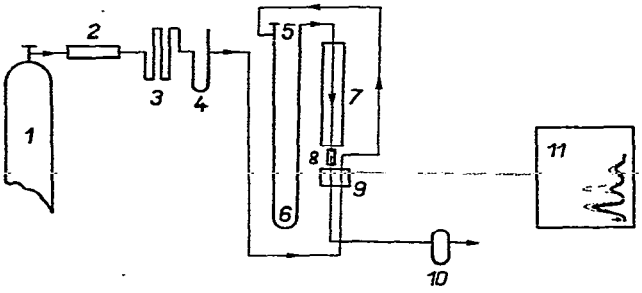

Fig. 1. Diagram of the apparatus used for destructive hydrogenation.

The mixture to be analyzed was injected into the purified carrier-gas stream (hydrogen) and was separated on the column. The carrier-gas flow-rate was 0.5–1 l/h. The gas purifier (2) consisted of three tubes connected in series: the first contained the catalyst CHZ 9025 for removal of oxygen; the second contained a molecular sieve and magnesium perchlorate for absorption of water; and the third contained phosphorus pentoxide deposited on cotton wool to remove the remaining traces of water. The dimensions of the tubes used were dependent on the conditions and the hydrogen purity.

The separated components of the mixture were led from the chromatographic column to the oven (7), which contained a quartz-glass tube (*ca.* 15 cm × 5 mm I.D.) packed with platinum gauze. The oven was heated by means of an electric resistance coil. The temperature of the platinum-gauze zone was maintained at 800°. A column length of 1 cm was used in order to avoid retardation of the methane passing through it. Sometimes, longer columns may be used, *e.g.*, 4 cm, so that the absorber need not be renewed too frequently. The sample size was the same as in normal chromatographic separations.

The length of the chromatographic column, the kind of packing and the tem-

perature were selected so as to achieve a good separation of the mixture. The chromatographic separation was first carried out without the hydrogenation oven and the absorber and the separated mixture from the chromatographic column was directly introduced into the detector. The separation was then carried out under the same conditions but with the hydrogenation oven connected. The peak magnitudes (the areas under the elution curve) were compared.

RESULTS AND DISCUSSION

As has already been pointed out, destructive hydrogenation occurs in a hydrogen stream over a platinum gauze at an elevated temperature, the aliphatic C–C bond being broken (80 kcal/mole) with formation of methane while the aromatic C=C bond remains intact (120 kcal/mole). Oxygen and nitrogen, if present, are converted into water and ammonia, respectively. If destructive hydrogenation is to be employed for the detection of C–C bonds in substances leaving a gas chromatograph, water, ammonia and aromatic hydrocarbons must be removed from the mixture to be analyzed. Moreover, pure methane is not always obtained from this procedure; with longer chains, ethane is also formed. All of these components were successfully removed by use of a short column of active charcoal containing 4% palladium; many varieties of absorber were tested, but this combination was found to be the most advantageous.

It is true that most chromatographed substances contain C–C bonds, but a closer study of destructive hydrogenation demonstrates the advantages of this method. For example, the area under the methane elution curve corresponds almost exactly

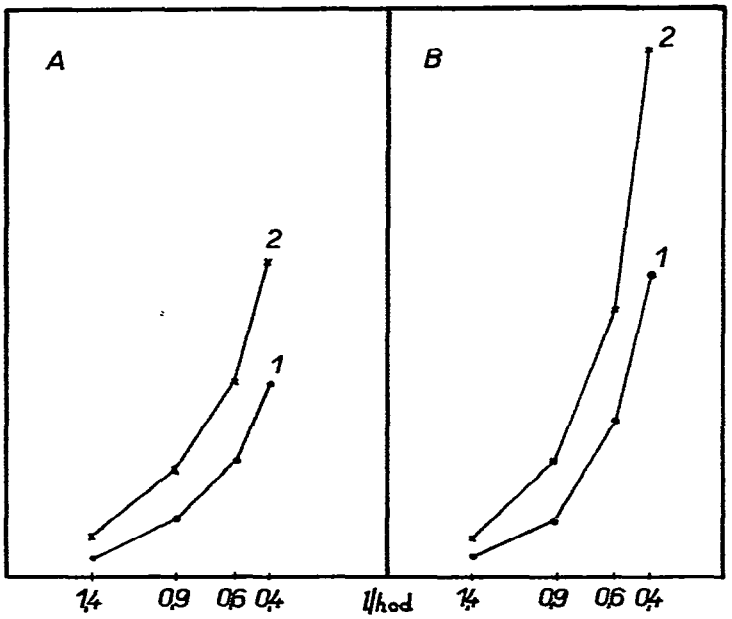

Fig. 2. The effect of the carrier-gas (hydrogen) flow-rate (horizontal axis) on the amount of methane formed using 10-cm (A) and 20-cm long (B) platinum gauzes.

to the number of $-CH_3$ groups bound to an aromatic ring. With alkyl groups other than $-CH_3$, the area is smaller. This is apparently caused by the fact that ethane and, to a lesser degree, higher hydrocarbons are formed in addition to methane when longer chains are present and are not eluted from the active charcoal in the absorber. Aliphatic and saturated cyclic substances yield, of course, larger amounts of methane

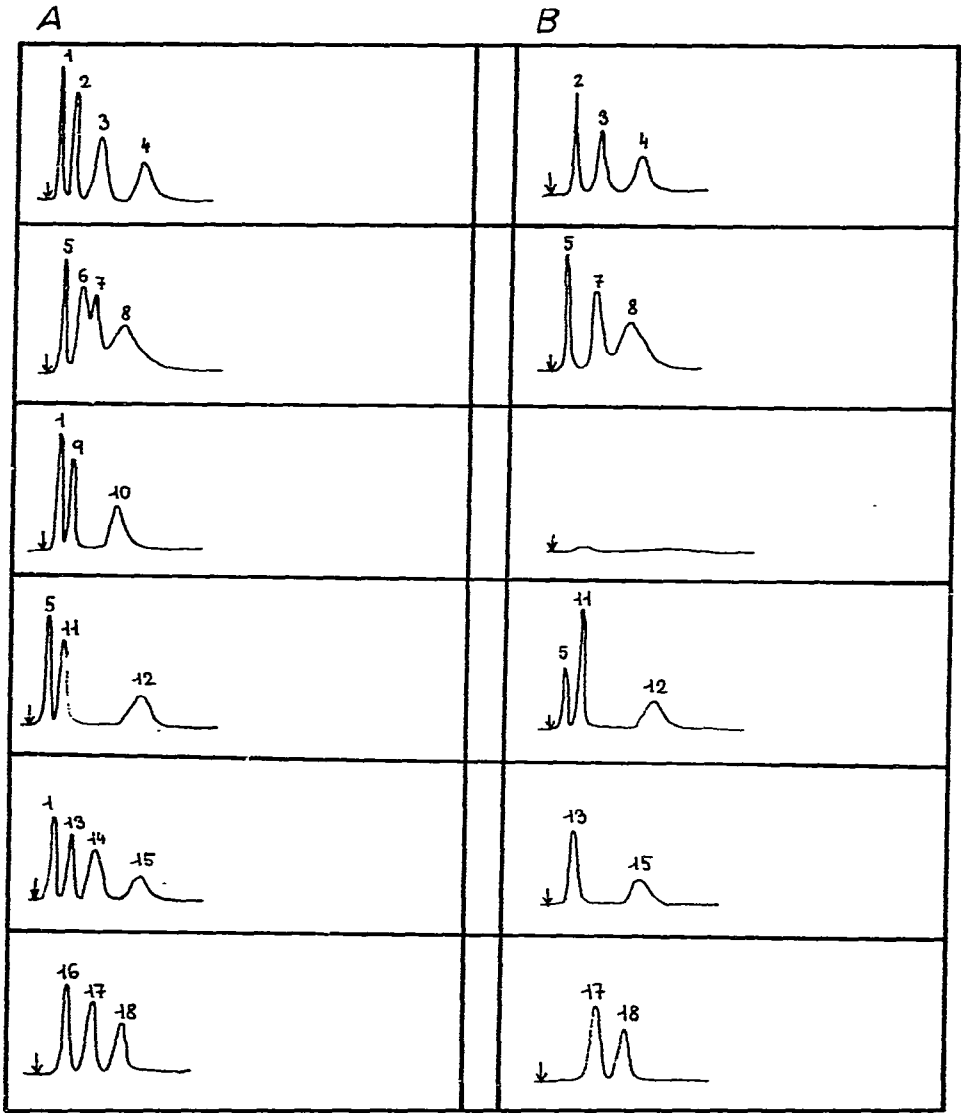

Fig. 3. Chromatograms of mixtures of substances obtained with and without destructive hydrogenation: A = original chromatogram, B = chromatogram after destructive hydrogenation. Peaks: 1 = benzene, 2 = anisole, 3 = acetophenone, 4 = *p*-methylacetophenone, 5 = toluene, 6 = phenol, 7 = *p*-cresol, 8 = *p*-ethylphenol, 9 = chlorobenzene, 10 = nitrobenzene, 11 = pseudocumene, 12 = *m*-nitrotoluene, 13 = *p*-xylidine, 14 = aniline, 15 = *m*-toluidine, 16 = pyridine, 17 = α-picoline and 18 = 2,6-lutidine.

than aromatic substances, so that there is a marked difference in the areas under the elution curves of the original chromatogram and the chromatogram after destructive hydrogenation. The same is also true for substances containing carbon bound to oxygen or nitrogen. When the same amounts of separated substances were compared, the methane peak areas were 2.0, 7.1 and 15.2 cm^2 for toluene, methanol and hexane, respectively. Derivatives of pyridine, quinoline, etc., behaved like aromatic compounds. Aldehydes behaved as if the aldehydic group were a $-CH_3$ group; the –COOH group behaved analogously. Substances remaining after destructive hydrogenation, and the unhydrogenated portions, were captured in quartz wool placed beyond the platinum gauze.

The effect of the carrier-gas flow-rate on the amount of methane formed during the hydrogenation was examined. From Fig. 2 it can be seen that the largest amount of methane was formed at a hydrogen flow-rate of 0.4 l/h. However, this flow-rate was too low for optimum chromatographic separation. A flow-rate of *ca.* 1 l/h was therefore used. The effect of the length of the platinum gauze was also investigated. At a hydrogen flow-rate of 0.4 l/h, the amount of methane formed on a 20-cm gauze was approximately twice that on a 10-cm gauze. The amount of methane formed was virtually constant at a flow-rate of *ca.* 1 l/h.

Fig. 3 gives examples of mixtures analyzed by this method. Although it is clear that the information obtained can only lead to a partial identification, this procedure is a suitable complement to the methods already developed[4–6] for the determination of the C:H, C:N and C:S ratios in substances separated by gas chromatography and for the determination of the number of double bonds[7].

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