Short Communication

Gas chromatographic separation of deuterated methanes

In this communication, the separation of deuterated methanes by gas–solid chromatography with an adsorption glass capillary column is described.

Fig. 1 shows a chromatogram of CH_4, CH_3D, CH_2D_2 and CD_4 resolved at low temperature (—188°). The samples were obtained by exposure to X rays (tungsten, 50 kV, 30 mA) of a mixture containing 45% deuterium, 45% xenon and 10% methane.

The column (0.30 mm internal diameter, and 35 m long) was prepared by passing a 20% sodium hydroxide solution through it for 6 h at 100°, in order to etch the internal surface of the glass[1]. The column was then washed to neutrality, dried and deactivated to a constant activity by passing pure nitrogen saturated with water at

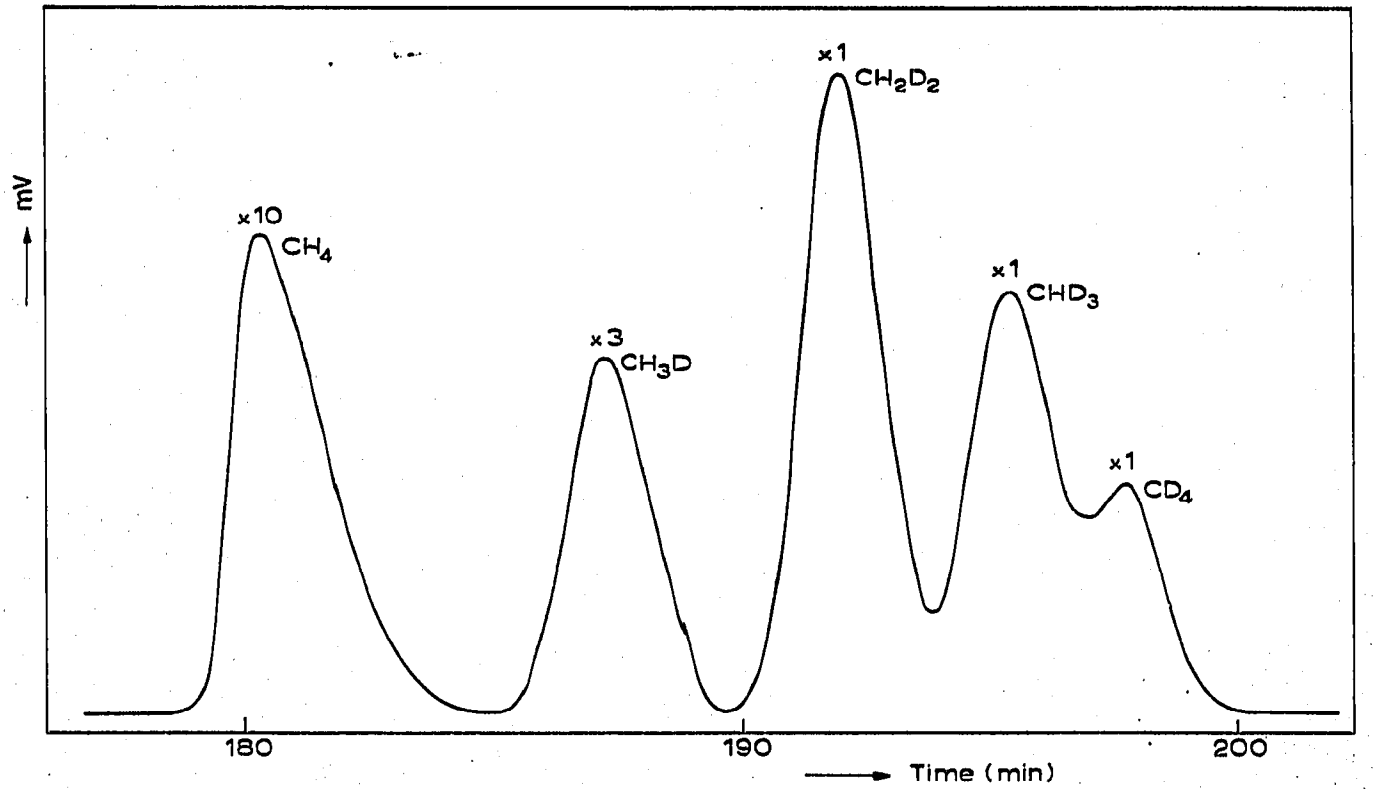

Fig. 1. Separation of deuterated methanes on an etched glass capillary column.

0° through it. An efficiency of about 55,000 theoretical plates was obtained for the methane peak. The working conditions for such a chromatogram are: column temperature: —188°; carrier gas: nitrogen with an inlet pressure of 32 mm Hg, and a flow rate of 0.62 ml/min. A home made gas chromatograph was employed; it was equipped with a flame ionization detector and a liquid nitrogen cryostat.

At the investigation temperature, methane has the lowest retention volume of the compounds in the mixture, since the "normal" isotopic effect is the predominant one. The separation between CH_3D and CH_4 is better than between CH_3D and CH_2D_2 and the same is observed for the other consecutive pairs of isotopically substituted molecules.

This behaviour could be connected with the dependence of the ratio of retention volumes (for each adjacent pair of isotopic compounds) on the ratio of their masses[2]; by plotting the log of the retention volume ratios *versus* $1 - m_1/m_2$, where m_1 and m_2 are the masses of the corresponding isotopic molecules, a straight line was obtained.

Similar relationships were found for the vapour pressure of different isotopes[3]. By gas chromatography it is possible to investigate these effects and to compare the values of the retention volumes with the vapour pressure measurement.

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Notes

Substituted hydrazones as derivatives of ketones in gas chromatography

It has recently been demonstrated that a variety of reactive ketones may function as reagents for primary amines, with the formation of the so-called Schiff bases or eneamines; these substances possess excellent gas-chromatographic properties[1]. In an analogous manner, compounds with reactive amino groups may function as reagents for ketones; thus N,N-dimethylhydrazine has been found to be useful in gas-chromatographic work with keto-steroids[2]. Other hydrazines and hydrazine-related compounds should also prove to be of value as reagents for ketones. We have investigated the gas-chromatographic properties of a number of these derivatives, including compounds obtained by reaction with N-aminopiperidine, N-aminohomopiperidine, pentafluorophenylhydrazine and phenylhydrazine[3,4].

Table I gives the retention data for the derivatives of di-*n*-hexyl and di-*n*-heptyl ketones, and for those of androstan-17-one.

The derivatives were prepared by reaction of the ketone with the appropriate reagent in ethyl acetate solution (acetic acid catalyst); complete condensation occur-