

The salient features for the over-all thermally initiated  $\text{CF}_3\text{CN}-\text{C}_2\text{H}_4$  reaction, at low values for the reactant ratio  $\text{C}_2\text{H}_4:\text{CF}_3\text{CN}$ , appear well-understood in the light of free-radical telomerization kinetics in which the  $\text{CF}_3\cdot$  radical is dominant in the chain-initiation step. These investigations are being extended to olefins and nitriles of related structures to gain a further insight on the reaction energetics; the question of using these processes with suitably selected experimental conditions, for the measurement

of  $\text{CF}_3\cdot$  radical affinities in the gas phase at moderately high temperatures, is also being explored as part of this work.

**Acknowledgment.**—This work has been possible, in large part, through grant-in-aid support from the American Chemical Society Petroleum Research Fund. Tenure of the Carbide Fellowship in Chemistry (1960–1961) and the American Chemical Society Petroleum Research Fellowship (1961–1964) by N. A. G. is gratefully acknowledged.

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## Chromatographic Separation of Isotopic Methanes

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RECEIVED JUNE 9, 1964

Isotopic methanes are separated chromatographically by using a charcoal column ( $-3.5$  to  $150^\circ$ ). Retention times progressively decrease with increasing D or T substitutions. This decrease is consistent with the expected decrease in polarizabilities with increasing D or T substitutions.

### Introduction

Isotopic molecules often exhibit markedly different retention times in gas-solid adsorption chromatography.<sup>1,2</sup> This fact is utilized in the present paper to develop a chromatographic technique for analyzing mixtures of deuterated and tritiated methanes.

### Experimental

The four D isomers were obtained from Merck Sharp and Dohme Co., Ltd., Montreal, Canada. A mixture containing four T isomers was prepared by allowing 0.016 mole of  $\text{CH}_4$  to stand for 2 months in the presence of 4.4 c. of  $\text{T}_2$ , which initiated tritiation by undergoing  $\beta$ -decay.<sup>3</sup> A chromatograph of the resulting mixture gave four peaks. These were identified by assuming that the peak sequence is the same as that observed with D isomers where  $\text{CD}_4$ ,  $\text{CD}_3\text{H}$ ,  $\text{CD}_2\text{H}_2$ , and  $\text{CDH}_3$  come off the column in this order. The identification was further checked in two ways. First,  $\text{CH}_3\text{T}$  was prepared by mercury-sensitized photolysis of a  $\text{CH}_4-\text{T}_2$  mixture. This photolysis was reported<sup>4</sup> to give predominantly monosubstituted methane, and the retention time of the principal peak coincided with that of a peak identified as  $\text{CH}_3\text{T}$ . A mixture of T isomers in which  $\text{CT}_4$  was the major component (mass spectrometry) was prepared as follows.  $\text{T}_2$  purchased from the Oak Ridge National Laboratories was found to contain small amounts of highly tritiated methane. This mixture was sparked with a Tesla coil and passed through a molecular sieve trap ( $-160^\circ$ ), which retained the methane but not tritium.<sup>5</sup> The methane recovered by subsequently warming the molecular sieve column gave a single peak whose retention time coincided with that of a peak originally identified at  $\text{CT}_4$ .

A 1520-cm. stainless steel column (0.152-cm. i.d.) was prepared by joining two 760-cm. columns which contained 0.0082 g./cm. of 80–100 mesh, high-activity charcoal purchased from Burrell Corp., Pittsburgh, Pa. Two such columns were prepared. One column was used for the experiments at  $-3.5$  and  $24^\circ$ , while the

other was used above  $50^\circ$ . Helium was used as a carrier gas, and the flow rate measured at the outlet was kept constant at 56.6 cc./min. regardless of column temperature.

To maintain the helium flow rate of 56.6 cc./min., it was necessary to employ high inlet pressures of above 10 atm. Sample injections at these pressures were accomplished with a gas-sampling valve, equipped with a Viton A O-ring, purchased from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

Experiments were performed using these mixtures: binary mixtures with 3:2 mole ratio of the components  $\text{CH}_4-\text{CD}_4$ ,  $\text{CH}_4\text{CHD}_3$ ,  $\text{CH}_4-\text{CH}_2\text{D}_2$ , and  $\text{CH}_3\text{D}-\text{CD}_4$ ; a mixture of  $\text{CH}_4$  with the four D isomers, each component having the same concentration; 4.4 c. of the four T isomers diluted in 0.016 mole of  $\text{CH}_4$ ; and 0.5 mc. of  $\text{C}^{14}\text{H}_4$  diluted in 0.016 mole of  $\text{CH}_4$ . In most experiments, sample size for a single injection was 1.3 moles of the mixture. A thermal conductivity cell was used for  $\text{CH}_4$  and D isomer detections, while a 3-cc. ion chamber was employed for  $\text{C}^{14}\text{H}_4$  and T isomer detections. Signals from both detectors were registered on a Brown dual-pen potentiometric recorder.

### Results and Discussion

Figure 1 gives a chromatogram containing peaks of  $\text{C}^{14}\text{H}_4$ ,  $\text{CH}_4$ , and  $\text{CH}_2\text{D}_2$ . The retention times of

TABLE I  
THE RATIO,  $t(\text{CH}_4)/t(\text{ISOTOPES})$ , OF RETENTION TIMES  
USING A CHARCOAL COLUMN

Isomers	$24^\circ$	$-3.5^\circ$
$\text{CH}_4^a$	1.000	1.000
$\text{CH}_3\text{D}$	1.015	1.016
$\text{CH}_2\text{D}_2$	1.029	1.033
$\text{CHD}_3$	1.042	1.051
$\text{CD}_4$	1.061	1.068
$\text{CH}_3\text{T}$	1.013	1.017
$\text{CH}_2\text{T}_2$	1.030	1.031
$\text{CHT}_3$	1.048	1.053
$\text{CT}_4$	1.068	1.078

<sup>a</sup>  $t(\text{CH}_4) = 78.0$  and  $180.3$  min. at  $24$  and  $-3.5^\circ$ , respectively.

TABLE II  
RETENTION TIMES AT DIFFERENT TEMPERATURES

Temp., $^\circ\text{C}$ .	$t(\text{CH}_4)$ , min.	$t(\text{CH}_4)/t(\text{CD}_4)$	$t(\text{CH}_4)/t(\text{CT}_4)$
50	41.63	1.049	1.065
75	26.70	1.041	1.052
100	19.30	1.035	1.043
125	14.40	1.027	1.030
150	11.25	1.014	1.014

(1) For the isotope effect in adsorption chromatography, see, for example, these references: (a) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **80**, 2909 (1958); (b) S. Ohkoshi, Y. Fujita, and T. Kwan, *Bull. Chem. Soc. Japan*, **31**, 770 (1958); (c) P. L. Gant and K. Yang, *Science*, **139**, 1548 (1959); (d) W. J. Hanbach and D. White, *J. chim. phys.*, **60**, 97 (1963); (e) E. Glueckauf, *Endeavour*, **20**, 42 (1961); (f) J. W. Root, E. K. Lee, and F. S. Rowland, *Science*, **143**, 676 (1964).

(2) For the isotope effect in partition chromatography, see, for example, these references: (a) K. E. Wilzbach and P. Riez, *ibid.*, **126**, 748 (1957); (b) R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963); (c) W. E. Falconer and R. J. Cvetanović, *Anal. Chem.*, **34**, 1064 (1962).

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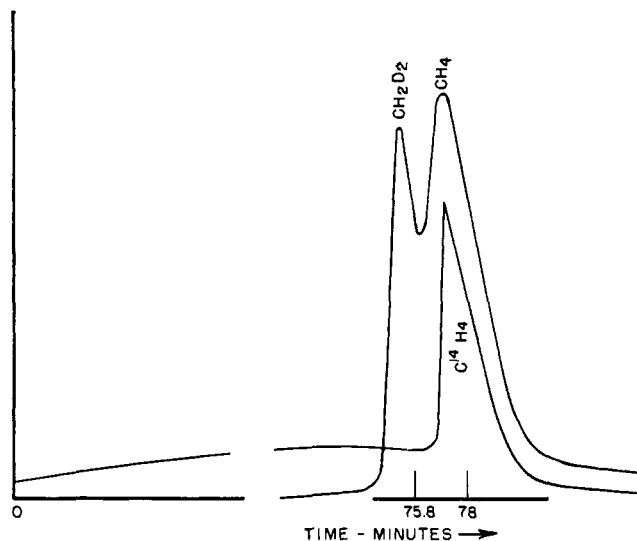


Fig. 1.—Chromatograms of  $\text{CH}_4$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{C}^{14}\text{H}_4$  at  $24^\circ$ .

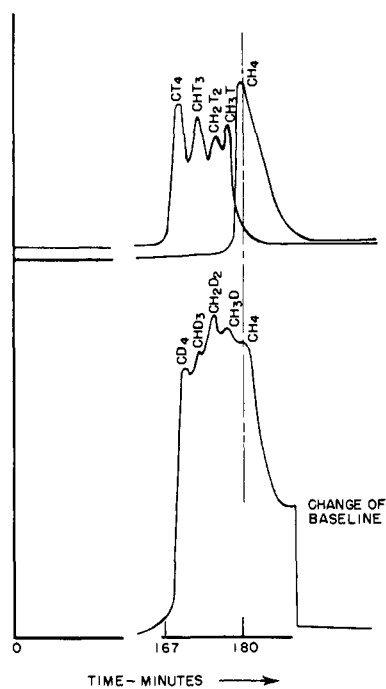


Fig. 2.—Chromatograms of mixtures containing  $\text{CH}_4$  and four D or T isomers at  $-3.5^\circ$ .

$\text{C}^{14}\text{H}_4$  and  $\text{CH}_4$  are the same, but that of  $\text{CH}_2\text{D}_2$  is shorter. This clearly indicates that the isotope effect is not due to the difference in total mass. Figure 2 indicates that both D and T isomers give four distinguishable peaks at  $-3.5^\circ$ . At  $24^\circ$ , only T isomers give four distinguishable peaks. This necessitated the use of different pairs of D isomers, as shown in Fig. 3. Table I summarizes relative retention times measured at peak maximum. Replacing H by either

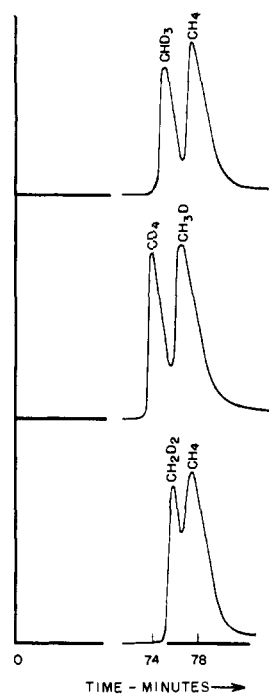


Fig. 3.—Chromatograms of some  $\text{CH}_4$ -D isomer pairs at  $24^\circ$ .

D or T results in a progressive decrease in retention times. To determine the possible dependence of the relative retention times on sample size, sample pressures in a 0.55-cc. loop at  $24^\circ$  were varied from 25 to 250 mm. Although this resulted in a 5% decrease in the retention time,  $t_1$ , of  $\text{CH}_4$ , the ratio  $t_1/t(\text{CD}_4)$  stayed constant with an average deviation of less than 0.2%.

Table II summarizes the retention times of  $\text{CH}_4$ ,  $\text{CD}_4$ , and  $\text{CT}_4$  between 50 and  $150^\circ$ . As temperature increases, the isotope effect decreases steadily. At  $150^\circ$ ,  $\text{CD}_4$  and  $\text{CT}_4$  no longer show distinguishable peaks; but even at this high temperature,  $\text{CH}_4$  separates from the other two.

Static adsorption data<sup>6</sup> indicate that the  $\text{CH}_4$ -charcoal has a deeper minimum than the  $\text{CD}_4$ -charcoal interaction. This is attributed to the fact that D substitution reduces the polarizability of methane.<sup>6</sup> Progressive decrease in retention times following D or T substitution, as observed in the present experiment, is explainable on the basis of this reduction in polarizabilities.

**Acknowledgment.**—Drs. L. O. Morgan and F. H. Dickey offered valuable discussion and advice. In a private communication, Drs. F. S. Rowland and E. K. C. Lee of the University of Kansas kindly informed us of their successful correlation of retention times with polarizabilities. These contributions are gratefully acknowledged.

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