The Gas-chromatographic Behavior of Perhaloalkanes

Ren IWATA, Yoshihiro MAKIDE, and Takeshi TOMINAGA*

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received July 1, 1974)

The retention indices of perhaloalkanes (perbromochlorofluoroalkanes, *etc.*) were measured by using a gas chromatograph with a squalane, Silicone DC 550, or Methoxy polyethylene glycol 350 column, and the correlation of the retention index with various physicochemical parameters was investigated. The retention index was found to correlate linearly with the composition of the halogen atoms in the perhaloalkane molecules; the correlation diagram appears to be of special analytical importance. The relationship between the retention index and the boiling point was also studied. The retention index was correlated linearly with the molar refractivity of the perhaloalkanes, irrespective of the polarity of the columns. The molar refractivity appears to be the inherent parameter which is most adequate for considering the regularity of the retention index. The effect of the polarity of the stationary phase on the retention index was also investigated.

In the course of our study of the recoil and radiolysis reactions in perchlorofluoroalkanes,[1-3] it became necessary to investigate systematically the gas-chromatographic behavior of perhaloalkanes (perbromochlorofluoroalkanes, *etc.*). If the correlation between the retention data and certain physicochemical parameters is established, it may facilitate the identification of unknown products gas-chromatographically without the need to refer to pure standard substances which are not readily available and without the aid of other, complementary means of analyses.

A number of works have been published on the gas-chromatographic behavior of homologous organic compounds. However, perhaloalkanes have received only a little attention,[4,5] and no systematic study of perbromochlorofluoroalkanes had been reported before our preliminary work.[6] The object of the present article is to determine the Kováts retention indices[7] for a number of perhaloalkanes and to study the correlation of those retention indices with various physicochemical parameters.

Experimental

Materials. CBr_3F, $CBrClFCClF_2$, $CBrClFCBrF_2$, and CBr_2FCBrF_2 were synthesized chemically in this laboratory. $CBrClF_2$, $CBrCl_2F$, $CBrF_2CF_3$, and $CBrF_2CClF_2$ were prepared by the γ-irradiation of mixtures of perchlorofluoroalkanes and bromine.[2] The other perhaloalkanes used in this work were obtained commercially from Matheson Gas Products, Inc., PCR, Inc., and the Tokyo Chemical Industry Co.

Determination of Retention Times and Retention Indices. The retention times were measured at a constant temperature between 0 and 100 °C by using a gas chromatograph equipped with a thermal conductivity detector. A water bath was used to keep the column temperature constant over the 0-60 °C range. A stainless steel column (I.D.: 3mm; length: 5m) was packed with squalane, Silicone DC 550, or Methoxy polyethylene glycol 350, 20%-coated on acid-washed Chromosorb W (80-100 mesh). The flow rate of the helium was 15 ml/min. The adjusted retention times obtained at 30 °C were first converted to specific retention volumes,[8] and then these in turn were converted to retention indices according to the following formula:

$$I_x = 100 \cdot \left[z + \frac{\log V_{g(x)} - \log V_{g(z)}}{\log V_{g(z+1)} - \log V_{g(z)}} \right]$$

where I_x denotes the retention index of a compound, x; $V_{g(x)}$, the specific retention volume of x, and $V_{g(z)}$ and $V_{g(z+1)}$, the specific retention volumes of two successive normal alkanes with carbon numbers of z and $z+1$ respectively, which were chosen so that $V_{g(z)} \leq V_{g(x)} < V_{g(z+1)}$.

Results and Discussion

The retention indices obtained for perhaloalkanes indicate an additivity with respect to the number of halogen atoms. Figures 1 and 2 reveal the correlation of the retention index, as measured by means of a Silicone DC 550 column, with the number of halogen atoms in perhalomethane and perhaloethane molecules respectively. The observed values for the γ-radiolysis products (closed circles in Figs. 1 and 2) are plotted nearly at the expected lattice positions of the correlation network. When a halogen atom is replaced by another halogen atom, the increase in the retention index due to the substitution was in the order: Br-for-Cl < Cl-for-F < Br-for-F. Furthermore, the magnitude of the change in the retention index for the same type of halogen substitution remains nearly identical, irrespective of the number of carbon atoms in the perhaloalkane molecules. This fact reveals that the regularity in the retention indices of C_1 and C_2 perhaloalkanes can be ascribed to the property inherent in each halogen atom rather than to that in a perhaloalkane molecule as a whole. We obtained diagrams similar to Figs. 1 and 2 for perhalomethanes and perhaloethanes on squalane and Methoxy polyethylene glycol 350 columns. The correlation was still good, irrespective of the polarity of the stationary phase, whereas the change in the retention index due to halogen substitution was enhanced by increasing the polarity.

While such a correlation appears to be very useful for analytical purposes, it cannot account for the essential nature of the observed regularity.[9] A linear correlation was obtained between the retention index and the boiling point, as is illustrated for perhaloalkanes on a squalane column in Fig. 3. The slope of the correlation curve (straight line) for perhaloethanes is larger than that for perhalomethanes. A similar relationship was obtained with a Silicone DC 550 column. Unlike on such a non-polar or slightly polar column, some plot-points deviate from the linear correlation

* To whom all correspondence should be addressed.

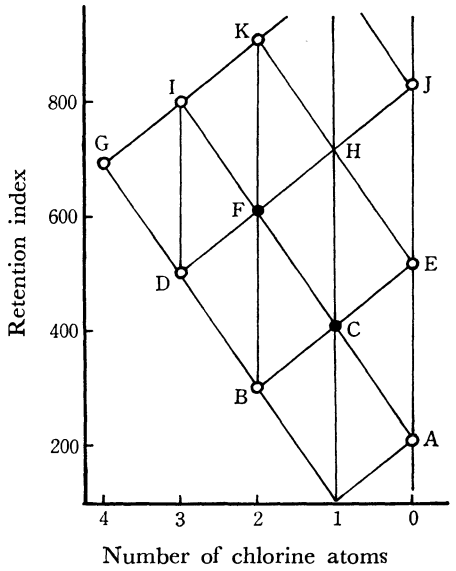

Fig. 1. Correlation between the retention index measured with a Silicone DC 550 column and the halogen composition of perhalomethanes.
In Fig. 1 and Figs. 3-6, (A): $CBrF_3$, (B): CCl_2F_2, (C): $CBrClF_2$, (D): CCl_3F, (E): CBr_2F_2, (F): $CBrCl_2F$, (G): CCl_4, (H): CBr_2ClF, (I): $CBrCl_3$, (J): CBr_3F, (K): CBr_2Cl_2

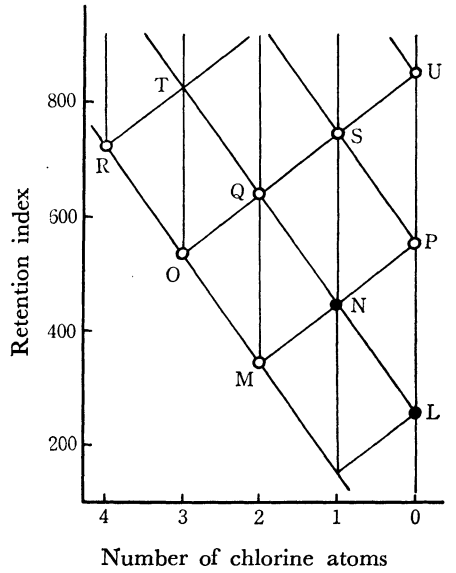

Fig. 2. Correlation between the retention index measured with a Silicone DC 550 column and the halogen compositlon of perhaloethanes.
In Figs. 2-6, (L): C_2BrF_5, (M): $C_2Cl_2F_4$, (N): C_2BrClF_4, (O): $C_2Cl_3F_3$, (P): $C_2Br_2F_4$, (Q): $C_2BrCl_2F_3$, (R): $C_2Cl_4F_2$, (S): $C_2Br_2ClF_3$, (T): $C_2BrCl_3F_2$, (U): $C_2Br_3F_3$

on a strongly polar Methoxy polyethylene glycol 350 column (Fig. 4), since the presence of bromine in the perhaloalkane molecules tends to increase their retention indices systematically (for example, the broken line in Fig. 4).

It is known that molar refractivity is an additive quantity and can be approximated by summing up the refractivities of the atoms composing the molecule.

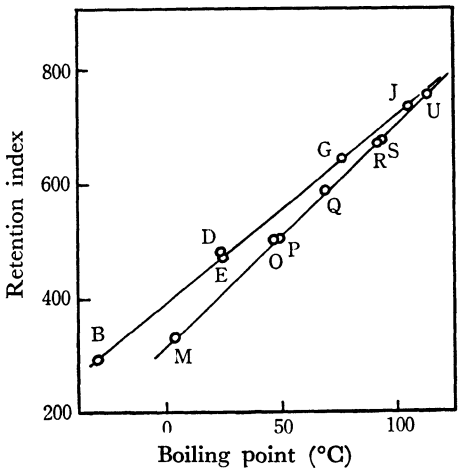

Fig. 3. Correlation between the retention index measured with a squalane column and the boiling point of perhaloalkanes.

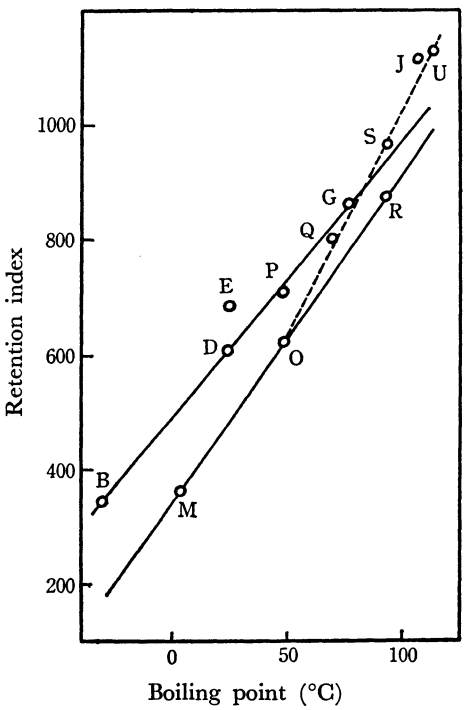

Fig. 4. Correlation between the retention index measured with a Methoxy polyethylene glycol 350 column and the boiling point of perhaloalkanes.

The molar refractivity can be linearly related to the electron polarizability taking part as dispersion and induction energies in the solvent-solute interactions. Hence, the molar refractivity can be taken as the parameter of the interaction between the solute (perhaloalkanes) and the solvent (stationary phase). The relationship between the molar refractivity[10] and the retention index of perhaloalkanes, as measured with a Silicone DC 550 column, is shown in Fig. 5. A linear correlation was observed with perhaloalkanes containing the same number of carbon atoms. Unlike the case of the correlation with the boiling point, the slopes of the correlation curves (straight lines) are nearly identical, irrespective of the number of carbon atoms.

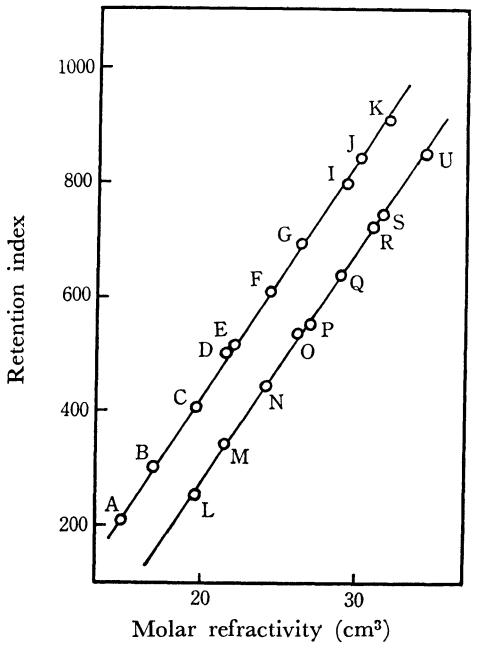

Fig. 5. Correlation between the retention index measured with a Silicone DC 550 column and the molar refractivity of perhaloalkanes.

Almost identical relationships were obtained with squalane and Methoxy polyethylene glycol 350 columns. These observations reveal that, for the perhaloalkanes studied in this work, the molar refractivity may be the inherent parameter, which is most suitable for considering the regularity of the retention index.

As in the case of Rohrschneider's characterization of the stationary phase,[11] we have investigated the influence of the polarity of the stationary phase on the retention indices of the perhaloalkanes. For convenience in comparing the polarity, the increase in the retention index of carbon tetrachloride obtained with an arbitrary polar stationary phase over that obtained with the non-polar stationary phase (squalane) is given as follows:

$$\Delta I_{CCl_4} = I_{CCl_4}(\text{polar}) - I_{CCl_4}(\text{non-polar})$$

Then, the value of ΔI_{CCl_4} obtained with an arbitrary stationary phase is presumed to be a measure for indicating the polarity of the stationary phase. In Fig. 6 are plotted the retention indices of perhaloalkanes against ΔI_{CCl_4}, or the polarity of the stationary phase. It is worth mentioning that the retention indices of all the perhaloalkanes studied in this work are correlated linearly with this measure. Since the retention indices for a new stationary phase can be predicted by measuring the retention index of CCl_4 with that stationary phase, the relationship illustrated in Fig. 6 appears to be very useful for the selection of a new stationary phase.

The present authors wish to express their thanks to Professor Nobufusa Saito, the University of Tokyo, for his encouragement and support.

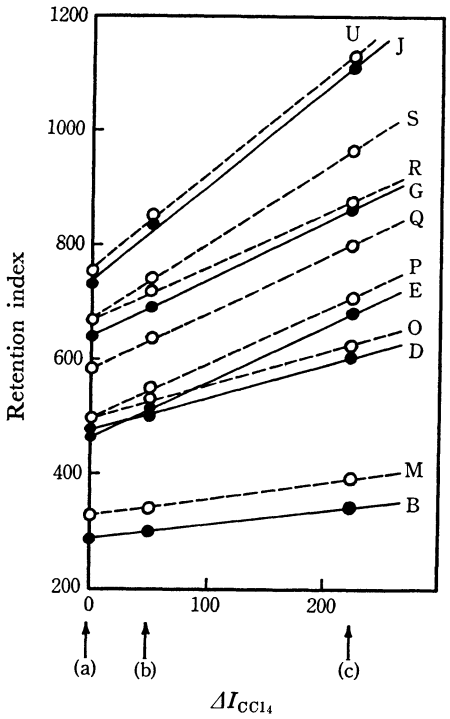

Fig. 6. The relationship of the retention index with the polarity of the stationary phase (in terms of ΔI_{CCl_4}). (a): squalane, (b): Silicone DC 550, (c): Methoxy polyethylene glycol 350.

References

1) T. Tominaga, Y. Makide, S. Okada, Y. Kunimasa, and K. Wada, *Radioisotopes*, **20**, 541 (1971).

2) T. Tominaga, R. Iwata, and Y. Makide, *Chem. Lett.*, **1972**, 871.

3) T. Tominaga, R. Iwata, and Y. Makide, This Bulletin, **46**, 1882 (1973).

4) H. Rotzsche, *Z. Anal. Chem.*, **175**, 338 (1960).

5) A. Foris and J. G. Lehman, *Sep. Sci.*, **4**, 225 (1969).

6) T. Tominaga, R. Iwata, and Y. Makide, *Chem. Lett.*, **1973**, 485.

7) E. Kovâts, *Helv. Chim. Acta*, **41**, 1915 (1958); ASTM, E 355-68 (1968).

8) Since boiling points of perhaloalkanes fall within a wide range, it is difficult to measure all the retention times at one common temperature. Accordingly, the retention times of higher boiling perhaloalkanes measured at higher temperatures were all converted to the values at 30 °C, by extrapolation of the linear correlation between the logarithm of the specific retention volume and the reciprocal of the absolute column temperature.

9) Similar correlation diagrams can be obtained with other additive parameters such as molecular weight. However, they do not represent linear correlations.

10) A. H. Fainberg and W. T. Miller, Jr., *J. Org. Chem.*, **30**, 864 (1965).

11) L. Rohrschneider, *Z. Anal. Chem.*, **236**, 149 (1968); *J. Chromatogr. Sci.*, **11**, 160 (1973).