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# Gas-chromatographic Behavior of $C_1$, $C_2$, and $C_3$-Halocarbons Containing Iodine

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**Synopsis.** The regularity of the specific retention volume ($V_g$) in gas chromatography was investigated on a number of $C_1$, $C_2$, and $C_3$ halocarbons containing iodine. The log $V_g$ value was found to correlate with the number of halogen and carbon atoms in the molecule.

Although the gas-chromatographic behavior of a number of $C_1$ and $C_2$ carbon mixed halides containing F, Cl, and Br has been investigated,[1,2] no extensive work has been reported on carbon mixed halides containing iodine. The object of this article is to report on our recent study of the regularity in the specific retention volume of $C_1$, $C_2$, and $C_3$ mixed halocarbons containing iodine in addition to F, Cl, and Br.

## Experimental

*Materials.* Twelve kinds of iodine-containing halocarbons were used in the present work. Of these, $CF_2ClI$, $CFCl_2I$, $CF_2BrI$, $C_2F_4ClI$, $C_2F_3Cl_2I$, $C_3F_6ClI$, and $C_3F_6BrI$ were prepared by the $\gamma$-irradiation of mixtures of adequate halocarbons and iodine.[3] $CF_3I$, $C_2F_5I$, $C_2F_4BrI$, $C_2F_4I_2$, $C_2F_3Cl_2I$, and $C_3F_7I$ were purchased from PCR, Inc., USA. The other halocarbons containing no iodine and used in this work were obtained as has been described previously.[2]

*Determination of Retention Volume.* The retention times of the halocarbons on a Silicone DC 550 column (20 wt% coated on acid-washed Chromosorb W80-100 mesh, 3 mm i.d.×5 m long) were measured at constant temperatures between 40 and 100 °C by using a gas chromatograph equipped with a thermal conductivity detector. The carrier gas was He, at the flow rate of 15 ml/min. The gas-chromatographic data were expressed in terms of the specific retention volume ($V_g$), normalized from the measured retention time.

## Results and Discussion

The logarithm of the specific retention volume of each halocarbon measured between 40 and 100 °C was linearly related to the reciprocal of the absolute temperature of the column; thus, the heat of vaporization from the solution in the Silicone DC 550 stationary phase remained constant over this range of column temperature. Furthermore, the heats of vaporization calculated for all the halocarbons from the slopes of the log $V_g - 1/T$ curves were correlated almost linearly with the logarithms of the specific retention volumes at any temperature.

Figure 1 reveals the correlation of the logarithm of the specific retention volume with the halogen composition for $C_2$-halocarbons.[4] The observed retention volumes of the $C_2$-halocarbons containing iodine (filled circles in Fig. 1) were plotted nearly at the lattice positions of the network for $C_2F_{6-x-y-z}Cl_xBr_yI_z$. Such results have also been obtained for the halocarbons containing no iodine,[1,2] which are

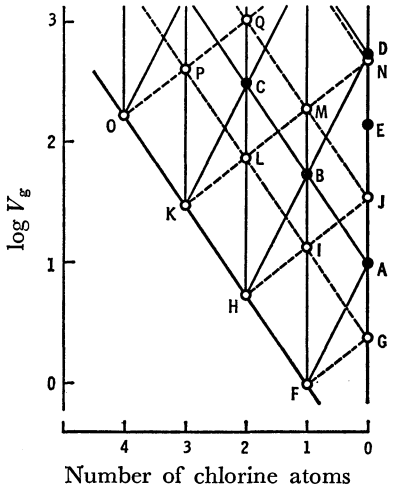


Fig. 1. Correlation between the logarithm of the specific retention volume on a Silicone DC 550 column (60 °C) and the halogen composition of $C_2$-halocarbons.
(A): $C_2F_5I$, (B): $C_2F_4ClI$, (C): $C_2F_3Cl_2I$, (D): $C_2F_4I_2$, (E): $C_2F_4BrI$, (F): $C_2F_5Cl$, (G): $C_2F_5Br$, (H): $C_2F_4Cl_2$, (I): $C_2F_4ClBr$, (J): $C_2F_4Br_2$, (K): $C_2F_3Cl_3$, (L): $C_2F_3Cl_2Br$, (M): $C_2F_3ClBr_2$, (N): $C_2F_3Br_3$, (O): $C_2F_2Cl_4$, (P): $C_2F_2Cl_3Br$, (Q): $C_2F_2Cl_2Br_2$.

represented by open circles in Fig. 1. A detailed examination of the additivity of log $V_g$ with respect to the halogen composition indicates that, upon halogen substitution, the log $V_g$ value is changed by a magnitude characteristic of the substitution: +0.76 by Cl-for-F, +1.17 by Br-for-F, and +1.76 by I-for-F (on a Silicone DC 550 column at 60 °C). The magnitude of the change in log $V_g$ for the same type of halogen substitution was found to be identical irrespective of the number of carbon atoms in the molecule. Accordingly, the log $V_g$ value of the halocarbons, $C_nF_{2n+2-x-y-z}Cl_xBr_yI_z$ ($n$=1, 2, and 3) on Silicone DC 550 at 60 °C, can be calculated as follows:

$$\log V_g = \alpha_n + 0.76x + 1.17y + 1.76z$$

where $\alpha_n$ is equal to −0.94, −0.80, and −0.61 for $n$=1, 2, and 3 (*i.e.*, $C_1$, $C_2$, and $C_3$) respectively.[5]

Figure 2 illustrates three-dimensionally the additivity of the log $V_g$ values of all the $C_2$-halocarbons with respect to the number of F, Cl, Br, and I in the molecule. The log $V_g$ value is expressed as the height from the ground plane. The four vertices of the larger tetrahedron correspond to $C_2F_6$, $C_2Cl_6$, $C_2Br_6$, and $C_2I_6$, while each edge includes $C_2$-halocarbons containing two kinds of halogens (*e.g.*, $C_2F_{6-x}Cl_x$ along the $C_2F_6$–$C_2Cl_6$ edge). $C_2$-halocarbons containing three kinds of halogens are located at the lattice positions on the surfaces of the tetrahedron except

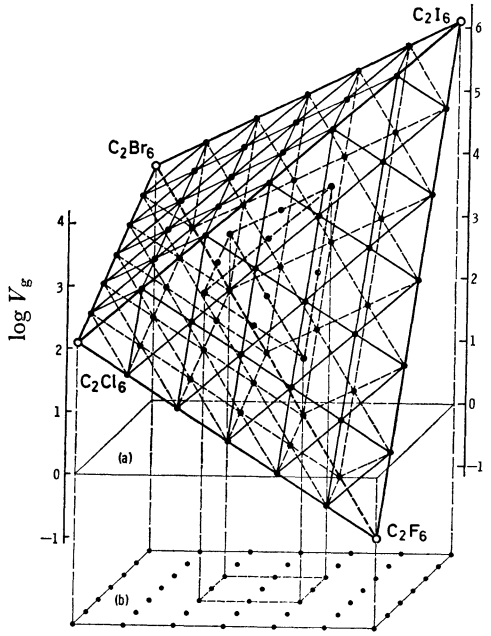


Fig. 2. Three dimensional diagram of the correlation between the logarithm of the specific retention volume and the halogen composition of $C_2F_{6-x-y-z}Cl_xBr_yI_z$.
(a): ground plane at log $V_g=0$.
(b): projection on a horizontal plane.

on the edges, while those which contain four kinds of halogens (*i.e.*, fluorochlorobromoiodocarbons) should be found along the edges of a smaller tetrahedron located inside (at the center) of the larger tetrahedron. The three-dimensional correlation diagram appears to be of analytical importance, since the order of elution or the relative difficulty of elution from a gas-chromatographic column can be predicted graphically for all the halocarbons. Such a correlation and relative order among these compounds can be retained at any temperature, although the absolute value of log $V_g$ will be changed. Therefore, we may choose adequate column conditions for these compounds by

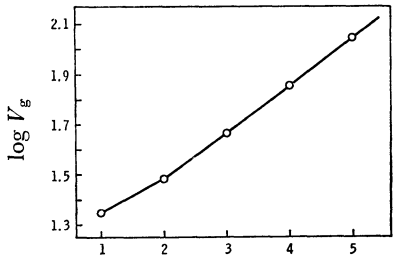


Fig. 3. Correlation between the logarithm of the specific retention volume and the number of carbon atoms in the series $C_nF_{2n-1}Cl_3$.

referring to the correlation diagram even if the log $V_g-1/T$ curves for all the compounds are not available.

In order to examine the dependence of log $V_g$ on the number of carbon atoms, a series of $C_nF_{2n-1}Cl_3$ halocarbons (*i.e.*, $CFCl_3$, $C_2F_3Cl_3$, $C_3F_5Cl_3$, $C_4F_7Cl_3$, and $C_5F_9Cl_3$) are illustrated in Fig. 3. The log $V_g$ value tends to increase with the number of carbon atoms, and the log $V_g$ *vs.* carbon number curve apparently approaches a straight line as the number of carbon atoms increases. All other series of halocarbons $C_nX_{2n+2}$ show similar behavior.

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## References

1) T. Tominaga, R. Iwata, and Y. Makide, *Chem. Lett.*, **1973**, 485.
2) R. Iwata, Y. Makide, and T. Tominaga, This Bulletin, **47**, 3071 (1974).
3) Details will be published shortly.
4) Very similar correlation diagrams were also obtained for $C_1$ and $C_3$-halocarbons. The same type of halogen substitution gave the identical slope in diagrams of $C_1$, $C_2$, and $C_3$-halocarbons.
5) Namely, $\alpha_n$ corresponds to the log $V_g$ value for $C_nF_{2n+2}$ ($n=1$, 2, and 3).