CHEMISTRY LETTERS, pp. 485-488, 1973. Published by the Chemical Society of Japan

GAS CHROMATOGRAPHIC BEHAVIOR OF PERHALOALKANES

Takeshi TOMINAGA, Ren IWATA, and Yoshihiro MAKIDE

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo
The Institute of Physical and Chemical Research, Wako-shi, Saitama

The gaschromatographic behavior of perhaloalkanes containing one or two carbon atoms and different kinds of halogen atoms in a molecule was investigated. The logarithm of the specific retention volume was correlated well with the halogen composition, the boiling point, the estimated volume of molecule and the molar refractivity of these compounds.

While the gas chromatographic behaviors of various organic compounds have been studied extensively, no systematic work has been reported on the gas chromatography of perhaloalkanes (perbromochlorofluoroalkanes, etc.). In the course of our investigation on the recoil and radiolysis reactions in perchlorofluoroalkanes,[1-3] it became necessary to establish a method for separation and identification of various products formed in such systems. Accordingly, we have initiated a systematic study on the gas chromatographic behavior of a number of perhaloalkanes containing different kinds of halogen atoms in the molecule.

In the present article are reported our recent data on the gas chromatography of perhaloalkanes containing one or two carbon atoms and different kinds of halogen atoms in the molecule, especially on the correlations of the retention volume with various chemical and physical parameters in these systems.

Most of the perhaloalkanes used in this work were either obtained commercially from P C R, Inc., Matheson Gas Products, Inc. and Tokyo Chemical Industry Co., or synthesized chemically by the methods described in the literature.[4] Otherwise, they were prepared by γ-irradiation of mixtures of perchlorofluoroalkanes and bromine.[2] Their retention times were determined with a 5-m Silicone DC 550 / Chromosorb W (20 % by weight, 80-100 mesh)column at 0-140°C in a helium stream (flow rate: 15 ml/min). Since the boiling points of perhaloalkanes fall within a wide temperature range, it is difficult to measure the retention times for all the compounds at one common temperature. Accordingly, the retention time data measured at various temperatures were all converted to the values at 0°C, by extrapolation of the specific retention volume——temperature correlation curves, and the results were summarized in terms of the specific retention volume (Vg) at 0°C.

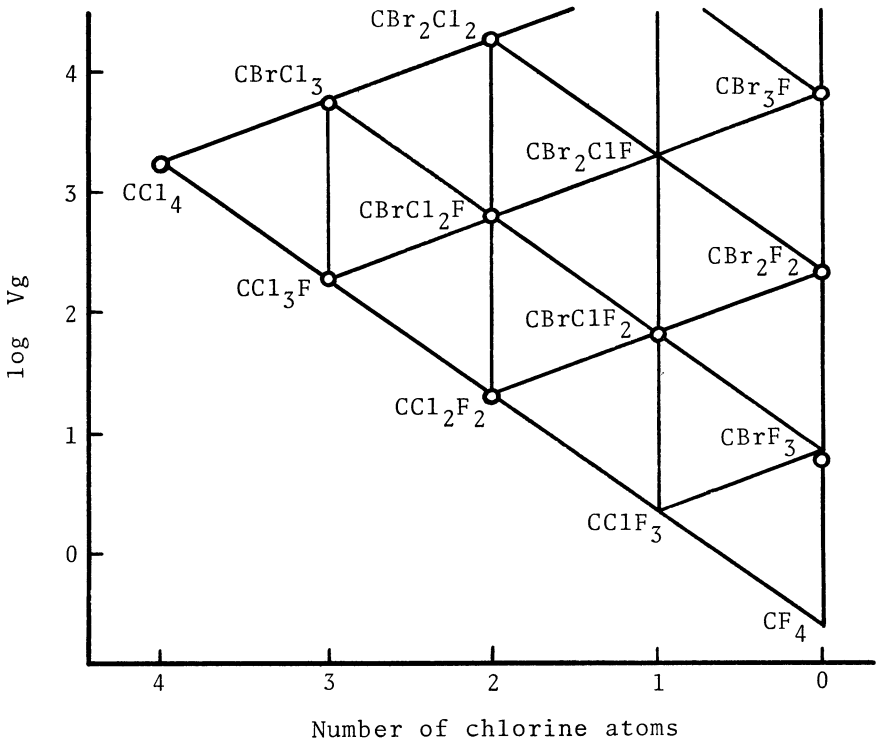

Fig.1. Correlation between the logarithm of the specific retention volume and the halogen composition of perhalomethanes.

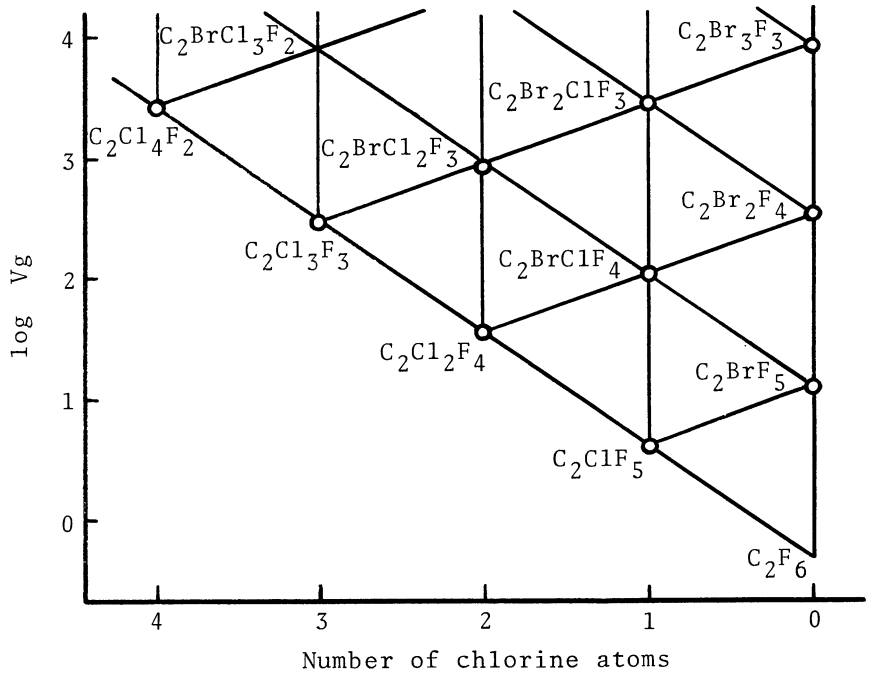

Fig.2. Correlation between the logarithm of the specific retention volume and the halogen composition of perhaloethanes.

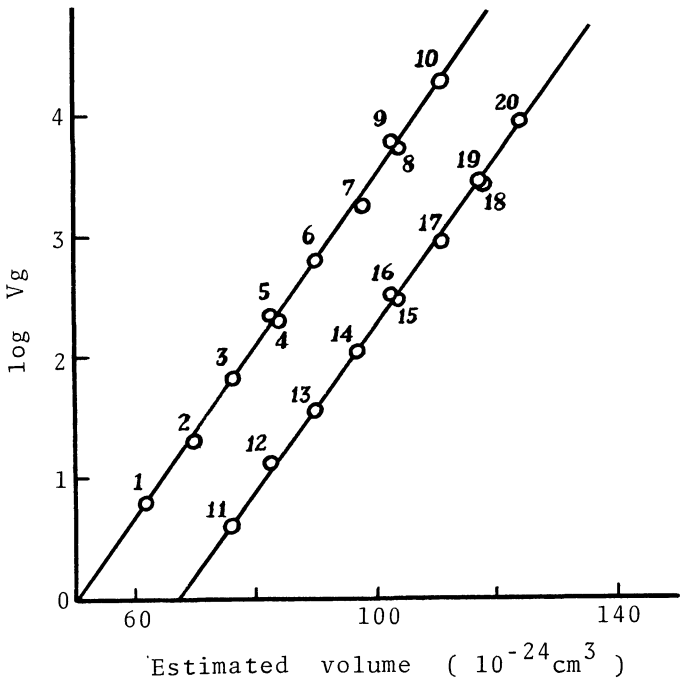

Fig.3. Correlation between the logarithm of the specific retention volume and the estimated volume of perhaloalkane molecule.

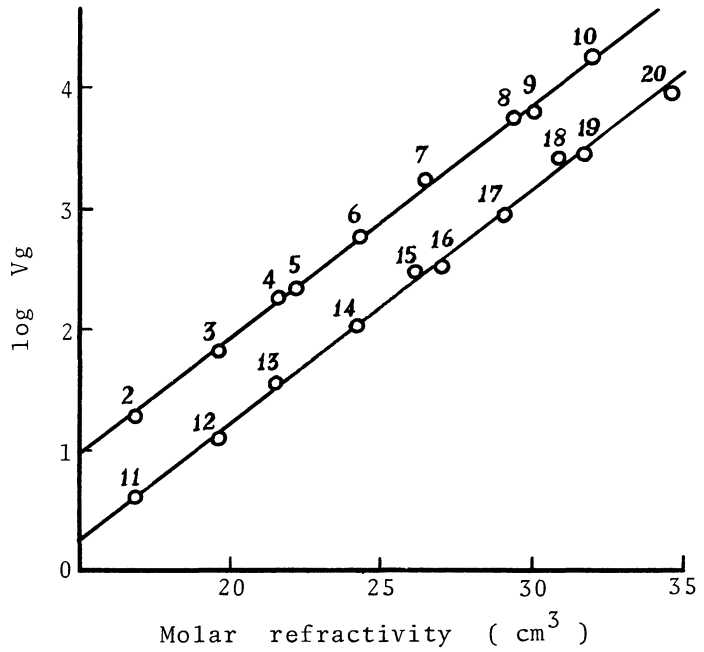

Fig.4. Correlation between the logarithm of the specific retention volume and the molar refractivity of perhaloalkanes.

Numbers in Figs. 3 and 4 correspond to the following perhaloalkanes:

1 : $CBrF_3$
2 : CCl_2F_2
3 : $CBrClF_2$
4 : CCl_3F
5 : CBr_2F_2
6 : $CBrCl_2F$
7 : CCl_4
8 : $CBrCl_3$
9 : CBr_3F
10 : CBr_2Cl_2
11 : C_2ClF_5
12 : C_2BrF_5
13 : $C_2Cl_2F_4$
14 : C_2BrClF_4
15 : $C_2Cl_3F_3$
16 : $C_2Br_2F_4$
17 : $C_2BrCl_2F_3$
18 : $C_2Cl_4F_2$
19 : $C_2Br_2ClF_3$
20 : $C_2Br_3F_3$

The following conclusions may be drawn from the experimental results:

1) We see in Figs. 1 and 2 that the logarithm of the specific retention volume (Vg) is correlated linearly with the composition of halogen atoms in perhalomethanes and perhaloethanes, respectively.[5] The regularity seems to be so perfect that all observed Vg values can be plotted nearly at the expected lattice positions of the correlation networks. Such correlation essentially indicates the additivity of the log Vg value with respect to the number of particular halogen atoms in the molecule. The correlation diagram appears to be of special analytical importance: it has been successfully applied to identification of unknown radiolysis and recoil products in irradiated perchlorofluoroalkane—bromine systems.[1-3]

2) As is often observed in homologous hydrocarbons, the logarithm of the specific retention volume was found to correlate linearly with the boiling point of perhaloalkanes containing the same number of carbon atoms in the molecule.

3) Figs. 3 and 4 indicate the linear correlations of the logarithm of the specific retention volume with the estimated volume of molecule and the molar refractivity of the perhaloalkanes, respectively. The volume of a molecule was roughly estimated by assuming that the molecule was composed of spheres with the Van der Waal's radii corresponding to halogen atoms. Molar refractivity was based on Fainberg and Miller's data.[6] It is Known that molar refractivity is also related to the volume of the molecule. Although different correlation curves correspond to the perhaloalkanes containing different number of carbon atoms in Fig.3 or Fig.4, they have identical slopes.

Further investigation of the dependence of log Vg on such volume parameters might afford clues to the elucidation of the mechanism governing the behavior of perhaloalkane molecules in gas chromatographic columns.

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

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, Bull. Chem. Soc. Japan, 46, in press.
4) Experimental details will be published elsewhere.
5) Very similar correlation was also observed in some perhalopropanes. Details will be published shortly.
6) A. H. Fainberg and W. T. Miller, Jr., J. Org. Chem., 30, 864 (1964).

(Received March 17, 1973)