The Gas Chromatographic Separation of Germanium Chlorobromides

Yoshihiro MAKIDE and Nobufusa SAITO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

The Institute of Physical and Chemical Research, Wako-shi, Saitama

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The formation of mixed halides of germanium in a mixture of germanium tetrachloride and germanium tetrabromide was observed by Delwaulle using Raman spectrometry.[1] However, the attempted mutual separation of these halides by distillation was reported to be unsuccessful.[2] In our recent study of the gas chromatographic behavior of inorganic halides, however, we have found that the mixed halides of germanium can indeed be separated by gas chromatography.

A gas chromatograph equipped with a thermal conductivity detector with platinum filaments was built in our laboratory. The path for the gas flow was made of glass and Teflon to avoid the contact of halides with metal. Kel-F Wax was used as the stationary liquid phase of the partition column. $GeCl_4$ and $GeBr_4$, prepared separately from the elements, were mixed and allowed to stand for a few days so that the halogen interchange equilibrium among the halides could be reached. The mass spectrum of their mixture was then measured by means of a double-focusing mass spectrometer. A mixture of these mixed halides with ^{82}Br-labeled arsenic tribromide was analyzed by means of a radio gas chromatograph. The separated halides were passed through a heated Teflon tube coil, and their activities were measured continuously by means of an NaI scintillation detector placed under the coil.

The formation of mixed halides ($GeCl_3Br$, $GeCl_2Br_2$, and $GeClBr_3$) in the mixture of $GeCl_4$ and $GeBr_4$ was confirmed by mass stectrometry.

The gas chromatogram of the $GeCl_4$–$GeBr_4$ mixture (Fig. 1) shows five peaks. The identification of the three intermediate peaks as mixed halides was confirmed by the following experimental results: (1) as Fig. 2 shows, the logarithm of the specific retention volume has an approximately linear relationship with the number of bromine atoms in a molecule, as in the case of $CCl_{4-n}Br_n$ and $SiCl_{4-n}Br_n$;[3] and (2) the radio gas chromatogram of the mixture with $As^{82}Br_3$ shows that the germanium mixed halides were labeled with ^{82}Br by isotopic exchange (as shown in Fig. 3). Their specific activities were proportional to the number of bromine atoms in the molecule.

Further studies of the gas chromatographic behavior of inorganic halides are in progress and will be published shortly.

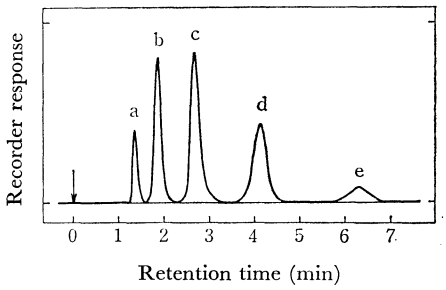

Fig. 1. Gas chromatogram of a mixture of $GeCl_4$ and $GeBr_4$.
Separation column: 200 cm×4 mm i.d., borosilicate glass, filled with 10% Kel-F Wax on silanized Chromosorb W (80—100 mesh). Column temperature: 100°C. Carrier gas: He, 30 ml/min.
a: $GeCl_4$; b: $GeCl_3Br$; c: $GeCl_2Br_2$; d: $GeClBr_3$; e: $GeBr_4$.

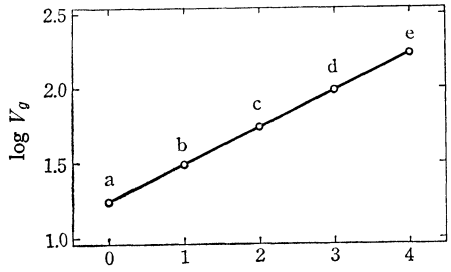

Fig. 2. Log specific retention volume *vs.* number of bromine atoms in a molecule for germanium halides.
a: $GeCl_4$; b: $GeCl_3Br$; c: $GeCl_2Br_2$; d: $GeClBr_3$; e: $GeBr_4$.

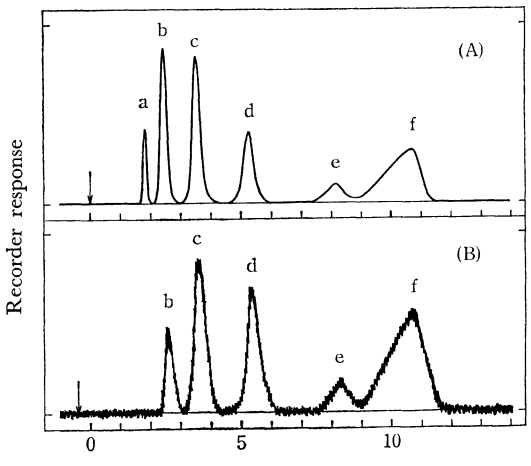

Fig. 3. Gas chromatogram (A) and radio chromatogram (B) of a mixture of $GeCl_4$, $GeBr_4$, and $As^{82}Br_3$.
Column and operating conditions: the same as in Fig. 1, with the exception of the flow rate (He): 20 ml/min. Radiation detector: 3″×3″ NaI(Tl).
a: $GeCl_4$; b: $GeCl_3Br$; c: $GeCl_2Br_2$; d: $GeClBr_3$; e: $GeBr_4$; f: $AsBr_3$.

1) M. L. Delwaulle, *Compt. Rend.*, **227**, 1229 (1948); **232**, 54 (1951); **234**, 2361 (1952).

2) G. S. Forbes and H. H. Anderson, *J. Amer. Chem. Soc.*, **66**, 931 (1944).

3) Y. Makide and N. Saito, presented at the 24th Annual Meeting of the Chemical Society of Japan (April 1971, Osaka).