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The Reaction of Germanium Atoms with Organic Halides

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Co-condensation of thermally evaporated germanium vapor with organic halides yields a mixture of trihalogermyl derivatives and tetrahalogermanes as major products. The nature of these reactions is discussed.

While the composition and physical properties of germanium atom have been amply investigated, the chemical properties of germanium atom have little been studied.[1-6)] On the other hand, the study of carbon and silicon atoms as homologue of germanium atom has been relatively investigated and been demonstrated to be useful for synthetic chemistry and reaction mechansim.[7)] Germanium atoms are also useful for preparation of various organogermanium compounds which are unobtainable by other methods, or which can be only in low yields. We now wish to report on reactions of thermally evaporated germanium vapor (atom) with organic halides (polyhaloalkanes and alkyl iodides). The present study is valuable for understanding not only of the chemical properties of germanium atoms but also of reactive intermediates in solutions.

A typical reaction of germanium atoms with organic halides by co-condensation under vacuum (5×10^{-3} Torr, 1 Torr=133.322 Pa) of thermally evaporated germanium vapor and a large excess of organic halides at 77 K is described. Germanium metal (0.5 g, 6.9 mmol) was evaporated using a resistively heated, alumina-coated tungsten spiral crucible for 1 h, while a large excess of organic halide (15-20 cm^3) was co-condensed on the walls of a quartz reaction flask containing the tungsten crucible and a perforated inlet tube through which the organic halide was introduced. The crucible was maintained at 1250-1350 ^oC and the reaction flask immersed in liquid nitrogen during germanium evaporation and introduction of the organic halide. After germanium evaporation and introduction of the organic halides, the reaction flask was warmed to room temperature and allowed to stand for 1.5 h. After removal of the reaction flask from a vacuum line, the products were identified by comparing their GC-MASS and retention times on GLC with those of authentic and similar samples.6,8)

Reactions of germanium atoms with polyhaloalkanes and alkyl iodides were examined. Germanium-containing products are summarized in Table 1. The reaction of germanium atoms with CCl_4 afforded $GeCl_4$ (ca. 50%), CCl_3GeCl_3 (7.0%), CCl_3CCl_3 (trace), and high-boiling products excluding germanium. McGlinchey and Tan found no $GeCl_4$ from the co-condensation of germanium atoms with CCl_4.4) The compound $GeCl_4$ presumably arises by abstraction of four chlorine atoms from CCl_4 by germanium atoms in a stepwise manner. Other process could occur such as abstraction of two chlorine atoms from CCl_4 by germanium atoms to give $GeCl_2$ followed by decomposition into $GeCl_4$ and germanium monochloride.9) However, the latter process would be thermally unfavorable under these co-condensation conditions. The compound CCl_3GeCl_3 probably is formed by C-Cl insertion of CCl_4 by germanium atoms to give $ClGeCCl_3$ followed by abstraction of two chlorine atoms from CCl_4. Other process could occur such as abstraction of two chlorine atoms from CCl_4 by germanium atoms to give $GeCl_2$ followed by C-Cl insertion of CCl_4. However, the former process is favored, since it has been reported that $GeCl_2$ does not insert into C-Cl of CCl_4 to give CCl_3GeCl_3.10) When $CFCl_3$ and $CHCl_3$ were used as substrate, the trihalogermyl compounds formed were $CFCl_2GeCl_3$ and $CHCl_2GeCl_3$, respectively. These germanium products indicate that no C-F and C-H insertion or abstraction by germanium atoms or germylenes occur. This may be a reflection of C-H, C-F, and C-Cl bond strengths. With $BrCCl_3$ germanium atoms inserted selectively into C-Br bond of $BrCCl_3$. Taking above results into consideration, the order of decreasing reactivity towards carbon-halogen insertion by germanium atoms is C-Br > C-Cl >> C-F. Germanium atoms reacted with dihalomethanes and alkyl iodides similarly to produce tetrahalogermanes and trihalogermyl derivatives predominantly. Me_2GeI_2 was also produced as a minor product in the co-condensation of germanium atoms with MeI.

Blank experiments were carried out under identical conditions. As a result, the products shown in Table 1 were attributable to the interaction of germanium atoms with starting organic halides.

A probable pathway for products shown in Table 1 is outlined in Scheme 1.

Table 1. The Reaction of Germanium Atoms with Organic Halides[a)]

Substrate	Products (Yield/%[b)])
CCl_4	$GeCl_4$ (ca. 50), CCl_3GeCl_3 (7.0)
$CFCl_3$	$GeCl_4$ (0.6), $CFCl_2GeCl_3$ (1.6)
$BrCCl_3$	$GeCl_4$ (5.8), $GeBrCl_3$ (1.1), $GeBr_3Cl$ (0.6), $GeBr_4$ (0.7), $CCl_3GeBrCl_2$ (0.6), CCl_3GeBr_3 (7.8)
$CHCl_3$	$GeCl_4$ (15.0), $CHCl_2GeCl_3$ (8.0)
CH_2Cl_2	$GeCl_4$ (1.6), $CH_2ClGeCl_3$ (0.3)
CH_2Br_2	$GeBr_4$ (2.0), $CH_2BrGeBr_3$ (0.7)
MeI	GeI_4 (14.0), $MeGeI_3$ (11.0), Me_2GeI_2 (0.5)
EtI	GeI_4 (17.0), $EtGeI_3$ (2.8)
n-PrI	GeI_4 (3.0), n-$PrGeI_3$ (2.7)
i-PrI	GeI_4 (5.1), i-$PrGeI_3$ (5.3)

a) Reactions were performed at room temperature for 1.5 h. b) Yields of products were determined on the basis of the amount of the consumed germanium metal on the assumption that all of the vaporized germanium metal completely reacted with organic halides.

Thermally evaporated germanium atoms possess ^3P ground state. ^3P germanium atoms inserted into carbon-halogen bonds of organic halides to form triplet divalent species (germylenes) (Eq. 1). The initially formed triplet germylenes rapidly relax to its singlet state (Eq. 2). Because the ground state of R_2Ge (R=H, Me) and GeI_2 has shown to be a singlet by quantum chemical calculations and chemical reactions [11-13)] The singlet germylenes abstract halogens from organic halides in a stepwise manner characteristic of germyl radicals (Eq. 3). The halogen abstraction has also been reported for singlet germylenes.[14)]

$$\ddot{\mathrm{Ge}}:(^3\mathrm{P}) \quad + \quad \mathrm{R\text{-}X} \longrightarrow {}^3[\mathrm{R\text{-}}\underset{\cdot}{\dot{\mathrm{Ge}}}\mathrm{\text{-}X}] \qquad (1)$$

$$ {}^3[\mathrm{R\text{-}}\underset{\cdot}{\dot{\mathrm{Ge}}}\mathrm{\text{-}X}] \longrightarrow {}^1[\mathrm{R\text{-}}\ddot{\mathrm{Ge}}\mathrm{\text{-}X}] \qquad (2)$$

$$\begin{tikzcd} & \mathrm{R}\dot{\mathrm{Ge}}\mathrm{X}_2 \arrow[r, "\mathrm{RX}"] & \mathrm{RGeX}_3 & (3) \\ {}^1[\mathrm{R\text{-}}\ddot{\mathrm{Ge}}\mathrm{\text{-}X}] \arrow[ur, "\mathrm{RX}"] \arrow[dr, "\mathrm{R\text{-}X}"'] & & & \\ & \mathrm{R}_2\mathrm{GeX}_2 & & (4) \end{tikzcd}$$

Scheme 1.

On the other hand, the singlet germylenes also undergo double insertions (Eq. 4). The carbon-halogen insertion and halogen abstraction by germanium atoms and germylenes presumably reflect the bond strength of carbon-halogen bonds.

Tetrahalogermanes arise by abstraction of four halogen atoms from organic halides by germanium atoms in a stepwise manner.

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