The Reaction of Germanium Atoms with Trimethylsilane

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Summary Co-condensation of thermally evaporated germanium vapour with trimethylsilane yields bis-trimethylsilylgermane, $Me_3SiGeH_2SiMe_3$.

Recently there has been considerable mechanistic and synthetic interest in the reactions of carbon, silicon and germanium atoms,[1,2] but a comparison of the reactions of nucleogenic and thermally generated atoms has not yet been achieved. Having begun a study of germanium atoms produced by nuclear recoil,[3,4] we have turned our attention to the reactions of thermally evaporated germanium atoms, on which only one previous report has appeared.[5]

We have studied the reaction of germanium atoms with trimethylsilane by co-condensation under vacuum of thermally evaporated germanium vapour and a large excess of trimethylsilane at 77 K. A resistively heated, alumina-coated molybdenum spiral crucible was employed, as described by Timms.[1] In a typical experiment 340 mg (4·7 mmol) of germanium metal was evaporated in 1 h while 10 ml of trimethylsilane was co-condensed on the walls of a one litre pyrex flask containing the crucible and a perforated inlet tube through which the Me_3SiH was admitted. The crucible was maintained at 1450 °C and the flask immersed in liquid nitrogen during germanium evaporation.

Fractionation of the reaction mixture by low pressure trap-to-trap distillation on a vacuum line yielded, in addition to unchanged Me_3SiH, hexamethyldisilane $Me_3SiSiMe_3$ (0·20 mmol), and a new compound, bis-trimethylsilylgermane $Me_3SiGeH_2SiMe_3$, in yields of 1·4 and 3·0% (isolated material, two experiments).

The structure of the product identified as bis-trimethylsilylgermane is apparent from its mass spectrum, parent ion at *m/e* 222 ($Me_3{}^{28}Si^{74}GeH_2{}^{28}SiMe_3$) with contributions from parent ions containing ^{70}Ge, ^{72}Ge, ^{73}Ge and ^{76}Ge in the correct natural abundances, and prominent fragment ions at *m/e* 207, 162, 147 and 73 (base peak). The n.m.r. spectrum consists of two singlet peaks in ratio 1 : 9 at δ 2·48 (Ge–H) and 0·24 (C–H) respectively.

A blank experiment was carried out under identical conditions except for a lower crucible temperature of 1100—

1200 °C, sufficient to melt the germanium but not to evaporate it during condensation of Me_3SiH. Fractionation of the volatile products yielded $Me_3SiSiMe_3$ (0·12 mmol) but no detectable $Me_3SiGeH_2SiMe_3$. Thus the only product attributable to the interaction of germanium vapour with trimethylsilane is the bis-trimethylsilylgermane.

Stepwise insertion is a reasonable mechanism for product formation (equations 1 and 2). While similar mechanisms have been proposed for the co-condensation of thermally evaporated silicon vapour with trimethylsilane[6] and for the reactions of nucleogenic germanium atoms with germane and germane–silane mixtures,[4] the present result is noteworthy when compared to the only other report of the reactivity of thermally generated germanium atoms.[5]

$$\mathrm{Ge} + \mathrm{HSiMe_3} \longrightarrow \mathrm{H\text{-}Ge\text{-}SiMe_3} \qquad (1)$$

$$\mathrm{Me_3SiGeH} + \mathrm{HSiMe_3} \longrightarrow \mathrm{Me_3SiGeH_2SiMe_3} \qquad (2)$$

McGlinchey and Tan found no double insertion products from the co-condensation of germanium vapour with CCl_4 and $SiCl_4$ respectively, and proposed an insertion–abstraction mechanism involving triplet germanium atoms and a triplet germylene (equation 3).[5]

$$\mathrm{Ge}(^3P) + \mathrm{Cl\text{–}CCl_3} \rightarrow {}^3[\mathrm{Cl\text{–}Ge\text{–}CCl_3}] \xrightarrow{\mathrm{CCl_4}} \mathrm{Cl_2GeCCl_3} \xrightarrow{\mathrm{CCl_4}} \mathrm{Cl_3GeCCl_3} \qquad (3)$$

Our result indicates no distinction between thermally generated and nucleogenic germanium atoms based on the product of reaction with SiH bonds.

The formation of $Me_3SiGeH_2SiMe_3$ by double insertion suggests that the intermediate Me_3SiGeH reacts as a singlet. It should be recalled that SiH_2 has a singlet ground state calculated to lie 46 kcal mol^{-1} below the lowest triplet state.[7] The ground state of GeH_2 is probably also a singlet. The chlorine abstraction observed by McGlinchey and Tan may well be due to a singlet intermediate, halogen abstraction being known for carbenes[8] and silylenes.[9] The initial insertion may be due to ^3P germanium atoms, the initially formed divalent germanium species rapidly relaxing to its ground singlet state. It is clearly premature however to definitely assign electronic states to either initial reacting atoms or to intermediates.

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