Kinetic Determination of the Bond Dissociation Energy $D(Me_3Ge–H)$ and Its Implications for Bond Strengths in Germanes†

By ALAN M. DONCASTER and ROBIN WALSH
(*Department of Chemistry, The University of Reading, Whiteknights, Reading* RG6 2AD)

Summary The kinetics of the gas-phase reaction between iodine and trimethylgermane are interpreted to provide a value for $D(Me_3Ge–H)$ of 342 kJ mol^{-1}.

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† No reprints available.

Bond dissociation energy measurements form the basis of free-radical thermochemistry without which the mechanistic interpretation of many chemical reactions would be difficult if not impossible. We have recently applied the kinetic technique of iodination, pioneered by Benson and his co-workers,[1] to the determination of Si–H bond dissociation energies in a variety of compounds.[2,3]. We now report a further extension of this technique to the determination of $D(Me_3Ge{-}H)$, the first example of its application to a germanium-containing compound. There is no previous measurement of $D(Me_3Ge{-}H)$.

We have investigated the gas-phase reaction of I_2 with Me_3GeH spectrophotometrically at 467 K. A combination of u.v., i.r., and mass spectrometric measurements shows the only products to be formed within a few hours are Me_3GeI and HI, although after a day secondary reactions set in. In particular MeI is absent ($\leqslant 5\%$ of Me_3GeI). The reaction occurs with a negligible pressure change. In a conditioned quartz vessel kinetic studies of iodine disappearance showed the reaction to obey equation (A) up to *ca.* 50% conversion

$$-\mathrm{d}[I_2]/\mathrm{d}t = k[I_2]^{1/2}\,[Me_3GeH] \qquad \text{(A)}$$

after which a slight inhibition was evident (as judged by curvature in the integrated plots). The rate data up to 50% conversion gave, at 467 K, $k = (1{\cdot}47 \pm 0{\cdot}10) \times 10^4\ \mathrm{Torr^{-1/2}\ s^{-1}}$. Inclusion of data up to 75% conversion would lower this figure by *ca.* 10%. The results are consistent with the mechanism in the Scheme. Assuming the rate of step (2) is slow compared with (3) in the early stages, then $k = k_1 K_{I_2}{}^{1/2}$. From the known value[4] of $K_{I_2}{}^{1/2}$, $k_1 = 1{\cdot}02 \times 10^5\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. The Arrhenius parameters of k_1 have not yet been determined‡ but we expect by analogy with both hydrocarbon[1] and silicon chemistry[2,3] that A_1 is *ca.* $10^{11{\cdot}0}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ in which case $E_1 = 53{\cdot}6\ \mathrm{kJ\ mol^{-1}}$. E_2 is not known but again by analogy[1–3] one would expect a value of *ca.* 5—15 kJ mol^{-1}. If $E_2 = 10\ \mathrm{kJ\ mol^{-1}}$, $\Delta H^\circ_{1{\cdot}2} = 44\ \mathrm{kJ\ mol^{-1}}$ and assuming a negligible effect of temperature, this implies $D(Me_3Ge{-}H,\ 298\ K) = D(H{-}I) + 44 = 342\ \mathrm{kJ\ mol^{-1}}$ (82 kcal mol^{-1}). This must be considered uncertain to $\pm$ 10 kJ mol^{-1} in view of the assumptions made.

$$I_2\ (+M) \rightleftharpoons 2I\cdot\ (+M) \qquad K_{I_2}$$

$$I\cdot + Me_3GeH \underset{2}{\overset{1}{\rightleftharpoons}} Me_3Ge\cdot + HI$$

$$Me_3Ge\cdot + I_2 \xrightarrow{3} Me_3GeI + I\cdot$$

Scheme

There is no previous measurement of $D(Me_3Ge{-}H)$ although there has been speculation as to its magnitude.[5] Comparison with $D(GeH_3{-}H)$ is worthwhile, since by analogy with Si–H dissociation energies,[6] little or no effect of methyl substitution is anticipated. For $D(GeH_3{-}H)$ Kim, Setser, and Bogan[7] have recently obtained an upper limit of 326 kJ mol^{-1} from i.r. chemiluminescence measurements,§ while earlier values comprise a higher upper limit of 386 kJ mol^{-1} from photoelectron detachment studies[8] and 365 kJ mol^{-1} from electron impact studies.[9] In general, the i.r. chemiluminescence method is reliable[10] and leads to values in good agreement with independent determinations. However, in the case of $D(SiH_3{-}H)$ a value of 363 kJ mol^{-1} was obtained, *ca.* 13 kJ mol^{-1} less than that[2] for $D(Me_3Si{-}H)$. While these discrepancies are not large we suspect that there may be some common effect in the chemiluminescence method leading to slightly low values for $D(SiH_3{-}H)$ and $D(GeH_3{-}H)$. Further independent determinations of these bond strengths are certainly called for. In the meantime we would favour a figure of 356 $\pm$ 16 kJ mol^{-1} for $D(GeH_3{-}H)$ in line with our determination for $D(Me_3Ge{-}H)$.

Our results also suggest that Ge–Me dissociation energies in methyl germanes are *ca.* 318 $\pm$ 16 kJ mol^{-1} on the assumption that Ge–Me and Ge–H bond dissociation energies differ by the same amount as their mean bond energies in GeH_4 and $GeMe_4$.[11] This, however, is not in agreement with the figure[11] of $D(Me_3Ge{-}Me) = 289\ \mathrm{kJ\ mol^{-1}}$ obtained from electron impact measurements.

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‡ Experiments to this end are underway.

§ A more recent reinvestigation gives $D^0_0(GeH_3{-}H) \leqslant 338\ \mathrm{kJ\ mol^{-1}}$, D. Setser, personal communication.

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