

**Kinetic Determination of the Bond Dissociation Energy $D(\text{Me}_3\text{Ge-H})$ and
Its Implications for Bond Strengths in Germanes†**

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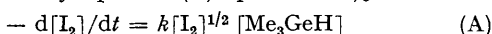
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Summary The kinetics of the gas-phase reaction between iodine and trimethylgermane are interpreted to provide a value for $D(\text{Me}_3\text{Ge-H})$ of 342 kJ mol^{-1} .

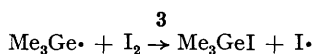
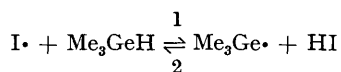
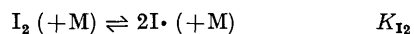
† No reprints available.

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 $D(\text{Me}_3\text{Ge-H})$, the first example of its application to a germanium-containing compound. There is no previous measurement of $D(\text{Me}_3\text{Ge-H})$.

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 ($\leq 5\%$ 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



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, $k = (1.47 \pm 0.10) \times 10^4 \text{ Torr}^{-1/2} \text{ s}^{-1}$. 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



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slow compared with (3) in the early stages, then $k = k_1 K_{\text{I}_2}^{1/2}$. From the known value⁴ of $K_{\text{I}_2}^{1/2}$, $k_1 = 1.02 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The Arrhenius parameters of k_1 have

‡ Experiments to this end are underway.

§ A more recent reinvestigation gives $D_0^\circ(\text{GeH}_3\text{-H}) \leq 338 \text{ kJ mol}^{-1}$, D. Setser, personal communication.

¹ D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.

² R. Walsh and J. M. Wells, *J.C.S. Faraday I*, 1976, **72**, 100; A. M. Doncaster and R. Walsh, unpublished experimental results.

³ R. Walsh and J. M. Wells, *J.C.S. Faraday I*, 1976, **1212**; A. M. Doncaster and R. Walsh, *Internat. J. Chem. Kinetics*, in the press.

⁴ J.A.N.A.F. Thermochemical Tables, 2nd edn., ed. D. R. Stull and H. Prophet, (N.S.R.D.S.-N.B.S. 37) National Bureau of Standards, 1971.

⁵ R. A. Jackson, in 'Essays on Free-Radical Chemistry,' *Chem. Soc. Special Publ.*, No. 24, 1970, 295.

⁶ A. Hosaka and F. S. Rowland, *J. Phys. Chem.*, 1973, **77**, 705.

⁷ K. C. Kim, D. W. Setser, and C. M. Bogan, *J. Chem. Phys.*, 1974, **60**, 1837.

⁸ K. J. Reed and J. I. Brauman, *J. Chem. Phys.*, 1974, **61**, 4830.

⁹ F. E. Saalfeld and H. J. Svec, *J. Phys. Chem.*, 1966, **70**, 1753.

¹⁰ W. H. Diewer and D. W. Setser, *J. Chem. Phys.*, 1973, **58**, 2310.

¹¹ M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, *J. Organometallic Chem.*, 1971, **29**, 195.

not yet been determined‡ but we expect by analogy with both hydrocarbon¹ and silicon chemistry^{2,3} that A_1 is ca. $10^{11.0} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in which case $E_1 = 53.6 \text{ kJ mol}^{-1}$. E_2 is not known but again by analogy¹⁻³ one would expect a value of ca. 5–15 kJ mol^{-1} . If $E_2 = 10 \text{ kJ mol}^{-1}$, $\Delta H_{1,2}^\circ = 44 \text{ kJ mol}^{-1}$ and assuming a negligible effect of temperature, this implies $D(\text{Me}_3\text{Ge-H}, 298 \text{ K}) = D(\text{H-I}) + 44 = 342 \text{ kJ mol}^{-1}$ (82 kcal mol^{-1}). This must be considered uncertain to $\pm 10 \text{ kJ mol}^{-1}$ in view of the assumptions made.

There is no previous measurement of $D(\text{Me}_3\text{Ge-H})$ although there has been speculation as to its magnitude.⁵ Comparison with $D(\text{GeH}_3\text{-H})$ is worthwhile, since by analogy with Si-H dissociation energies,⁶ little or no effect of methyl substitution is anticipated. For $D(\text{GeH}_3\text{-H})$ Kim, Setser, and Bogan⁷ 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 studies⁸ and 365 kJ mol^{-1} from electron impact studies.⁹ In general, the i.r. chemiluminescence method is reliable¹⁰ and leads to values in good agreement with independent determinations. However, in the case of $D(\text{SiH}_3\text{-H})$ a value of 363 kJ mol^{-1} was obtained, ca. 13 kJ mol^{-1} less than that² for $D(\text{Me}_3\text{Si-H})$. 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 $D(\text{SiH}_3\text{-H})$ and $D(\text{GeH}_3\text{-H})$. Further independent determinations of these bond strengths are certainly called for. In the meantime we would favour a figure of $356 \pm 16 \text{ kJ mol}^{-1}$ for $D(\text{GeH}_3\text{-H})$ in line with our determination for $D(\text{Me}_3\text{Ge-H})$.

Our results also suggest that Ge-Me dissociation energies in methyl germanes are ca. $318 \pm 16 \text{ kJ mol}^{-1}$ 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 figure¹¹ of $D(\text{Me}_3\text{Ge-Me}) = 289 \text{ kJ mol}^{-1}$ obtained from electron impact measurements.

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