Kinetically Determined Bond Dissociation Energies in Hexamethyldisilane

By Iain M. T. Davidson* and Anthony B. Howard
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary A re-investigation of the thermolysis of hexamethyldisilane gives $D(\mathrm{Me_3Si{-}SiMe_3})$ as 337 kJ mol^{-1} (80·5 kcal mol^{-1}), the Arrhenius A factor for this dissociation being $10^{17\cdot53}\mathrm{s}^{-1}$; $D(\mathrm{Me_3Si{-}H})$ is estimated as 368 kJ mol^{-1}.

The thermolysis of hexamethyldisilane at low pressure has been interpreted in terms of a radical non-chain sequence, to give Arrhenius parameters for the rupture of the silicon–silicon bond,[1] but the A factor thus obtained is unreasonably low in relation to recent values[2,3] of the rate constant for recombination of trimethylsilyl radicals. We have therefore re-investigated this thermolysis in a stirred-flow system between 770 K and 872 K, with low concentrations of hexamethyldisilane ($4\cdot3 \times 10^{-9}$ to $3\cdot6 \times 10^{-7}$ mol cm^{-3}) in a nitrogen stream above atmospheric pressure, excess of *m*-xylene being present in some runs.

With no xylene present, the main product was trimethylsilane, with smaller amounts of tetramethylsilane, the isomer of hexamethyldisilane[4] [$\mathrm{Me_3SiCH_2Si(H)Me_2}$], and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. With added xylene, trimethylsilane and the isomer of hexamethyldisilane were formed at reduced rates, while the formation of the disilacyclobutane was suppressed. First-order rate constants for the formation of trimethylsilane in xylene were given by $k/\mathrm{s}^{-1} = 10^{17\cdot 53 \pm 0\cdot 25}\exp(-336\cdot 6 \pm 4\cdot 0/RT)$(activation energy in kJ mol^{-1}). The following sequence of reactions accounts for the thermolysis of hexamethyldisilane in *m*-xylene (RH).

$$\mathrm{Me_3SiSiMe_3} \rightarrow \mathrm{2Me_3Si\cdot} \qquad (1)$$

$$\mathrm{Me_3Si\cdot + RH} \rightarrow \mathrm{Me_3SiH + R\cdot} \qquad (2)$$

$$\mathrm{R\cdot + Me_3SiSiMe_3} \rightleftharpoons \mathrm{RH + Me_5Si_2\dot{C}H_2} \qquad (3), (-3)$$

$$\mathrm{Me_5Si_2\dot{C}H_2} \rightarrow \mathrm{Me_3SiCH_2\dot{S}iMe_2} \qquad (4)$$

$$\mathrm{Me_3SiCH_2\dot{S}iMe_2 + RH} \rightarrow \mathrm{Me_3SiCH_2Si(H)Me_2 + R\cdot} \qquad (5)$$

$$\mathrm{2\,R\cdot} \rightarrow \mathrm{R_2} \qquad (6)$$

It appears that the added xylene inhibits a chain reaction which produces all of the disilacyclobutane and the extra trimethylsilane formed in the absence of xylene, the chain propagating step being

$$\mathrm{Me_3SiCH_2\dot{S}iMe_2} \rightarrow \mathrm{Me_3Si\cdot + CH_2\!:\!SiMe_2} \qquad (7)$$

In xylene, reaction (7) cannot compete with reaction (5).

Hence, the thermolysis of hexamethyldisilane at low pressure is not a non-chain process, as was previously believed,[1,5] but proceeds by a chain of short length (between 4·5 and 2·1 under the above conditions). Consequently the Arrhenius parameters for the formation of trimethylsilane in the presence of excess of xylene are the best available measure of k_1. The A factor of $10^{17\cdot 53}\,\mathrm{s}^{-1}$ is now satisfactorily consistent with that[3] for reaction (−1), and while a value of 337 kJ mol^{-1} (80·5 kcal mol^{-1})† for $D(\mathrm{Me_3Si{-}SiMe_3})$ represents a substantial increase on the previously accepted value[5] there is other evidence in support of it; recent electron impact experiments[6] give $D(\mathrm{Me_3Si{-}H}) - D(\mathrm{Me_3Si{-}SiMe_3}) = 31$ kJ mol^{-1} whence $D(\mathrm{Me_3Si{-}H}) = 368$ kJ mol^{-1} (88 kcal mol^{-1}), in good agreement with the value of approximately 372 kJ mol^{-1} (89 kcal mol^{-1}) obtained by Walsh from experiments on the rate of iodination of trimethylsilane.[7]

The tetramethylsilane may be formed by direct silylene elimination

$$\mathrm{Me_3Si{-}SiMe_3} \rightarrow \mathrm{Me_4Si + Me_2Si} \qquad (8)$$

and the earlier Arrhenius parameters[1] probably related to this process rather than to the rupture of the silicon–silicon bond.

We thank the S.R.C. for financial support.

(*Received*, 5*th March* 1973; *Com.* 295.)

---

† 1 Thermochemical calorie = 4·184J.

[1] I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc.* (*A*), 1968, 282.

[2] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

[3] P. Cadman, G. M. Tilsley, and A. F. Trotman-Dickenson, *J.C.S. Faraday I*, 1972, **68**, 1849.

[4] H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Comm.*, 1968, 930; C. Eaborn and J. M. Simmie, *ibid.*, p. 1426.

[5] I. M. T. Davidson, *Quart. Rev.*, 1971, **25**, 111.

[6] I. M. T. Davidson, M. Jones, and H. F. Tibbals, unpublished results.

[7] R. Walsh, reported at Gas Kinetics Discussion Group Meeting, Leicester, 1972.