

Kinetics of the Gas-phase Reaction between Iodine and Trimethylsilane and the Bond Dissociation Energy $D(\text{Me}_3\text{Si-H})^\dagger$

By ROBIN WALSH* and MISS J. M. WELLS

(Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 2AD)

Summary The kinetics of the title reaction support an iodine atom abstraction mechanism and a value of $D(\text{Me}_3\text{Si-H})$ considerably higher than previous estimates.

BENSON and co-workers¹ have used gas phase kinetic studies of the reactions of iodine and organic species to obtain reliable (C-H) bond dissociation energies. For X other than a first row element the data on X-H bond strengths is sparse² and many values are subject to uncertainty. For X = Si most bond strengths are based on $D(\text{Me}_3\text{Si-H}) = 340 \text{ kJ mol}^{-1}$, a value obtained by Davidson from studies³ of the pyrolysis of Me_3SiH .

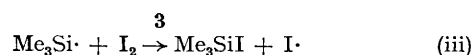
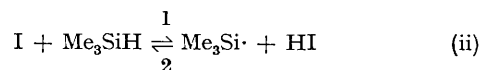
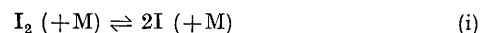
We have investigated the reaction of iodine with Me_3SiH in the gas phase at 546 K using a spectrophotometric analytical technique. U.v. measurements throughout the course of the reaction indicate the formation of both Me_3SiI and HI in approximately equal quantities. Gas chromatographic analysis of product samples showed that, apart from HI, only Me_3SiI and its hydrolysis products were present. In particular, MeI, CH_4 , and H_2 were all shown to

be absent (less than a few per cent). The reaction occurred with a negligible pressure change. In a conditioned quartz vessel kinetic studies of iodine disappearance showed the reaction to obey equation (1) up to about 50% conversion

$$\frac{-d[\text{I}_2]}{dt} = k[\text{I}_2]^\dagger[\text{Me}_3\text{SiH}] \quad (1)$$

after which a slight inhibition (hardly greater than experimental error) was evident. The data gave, at 546 K, $k = (2.0 \pm 0.2) \times 10^5 \text{ Torr}^{-\frac{1}{2}} \text{ s}^{-1}$.

The results suggest the mechanism shown in (i), (ii), and (iii). Assuming the rate of step (2) is negligible compared



† First reported at a meeting of the Gas Kinetics Discussion Group of the Chemical Society at Leicester, September 25th, 1972.

with (3) in the early stages, then $k = k_1 K_1^\ddagger$, which from the known value of K_1^\ddagger yields $k_1 = 9.6 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$. The Arrhenius parameters of k_1 have not yet been determined, but we expect by analogy with hydrocarbon chemistry¹ A_1 is *ca.* $10^{10.9} \text{ M}^{-1} \text{ s}^{-1}$, in which case $E_1 = 83 \text{ kJ mol}^{-1}$. E_2 is not known but is likely to be smaller than the activation energy of the analogous reaction of $\text{Me}_3\text{C}^\cdot$ (5 kJ mol^{-1}). If $E_2 = 5 \text{ kJ mol}^{-1}$, $\Delta H_{1,2}^\ddagger = 78 \text{ kJ mol}^{-1}$ and assuming a negligible effect of temperature this implies $D(\text{Me}_3\text{Si-H}, 298 \text{ K}) = D(\text{H-I}) + 78 = 376 \text{ kJ mol}^{-1}$ (90 kcal mol^{-1}). This value, although subject to the uncertainty of the assumptions stated, is considerably higher than the previous figure.³ It implies that, in the pyrolyses of both Me_3SiH^3 and $\text{Me}_3\text{Si-SiMe}_3$,⁴ in contrast to previous suggestions, short chains occur and these lower the overall

activation energies below those of the initiation steps. A very recent reinvestigation on the latter pyrolysis⁵ bears this out. This value of the bond strength also helps to remove an apparent anomaly⁶ in relative rates of hydrogen abstraction from Me_3SiH^7 and SiH_4 by methyl radicals.^{7,8} The activation energies for these abstractions differ by only 4 kJ mol^{-1} , a figure more easily reconciled with a bond strength difference of 21 kJ mol^{-1} from the new figures, rather than 59 kJ mol^{-1} from the old.

Measurements of X-H bond strengths for compounds containing other elements are planned.

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² For a recent review see K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, in the press.

³ I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. (A)*, 1971, 882. See also I. M. T. Davidson, *Quart. Rev.*, 1971, **25**, 111.

⁴ I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. (A)*, 1968, 282.

⁵ I. M. T. Davidson and A. V. Howard, Gas Kinetics Discussion Group Meeting, Cardiff, April 5th 1973.

⁶ E. Whittle, 'Chemical Kinetics,' M. T. P. International Review of Science, Physical Chemistry, Ser. 1, **9**, ed. J. C. Polanyi, 1972, p. 75.

⁷ E. R. Morris and J. C. J. Thynne, *J. Phys. Chem.*, 1969, **73**, 3294.

⁸ O. P. Strausz, E. Jacobowski, H. S. Sandhu, and H. E. Cumming, *J. Chem. Phys.*, 1969, **51**, 552.