

Kinetic Determination of the Bond Dissociation Energy $D(\text{SiH}_3\text{-H})$ and its Implications for Bond Strengths in Silanes

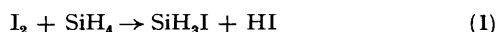
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Summary The kinetics of the gas-phase reaction between iodine and monosilane are interpreted to provide a value for $D(\text{SiH}_3\text{-H})$ of 376 kJ mol^{-1} .

WHEREAS C-H bond dissociation energies in alkanes are well established and values have hardly been modified for 30 years,¹ Si-H bond dissociation energies are still somewhat uncertain and by no means agreed. It is important to obtain reliable values since they form the thermochemical basis for the underpinning of reaction mechanisms in silicon and organosilicon chemistry. We have recently embarked on a program of such measurements in a variety of compounds.² We now report an extension of the technique to the simplest silane of all, *viz.* monosilane. Existing values for $D(\text{SiH}_3\text{-H})$ vary between 363 and 398 kJ mol^{-1} .³⁻⁶

The method involves the study of the kinetics of the gas-phase reaction of SiH_4 with I_2 . The reaction is monitored spectrophotometrically. U.v. spectral changes indicate the formation of HI and one or more iodides depending on conditions. A combination of i.r. and microwave spectroscopy shows SiH_3I to be the most prominent iodide formed initially. H_2 is absent and there is no pressure change during the reaction. These observations support the occurrence of reaction (1) in the early stages. There is no reaction, under the experimental conditions, of SiH_4 with HI but there is evidence (*vide infra*) of secondary reactions, most probably of SiH_3I with I_2 .

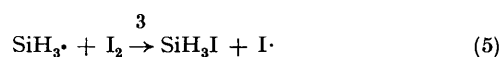
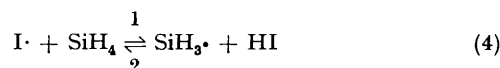
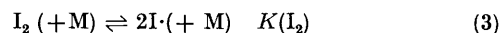


The kinetics of iodine disappearance in a well conditioned quartz vessel were studied at 537.9 K. Initial rates (obtained by computerised curve fitting) were found to fit the rate equation (2) for a range of I_2 pressures from

$$-d[\text{I}_2]/dt = k[\text{I}_2]^\dagger[\text{SiH}_4] \quad (2)$$

0.26–3.0 Torr and SiH_4 pressures from 9.4–44.4 Torr. The data from 14 runs gave a value of $k = (4.55 \pm 0.28)$

$\times 10^{-5} \text{ Torr}^{-\frac{1}{2}} \text{ s}^{-1}$. Integrated plots of equation (2) up to 65% conversion also fitted the data with the same rate constant provided (i) $[\text{SiH}_4]_0/[\text{I}_2]_0$ was > 50 and (ii) allowance was made for a slight inhibition effect by HI which became more serious as the reaction proceeded. At lower values of the ratio $[\text{SiH}_4]_0/[\text{I}_2]_0$, the I_2 time evolution showed significant departure from the integrated form of equation (2) in a direction indicative of reaction between I_2 and an initially formed product. The results in the initial stages offer strong support for the mechanism shown in equations (3)–(5). Assuming the rate of step (2) is slow



$$\log k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = (11.56 \pm 0.34) - (83.2 \pm 3.5 \text{ kJ mol}^{-1})/RT \ln 10 \quad (6)$$

compared with (3) initially, then $k = k_1 K(\text{I}_2)^\dagger$. From the known value⁷ of $K(\text{I}_2)^\dagger$, $k_1 = 2.75 \pm 0.17 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Further measurements of k_1 in the temperature range 507–547 K give the Arrhenius equation (6).

The A factor is in good agreement with expectations based on both hydrocarbon⁸ and silicon chemistry.² Further rate measurements carried out in the presence of HI give values of rate constant ratio k_2/k_3 in the range 0.08–0.12. It is difficult to measure the Arrhenius parameters for this ratio with reliability (because of secondary reactions) but the data are consistent with $E_2 - E_3 = 5 \pm 7 \text{ kJ mol}^{-1}$. E_3 cannot be obtained separately but by analogy with hydrocarbon chemistry⁸ one would expect $E_3 = 0$ and therefore $E_2 = 5 \pm 7 \text{ kJ mol}^{-1}$. Thus $\Delta H_{13}^\circ = E_1 - E_2 = 78 \pm 8 \text{ kJ mol}^{-1}$ and assuming a negligible effect of temperature, this implies $D(\text{SiH}_3\text{-H}, 298 \text{ K}) = D(\text{H-I}) + (78 \pm 8) = 376 \pm 8 \text{ kJ mol}^{-1}$ ($90 \pm 2 \text{ kcal mol}^{-1}$).

Amongst existing values for $D(\text{SiH}_3\text{-H})$ the most commonly quoted figures are the electron impact based values of 393³ and 398 kJ mol⁻¹.⁴ More recently Reed and Brauman⁶ obtained an upper limit of 386 kJ mol⁻¹ by photoelectron detachment and Duewer and Setser an apparent upper limit⁵ of 363 kJ mol⁻¹ by measurement of HF i.r. chemiluminescence in the reaction of $\text{F}\cdot + \text{SiH}_4$. These latter methods have some uncertainties associated with them and the reasonably close agreement with our result adds weight to it. It also indicates, as has often been the case in the past, that the electron impact values are in error.

Our new value for $D(\text{SiH}_3\text{-H})$ is very close to our earlier figure of 378 kJ mol⁻¹ for $D(\text{Me}_3\text{Si-H})$ ^{2a} and indicates an extremely small (if anything strengthening) effect of methyl groups on Si-H bond strengths. This is consistent with measurements of H abstraction by both $\text{CH}_3\cdot$ radicals⁹ and hot T atoms.¹⁰

The new figure for $D(\text{SiH}_3\text{-H})$ also permits calculation of $\Delta H_f^\circ(\text{SiH}_3) = 193 \pm 8 \text{ kJ mol}^{-1}$ [via the known value¹¹ for $\Delta H_f^\circ(\text{SiH}_4)$]. This in turn enables us to estimate $D(\text{SiH}_3\text{-SiH}_3) = 305 \pm 11 \text{ kJ mol}^{-1}$. This figure is significantly less than that of 337 kJ mol⁻¹ for $D(\text{Me}_3\text{Si-SiMe}_3)$ ¹² and is in contrast to the bond strengths¹ in the analogous hydrocarbons where $D(\text{CH}_3\text{-CH}_3) > D(\text{Me}_3\text{C-CMe}_3)$. Although the hydrocarbon case is complicated by steric effects, this result suggests that in silanes (or at least disilanes) methyl groups are bond strengthening rather than weakening. A comparison of the Pauling electronegativities for C (2.5) and Si (1.8) supports the idea that CH_3 groups on Si may act via inductive electron withdrawal.

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