# Kinetics of the Reaction of Silylene with Hydrogen and a Possible Resolution of Discrepancies over $\Delta H_f^{\ominus}$ (SiH$_2$)

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RRKM (Rice–Ramsperger–Kassel–Marcus) calculations, carried out to fit some new experimental data, are found to reconcile apparent differences in two recent studies of the fast reaction between SiH$_2$ and H$_2$: the calculations lead to $\Delta H_f^{\ominus}$ (SiH$_2$) = 65.3 ± 1.5 kcal mol$^{-1}$.†

In a recent time-resolved, laser absorption study of the reaction of SiH$_2$ with D$_2$, Jasinski[1] obtained a rate constant of $(2.6 \pm 0.7) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, a value *ca.* 10$^4$ higher than that estimated from previous static system pyrolysis studies.[2] Moreover he argued that his rate constant (closely approximating the second order limiting value) implied a value for $\Delta H_f^{\ominus}$ (SiH$_2$) consistent with a recent theoretical estimate[3] of 68.1 kcal mol$^{-1}$, itself considerably higher than the previously accepted value[2] of *ca.* 58 kcal mol$^{-1}$. Jasinski argued that his rate constant implied an activation energy of <1 kcal mol$^{-1}$ for SiH$_2$ with D$_2$, a figure in apparent agreement with the most recent theoretical calculation but considerably lower than several previous estimates.[4]

† 1 cal = 4.184 J.
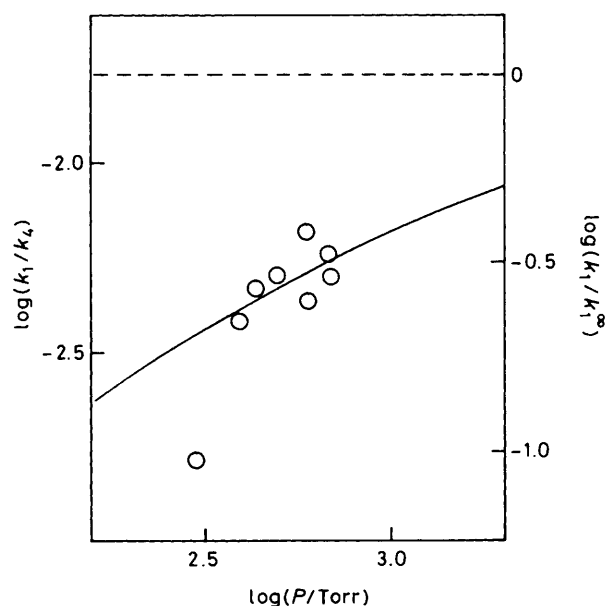
**Figure 1.** Pressure dependence of reaction of $SiH_2$ with $H_2$ (relative to reaction with phenylsilane). Solid line: RRKM calculated: dotted line corresponds to $k_1^\infty$

In another time-resolved study using laser induced fluorescence detection, Inoue and Suzuki[5] have obtained $k = (1.0 \pm 0.4) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction (1) of $SiH_2$ with $H_2$, a value differing by a factor of between 13 and 55 from that of Jasinski. The substantially higher figure for $\Delta H_f^\circ(SiH_2)$ implies a $\Delta H^\circ$ value for reaction (2) greater than the measured[6,7] activation energy of 48.8 kcal mol$^{-1}$. In an effort to resolve these problems we have carried out (a) an experimental study of reaction (1) and (b) RRKM (Rice–Ramsperger–Kassel–Marcus) calculations on both reactions (1) and (2).

$$SiH_2 + H_2(+M) \xrightarrow{k_1} SiH_4(+M) \qquad (1)$$

$$Si_2H_6 \xrightarrow{k_2} SiH_4 + SiH_2 \qquad (2)$$
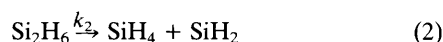
We have exploited a recently developed method[8] using the 206 nm photolysis of phenylsilane as the $SiH_2$ source, *viz.* reaction (3). Experiments were carried out in heated quartz vessel (100 °C) using appropriate mixtures of phenylsilane, hydrogen, and inert gas.

$$C_6H_5SiH_3 \xrightarrow{k_3} C_6H_6 + SiH_2 \qquad (3)$$
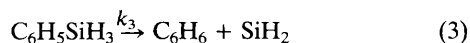
The competition between the steps in reactions (4) and (1) was followed by studying the reduction of phenyldisilane yields relative to primary benzene formation caused by addition of varying quantities of $H_2$. $SiH_4$ was detected but our analytical sensitivity was too low to use its formation as a quantitative monitor of step (1). Further details of the method are given in reference 8. In a series of experiments at a constant $H_2$ pressure of 300 Torr and varying argon up to 700

Torr, measurements of $k_1/k_4$, although scattered, showed a trend with pressure, as indicated in Figure 1.

$$SiH_2 + C_6H_5SiH_3 \xrightarrow{k_4} C_6H_5Si_2H_5 \qquad (4)$$
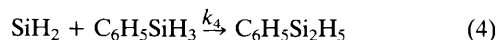
In order to try to fit these data, RRKM calculations on step (1) were carried out with weak collisional stabilisation using the current high pressure rate constant estimate,[9] $\log(k_{\infty1}^{\infty}/\text{s}^{-1})$ = 15.5 − 58.0 kcal mol$^{-1}$/$RT$ ln 10, as the basis for defining an activated complex. With a stepladder model using $<\Delta E>_{\text{down}}$ = 200 cm$^{-1}$,[10] the line shown in Figure 1 was obtained. It was matched to the data using the previously evaluated result[8] of $k_4 = 1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (assumed $T$ independent). This calculation yielded a value of $k_1^\infty = 1.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with an uncertainty of a factor of *ca.* 2 related to the uncertainty in the value of $<\Delta E>_{\text{down}}$. Within error this calculation and our measurements confirm Jasinski's result.

When the RRKM calculation was repeated under the conditions of Inoue and Suzuki's study, $k_1/k_1^\infty$ values of between 0.01 and 0.02 were obtained. Within the uncertainties of the calculations and the experiments this supports the contention that the apparent discrepancy between this study and Jasinski's is that reaction (1) is substantially into the pressure dependent (3rd order) region.

Taking Jasinski's value as the most reliable current estimate of $k_1^\infty$ at 298 K, in combination with the $k_{-1}^\infty$ calculated from the Arrhenius equation[9] given, $K_{-1,1} = 1.42 \times 10^{-35}$ atm and $\Delta G_{-1,1}^\circ = 47.5$ kcal mol$^{-1}$. Use of tabulated entropy values[11–13] leads to $\Delta S_{-1,1}^\circ = 31.9$ cal K$^{-1}$ mol$^{-1}$ and therefore $\Delta H_{-1,1}^\circ = 57.0$ kcal mol$^{-1}$. Taken with the current $\Delta H_f^\circ(SiH_4)$[11] this yields $\Delta H_f^\circ(SiH_2) = 65.2$ kcal mol$^{-1}$. Uncertainties should amount to no more than $\pm 1.5$ kcal mol$^{-1}$.

A principal difficulty with this value is its apparent inconsistency with the thermochemistry of step (2). This may be checked with the aid of another of the new, directly-obtained rate constants,[5] $k_{-2} = 1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. If it is reasonably assumed to be temperature independent, it may be combined with the separately measured $k_2 = 1.33 \times 10^{-4}$ s$^{-1}$ to give $K_{2,-2} = 9.5 \times 10^{-14}$ atm and $\Delta G_{2,-2}^\circ = 34.8$ kcal mol$^{-1}$ at 585 K. Combination, as before, with $\Delta S_{2,-2}^\circ$ and temperature correction yields $\Delta H_{2,-2}^\circ = 54.5$ kcal mol$^{-1}$ at 298 K. Taken with the current $\Delta H_f^\circ(Si_2H_6)$[12] and $\Delta H_f^\circ(SiH_4)$[11] this yields $\Delta H_f^\circ(SiH_2) = 65.4$ kcal mol$^{-1}$. Thus the directly measured $SiH_2$ rate constants and the older pyrolysis results are consistent in an *absolute* sense.

The difficulty with the latter calculation is that it implies for step (2), $\log k_2^\infty/\text{s}^{-1} = 16.0 − 53.2$ kcal mol$^{-1}$/$RT$ ln10 which disagrees with the measured[6,7] Arrhenius equation. However, the latter is derived, in part, from shock tube measurements at high dilution in argon in the range 850—1000 K. Dzarnoski *et al.*[6] noted the requirement to make unimolecular fall-off corrections in this range and estimated $k_2/k_2^\infty$ to be in the range 0.9—0.7 under experimental conditions. We have repeated these RRKM calculations for a transition state model consistent with the above Arrhenius equation with weak collisional activation. Using a stepladder model with $<\Delta E>_{\text{down}} = 300$ cm$^{-1}$ (consistent with other evidence on such systems[10]) we find $k_2/k_2^\infty$ to lie in the considerably lower range 0.3—0.13. The absolute rate constants ($k_2$) with our model are in reasonable agreement with experiment[6] and give ($P = 2500$ Torr) $\log(k_2/\text{s}^{-1}) = 13.25 − 44.3$ kcal mol$^{-1}$/$RT$ ln10, also in tolerable agreement. We cannot be certain that all the parameters of our calculation are correct but neither can Dzarnoski *et al.*[6] and the *measured* rate constants can be as

well accommodated to this alternative Arrhenius equation. This makes further experimentation on $Si_2H_6$ decomposition desirable and for the present removes this system as an impediment to the revised $\Delta H_f^{\circ}(SiH_2)$.

There are other systems whose analysis apparently conflicts with this new figure but we cannot discuss them all within the confines of this communication. It is, however, worthwhile to consider one important one. John and Purnell[2] studied the pyrolysis of $Si_2H_6$ in the presence of hydrogen and found no inhibition of $Si_3H_8$ formation *via* reaction (5) and hence argued that step (1) must be slow. However, our RRKM calculations on $k_1$ taken with the value of $k_5$[5] show that virtually no inhibition (only *ca.* 3%) is to be expected even with the high value of $k_1^{\circ}$.

$$SiH_2 + Si_2H_6 \xrightarrow{k_5} Si_3H_8 \qquad (5)$$
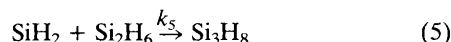
We conclude that the older pyrolysis data are not in conflict with the upward revision of $\Delta H_f^{\circ}(SiH_2)$ to $65.3 \pm 1.5$ kcal mol$^{-1}$, a value in more satisfactory agreement with the recent theoretical calculations[3,4] and further experimental work.[14]

*Received, 30th April 1986; Com. 572*

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