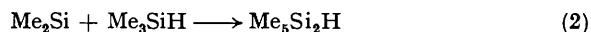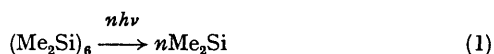# Kinetics of Insertion Reactions of Dimethylsilylene

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*Summary* Dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane, inserts into the silicon–hydrogen bond in trimethylsilane and pentamethyldisilane with approximately zero activation energy, while insertion into hydrogen chloride requires an activation energy of 28 kJ mol$^{-1}$; the results for silicon–hydrogen insertion shed some light on the mechanism of the thermolysis of pentamethyldisilane.

THERE is considerable interest in the chemistry of silicon-containing intermediates, but little kinetic information about their reactions. We report the first measurement of relative activation energies and rates for some gas-phase insertion reactions of dimethylsilylene. These results help to explain some curious kinetic features of the thermolysis of pentamethyldisilane.[1]

Photolysis of dodecamethylcyclohexasilane at 254 nm was used as the source of dimethylsilylene. This is a clean source in solution[2,3] found by us to be slightly complicated in the gas phase by successive elimination of dimethylsilylene and by minor reactions involving dimethylsilyl and trimethylsilyl radicals. Mixtures of dodecamethylcyclohexasilane (6 mmHg) and trimethylsilane (40 mmHg) were photolysed for a fixed time between 413 and 510 K. The only measurable products were pentamethyldisilane (2·1 mmHg) and heptamethyltrisilane (0·6 mmHg), both yields being invariant with temperature within 5%. These results are consistent with the sequence shown in reactions (1)—(4). Reaction (4) is known to be rapid in the thermolysis of pentamethyldisilane,[1] and is likely to occur here to

$$\overset{nh\nu}{(Me_2Si)_6 \longrightarrow nMe_2Si} \qquad (1)$$

$$Me_2Si + Me_3SiH \longrightarrow Me_5Si_2H \qquad (2)$$

$$Me_2Si + Me_5Si_2H \longrightarrow Me_7Si_3H \qquad (3)$$

$$Me_2Si \longrightarrow \text{surface polymer} \qquad (4)$$

some extent. From the product yields, $k_3/k_2 = ca.$ 3 over the temperature range. The steady-state expressions for the formation of these products both contain $k_2$, $k_3$, and $k_4$; since the yields were independent of temperature, $E_2 = E_3 = E_4$ (between 413 and 510 K an uncertainty of 5% in the yields corresponds to a variation of less than 1 kJ mol$^{-1}$ in activation energy). In otherwise identical experiments with a mixture of pentamethyldisilane (17·8 mmHg) and *sym*-tetramethyldisilane (2·2 mmHg) instead of the tri-methylsilane, the reactions were (1), (3), (4), and (5). The

$$Me_2Si + Me_4Si_2H_2 \rightarrow Me_6Si_3H_2 \qquad (5)$$

yields of heptamethyltrisilane (3·4 mmHg) and hexamethyl-trisilane (0·6 mmHg) were likewise independent of temperature within 5%, with $k_5/k_3 = ca.$ 1·4. Hence $E_2 = E_3 = E_4 = E_5$ and $k_2:k_3:k_5 = ca.$ 1:3:4.

Photolysis of dodecamethylcyclohexasilane (6 mmHg) with hydrogen chloride (40 mmHg) proceeded by reactions (1), (4), and (6). However, the yields of dimethylchloro-silane varied with temperature from 1·2 mmHg at 423 K to

$$Me_2Si + HCl \rightarrow Me_2SiHCl \qquad (6)$$

9·4 mmHg at 478 K, corresponding to an activation energy of 27·7 $\pm$ 1 kJ mol$^{-1}$. Attempts to carry out similar experiments with chlorosilanes were unsuccessful, as they were in solution.[2]

In the absence of a known reference reaction, Arrhenius parameters for reactions (2), (3), (5), and (6) cannot be evaluated absolutely. However, considering the close equality of $E_2$, $E_3$, $E_4$, and $E_5$, and the nature of reaction (4), it is very likely that these activation energies are all close to zero. If so, $E_6$ would be 28 kJ mol$^{-1}$, which is reasonable in relation to the estimate[4] of 23 kJ mol$^{-1}$ for SiH$_2$ + H$_2$ → SiH$_4$.

Our results for reactions (2) and (3) are of interest in relation to earlier work on the thermolysis of pentamethyl-disilane.[1] The reaction sequence (−2), (2), (3), (−3) was expected, by analogy with disilane[5] and methyldisilane.[6]

$$Me_5Si_2H \rightleftharpoons Me_2Si + Me_3SiH \qquad (-2), (2)$$

$$Me_2Si + Me_5Si_2H \rightleftharpoons Me_7Si_3H \qquad (3), (-3)$$
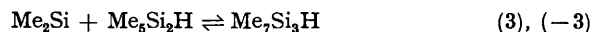
For up to 5% decomposition there was clear evidence for reaction $(-2)$, which had Arrhenius parameters consistent with expectation;[5—7] but no heptamethyltrisilane was observed, whereas trisilanes were found from the other disilanes.[5,6] When kinetic measurements were continued beyond 5%, the onset of the reverse reaction (2) caused curvature in the integrated rate plots, this curvature occurring at ca. 7% decomposition at 620 K, but not until at least 20% decomposition at 699 K. This behaviour raised questions[1] about the size of $E_2$ and $E_3$.

We have now simulated the experimental results by computer-aided numerical integration,[8] using the experimental Arrhenius parameters[1] for reaction $(-2)$, with $E_2 = E_3 = 0$ and $A_3 = (3 \times A_2)$. The reasonable (but not unique) estimates of the Arrhenius parameters in the Table gave excellent agreement with experiment. This agreement was destroyed when $E_2 = E_3 \geqslant 5$ kJ mol$^{-1}$.

TABLE. Arrhenius parameters for thermolysis of pentamethyldisilane.

| Reaction | $(-2)$ | $(2)$ | $(3)$ | $(-3)$ | $(4)$ |
|---|---|---|---|---|---|
| $\log_{10} A$ | 12·93 | 9·0 | 9·5 | 13·0 | 5·0 |
| $E$/kJ mol$^{-1}$ | 198 | 0 | 0 | 150 | 0 |

a First order $A$ factors are in s$^{-1}$ and second order in dm$^3$ mol$^{-1}$ s$^{-1}$.

The temperature-dependence of the onset of reaction (2) in the thermolysis simply arose because $k_{-2}$ becomes larger relative to the other rate constants as the temperature is raised, thus maintaining first-order behaviour to higher percentage decomposition.

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