Reaction of Trimethyl- and Dimethyl-Silyl Radicals with Pentamethyldisilane

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The rate constant for the H atom abstraction of trimethylsilyl radicals from pentamethyldisilane ($k(4)$) was measured relative to the trimethylsilyl combination reaction $k(3)$. A value for $\frac{k(4)}{\sqrt{k(3)}} = (8.53 \pm 0.08) \cdot 10^{-11}\ \mathrm{cm}^{3/2}\ \mathrm{s}^{-1/2}$ was obtained. For the dimethylsilyl radical, a smaller value for the corresponding rate constant ratio $(5.9 \pm 0.2) \cdot 10^{-11}\ \mathrm{cm}^{3/2}\ \mathrm{s}^{-1/2}$ was measured, and this was attributed to a disproportionation reaction between the dimethylsilyl and the pentamethyldisilyl radical leading to dimethylsilylene.

Key words: Hydrogen abstraction, silyl radicals, pentamethyldisilane, disproportionation reaction.

Introduction

Our investigation of the mercury-sensitized photolysis of pentamethyldisilane [1] indicates a relatively fast H atom abstraction from Me_5Si_2H by silyl radicals. Such reactions are scarce in the literature. The main reason lies in a lack of suitable silyl radical sources. The cleanest way to produce silyl radicals is by hydrogen abstraction from the corresponding silane. In [2] it has been shown that in the case of Me_3SiH, excited mercury abstracts hydrogen 26 ± 11 times faster from the Si–H bond than from the C–H bonds. For H atoms this value increases to 308 ± 107. However, the major disadvantage of this method is that the stable product of the abstraction process and the radical precursor are identical. Therefore Gammie et al. [3] used bis-trimethylsilylmercury as a radical source, and their work represents the only source of relative rate constants for this type of reaction. In our investigation, we used H atoms to generate di- and tri-methylsilyl radicals from di- and tri-methylsilane. The reaction conditions chosen were such that the extent of the reaction could be followed by a stable product.

Mixtures of Hg, $1.7 \cdot 10^{19}\ \mathrm{cm}^{-3}$ H_2, $9 \cdot 10^{17}\ \mathrm{cm}^{-3}$ Me_3SiH or Me_2SiH_2, and Me_5Si_2H in the concentration range of $5.4 \cdot 10^{14}\ \mathrm{cm}^{-3} - 5.2 \cdot 10^{15}\ \mathrm{cm}^{-3}$ were exposed to 254 nm Hg resonance radiation. The photoproducts were quantified by GC(FID) [4].

The excited Hg atoms are almost exclusively quenched by H_2 [5]:

$$Hg^* + H_2 \rightarrow 2H + Hg. \tag{1}$$

The H atoms react largely ($\approx 98\%$) with the monosilane [6] RH ($R = Me_3Si, Me_2SiH$):

$$H + RH \rightarrow H_2 + R. \tag{2}$$

The radical R may then react in two ways:

$$2R \rightarrow R_2, \tag{3}$$

$$R + Me_5Si_2H \rightarrow RH + Me_5Si_2. \tag{4}$$

If the chosen conditions are such that $k(3)[R] \gg k(4)[Me_5Si_2H]$, and under the provision that the rate constants for the radical combination and cross-combination

$$2Me_5Si_2 \rightarrow Me_{10}Si_4 \tag{5}$$

and

$$Me_5Si_2 + R \rightarrow Me_5Si_2R \tag{6}$$

do not differ greatly, the condition of $[R]_{ss} \gg [Me_5Si_2]_{ss}$ will hold. In such a case, (6) will be the main reaction path for the Me_5Si_2 radical, and in a very good approximation $[Me_5Si_2R]$ will be equal to the (not measurable) concentration of RH formed in reaction (4). In agreement with these considerations, no $Me_{10}Si_4$ was found in our experiments.

A plot of $[Me_5Si_2R]/([R_2]t)^{1/2}$ versus $[Me_5Si_2H]$ should give a straight line (Figure 1). The slope of this

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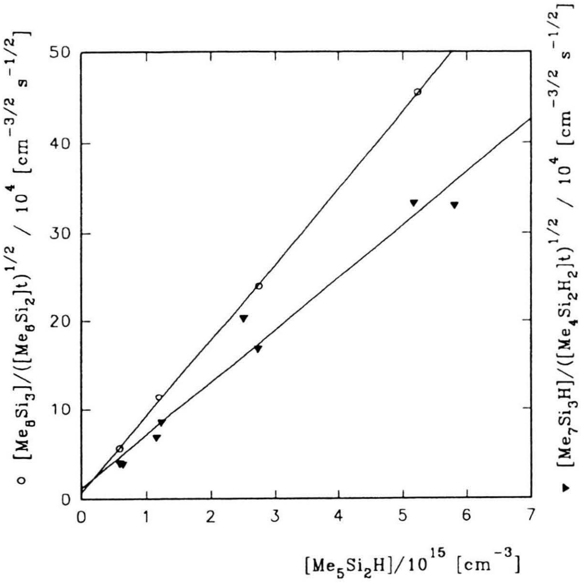

Fig. 1. Plot of $[Me_5Si_2R]/([R_2]t)^{1/2}$ versus $[Me_5Si_2H]$ ($R = Me_3Si$, Me_2SiH).

line is given by $k(4)/k(3)^{1/2}$. For Me_3Si we find

$$\frac{k(4)}{\sqrt{k(3)}} = (8.53 \pm 0.08) \cdot 10^{-11}\ \mathrm{cm}^{3/2}\,\mathrm{s}^{-1/2},$$

and for Me_2SiH

$$\frac{k(4)}{\sqrt{k(3)}} = (5.9 \pm 0.2) \cdot 10^{-11}\ \mathrm{cm}^{3/2}\,\mathrm{s}^{-1/2}.$$

If we take a value $k(3) = 3 \cdot 10^{-11}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$ [7, 8] for the recombination of R, $k(4)$ can be calculated to be $4.7 \cdot 10^{-16}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$ for Me_3Si and $3.2 \cdot 10^{-16}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$ for Me_2SiH. A number of reasons could be responsible for the different relative abstraction rate constants for Me_3Si and Me_2SiH. For example, the abstraction reaction rate constant $k(4)$ could be smaller for Me_2SiH than for Me_3Si, or the combination rate constant $k(3)$ could be larger for Me_2SiH than for Me_3Si. Neither of these two possibilities can be excluded by us. There exists yet another possibility, disproportionation reactions

$$2\,Me_2SiH \rightarrow Me_2Si + Me_2SiH_2, \qquad (7)$$

$$Me_2SiH + Me_5Si_2 \rightarrow Me_2Si + Me_5Si_2H \qquad (8)$$

in the case of Me_2SiH may be prominent.

The Me_2Si may insert into the Si–H bond of Me_2SiH_2 or Me_5Si_2H:

$$Me_2Si + Me_2SiH_2 \rightarrow Me_4Si_2H_2, \qquad (9)$$

$$Me_2Si + Me_5Si_2H \rightarrow Me_7Si_3H. \qquad (10)$$

The occurrence of (8) in competition with (6) leads to a decrease of Me_5Si_2R under the prevailing conditions $k(9)[Me_2SiH_2] \gg k(10)[Me_5Si_2H]$ [9]. Taking (7)–(9) into account, we arrive at the following equation

$$\frac{[Me_7Si_3H]}{[Me_5Si_2H]t} = \frac{k(6)}{k(6)+k(8)}\,\frac{k(4)}{\sqrt{k(3)+k(7)}}\sqrt{I_{\mathrm{abs}}} - \frac{k(6)}{k(6)+k(8)}\,\frac{k(4)}{2(k(3)+k(7))}[Me_5Si_2H]. \qquad (11)$$

For Me_2SiH as well as for Me_3Si we plotted the data according to (11) (Figure 2). The slope is small and loaded with a large error, but the intercept can be determined reasonably well. For Me_2SiH we get

$$\left(\frac{k(6)}{k(6)+k(8)}\,\frac{k(4)}{\sqrt{k(3)+k(7)}}\sqrt{I_{\mathrm{abs}}}\right) = (2.93 \pm 0.15) \cdot 10^{-4}\ \mathrm{s}^{-1},$$

and for Me_3Si we get an intercept of $(4.44 \pm 0.06) \cdot 10^{-4}\ \mathrm{s}^{-1}$. In the case of Me_3Si, $k(8)$ equals zero, and if we assume identical values for the second factor we

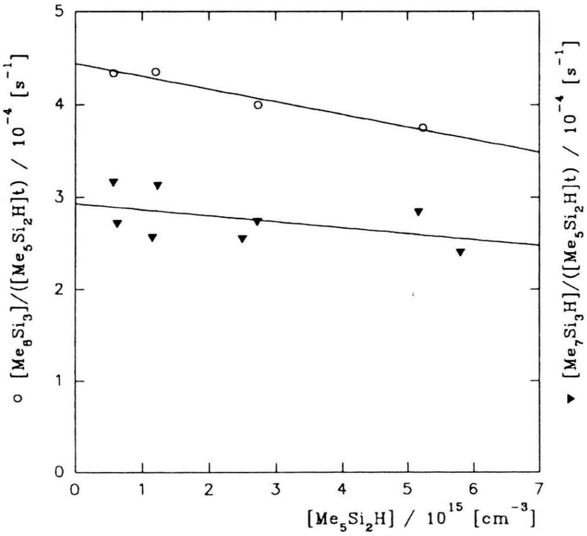

Fig. 2. Plot of $[Me_5Si_2R]/([Me_5Si_2H]t)$ versus $[Me_5Si_2H]$ ($R = Me_3Si$, Me_2SiH).

arrive at

$$\frac{k(6)}{k(6)+k(8)} = 0.66 \pm 0.16\,.$$

The above value seems appropriate, since it compares well with the branching ratio for Me_2SiH [10] $k(7)/(k(7)+k(3)) = 0.64$.

Our value for the relative rate constant for the H atom abstraction from Me_5Si_2H by Me_3Si is almost a factor of ten smaller than the value for $Me_3Si + Si_2H_6$ [3], despite the smaller bond dissociation energy of Me_5Si_2H ($DH^\theta(Si_2H_5-H) = 372$ kJ/mol [11], $DH^\theta(Me_5Si_2-H) = 357$ kJ/mol [12], $DH^\theta(Me_3Si-H) = 397$ kJ/mol [13]). Our results with GeH_4 [14] suggest that the rate constant for H abstraction by Me_3Si depends very sensitively on the dissociation energy of the X–H bond which is to be broken. Therefore we think that the results presented here are incompatible with the results given in [3], and that the main reason is the different Me_3Si source used in these experiments. At first glance, $(Me_3Si)_2Hg$ looks very attractive as a source of Me_3Si radicals. But the photochemistry of this compound seems to offer a number of surprises. Lehnig et al. [15], e.g., have shown that Me_3Si radicals undergo substitution reactions at the Si as well as at the Hg-center. This Me_3Si source was found to be unsuitable by us because of severe surface problems.

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