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Rate constants for H + $(CH_3)_{4-n}SiH_n$, $n = 1$–4

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Abstract

Rate constants for the reactions of H atoms with SiH_4 and the methylsilanes, $(CH_3)_{4-n}SiH_n$, $n = 1$–4, have been measured at 298 K in pulsed photolysis experiments with H atoms produced by the mercury-sensitised photolysis of H_2 and monitored by Lyman-α absorption. The values obtained, for $n = 1$–4, respectively, are: $k_1 = (2.70 \pm 0.20) \times 10^{-13}$, $k_2 = (3.94 \pm 0.29) \times 10^{-13}$, $k_3 = (3.88 \pm 0.21) \times 10^{-13}$, and $k_4 = (3.38 \pm 0.16) \times 10^{-13}$ cm^3 s^{-1}. These results show that methyl substitution enhances the reactivity of the Si–H bond towards H atom attack, and comparisons are made with the corresponding reactions of Cl, Br and O atoms. © 1998 Elsevier Science B.V.

1. Introduction

Whether methyl substitution has an effect on the strength and reactivity of the Si–H bond in SiH_4 is a contentious topic [1]. The results of Ding and Marshall [1,2] indicate that for Cl and Br attack the room temperature rate constant corrected for reaction path degeneracy, k/n, is higher for $(CH_3)_3SiH$ than SiH_4 by a factor of about 4. Although in each case this was accompanied by an increase in A-factor, an increase in activation energy was also observed, from which they deduced that the dissociation energy of the Si–H bond in $(CH_3)_3SiH$ is 14 kJ mol^{-1} higher than in SiH_4. By contrast, for O atom attack, Horie et al. [3] found that k/n was greater for $(CH_3)_3SiH$ than SiH_4 by a factor of 35. According to unpublished results referred to by Ding and Marshall [1], this is because the activation energy of the $(CH_3)_3SiH$ reaction is about 5 kJ mol^{-1} less than for SiH_4, a result which could be interpreted as an indication that methyl substitution reduces the Si–H dissociation energy. Both of these conclusions are contrary to the hitherto accepted view that methylation has no discernible effect on the strength of the Si–H bond [4].

The reactions of H atoms offer a less complicated yardstick of reactivity than attack by more complex species, and therefore occupy a central position in this discussion. Unfortunately, although many investigations of the reactions of H atoms with SiH_4 and the methysilanes have been reported, the values of the rate constants obtained cover a wide range, making it difficult to establish reactivity patterns. Further uncertainty has been introduced recently by Marshall and coworkers [5], who have called into question the results of Potzinger and coworkers [6] for SiH_4, results which until then had been regarded as the most reliable available. This in turn casts doubt on their [6] data for the methylsilane reactions, and in view of the topicality of the effect of methyl substitution on the reactivity of the Si–H bond and the thermochemistry of the corresponding silyl radicals [1,4,7], the kinetics of H atom attack on the methylsilanes are now likely to become the subject of renewed interest. We have therefore undertaken a fresh investigation of the reactions of H atoms with SiH_4

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and the methylsilanes. The values of the rate constants obtained are compared with those found in previous studies, and with results reported for attack by Cl, Br and O atoms.

2. Experimental

The pulsed photolysis system used in these experiments has been described previously [8]. Briefly, H atoms are produced by mercury-sensitized photolysis (253.7 nm) of H_2 by flowing a dilute substrate-H_2 mixture over a drop of mercury in a thermostatted reservoir, and then through a quartz reaction cell, where it is illuminated with light from a pulsed low-pressure mercury lamp. The concentration of H atoms is followed after the photolysis pulse by monitoring the radiation transmitted through the cell from a Lyman-α lamp situated perpendicular to the photolysis lamp. The Lyman-α line (121.6 nm) is selected by a vacuum-ultraviolet monochromator and detected by a solar-blind photomultiplier, the output from which is amplified, digitised and then counted on a multichannel scaler card installed in a PC. The PC also controls the variables that define the experimental reaction conditions (length of the photolysis pulse, period between pulses, flow rates, temperature and data collection time) by means of a file created for each series of runs. In these experiments, good quality data were obtained between 15 and 60 min.

Mixtures of silane (0.80–1.10 Torr) and H_2 ($\approx$ 900 Torr) were prepared in a 20 l bulb, allowed to stand overnight to allow complete mixing, and used within 48 h to ensure constancy of composition. To achieve the desired concentration, the silane–H_2 mixture (flow rate 1–10 standard $cm^3\ min^{-1}$) was diluted by combining it with a stream of hydrogen in a mixing chamber, the total flow rate being maintained at 500 standard $cm^3\ min^{-1}$. The pressure in the reaction cell was held constant at 500 Torr.

H_2 (Linde, 99.999%) was passed through an Oxytrap and an Indicating Oxytrap (Alltech) to absorb any residual traces of oxygen and water. SiH_4 (Matheson, 99.99%), and the methylsilanes (Peninsular ChemResearch, 99%) were further purified by low-temperature trap-to-trap fractionation, and thoroughly degassed.

3. Results

In order to ensure that pseudo first-order conditions prevailed in our work, the concentration of H atoms produced by the photolytic pulse was determined in a separate set of experiments by the method described in detail in previous papers [8,9]. The resultant calibration plot relating $\ln(I_0/I)$ to [H], where I_0/I is the Lyman-α transmittance, showed that Beer–Lambert behaviour was followed up to [H] $\approx 3.0 \times 10^{12}$ cm^{-3}, corresponding to a photolysis pulse length of 3.8 ms for the methylsilanes, and 6.0 ms for SiH_4, where a mesh was inserted between the photolysis lamp and the reaction cell. All rate constant measurements were therefore carried out with maximum pulse lengths less than these values, and the resultant H atom concentrations led to [silane]/[H] ratios in the range 10–500.

Under these conditions, the variation of [H] with time immediately after the photolysis pulse is given by $[H] = [H]_0 \exp(-k^1 t)$, where k^1 is the pseudo first-order rate constant. Substitution of the Beer–Lambert expression yields $I = I_0 \exp\{-P \exp(-k^1 t)\}$, where $P = Q[H]_0$, and Q is the slope of the calibration plot. The value of k^1 was obtained by fitting this double exponential function to the experimental decay data by a non-linear least-squares procedure (Wavemetrics Igor Pro) with I_0, P and k^1 as adjustable parameters.

As we have pointed out previously [9], the value of k^1 determined in this manner does not rely on absolute values of [H] being known, and hence does not depend on the values of the intensity of the absorbed photolysis light and the rate constants of the reactions leading to the production of H atoms in the Hg-sensitized photolysis of H_2. The only conditions that need to be fulfilled are that pseudo first-order concentration ratios be established, and H atom concentrations be restricted to the Beer–Lambert region.

The values of k^1 obtained increased strongly with photolysis pulse length. As has been shown previously [6,8], this behaviour can be accounted for by the occurrence of secondary reactions between the H atom and the silyl radical formed by H-abstraction from the silane. As before, to obtain the true value of k^1, several experiments were carried out at different pulse lengths, and the results extrapolated to zero.

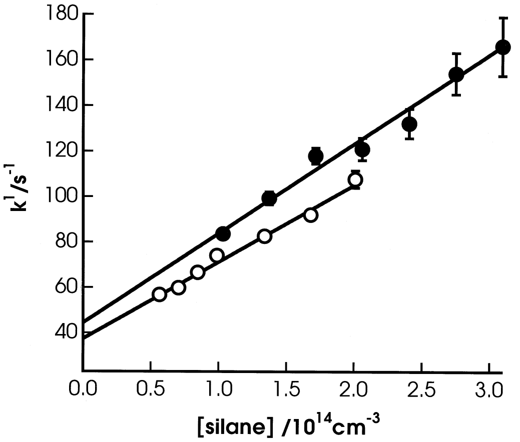

Fig. 1. Plot of k^1 versus [silane] for the evaluation of k: (○) SiH_4; (●) $(CH_3)_2SiH_2$.

The bimolecular rate constant for H atom attack on the silane, k, is related to k^1 by $k^1 = k[\text{silane}] + k_w$, where k_w is the rate constant for the diffusion of H atoms out of the Lyman-α observation zone. Values of k^1 were determined at several silane concentrations, and k was then evaluated from the slope of a plot of k^1 versus [silane]. Typical plots, for SiH_4 and $(CH_3)_2SiH_2$, are shown in Fig. 1, and the values of k obtained for $(CH_3)_{4-n}SiH_n$, $n = 1$–4, are: $k_1 = (2.70 \pm 0.20) \times 10^{-13}$, $k_2 = (3.94 \pm 0.29) \times 10^{-13}$, $k_3 = (3.88 \pm 0.21) \times 10^{-13}$ and $k_4 = (3.38 \pm 0.16) \times 10^{-13}$ cm^3 s^{-1}, where the error limits correspond to one standard deviation.

4. Discussion

4.1. $H + SiH_4$

The rate constants determined in this work are compared with previously reported values in Table 1 (also see Refs. [21,22]). Setting aside the anomalously high values, we see that the remaining nine rate constants fall within the range 2.0–4.6 $\times 10^{-13}$ cm^3 s^{-1}. It is interesting to note that the average of these is $(3.4 \pm 0.5) \times 10^{-13}$ cm^3 s^{-1}, the same as that found in this work, and close to the best value suggested by Arthur and Bell [23] in their review of data published prior to 1978, $(3.5 \pm 0.7) \times 10^{-13}$ cm^3 s^{-1}.

Inspection of Table 1 shows that our value of the rate constant is a factor of 1.7 higher than that of Potzinger and coworkers [6]. This difference in results is unexpected, as our experimental system is based on an earlier version constructed by Potzinger, Reimann and coworkers [6,10]. The reason for the disparity is not obvious, but may be connected with the H atom concentrations employed in our work, which are at least a factor of 10 less than those in the experiments of Potzinger and coworkers. This allows the experimental Lyman-α decay curve to be fitted to a double exponential function to evaluate k^1, rather than the triple exponential function used in the earlier work, and consequently extrapolation of k^1 values to zero pulse-length is now more straightforward. In addition, the automation of some aspects of the experiment, described previously [8], has led to much more data being collected for a particular reaction system than formerly, and this may also contribute to more reliable and consistent results being obtained.

The most recent study of $H + SiH_4$ is that of Marshall and coworkers [5]. Our only reservation concerning their work is that H atom concentrations were not independently determined, and although it is unlikely that pseudo first-order conditions did not apply in their work, it was not verified. Their rate constant is 18% lower than ours, but having regard

Table 1
Rate constants for $H + SiH_4$

T (K)	k (10^{-13} cm^3 s^{-1})	Ref.
298	> 2.2	[11]
room	21 ± 7[a]	[12]
room	26 ± 3	[13]
300	85 ± 34	[14]
300	4.6 ± 0.3	[15]
305	4.4 ± 1.0[b]	[16]
room	4.4 ± 0.7	[17]
294	2.0 ± 0.1	[6]
293	2.2 ± 0.2	[18]
room	4.0	[19]
room	2.5 ± 0.5	[20]
298	2.8 ± 0.3[c]	[5]
298	3.4 ± 0.3	this work

[a] Relative to $k(H + C_2H_2) = (3.78 \pm 0.30) \times 10^{-13}$ cm^3 s^{-1} [21].
[b] Relative to $k(H + C_2H_4) = (1.24 \pm 0.22) \times 10^{-12}$ cm^3 s^{-1} [22].
[c] Evaluated at 298 K from quoted Arrhenius parameters.

Table 2
Rate constants for $H+(CH_3)_{4-n}SiH_n$, $n=1$–3

T (K)	k (10^{-13} cm^3 s^{-1})	Ref.
	CH_3SiH_3	
room	12.6 ± 3.8^a	[12]
room	11.5 ± 2.0	[13]
305	6.3 ± 1.2^b	[16]
room	3.8 ± 0.2	[17]
291	4.0 ± 0.1	[6]
298	3.9 ± 0.2	this work
	$(CH_3)_2SiH_2$	
room	17.6 ± 4.8^a	[12]
room	4.1 ± 0.9	[13]
305	6.8 ± 1.3^b	[16]
room	2.8 ± 0.2	[17]
292	3.1 ± 0.1	[6]
298	3.9 ± 0.3	this work
	$(CH_3)_3SiH$	
room	15.9 ± 4.0^a	[12]
room	3.7 ± 1.0	[13]
305	5.8 ± 1.2^b	[16]
290	2.6 ± 0.1	[6]
298	2.7 ± 0.2	this work

[a] Relative to $k(H+C_2H_2)=(3.78\pm0.30)\times10^{-13}$ cm^3 s^{-1} [21].
[b] Relative to $k(H+C_2H_4)=(1.24\pm0.22)\times10^{-12}$ cm^3 s^{-1} [22].

to the range of values reported for this reaction, this constitutes an acceptable degree of agreement.

4.2. $H+(CH_3)_{4-n}SiH_n$, $n=1$–3

Before ascribing the measured rate constants to attack on the Si–H bonds in the methylsilanes, the possibility must be considered that attack also occurs on their methyl groups. Arrhenius parameters for the reaction of H atoms with $(CH_3)_4Si$ have been determined by Potzinger and coworkers [24], and the rate constant evaluated at 298 K is 1.15×10^{-16} cm^3 s^{-1}. Taking into account the number of methyl groups in the various methylsilanes, the resultant rate constants are 0.03, 0.02 and 0.01% of the experimental values for $n=1$–3, respectively. The rate constants obtained in this work can therefore be confidently attributed to attack solely on the Si–H bonds of the methylsilanes.

Rate constants for H atom attack on the methylsilanes from this and previous studies are listed in Table 2. There is a clear separation between the values of Hong [12], Cowfer et al. [13], and Austin and Lampe [16], and those reported by Wörsdorfer et al. [17], Potzinger and coworkers [6], and in this work, the early values being much higher than the later ones.

The work of Wörsdorfer et al. and Potzinger and coworkers is from the same laboratory, the former employing the discharge-flow technique, the latter, pulsed photolysis-resonance absorption. While there is reasonable agreement between their rate constants for CH_3SiH_3 and $(CH_3)_2SiH_2$, the value obtained for SiH_4 in the discharge-flow experiments is more than twice that found by pulsed photolysis. Potzinger and coworkers have suggested that surface effects may have influenced the results of the earlier work, but as has been pointed out above, their value for SiH_4 now appears to be low compared with our value and that of Marshall and coworkers [5].

Comparison of our results for the methylsilanes with those of Potzinger and coworkers shows that there is agreement only for CH_3SiH_3. For both $(CH_3)_2SiH_2$ and $(CH_3)_3SiH$ our values are higher, the difference in the case of $(CH_3)_2SiH_2$ being particularly marked.

4.3. Reactivity trends

The effect of increasing methyl substitution on the reactivity of the Si–H bond can be seen by evaluating k/n, the rate constant corrected for reaction-path degeneracy, where n is the number of Si–H bonds.

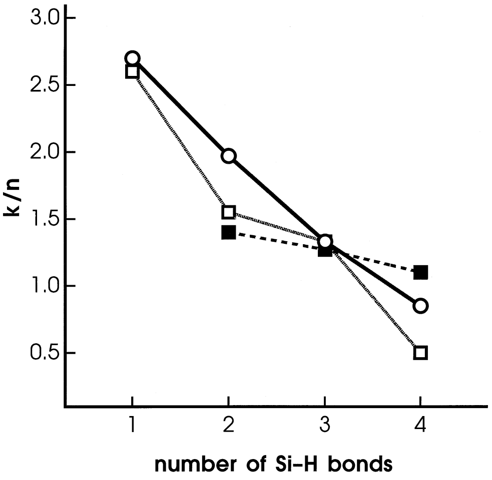

Fig. 2. Effect of methyl substitution on Si–H bond reactivity: (○) this work; (□) Ref. [6]; (■) Ref. [17].

A plot of k/n versus n comparing our results with those of Potzinger and coworkers and Wörsdorfer et al. is shown in Fig. 2. Our values show that methyl substitution leads to a progressive increase in Si–H bond reactivity. The same trend is followed by the values of Potzinger and coworkers, but as a result of their low rate constants for $(CH_3)_2SiH_2$ and SiH_4, their values are rather scattered. The data of Wörsdorfer et al. show little variation for the three silanes studied.

A comparison of the reactivity of $(CH_3)_3SiH$ and SiH_4 towards attack by various atoms is shown in Table 3. The ratios of the k/n values for $(CH_3)_3SiH$ and SiH_4 are 3.2, 2.8, 4.6 and 35, for H, Cl, Br and O attack, respectively. Thus the introduction of methyl groups enhances the reactivity of the Si–H bond to a similar extent for the H, Cl and Br reactions, but for O atom attack the effect is much more striking. For both the Cl and Br atom reactions, the Arrhenius parameters of Ding and Marshall [1,2] show that the observed reactivity increase from SiH_4 to $(CH_3)_3SiH$ is the result of an increase in the value of A/n, offset to some extent by an increase in activation energy. In the case of the O atom reactions, however, the unpublished results of Ding and Marshall [1] indicate that the activation energy for $(CH_3)_3SiH$ is substantially less than for SiH_4, and this leads to the much greater increase in k/n observed for these reactions. For H atom attack, despite an oddly low value for $(CH_3)_3SiH$, Potzinger and coworkers came to the conclusion that the activation energy was unaffected by methylation, and that the main contribution to the change in k/n along the series was a parallel change in A-factor.

The conflicting behaviour shown by the different attacking species points to the need for further studies of the temperature dependence of these reactions, particularly those involving H and O atom attack.

Table 3
Reactivity of $(CH_3)_3SiH$ and SiH_4 to atom attack

Silane	k/n (10^{-13} cm^3 s^{-1})	Ref.
	H	
$(CH_3)_3SiH$	2.7×10^{-13}	this work
SiH_4	0.85×10^{-13}	this work
	Cl	
$(CH_3)_3SiH$	1.56×10^{-10}[a]	[1]
SiH_4	0.554×10^{-10}[a]	[2]
	Br	
$(CH_3)_3SiH$	5.23×10^{-12}[a]	[1]
SiH_4	1.14×10^{-12}[a]	[2]
	O	
$(CH_3)_3SiH$	3.06×10^{-12}[b]	[3]
SiH_4	0.88×10^{-13}[b]	[3]

[a] Evaluated at 298 K from Arrhenius parameters.
[b] Room temperature.

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