Kinetic Studies and *ab initio* Investigations of the Reactions of Atomic Bromine with Methylsilane and Dimethylsilane

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The kinetics of the reactions of $\text{Br}[4p(^2P_J)]$ with CH_3SiH_3 (1) and $(\text{CH}_3)_2\text{SiH}_2$ (2) have been measured using flash photolysis/time-resolved atomic resonance spectroscopy over the temperature ranges 350–550 and 390–550 K, respectively. The results are $k_1 = (4.0 \pm 0.5) \times 10^{-10} \exp(-19.7 \pm 0.5 \text{ kJ mol}^{-1}/RT)$ and $k_2 = (4.3 \pm 0.8) \times 10^{-10} \exp(-21.6 \pm 0.7 \text{ kJ mol}^{-1}/RT)$ in units of $\text{cm}^3 \text{ s}^{-1}$, with confidence limits of ca. $\pm 13\%$. Assumed activation energies for the reverse reactions yield Si–H bond dissociation enthalpies, D_{298} , of 388 ± 5 and $392 \pm 5 \text{ kJ mol}^{-1}$ in methylsilane and dimethylsilane, respectively. These values and the Arrhenius parameters are intermediate between earlier results for $\text{Br} + \text{SiH}_4$ and $\text{Br} + (\text{CH}_3)_3\text{SiH}$, although the uncertainty in D_{298} is too great to establish a firm trend in D_{298} with the degree of methylation. The silanes and corresponding silyl radicals are characterized by *ab initio* methods at up to the MP4/6-31G*//HF/6-31G* level.

Fundamental thermochemical data such as bond strengths are important for the assessment of proposed reaction mechanisms and intermediates. In silicon chemistry, the Si–H bond dissociation enthalpies (D_{298}) in methyl-substituted silanes have been recommended to be the same as in SiH_4 .¹ We have recently suggested that $D_{298}[(\text{CH}_3)_3\text{Si}-\text{H}]$ is greater than $D_{298}(\text{SiH}_3-\text{H})$,² while contrary evidence of bond weakening comes from the spectroscopy of high overtones in silanes.^{3,4} Here we present the first kinetic measurements for the reactions

The results are combined with assumed activation energies for the reverse reactions, based on the analogous hydrocarbon reactions, to estimate $D_{298}(\text{Si}-\text{H})$ in methylsilane and dimethylsilane. The CH_3SiH_2 and $(\text{CH}_3)_2\text{SiH}$ radicals are characterized by *ab initio* methods and the results employed to derive independent estimates of D_{298} for comparison. The kinetic and thermochemical results are compared with our earlier measurements^{2,5} on

and allow us to look for trends in the Arrhenius parameters for the reactions of atomic bromine with silanes.

Methodology

Experimental Method

Details of the variable-temperature reactor and the experimental techniques for generating and monitoring halogen atoms in the gas phase have been given previously,^{5,6} and are described briefly. CH_3SiH_3 and $(\text{CH}_3)_2\text{SiH}_2$ (Hüls, minimum purity 97%) were separated from any non-condensable impurities by three freeze-pump-thaw cycles at 77 K. Atomic bromine, $4p(^2P_J)$, is formed by pulsed photolysis of CH_2Br_2 with a small flashlamp. The Br then reacts with an excess of silane under pseudo-first-order conditions, with an exponential decrease of $[\text{Br}]$ characterized by a decay coefficient k_{psl} between 10 and 1000 s^{-1} . The relative concentration of $[\text{Br}]$ is measured by time-resolved atomic resonance fluorescence at $\lambda = 149\text{--}163 \text{ nm}$.⁷ Repetitive pulsing (1–2 Hz) and signal averaging are employed. Fresh gas mixtures flow into the reactor to replenish the reagents between photolysis flashes,

but the gas residence time τ_{res} is long compared with the kinetic timescale so the conditions are pseudo-static. The slopes of plots of k_{psl} vs. silane concentration yield the second-order rate constants for (1) and (2), k_1 and k_2 . The initial $[\text{Br}]$ was varied by changing the flashlamp energy E_F to see whether this affected the measured k_1 and k_2 .

As in previous experiments,^{5,6} the temperature of the gas in the reaction zone was measured before and after each k determination with a Type K thermocouple sheathed to prevent chemical and mechanical damage, but not shielded against radiative heat transfer to or from the walls of the reactor. Radiation errors⁸ were determined in separate experiments where the unshielded thermocouple was alternately uncovered and covered with a moveable radiation shield. The resulting change in measured T , ΔT , was fitted as a cubic function of T . ΔT was observed to be essentially independent (to within $\pm 2 \text{ K}$ or less) of the bath gas pressure and velocity over a wide range of conditions. The radiation error is inversely proportional to $n+1$, where n is the number of shields employed,⁸ and thus the correction to the unshielded thermocouple reading is $-\Delta T$, which is zero at the extremes of the range 290–850 K, and reaches a peak of 10 K at ca. 520 K. After this correction we allowed for a $\pm 2\%$ uncertainty in T to cover errors in the correction procedure and uncertainty in the thermocouple calibration.

Ab initio Calculations

$D_0(\text{Si}-\text{H})$ in a general silane R_3SiH is related to the known⁹ $D_0(\text{SiH}_3-\text{H})$ by the homodesmotic reaction

which conserves the number and type of each bond, and for which ΔH_0 equals $D_0(\text{R}_3\text{Si}-\text{H}) - D_0(\text{SiH}_3-\text{H})$. The geometry of each species was obtained at the Hartree–Fock (HF) level of theory, using *ab initio* methods¹⁰ implemented in the Gaussian 90 program.¹¹ The split-valence plus polarization 6-31G* atomic basis set was employed. Harmonic vibrational frequencies were calculated at each minimum-energy structure and were then scaled by a factor of 0.89 to correct for known deficiencies in the HF frequencies. The scaled frequencies yield the zero-point vibrational energy (ZPE). An energy correction for electron correlation was made with Møller–Plesset perturbation theory at up to fourth order with the 6-31G* basis set, using the frozen core approximation, and the results are denoted as MP4/6-31G*.

Results

Kinetic Analysis

Initial checks showed that photolysis of the silanes alone yielded no detected H atoms, and that there was no interference with the fluorescence detection of Br. Eighteen k_1 measurements are summarized in Table 1. The $\pm\sigma_{k_1}$ values listed in Table 1 reflect factors that contribute to the uncertainty of k_1 derived from each set of k_{psl} measurements as a function of $[\text{CH}_3\text{SiH}_3]$, primarily the scatter in the plot of k_{psl} vs. $[\text{CH}_3\text{SiH}_3]$. An improvement over our previous experiments^{2,5} is the use of smaller $[\text{CH}_2\text{Br}_2]$, which leads to reduced initial $[\text{Br}]$ and thus less consumption of Br by secondary radical reactions. The observed independence of k_1 from E_{F} shows that reaction (1) has been isolated from secondary processes such as $\text{Br} + \text{CH}_3\text{SiH}_2 \rightarrow \text{products}$. k_1 does not depend on τ_{res} , indicating that thermal decomposition of CH_3SiH_3 is unimportant. Fig. 1 shows an Arrhenius plot of the k_1 measurements, and for the temperature range 350–550 K these may be summarized in the form $A \exp(-E_a/RT)$ as

$$k_1 = (4.0 \pm 0.5) \times 10^{-10} \exp(-19.7 \pm 0.5 \text{ kJ mol}^{-1}/RT) \quad \text{cm}^3 \text{ s}^{-1} \quad (\text{I})$$

where the errors are $\pm 1\sigma$. The variance and covariance¹² of A and E_a yield the statistical uncertainty in k_1 , which is combined with an allowance of $\pm 5\%$ for possible but unrecognized systematic errors to yield 95% confidence limits of ca. $\pm 13\%$ of k_1 . This takes account of the scatter between different k_1 determinations under different conditions.

22 measurements of k_2 are summarized in Table 2, and are similarly independent from E_{F} and τ_{res} . The Arrhenius fit over the range 390–550 K of

$$k_2 = (4.3 \pm 0.8) \times 10^{-10} \exp(-21.6 \pm 0.7 \text{ kJ mol}^{-1}/RT) \quad \text{cm}^3 \text{ s}^{-1} \quad (\text{II})$$

is plotted on Fig. 1. Confidence limits for k_2 , derived as for k_1 , are ca. $\pm 12\%$ of k_2 .

Thermochemical Analysis

A reasonable estimate of the activation energy for the reverse of reaction (1), E'_a , was obtained by averaging the measured E_a for the reactions of the carbon analogue, CH_3CH_2 , and

SiH_3 with HBr, which are $-4.2 \pm 1.2^{13}\dagger$ and $-0.7 \pm 1.2 \text{ kJ mol}^{-1,9}$ respectively. This leads to $E'_a \approx -2.5 \text{ kJ mol}^{-1}$, with an assumed uncertainty of $\pm 5 \text{ kJ mol}^{-1}$ to allow for errors in this estimation. ΔC_p is negligible,² so that to a good approximation $\Delta_{298}H$ for reaction (1) is $E_a - E'_a = 22.2 \pm 5 \text{ kJ mol}^{-1}$. $\Delta_{298}H$ is also equal to $D_{298}(\text{CH}_3\text{SiH}_2-\text{H}) - D_{298}(\text{H}-\text{Br})$ which, coupled with $D_{298}(\text{H}-\text{Br}) = 366.3 \text{ kJ mol}^{-1,14}$ implies that $D_{298}(\text{CH}_3\text{SiH}_2-\text{H}) = 388.5 \pm 5 \text{ kJ mol}^{-1}$. A similar analysis was made for reaction (2), where E_a for $(\text{CH}_3)_2\text{CH} + \text{HBr}$ has been measured to be $-6.4 \pm 0.9 \text{ kJ mol}^{-1,13}$. This leads to an assumed E'_a of $-3.6 \pm 5 \text{ kJ mol}^{-1}$. $\Delta_{298}H$ for reaction (2) of $25.2 \pm 5 \text{ kJ mol}^{-1}$ and an estimated $D_{298}[(\text{CH}_3)_2\text{SiH}-\text{H}]$ of $391.5 \pm 5 \text{ kJ mol}^{-1}$. These results are compared below to $D_{298}(\text{SiH}_3-\text{H}) = 384.1 \pm 2.0 \text{ kJ mol}^{-1}$ measured by Seetula *et al.*,⁹ who determined both E_a and E'_a for reaction (4) directly, and to $D_{298}[(\text{CH}_3)_3\text{Si}-\text{H}]$ (we had previously derived $D_{298} = 397.6 \text{ kJ mol}^{-1,2}$ the revised E'_a ¹³ now leads to $D_{298} = 398.6 \pm 6 \text{ kJ mol}^{-1}$).

Ab initio Analysis

The calculated HF/6-31G* structures for CH_3SiH_3 , $(\text{CH}_3)_2\text{SiH}_2$ and the corresponding silyl radicals are given in

Fig. 1 Arrhenius plot of the rate constant measurements for the reactions of atomic bromine with methylsilane (O) and dimethylsilane (●)

† The negative activation energies for alkyl radicals plus HBr have recently been revised to be slightly more negative, by up to 2 kJ mol^{-1} , and these newer values are employed, see ref. 13(b).

Table 1 Summary of rate constant measurements for $\text{Br} + \text{CH}_3\text{SiH}_3$

T/K	p/kPa	$([\text{M}] \approx [\text{Ar}])/10^{18} \text{ cm}^{-3}$	$\tau_{\text{res}}/\text{s}$	E_{F}/J	$[\text{CH}_2\text{Br}_2]/10^{14} \text{ cm}^{-3}$	$[\text{CH}_3\text{SiH}_3]_{\text{max}}/10^{14} \text{ cm}^{-3}$	$(k_1 \pm \sigma_{k_1})/10^{-13} \text{ cm}^3 \text{ s}^{-1}$
351	6.77	1.64	1.1	2.45	0.97	5.04	4.16 ± 0.09
351	6.77	1.64	1.1	1.25	0.97	5.04	3.96 ± 0.24
365	6.64	1.61	1.1	2.45	0.96	3.24	6.76 ± 0.38
365	6.69	1.63	2.1	2.45	0.97	3.18	7.47 ± 0.27
390	6.63	1.61	1.1	3.20	0.97	3.24	9.54 ± 0.45
390	6.63	1.61	1.1	2.45	0.97	3.24	9.86 ± 0.47
390	6.63	1.61	1.1	1.25	0.97	3.24	8.84 ± 0.12
419	13.3	3.24	1.1	3.20	0.99	2.21	13.6 ± 0.6
419	13.3	3.24	1.1	2.45	0.99	2.21	13.0 ± 0.4
419	13.3	3.24	1.1	1.25	0.99	2.21	14.0 ± 0.5
449	13.3	3.23	1.1	2.45	0.96	1.08	19.6 ± 0.5
451	13.4	3.25	2.1	2.45	1.17	1.04	22.8 ± 0.6
490	6.73	1.64	1.1	2.45	0.98	0.79	33.4 ± 1.9
490	10.1	2.44	1.1	2.45	0.97	0.59	31.8 ± 1.6
518	6.68	1.62	1.1	2.45	1.00	0.38	40.9 ± 0.8
519	6.77	1.64	2.1	2.45	1.02	0.37	44.0 ± 1.6
550	13.3	3.22	1.1	2.45	1.00	0.39	48.5 ± 0.5
550	13.3	3.24	2.2	2.45	1.03	0.37	56.6 ± 0.9

Table 2 Summary of rate constant measurements for $\text{Br} + (\text{CH}_3)_2\text{SiH}_2$

T/K	p/kPa	$([\text{M}] \approx [\text{Ar}])/10^{18} \text{ cm}^{-3}$	$\tau_{\text{res}}/\text{s}$	E_{F}/J	$[\text{CH}_2\text{Br}_2]/10^{14} \text{ cm}^{-3}$	$(\text{CH}_3)_2\text{SiH}_2]_{\text{max}}/10^{14} \text{ cm}^{-3}$	$(k_2 \pm \sigma_{k_2})/10^{-13} \text{ cm}^3 \text{ s}^{-1}$
386	9.99	2.43	1.1	4.05	1.00	3.74	4.65 ± 0.68
386	9.99	2.43	1.1	2.45	1.00	3.74	5.00 ± 0.28
386	9.99	2.43	1.1	1.25	1.00	3.74	5.02 ± 0.10
387	10.1	2.44	2.1	2.45	1.13	4.93	5.66 ± 0.16
401	6.64	1.61	1.1	4.05	0.98	3.91	6.23 ± 0.40
401	6.64	1.61	1.1	2.45	0.98	3.91	6.48 ± 0.35
401	6.64	1.61	1.1	1.25	0.98	3.91	5.82 ± 0.40
419	13.2	3.21	1.1	2.45	0.98	3.98	7.56 ± 0.50
420	13.4	3.26	2.2	2.45	1.01	3.94	9.90 ± 0.09
429	13.3	3.24	1.1	4.05	1.02	2.55	9.69 ± 0.28
429	13.3	3.24	1.1	2.45	1.02	2.55	9.83 ± 0.09
429	13.3	3.24	1.1	1.25	1.02	2.55	9.59 ± 0.29
431	6.71	1.63	1.1	4.05	1.02	2.53	11.5 ± 0.6
431	6.71	1.63	1.1	2.45	1.02	2.53	12.0 ± 0.7
431	6.71	1.63	1.1	1.25	1.02	2.53	11.4 ± 0.6
462	6.67	1.62	1.1	5.00	0.95	2.51	16.4 ± 0.6
462	6.67	1.62	1.1	2.45	0.95	2.51	17.3 ± 0.5
462	6.67	1.62	1.1	1.25	0.95	2.51	15.9 ± 0.4
500	6.67	1.62	2.1	2.45	0.99	1.10	25.1 ± 1.3
501	6.71	1.63	1.1	2.45	0.96	1.16	26.7 ± 0.7
544	13.2	3.20	1.1	2.45	1.04	1.15	31.9 ± 1.5
546	13.5	3.28	2.1	2.45	1.11	1.13	35.4 ± 1.3

Fig. 2 and 3. The geometry for CH_3SiH_3 is close to that published by Gordon and Volk,¹⁵ while the other species do not appear to have been characterized theoretically. A consistent consequence of H-atom loss for each silane, including trimethylsilane,² is a slight shortening of the Si—C bonds by 0.006 Å. There is also a slight change of the hybridization on Si from sp^3 towards sp^2 . For example, in SiH_4 the sum of three H—Si—H angles is 328.4° , while in SiH_3 this sum is 332.6° , indicating some flattening of the SiH_3 group. In

$(\text{CH}_3)_3\text{SiH}$ the sum of the C—Si—C angles is 331.1° , perhaps reflecting steric repulsion between the methyl groups, and increases by only 0.4° upon loss of H. The other silanes are intermediate. Methylation also increases the Si—H distance from 1.475 Å in SiH_4 to 1.484 Å in $(\text{CH}_3)_3\text{SiH}$, and at the same time the (average) scaled vibrational frequencies of the normal mode(s) corresponding to the Si—H stretch(es) decrease from 2138 cm^{-1} in SiH_4 to 2070 cm^{-1} in $(\text{CH}_3)_3\text{SiH}$.

The vibrational frequencies and total electronic energies at the HF, MP2, MP3 and MP4 levels of theory are listed in Table 3, and are employed to calculate ΔH_0 (including ZPE)

Fig. 2 HF/6-31G* structures of methylsilane and methylsilyl. CH_3SiH_3 is C_{3v} ; $\angle \text{H}_a\text{CH}_b = 107.8^\circ$, $\angle \text{H}_a\text{CSi} = 111.1^\circ$, $\angle \text{H}_c\text{SiH}_d = 108.3^\circ$, $\angle \text{H}_c\text{SiC} = 110.6^\circ$. CH_2SiH_2 is C_s ; $\angle \text{H}_a\text{CH}_b = 107.9^\circ$, $\angle \text{H}_a\text{CSi} = 111.1^\circ$, $\angle \text{H}_b\text{CSi} = 111.0^\circ$, $\angle \text{H}_c\text{SiH}_d = 109.2^\circ$, $\angle \text{H}_c\text{SiC} = 111.6^\circ$.

Fig. 3 HF/6-31G* structures of dimethylsilane and dimethylsilyl. $(\text{CH}_3)_2\text{SiH}_2$ is C_{2v} ; $\angle \text{H}_a\text{CH}_b = 107.7^\circ$, $\angle \text{H}_a\text{CSi} = 111.2^\circ$, $\angle \text{H}_b\text{CSi} = 111.3^\circ$, $\angle \text{H}_c\text{SiH}_d = 107.5^\circ$, $\angle \text{H}_c\text{SiC} = 109.4^\circ$, $\angle \text{CSiC} = 111.5^\circ$. $(\text{CH})_2\text{SiH}$ is C_s ; $\angle \text{H}_a\text{CH}_b = 107.8^\circ$, $\angle \text{H}_a\text{CSi} = 111.1^\circ$, $\angle \text{H}_b\text{CSi} = 111.1^\circ$, $\angle \text{H}_c\text{SiC} = 110.1^\circ$, $\angle \text{CSiC} = 111.7^\circ$.

Table 3 Summary of *ab initio* results^a

species	scaled frequencies/cm ⁻¹	total electric energy HF ^b	$\langle S^2 \rangle$	total electronic energy ^b		
				MP2	MP3	MP4
CH ₃ SiH ₃	173, 502, 503, 648, 867 (2), 929, 934 (2), 1299, 1435 (2), 2109 (2), 2120, 2855, 2919 (2)	-330.272 41	0	-330.485 05	-330.513 42	-330.524 61
CH ₃ SiH ₂	166, 507, 569, 644, 843, 866, 908, 1292, 1434 (2), 2094, 2102, 2853, 2915, 2926	-329.651 81	0.753	-329.851 16	-329.877 14	-329.887 78
(CH ₃) ₂ SiH ₂	139, 154, 196, 447, 567, 607, 631, 674, 843, 866, 869, 910, 941, 1296, 1301, 1430, 1433, 1438, 1440, 2089, 2100, 2850 (2), 2909, 2911, 2914 (2)	-369.319 60	0	-369.663 66	-369.701 98	-369.718 61
(CH ₃) ₃ SiH	128, 140, 190, 501, 596, 598, 662, 708, 847, 860, 877, 1288, 1295, 1429, 1431, 1436, 1439, 2074, 2847 (2), 2905, 2906, 2921 (2)	-368.697 50	0.753	-369.028 45	-369.064 27	-369.080 44

^a With the 6-31G* basis set at HF/6-31G* geometries. ^b Total electronic energies at the given levels of theory in au; 1 au $\approx$ 2625 kJ mol⁻¹.

for reaction (5). The expectation values derived for S^2 are very close to the ideal value of 0.75 for doublet states so spin-contamination of the HF wavefunctions is negligible. Calculated ΔC_p values¹⁶ are used to extrapolate ΔH to 298 K, although this is, in fact, a very small correction (-0.2 kJ mol⁻¹). The results yield $\Delta D = D_{298}(\text{R}_3\text{Si-H}) - D_{298}(\text{SiH}_3\text{-H})$ and are summarized in Table 4. As may be seen, $\Delta D \approx 0$ for CH₃SiH₃ and (CH₃)₂SiH₂, by contrast to $\Delta D \approx 14$ kJ mol⁻¹ for (CH₃)₃SiH.

Discussion

There appear to be no previous determinations of k_1 or of k_2 for comparison with the present results. The Arrhenius parameters are compared with those for reactions (3) and (4) in Table 4, and there are monotonic increases in A and E_a with the number of methyl groups. A consequence of the greater A for reactions (1) and (2) than for (4) is that k_1 and k_2 are larger than k_4 over the temperature range studied, even though reaction (4) has the lower E_a .

E_a for the forward reaction is seen to increase slightly as the number of methyl groups goes up, in accord with the idea that methyl substitution slightly increases the Si-H bond strength *i.e.* $\Delta D > 0$.² However, there are alternative interpretations which are both consistent with the experiments: (a) $D_{298}(\text{Si-H})$ in SiH₄, CH₃SiH₃ and (CH₃)₂SiH₂ is really the same, as argued by Walsh,¹ and the observed variation in ΔD can be accommodated by reasonable variations in the assumed E_a' for the reverse reactions. Thus ΔD is not significantly different from zero, as seen in the uncertainties of Table 4. (CH₃)₃SiH might therefore be an anomalous molecule where the derived $D_{298}(\text{Si-H})$ disagrees with $\Delta D = 0$. (b) Successive methyl groups contribute around $+4$ kJ mol⁻¹ each to ΔD . The *ab initio* thermochemistry is in accord with (a), although it is hard to assess its detailed reliability without prior knowledge of the effect we are trying to determine!

An unresolved disagreement exists between the experiments and theory discussed above, which all suggest $\Delta D \geq 0$, and results from high overtone spectroscopy of local Si-H stretching modes in silanes by McKean *et al.*³ and Bernheim *et al.*,⁴ where $D_0(\text{Si-H})$ was derived from Birge-Sponer plots. They found $D_0(\text{SiH}_3\text{-H}) = 381$ kJ mol⁻¹, in good accord with the kinetic result of Seetula *et al.*,⁹ but concluded that successive methyl substitutions led to lower bond strengths. For CH₃SiH₃ the two groups found $\Delta D = -12$ and -6 kJ mol⁻¹,^{3,4} respectively, for (CH₃)₂SiH₂, $\Delta D = -18$ and -16 kJ mol⁻¹, and for (CH₃)₃SiH, $\Delta D = -24$ and -57 kJ mol⁻¹. These ΔD values imply that E_a' for reactions (1)–(3) must be increasingly positive, up to, *e.g.*, around $+30$ kJ mol⁻¹ for reaction (3). The measured Si-H stretching frequencies of, *e.g.*, McKean *et al.*³ show the same trend as the *ab initio* data discussed above (the theoretical values are consistently 50 cm⁻¹ below the observed values), thus the disagreement over the implied bond strength concerns the interpretation of the measured frequencies, and not the measurements themselves.

Direct measurements of the reverse of reactions (1)–(3) are required to eliminate the need for assumed E_a' values, and thereby reduce the uncertainty in ΔD : we plan to carry out such experiments in the future.

Conclusions

The first kinetic studies of the reactions of Br atoms with methylsilane and dimethylsilane have been made, and the Arrhenius parameters lie between those for Br + SiH₄ and Br + (CH₃)₃SiH. The E_a values, when combined with assumed E_a' for the reverse reactions based on known E_a' for the carbon analogues, yield Si-H bond dissociation enthalpies between those for SiH₄ and (CH₃)₃SiH, but not significantly different from $D_{298}(\text{SiH}_3\text{-H})$. Alternative interpretations are that substitution of methyl groups in SiH₄ raises the Si-H bond strength by *ca.* 4 kJ mol⁻¹ per methyl,

Table 4 Comparison of Br + silane reactions

silane	ref.	$A/10^{-10}$ cm ³ s ⁻¹	$E_a/\text{kJ mol}^{-1}$	$E_a'/\text{kJ mol}^{-1}$ ^a	ΔD^b				
					expt.	HF	MP2	MP3	MP4
SiH ₄	9	1.6 ± 0.6	18.0 ± 1.3	-0.7 ± 1.2^c	(0)	—	—	—	—
SiH ₄	5	0.9 ± 0.15	17.0 ± 0.6	—	—	—	—	—	—
CH ₃ SiH ₃	this work	4.0 ± 0.5	19.7 ± 0.5	-2.5 ± 5	4 ± 5	-0.2	-0.2	-0.2	-0.2
(CH ₃) ₂ SiH ₂	this work	4.3 ± 0.8	21.6 ± 0.7	-3.6 ± 5	7 ± 5	-0.2	-0.2	-0.2	-0.2
(CH ₃) ₃ SiH	2 ^d	7.6 ± 3.3	28.4 ± 1.3	-4.3 ± 5	15 ± 6	13.9	12.6	13.5	—

^a Assumed reverse activation energy (see text). ^b $D_{298}(\text{Si-H})$ relative to SiH₄. ^c Measured quantity. ^d See text.

or instead that D_{298} is independent of the degree of methylation but with trimethylsilane as an exception.

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