

**An Investigation of the Gas-Phase Reaction of Atomic Bromine with Disilane:
Implications for the Si₂H₅-H Bond Strength**

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Abstract

The rate constant for the reaction $\text{Br}(4p)^2P_1 + \text{Si}_2\text{H}_6$ has been measured with the flash-photolysis/resonance fluorescence technique to be $(1.35 \pm 0.12) \times 10^{-10} \exp(-3.05 \pm 0.3 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1}$ over the temperature range 295-565 K. The uncertainties represent $\pm 1\sigma$ in the Arrhenius parameters, while 95% accuracy limits are about $\pm 12\%$. The results are combined with an assumed activation energy for the reaction $\text{Si}_2\text{H}_5 + \text{HBr} \rightarrow \text{Si}_2\text{H}_6 + \text{Br}$ to yield an estimated Si-H bond dissociation enthalpy of $372 \pm 5 \text{ kJ mol}^{-1}$ at 298 K, which is in accord with most previous experimental and *ab initio* estimates, and thence $\Delta H_{f,298}(\text{Si}_2\text{H}_5) = 234 \pm 5 \text{ kJ mol}^{-1}$.

1. INTRODUCTION

Kinetic studies of the reactions of atomic oxygen with SiH_4 and other substituted silanes [1][2][3] have shown that there is not a straightforward relationship between the dissociation enthalpy D_{298} of the Si-H bond being broken and the rate constant or activation energy E_a for abstraction. In particular, while $D_{298}(\text{Si-H})$ in the series of methyl-substituted silanes either increases slightly [4][5] or remains constant as the number of methyl groups goes up [6], the rate constant increases. As part of a continuing study to relate silane reactivity to fundamental molecular properties, we have extended our earlier halogenation experiments on silanes [4][5][7] to the reaction of ground-state bromine atoms, $\text{Br}(4p)^2P_1$, with disilane:



The results are compared with those for $\text{Br} + \text{SiH}_4$ [7][8], and when combined with an assumed activation energy for the reverse reaction yield an estimate of $D_{298}(\text{Si}_2\text{H}_5\text{-H})$. This quantity has featured in several recent *ab initio* investigations [9][10][11][12], but there are only two previous experimental estimates. These estimates are $361 \pm 8 \text{ kJ mol}^{-1}$ based on unpublished iodination data [13], subsequently revised to 367 kJ mol^{-1} [14], and results from photoionization studies [15] which, combined with $\Delta H_{f,298}(\text{Si}_2\text{H}_6)$ [16], yield an upper limit of 391 kJ mol^{-1} and a most probable value of 374 kJ mol^{-1} . Our measurements are also compared with a computational assessment of $D_{298}(\text{Si}_2\text{H}_5\text{-H})$ obtained from analysis of the homodesmic process



and the results of previous *ab initio* investigations.

2. EXPERIMENTAL TECHNIQUE

Si_2H_6 (Matheson, 97% min.) was purified with several freeze-pump-thaw cycles before use. At the low concentrations of Si_2H_6 employed we found it necessary to flow mixtures through the reactor for about 15 minutes before reproducible data were obtained, which we attribute to adsorption of Si_2H_6 on the reactor walls. Experiments were carried out in a large excess of Ar bath gas, and the temperature T was measured at the beginning and end with a moveable thermocouple corrected for radiation errors ($\sigma_T/T \approx 2\%$) [5]. Kinetic measurements were made using the flash-photolysis resonance-fluorescence technique as described previously [7][17] and where details may be found. Bromine atoms were generated by flash lamp photolysis of CH_2Br_2 , and were monitored by time-resolved atomic resonance fluorescence excited from a microwave discharge lamp, as they reacted with an excess of Si_2H_6 under pseudo-first-order conditions, on a timescale of the order of 1 - 10 ms. As argued earlier [7], we expect the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ states to remain in equilibrium. The second-order rate constant k_1 is derived from the slopes of plots of the pseudo-first-order decay coefficients k_{ps1} vs. $[\text{Si}_2\text{H}_6]$ such as Fig. 1, where

$$-d[\text{Br}]/dt = k_1[\text{Br}][\text{Si}_2\text{H}_6] + k_{\text{diff}}[\text{Br}] = k_{ps1}[\text{Br}] \quad (3)$$

and k_{diff} accounts for loss of Br by pathways other than reaction (1), primarily diffusion. The uncertainty in the slopes of plots like Fig. 1 is the dominant contribution to the precision σ_{k_1} . The energy, F , of the discharge through the flashlamp and $[\text{CH}_2\text{Br}_2]$ were varied to see if the measurements depended on $[\text{Br}]_{t=0}$. Additionally, $[\text{CH}_2\text{Br}_2]$ was sometimes varied during each set of determinations of k_{ps1} as a function of $[\text{Si}_2\text{H}_6]$, from 0 to $[\text{Si}_2\text{H}_6]_{\text{max}}$, with all other

experimental parameters held constant. The average gas residence time inside the heated reactor before photolysis, τ_{res} , was varied to check for possible thermal decomposition of Si_2H_6 .

3. RESULTS

Twenty nine measurements of k_1 are summarized in Table 1. No consistent variations with the experimental parameters P (pressure), τ_{res} , F and $[\text{CH}_2\text{Br}_2]$ were found, which is consistent with the attainment of pseudo-first-order conditions, demonstrates that decomposition of Si_2H_6 was unimportant and shows that reaction (1) was successfully isolated from any secondary chemistry. The results are plotted in Arrhenius form on Fig. 2. Also shown there is the fit to the form $k = A \exp(-E_a/RT)$, where σ_{k_1} and σ_T contribute to the weighting of each point:

$$k_1 = (1.35 \pm 0.12) \times 10^{-10} \exp(-3.05 \pm 0.3 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (4)$$

for $295 \text{ K} \leq T \leq 565 \text{ K}$. The uncertainties in A and E_a represent $\pm 1\sigma$, while consideration of the covariance [18] of A and E_a yields the 95% precision of k_1 as about $\pm 7\%$. Allowance for unrecognized but potential systematic errors leads to estimated accuracy limits of $\pm 12\%$ of k_1 .

4. DISCUSSION

4.1 Comparison with $\text{Br} + \text{SiH}_4$

No previous determinations of k_1 have been reported, so we compare reaction (1) with the process



The preexponential A factor for reaction (5) has been measured twice, over temperature ranges comparable to that employed here, to be (0.9 ± 0.15) [8] and $(1.6 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [7]. The similar A factor measured here for reaction (1) is consistent with a similar mechanism, i.e. H-atom abstraction, although the present results do not rule out more complicated pathways such as formation of $\text{SiH}_3\text{Br} + \text{SiH}_3$. E_a for reaction (5) was found to be 18.0 ± 1.3 [8] and $17.0 \pm 0.6 \text{ kJ mol}^{-1}$ [7]: the smaller E_a measured here indicates that reaction (1) is less endothermic than reaction (5), and confirms the suggestion by Walsh [13] that silyl substitution weakens the Si-H bond.

4.2 Thermochemical Analysis

The k_1 results can be used to derive $D_{298}(\text{Si}_2\text{H}_5\text{-H})$ given two assumptions. The first is that the dominant products of reaction (1) are $\text{Si}_2\text{H}_5 + \text{HBr}$. The second is the magnitude of E_a' , the activation energy for the reverse of reaction (1). We *approximate* this by averaging the known E_a' for the reactions $\text{SiH}_3 + \text{HBr}$ [8] and $\text{C}_2\text{H}_5 + \text{HBr}$ [19] of -0.7 ± 1.2 and $-4.2 \pm 1.2 \text{ kJ mol}^{-1}$, respectively. This leads to $E_a' \approx -2.5 \text{ kJ mol}^{-1}$, with an uncertainty of $\pm 5 \text{ kJ mol}^{-1}$ to allow for errors in this estimation method (we present data to a precision of 0.1 kJ mol^{-1} to avoid accumulation of roundoff errors when thermochemical data are combined, without implication of this degree of accuracy). The contribution of ΔC_p to ΔH over the temperature range investigated is negligible compared to the $\pm 5 \text{ kJ mol}^{-1}$ uncertainty [4], so that to a good approximation ΔH_{298} for reaction (1) is $E_a - E_a' = 5.6 \pm 5 \text{ kJ mol}^{-1}$. At the same time ΔH_{298} is equal to the difference in bond dissociation enthalpies $D_{298}(\text{Si}_2\text{H}_5\text{-H}) - D_{298}(\text{H-Br})$ which, combined with $D_{298}(\text{H-Br}) = 366.3 \text{ kJ mol}^{-1}$ [20], implies $D_{298}(\text{Si}_2\text{H}_5\text{-H}) = 371.9 \pm 5 \text{ kJ mol}^{-1}$.

mol⁻¹. This value is larger than the original estimate by Walsh [13] based on experiments involving



of 361 ± 8 kJ mol⁻¹, partly because E_a' for reaction (6) was formerly thought to be *positive* and in the range 0-8 kJ mol⁻¹. New evidence concerning E_a' for analogous processes has since led to an upward revision of $D_{298}(\text{Si}_2\text{H}_5\text{-H})$ to 367 kJ mol⁻¹ [6, 14], which lies well within the combined error limits. Our $D_{298}(\text{Si}_2\text{H}_5\text{-H})$ estimate is close to the "most probable" value of 373.7 kJ mol⁻¹ obtained from the photoionization mass spectrometry experiments of Ruscic and Berkowitz [15], and together with $\Delta H_{f,298}(\text{Si}_2\text{H}_6) = 79.9$ kJ mol⁻¹ [16] implies $\Delta H_{f,298}(\text{Si}_2\text{H}_5) = 233.8 \pm 5$ kJ mol⁻¹.

4.3 Theoretical analysis

We obtained geometries and scaled vibrational frequencies for the species in reaction (2) at the HF/6-31G* level using standard methods [21] implemented with the GAUSSIAN90 program [22], and the results agree with previous calculations [21][23]. Total electronic energies of SiH₃ and SiH₄ calculated at these geometries at up to the MP4/6-31G* level have been given earlier [4]; those for Si₂H₅ and Si₂H₆ are shown in Table 2. The *ab initio* electronic and zero-point vibrational energies were then employed to calculate ΔH_0 for reaction (2), and all gave similar values ranging from 12.1 (HF) to 11.8 (MP4) kJ mol⁻¹. Consideration of $H_{298}\text{-}H_0$ for each species [4][15] yields an MP4/6-31G* estimate for ΔH_{298} of 12.2 kJ mol⁻¹, which when coupled with the experimental $D_{298}(\text{SiH}_3\text{-H})$ of 384.1 ± 2.0 kJ mol⁻¹ [8] yields $D_{298}(\text{Si}_2\text{H}_5\text{-H}) = 371.9$ kJ mol⁻¹, in excellent accord with the experimental results. This accord validates the two assumptions of Section 4.2. Thus analysis of homodesmotic reactions appears, when applied to Si-

H bond dissociation enthalpies, to give excellent agreement with experiment while requiring only modest computing resources.

Other recent *ab initio* studies by Horowitz and Goddard [9], Ho and Melius [10], Sax and Kalcher [11], and Curtiss *et al.* [12] yielded values for $\Delta H_{f,298}(\text{Si}_2\text{H}_5)$ of 263.6, 231.8, 236.0 and 223.4 kJ mol⁻¹, respectively. With the exception of the earliest calculation, those studies are in accord with the value suggested above. The latest estimate appears to be about 10 kJ mol⁻¹ too small but, bearing in mind our ± 5 kJ mol⁻¹ uncertainty, it lies within the 8 kJ mol⁻¹ target accuracy for the Gaussian-2 method [24][25][26].

5. CONCLUSIONS

The first kinetic measurements for $\text{Br} + \text{Si}_2\text{H}_6$ yield a preexponential factor similar to that for $\text{Br} + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{HBr}$. The measured activation energy was combined with an assumed value for the reaction $\text{Si}_2\text{H}_5 + \text{HBr}$, based on literature data for $\text{SiH}_3 + \text{HBr}$ and $\text{C}_2\text{H}_5 + \text{HBr}$, to obtain a value for $D_{298}(\text{Si}_2\text{H}_5\text{-H})$ which is about 12 kJ mol⁻¹ smaller than $D_{298}(\text{SiH}_3\text{-H})$, and confirms that silyl substitution weakens the Si-H bond. The thermochemical results are in excellent accord with an *ab initio* analysis.

6. ACKNOWLEDGMENTS

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Table 1. Summary of rate constant measurements for Br + Si₂H₆

T, K	P, mbar	τ_{res} , s	F, J	[CH ₂ Br ₂], 10 ¹⁴ cm ⁻³	[Si ₂ H ₆] _{max} , 10 ¹² cm ⁻³	$k_1 \pm \sigma_{k_1}$, 10 ⁻¹¹ cm ³ s ⁻¹
295	69.2	1.5	4.05	6.03	16.6	3.25 ± 0.20
295	134.8	4.4	4.05	23.60	10.4	4.33 ± 0.20
295	140.6	4.5	5.00	16.00	9.6	4.42 ± 0.69
295	140.6	4.5	2.45	16.00	9.4	4.33 ± 0.16
296	130.6	2.2	4.05	3.76	12.7	4.21 ± 0.12
296	137.8	2.2	4.05	8.05	13.4	5.81 ± 0.34
296	68.8	1.5	4.05	5.00	16.6	4.12 ± 0.10
296	68.0	1.5	5.00	6.00	14.3	4.22 ± 0.25
296	68.0	1.5	2.45	6.00	14.3	4.08 ± 0.11
312	69.2	1.4	4.05	5.71	15.6	3.86 ± 0.20
313	136.6	4.1	4.05	15.90	8.4	3.42 ± 0.13
314	75.5	1.6	4.05	5.91	13.9	3.64 ± 0.15
315	68.6	1.4	4.05	5.60	15.5	4.31 ± 0.13
334	75.4	1.5	4.05	5.33	13.1	4.23 ± 0.12
335	69.0	1.3	4.05	4.40	14.6	3.92 ± 0.83
337	72.6	1.4	4.05	5.26	12.5	4.11 ± 0.17
338	68.6	1.3	4.05	5.20	14.4	4.73 ± 0.21
359	79.0	1.4	4.05	6.14	12.7	4.43 ± 0.15
363	68.0	1.8	4.05	8.03	15.5	4.33 ± 0.13
381	67.3	1.1	5.00	3.86	11.0	5.17 ± 0.17
381	67.3	1.1	2.45	3.86	11.0	5.03 ± 0.15
420	67.7	1.6	4.05	5.92	13.4	4.79 ± 0.20
420	71.8	1.1	4.05	4.57	10.1	6.00 ± 0.14
485	66.2	1.3	4.05	6.79	10.9	5.43 ± 0.22
487	67.5	1.3	4.05	4.89	10.4	6.42 ± 0.15
487	71.6	0.9	4.05	3.91	8.1	6.79 ± 0.17
536	72.8	0.7	4.05	3.62	7.9	7.82 ± 0.28
542	77.2	1.4	4.05	5.04	12.5	6.61 ± 0.20
565	72.6	0.6	4.05	3.07	8.2	7.25 ± 0.17

Table 2. Ab initio energies calculated with the 6-31G* atomic basis set^a

Species	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*
Si ₂ H ₅	-580.69070	-580.83645	-580.86699	-580.87729
Si ₂ H ₆	-581.30509	-581.46452	-581.49731	-581.50833

^a At the HF/6-31G* optimized geometries. Electronic energies are quoted in atomic units: 1 Hartree \approx 2625 kJ mol⁻¹.

FIGURE CAPTIONS

Fig. 1 Plot of k_{ps1} versus $[\text{Si}_2\text{H}_6]$ at $P = 72$ mbar and $T = 487$ K, to obtain k_1 from the slope.

Fig. 2 Arrhenius plot of k_1 for $\text{Br} + \text{Si}_2\text{H}_6$.

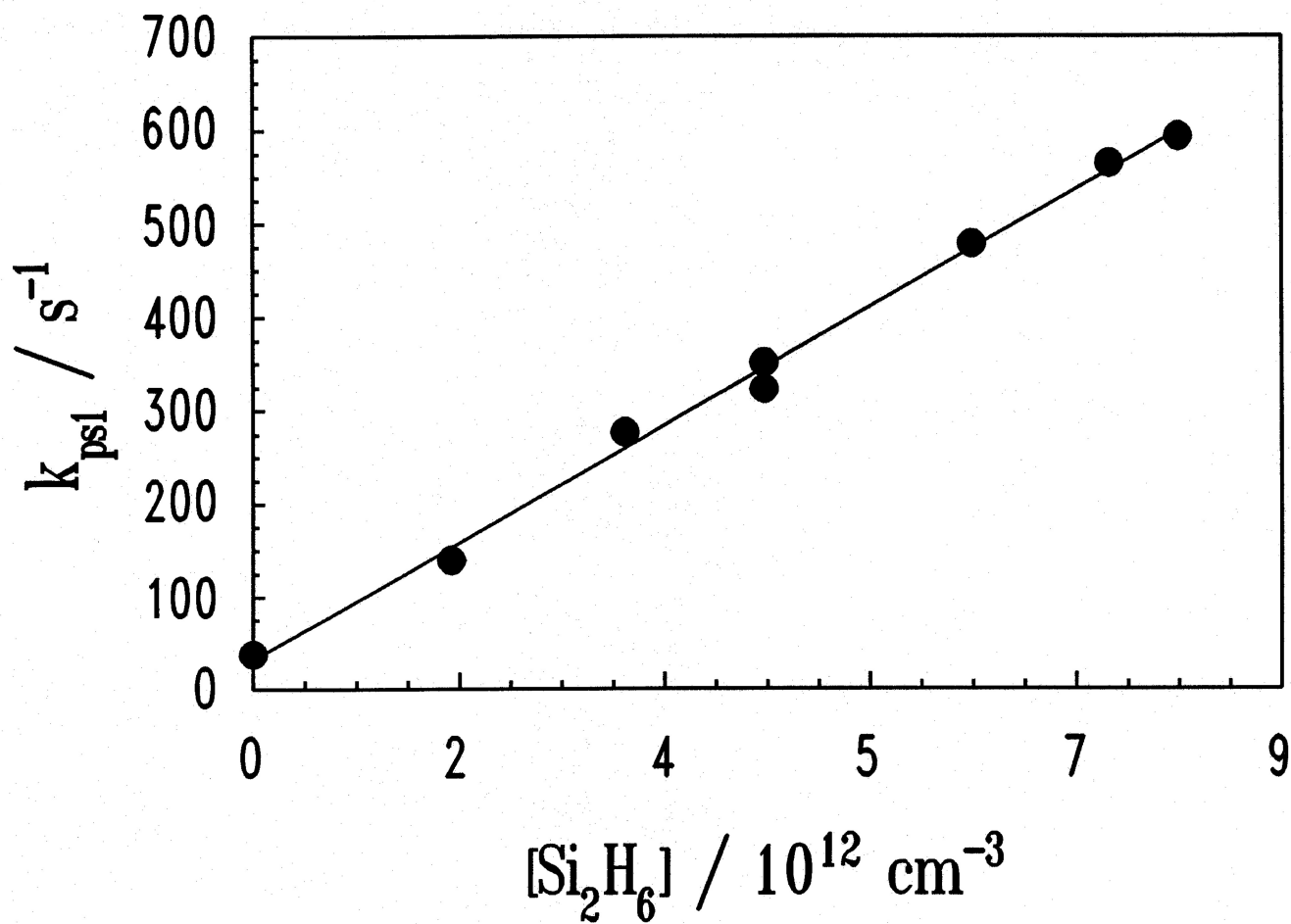


Fig. 1 Plot of k_{ps1} versus $[Si_2H_6]$ at $P = 72$ mbar and $T = 487$ K, to obtain k_1 from the slope.

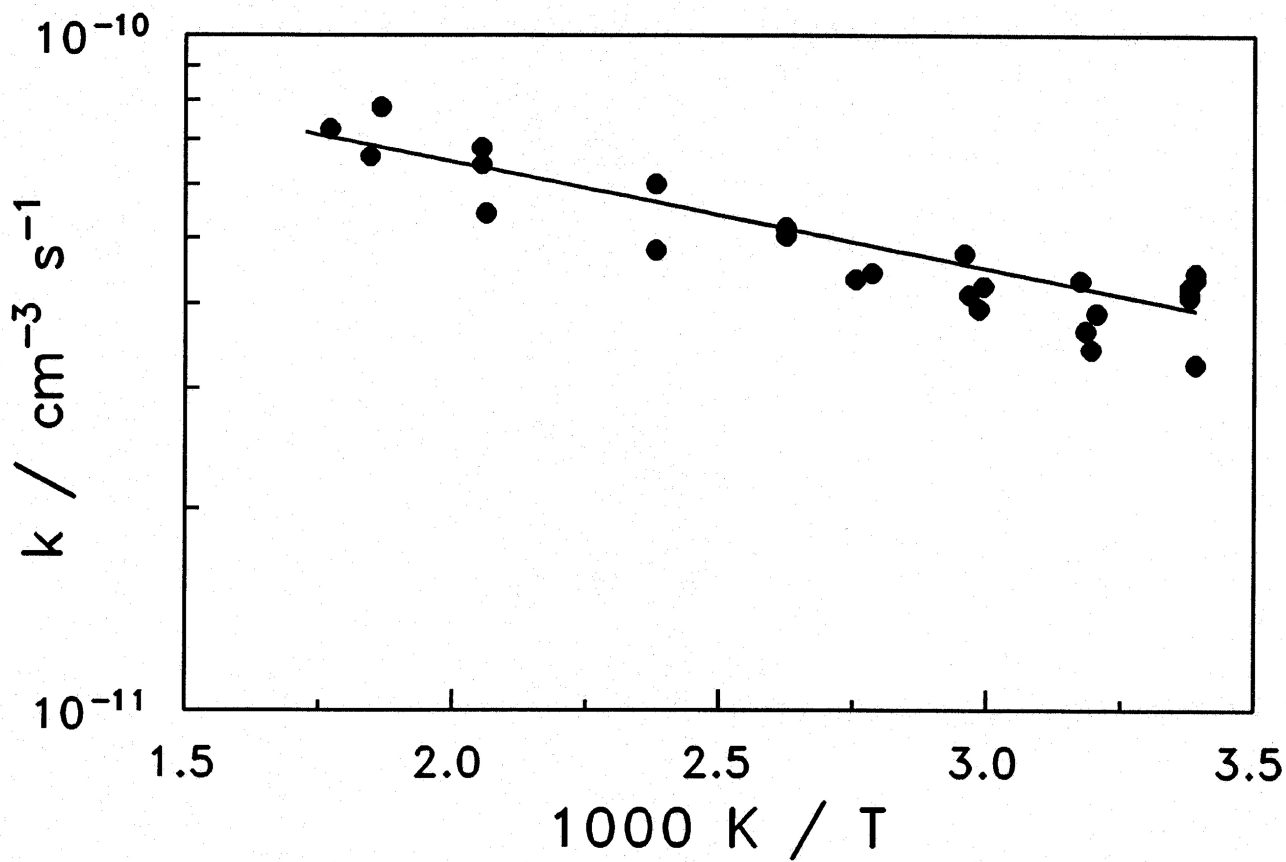


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