**A Discharge-Flow/Chemiluminescence Study of the Reaction $\text{O} + \text{Si}_2\text{H}_6$
at Room Temperature.**

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Abstract

Discharge-flow kinetic studies using NO_2 chemiluminescence detection of O yielded a rate constant for $\text{O} + \text{Si}_2\text{H}_6$ of $(6.0 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 295 K, where the 95% confidence interval includes both precision and accuracy. Insertion and abstraction mechanisms are discussed, and on the assumption that H-atom abstraction dominates, a likely activation energy is about 8 kJ mol^{-1} . This is an upper limit if insertion into the Si-Si bond is significant.

1. INTRODUCTION

Disilane has been employed for chemical vapor deposition (CVD) of silicon oxide [1], and the reaction

is a likely initial step in systems where atomic oxygen is present, e.g. plasma-enhanced CVD or photochemical vapor deposition from $\text{Si}_2\text{H}_6/\text{N}_2\text{O}_3$ mixtures [2]. Modeling of CVD mechanisms requires kinetic information about the individual elementary reactions, which has motivated this first characterization of the rate constant k_1 for reaction (1). The results are also compared with recent measurements of the kinetics of the reactions of atomic oxygen with SiH_4 [3][4][5][6] and methyl-substituted silanes [5][7], which indicate that increasing methylation increases the room temperature rate constant. This is perhaps surprising given that methyl substitution is thought either to leave the Si-H bond dissociation enthalpy D_{298} essentially unchanged [8] or to raise D_{298} slightly [9]. Horie *et al.* [5] have rationalized this reactivity trend by relating the room temperature rate constants to the ionization potential of the silane, which reflects the ease of electron transfer to the attacking oxygen atom. The present results permit a test of this correlation where H in SiH_4 is substituted by an electropositive SiH_3 group, rather than electronegative CH_3 groups.

2. EXPERIMENTAL TECHNIQUE

We employed the discharge-flow technique as described in our previous study [6] of

Briefly, $\text{O}(2p^3P)$ atoms were generated by a microwave discharge through a dilution of N_2O in

Ar, or through impurities in a large flow of 99.998% Ar, and were detected by O/NO chemiluminescence at a wavelength of about 510 nm. Absolute [O] were determined via the O + NO₂ titration reaction and pseudo-first-order conditions [O] << [Si₂H₆] were maintained. A new, narrower Pyrex flow tube was constructed with an i.d. of 2.2 cm, to yield higher mean gas velocities v than in the previous apparatus [6], and thus to permit use of shorter reaction times $t = l/v$, where l is the distance from the O-atom injector to the observation window. In each experiment the distance l and [NO] were held constant while [Si₂H₆] was varied, and therefore any diffusional loss of O to the reaction tube walls k_{diff} was constant. Typically $v \approx 20 \text{ ms}^{-1}$ which leads to a negligible pressure drop along the reaction zone of about 4 Pa according to the Poiseuille equation. As discussed earlier [6], the measured chemiluminescence intensity I is given by

$$I = A[\text{NO}][\text{O}]_0 \exp(-(2k_{\text{O}+\text{NO}}[\text{Ar}][\text{NO}] + k_{1,\text{obs}}[\text{Si}_2\text{H}_6] + k_{\text{diff}})t) \quad (3)$$

where A is an arbitrary constant. An example of a plot of $\ln I$ vs. [Si₂H₆] is shown in Fig. 1 and has a slope of $-k_{1,\text{obs}}t$, where $k_{1,\text{obs}}$ is the observed or effective value of k_1 .

3. RESULTS

Thirty-one $k_{1,\text{obs}}$ measurements at $295 \pm 3 \text{ K}$ are listed in Table 1. l was varied by a factor of 2, the pressure P by a factor of 4 and [O]₀ by a factor of 5. These $k_{1,\text{obs}}$ values were corrected for possible secondary reactions by means of computer simulations with the ACUCHEM program [10], according to the scheme given in Table 2, and for axial diffusion [11], to yield k_1 .

Table 2. Reaction scheme for secondary chemistry in O + Si₂H₆

Reaction		k(298 K), cm ³ s ⁻¹	Ref.
O + Si ₂ H ₆ → OH + Si ₂ H ₅	(1)	6.7 x 10 ⁻¹²	this work ^a
O + OH → O ₂ + H	(4)	3.3 x 10 ⁻¹¹	[12]
OH + Si ₂ H ₆ → H ₂ O + Si ₂ H ₅	(5)	1.4 x 10 ⁻¹¹	[3] ^b
OH + NO + Ar → HONO + Ar	(6)	1.2 x 10 ^{-13 c}	[12]
OH + OH → O + H ₂ O	(7)	1.8 x 10 ⁻¹²	[12]
O + Si ₂ H ₅ → products	(8)	1.4 x 10 ⁻¹⁰	see text
Si ₂ H ₅ + NO + Ar → Si ₂ H ₅ NO + Ar	(9)	1.3 x 10 ^{-12 c}	[13] ^b

^a Initial experimental estimate.

^b Value for analogous SiH₄ reaction employed.

^c Third-order rate constant employed: effective second-order rate constant at 0.67 kPa quoted.

Reaction (4) was found to be an unimportant route for O-atom loss because [OH] is quickly removed, mainly by Si₂H₆. Si₂H₅ could potentially consume O in the fast reaction (8), for whose rate constant we have assumed a nearly gas-kinetic value by analogy with O + CH₃ [12]. At the same time Si₂H₅ will recombine with the NO (added to detect the O atoms) via reaction (9). This removal of Si₂H₅ eliminates much of the potential O-atom loss through reaction (8). k_9 was assumed to equal the measured SiH₃ + NO rate constant [13], although the larger number of degrees of freedom in Si₂H₅NO as compared to SiH₃NO mean that this k_9 is an underestimate, and therefore that the effect of the secondary chemistry in Table 2 is overestimated. The effects of other reactions not considered here will tend to oppose this error. The resulting k_1 values are typically up to about 10% smaller than $k_{1,obs}$ (Table 1), showing that secondary chemistry is minor.

The mean k_1 is $6.04 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ with a statistical error of $\sigma = 0.22 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The 2σ precision limits together with a $\pm 10\%$ allowance for any unrecognized sources of systematic error [14] yield 95% confidence limits of $\pm 1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

4. DISCUSSION

Reaction (1) is approximately 20 times faster than $\text{O} + \text{SiH}_4$, reaction (2), at 295 K. There is evidence that the dominant channel for (2) is H-atom abstraction [5][15][16][17] so this is a plausible channel for (1) as well. Recent measurements in our laboratory [7] yielded $k_2 = 1.2 \times 10^{-10} \exp(-14.4 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1}$, thus a reasonable estimate of A for reaction (1) based on a similarly loose transition state is $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value is supported by a preliminary transition state theory analysis based on *ab initio* HF/6-31G* data for an abstraction pathway. For comparison, over the temperature range 400-600 K Arrhenius fits to the abstraction reactions $\text{O} + \text{CH}_4$ and $\text{O} + \text{C}_2\text{H}_6$ [17], which also proceed via loose transition states [18], yield similar preexponential A factors of $(1-2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [17], even though the C-H bond is less polar than the Si-H bond. Combination of the present measurement with the assumed A factor for reaction (1) yields an activation energy E_a of about 8 kJ mol^{-1} , and provides a possible extrapolation of k_1 to elevated temperatures. The E_a is 6 kJ mol^{-1} below that for reaction (2), which is reasonable in view of $D_{298}(\text{Si}_2\text{H}_5\text{-H})$ lying approximately 17 kJ mol^{-1} below $D_{298}(\text{SiH}_3\text{-H})$ [8]. Horie *et al.* [5] proposed that the room temperature rate constants for H-atom abstraction by O from substituted silanes are correlated to the ionization potential (I.P.); because the I.P.s for Si_2H_6 and $(\text{CH}_3)_3\text{SiH}$ are similar [19] a similar rate constant per Si-H bond of $3.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [5] might be expected, i.e. $k_1 \approx 2$

$\times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. This is about a factor of 3 larger than measured here, which may indicate uncertainty in the correlation or that it cannot be extended beyond methyl substitution.

However, other reaction channels apart from abstraction are possible, which makes the proposed E_a an upper limit. For example, Hoffmeyer *et al.* have studied the reaction

at room temperature and obtained $k_{10} = 1.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [20], and the mechanism they deduced involves O-atom insertion into the Si-Si bond followed by fragmentation of excited siloxane. k_{10} is about 50 times smaller than k_1 . If both reactions proceed via the same mechanism and have similar A factors, this implies $E_{a,1} \approx E_{a,10} - 9 \text{ kJ mol}^{-1}$. This difference in E_a would be consistent with $D_{298}(\text{H}_3\text{Si-SiH}_3) \approx D_{298}((\text{CH}_3)_3\text{Si-Si}(\text{CH}_3)_3) - 17 \text{ kJ mol}^{-1}$ [9].

It may be possible to distinguish between insertion and abstraction through consideration of the Arrhenius parameters, since formation of a singlet intermediate adduct [20] is non-adiabatic with respect to spin and therefore may have a reduced A factor. These parameters are presently unavailable and will be the subject of a future study. Experimental detection of the possible OH product of reaction (1) is also desirable.

5. CONCLUSIONS

The room temperature rate constant for $\text{O} + \text{Si}_2\text{H}_6$ has been determined to be $(6 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. On the assumption that H-atom abstraction dominates, a likely activation energy is about 8 kJ mol^{-1} . This is an upper limit if other channels, such as insertion into the Si-Si bond, are also important.

6. ACKNOWLEDGMENTS

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Table 1. Summary of O + Si₂H₆ measurements at 295 ± 3 K.

l cm	v cm s ⁻¹	P kPa	[N ₂ O]/10 ¹² cm ⁻³	[NO]/10 ¹⁴ cm ⁻³	[Si ₂ H ₆] _{max} /10 ¹³ cm ⁻³	[O]/10 ¹¹ cm ⁻³	k _{1,obs} /10 ⁻¹² cm ³ s ⁻¹	k ₁ /10 ⁻¹² cm ³ s ⁻¹
7.5	2390	0.25	0.9	3.7	7.9	7.6	9.14	8.10
7.5	2210	0.43	1.3	3.8	7.9	6.7	8.01	7.26
7.5	2130	0.52	1.7	3.8	9.1	7.9	7.11	6.44
7.5	2050	0.67	1.9	3.9	9.1	4.9	6.50	6.10
7.5	2050	0.76	2.1	3.6	7.2	4.5	7.08	6.64
7.5	2020	0.83	2.2	3.5	6.9	3.7	6.65	6.35
7.5	1870	0.93	2.6	3.6	8.3	3.9	5.74	5.48
10.0	2460	0.28	0	4.3	5.2	2.2	8.74	8.29
10.0	2160	0.29	0.8	4.8	8.0	4.3	6.45	6.02
10.0	2240	0.35	0.6	3.9	4.3	4.0	8.63	7.88
10.0	2160	0.37	0	4.0	3.7	1.5	7.53	7.26
10.0	1950	0.41	1.2	4.4	7.6	4.9	5.41	5.04
10.0	1890	0.56	1.8	4.2	8.5	6.8	4.86	4.52
10.0	2120	0.61	0	5.3	6.1	1.6	5.51	5.41
10.0	1970	0.67	1.0	4.5	5.2	2.1	6.80	6.62
10.0	1900	0.71	2.6	5.5	9.4	4.1	4.13	4.02
10.0	1980	0.75	0	5.0	8.9	3.5	4.20	4.09
10.0	2050	0.85	0	5.0	6.7	1.5	4.92	4.88
10.0	1950	0.94	0	4.9	6.6	2.2	5.16	5.07
10.0	1860	0.98	3.7	5.3	9.7	4.7	4.29	4.18

15.0	2160	0.29	0.8	4.8	4.9	2.6	6.05	5.73
15.0	2010	0.32	0.6	3.9	9.6	1.7	4.05	3.96
15.0	2000	0.40	1.0	4.8	5.1	3.6	6.10	5.72
15.0	2020	0.41	0.8	3.6	4.4	3.5	7.30	6.72
15.0	1950	0.47	0	4.4	3.6	2.2	6.18	5.90
15.0	2040	0.67	1.9	4.4	4.9	6.4	7.47	6.81
15.0	1970	0.67	1.2	3.6	5.1	3.4	6.86	6.55
15.0	1920	0.71	0	4.3	5.0	2.3	6.19	6.02
15.0	1890	0.88	2.1	3.5	5.7	3.9	5.93	5.66
15.0	1920	0.93	3.1	4.0	4.3	6.0	7.44	6.97
15.0	1880	0.94	0	4.2	3.6	2.6	7.57	7.43

Figure caption

Fig. 1 Plot of $\ln I$ vs. disilane concentration to obtain k_1 from the slope.