Discharge-Flow/Chemiluminescence and Flash-Photolysis/Resonance Fluorescence

Studies of the Reaction $\text{O} + \text{SiH}_4$ at Room Temperature.

Craig A. Taylor, Luying Ding and Paul Marshall*

Department of Chemistry, University of North Texas

P.O. Box 5068, Denton, Texas 76203-5068

Abstract

DF-CL studies using NO_2 chemiluminescence detection of O yielded a rate constant k_1 for $\text{O} + \text{SiH}_4$ of $(2.6 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 295 K, where the 95% confidence interval reflects accuracy. FP-RF studies using flash photolysis of SO_2 followed by time-resolved vuv fluorescence detection of O at 295 K yielded $k_1 = (3.0 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. These results are in good accord with most previous measurements and lead to a combined best estimate of $k_1 = (3.2 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. The DF-CL and FP-RF methods appear to have little unrecognized systematic error.

1. INTRODUCTION

The reaction of atomic oxygen, $O(2p^3P)$, with silane is an important step in silane combustion, and is included in models of SiH_4 oxidation. These studies have been carried out to characterize the possible hazard of SiH_4 explosions [1], and to investigate the possible use of SiH_4 to enhance ignition of hydrogen and hydrocarbon fuels in supersonic combustion ramjet engines [2][3]. The reaction is also a likely step in the plasma-enhanced and low-temperature chemical vapor deposition of silicon oxide from mixtures of silane and nitrous oxide or oxygen [4][5][6][7]. The dominant product channel is to $OH + SiH_3$, which was suggested by chemiluminescence and laser-induced fluorescence studies of OH by Agrawalla and Setser [8] and Park *et al.* [9], as well as a mass-spectrometric product study by Horie *et al.* [10]. A dissenting view was presented by Withnall and Andrews [11] who observed silanol formation in matrix isolation experiments, and proposed an insertion mechanism proceeding via triplet silanol, but Herron [12] has suggested that the SiH_3OH was formed by recombination of SiH_3 and OH after the primary step

Three previous kinetic measurements have been reported. The first was by Atkinson and Pitts [13], who measured the rate constant k_1 to be $(4.8 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 298 K by means of a flash-photolysis/chemiluminescence (FP-CL) technique, while Mkryan *et al.* [14] obtained $k_1 = (2.7 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ with a discharge-flow/ESR method. Recently Horie *et al.* [10] derived an intermediate value of $3.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ from measurements with a discharge-flow/mass spectrometry (DF-MS) system, although this value includes a 50% correction (derived from comparisons with other well-characterized O-atom reactions) of

unknown origin.

The present work has two aims. The first is to check for any systematic errors in the flash-photolysis/resonance fluorescence (FP-RF) system we have used for other studies of silane plus halogen kinetics [15][16], by measuring the same reaction in this system and in a new discharge-flow/chemiluminescence (DF-CL) apparatus. The second aim is to reduce the uncertainty in k_1 by experiments that employ both these independent techniques.

2. EXPERIMENTAL TECHNIQUES

2.1 *Gas-Handling System*

Gas mixtures were prepared as described elsewhere [17], and all experiments were carried out with a large excess of Ar bath gas. Ar (Linde 99.997% and Big Three Industries 99.998%), O₂ (MG Industries, UHP 99.99%) and N₂ (Big Three Industries 99.998%) gas were used as supplied. SO₂ (J.T. Baker 99.96%) and SiH₄ (Matheson semiconductor grade) were degassed by three "freeze-pump-thaw" cycles at 77 K (we found the commercial SiH₄ to contain a large fraction, around 25%, of noncondensable gas, presumably H₂). NO (Linde 98.5%) was separated from other less volatile nitrogen oxides by distillation from a trap cooled by a liquid N₂/ethanol slush (156 K). NO₂ (Matheson 99.5%) was purified by condensation at 156 K. Gas flows were measured either with electronic flow meters (Omega FMA-5000 series) or flow controllers (MKS Instruments 1159A and 1159B), calibrated against a bubble meter (Teledyne-Hastings HBM-1A) [18].

2.2 *Discharge-Flow/Chemiluminescence Method*

A schematic diagram of the apparatus, constructed from Pyrex glass, is shown in Fig. 1, and the principles of operation follow those outlined by Kaufman for monitoring NO_2 chemiluminescence [19][20] from the reaction:

If an O atom reacts via reaction (2), under our conditions, the NO_2 molecule formed rapidly consumes a second O atom and reforms NO via the reaction

and thus $[\text{NO}]$ is constant. An O-atom precursor diluted in Ar is dissociated by a microwave discharge, and the O atoms are carried into the reaction tube (i.d. $d = 3.90$ cm) via a moveable injector (i.d. 1.0 cm). The inside of the injector was coated with Teflon (Chemical Rubber Co. "Fluoro-Glide") to inhibit O-atom recombination at the walls. The exterior of the injector was painted black, and two right-angle bends with light traps were formed in the injector, to reduce the amount of light from the microwave discharge reaching the reaction tube. Small holes at the end of the injector introduced O atoms normal to the flow of gas along the tube. Visual inspection of the chemiluminescence revealed that mixing was complete within 0.1 cm. Reagents diluted in Ar were introduced at one end of the (uncoated) reaction tube, which was evacuated through a rotary pump (Sargent-Welch 1397, 500 l min^{-1}). About half the Ar flow was diverted through the injector to prevent back diffusion of reactants into the injector. The pressure in the reaction tube was measured with a capacitance manometer (MKS Instruments 122A or 222C) opposite the 2.5 cm dia. Vycor optical port. The pressure drop along the tube was estimated via consideration of the viscosity of Ar to be negligible (≈ 1 Pa).

For preliminary experiments the optical detection system consisted of a photomultiplier

tube (PMT, Hamamatsu IP28) and a monochromator (Oriel 77250), which was calibrated against the Hg spectrum. The PMT output current was passed through a $1\text{ M}\Omega$ resistor and the resulting voltage was monitored with a digital voltmeter (Beckman 850). This signal I is proportional to the light intensity. In all experiments the background signal obtained when $[\text{NO}] = [\text{SiH}_4] = 0$, arising from scattered light in the reaction tube, was subtracted from I before further analysis. The preliminary work showed that the maximum chemiluminescence signal was obtained at a wavelength of about 520 nm, which reflects a combination of the absolute emission intensity that peaks at 630 nm [21] and the PMT efficiency which improves towards shorter wavelengths. Kinetic measurements on $\text{O} + \text{SiH}_4$ were made with an improved detector system where the monochromator was replaced with an interference filter centered at 510 nm (FWHM = 11 nm, 58% peak transmittance) and an amplifier (Thorn EMI C632-A1) replaced the resistor. The absolute calibration of the detection system at different PMT voltages was determined by titrations [22] of atomic O using reaction (3).

In each experiment the distance from the injector tip to the observation window l was held constant, and the residence time t of the mixed gases before reaching the window is l/v where v is the mean gas velocity. Any diffusional loss of O to the reaction tube walls is therefore constant, although preliminary experiments revealed no detectable losses in the absence of reagents.

The measurements of k_1 were carried out under pseudo-first-order conditions with $[\text{O}]_0 \ll [\text{SiH}_4]$ so that $[\text{SiH}_4]$ was essentially constant. Sufficient O atoms were produced by passing "pure" Ar through the microwave discharge, from trace impurities and/or minor air leaks in the apparatus. A fixed $[\text{NO}]$ was introduced to monitor $[\text{O}]$. O atoms are lost via reactions (1) and

(2) and possibly diffusion, characterized by k_{diff} . Thus an exponential decay of [O] is expected,

$$[\text{O}] = [\text{O}]_0 \exp(-(2k_2[\text{Ar}][\text{NO}] + k_1[\text{SiH}_4] + k_{\text{diff}})t) \quad (4)$$

where $[\text{O}]_0$ is the initial [O]. Kaufman [20] has shown that the chemiluminescence intensity is proportional to the product $[\text{O}][\text{NO}]$ and therefore

$$I = A[\text{NO}][\text{O}]_0 \exp(-(2k_2[\text{Ar}][\text{NO}] + k_1[\text{SiH}_4] + k_{\text{diff}})t) \quad (5)$$

where A is an arbitrary constant. A plot of $\ln I$ vs. $[\text{SiH}_4]$ should be linear with slope $-k_1 t$, and an example is shown in Fig. 2. By working at a fixed l (fixed t) and variable $[\text{SiH}_4]$ k_1 was separated from both k_2 and k_{diff} . The observed $k_{1,\text{obs}}$ values were then corrected for axial diffusion [23]:

$$k_1 = k_{1,\text{obs}} (1 + aD/v) \quad (6)$$

a is $-d \ln([\text{O}]/[\text{O}]_0)/dl$ and D is the diffusion coefficient of atomic O. Axial diffusion arises when O atoms diffuse along the concentration gradient along the reaction tube; calculations based on an estimated $D = 0.2 \text{ cm}^2 \text{ s}^{-1}$ at 10^5 Pa [24] yielded corrections from 0.8 to 5.6%. Our experiments were carried out with Reynolds numbers in the range 10-50, which correspond to lengths required to develop laminar flow of 5-25 cm. Typical values of l were in this range, so that experiments were performed in a region of incompletely developed laminar flow. Because wall losses were negligible no correction for velocity profile effects is required [25].

2.3 Flash-Photolysis/Resonance Fluorescence Method

Details of the reactor have been described before in our previous study of atomic halogen reactions with SiH_4 [15] so a summary and modifications for the study of atomic O are presented here. The reactor is a stainless-steel six-way cross, and the intersection of the sidearms defines

the reaction zone where atomic O was generated and monitored. Actinic radiation entered along one sidearm, resonance radiation entered at right-angles through a second, and fluorescence was observed through a third mutually perpendicular sidearm. O atoms were generated by photolysis of SO₂ with a small flashlamp at wavelengths down to about 120 nm through magnesium fluoride optics, where the output pulse has a width of about 7 μ s. The O atoms then reacted with excess SiH₄ under pseudo-first-order conditions. The relative concentration of O was monitored by time-resolved resonance fluorescence at 130 nm, (3s)³S $\rightarrow$ (2p)³P_J [26], with signal averaging. Resonance radiation was excited by a cw microwave discharge through a flow of 0.1% O₂ in Ar at a pressure of about 200 Pa. The fluorescence was viewed by a solar-blind PMT through a calcium fluoride filter to block any Lyman- α radiation from H atoms. Current pulses from individual photons passed through an amplifier/discriminator, were counted as a function of time after the photolysis flash by a multichannel scaler, and were analyzed with a microcomputer.

O atoms were lost from the reaction zone mainly by reaction (1) and diffusion, described by k_{diff} , so that the pseudo-first-order decay constant for [O] is

$$k_{\text{ps1}} = k_1[\text{SiH}_4] + k_{\text{diff}} \quad (7)$$

and

$$[\text{O}] = [\text{O}]_0 \exp(-k_{\text{ps1}} t) \quad (8)$$

where t is the time after the photolysis pulse. k_{ps1} was determined by fitting the decay of fluorescence to the sum of an exponential curve plus a constant (to account for a constant background of scattered light); k_1 was obtained from the slope of a weighted linear plot of k_{ps1} vs. [SiH₄] together its statistical uncertainty σ_{k_1} [27].

3. RESULTS

Twelve DF-CL measurements of k_1 are listed in Table 1. After correction for axial diffusion, the mean k_1 is $3.08 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ with $\sigma = 0.09 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. A potential source of systematic error is consumption of atomic O by processes other than (1), which is likely because the products of reaction (1) may react rapidly with O atoms. We have carried out kinetic modeling [28] to investigate the effects of the possible secondary reactions summarized in

Table 2. Reaction scheme for secondary chemistry in O + SiH₄

Reaction		$k(298 \text{ K}), \text{ cm}^3 \text{ s}^{-1}$	Ref.
$\text{O} + \text{SiH}_4 \rightarrow \text{OH} + \text{SiH}_3$	(1)	3.5×10^{-13}	[10]
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	(9)	3.3×10^{-11}	[29]
$\text{OH} + \text{SiH}_4 \rightarrow \text{H}_2\text{O} + \text{SiH}_3$	(10)	1.4×10^{-11}	[13]
$\text{OH} + \text{NO} + \text{Ar} \rightarrow \text{HONO} + \text{Ar}$	(11)	$1.2 \times 10^{-13} \text{ }^a$	[29]
$\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	(12)	1.8×10^{-12}	[29]
$\text{O} + \text{SiH}_3 \rightarrow \text{products}$	(13)	1.4×10^{-10}	see text
$\text{SiH}_3 + \text{NO} + \text{Ar} \rightarrow \text{SiH}_3\text{NO} + \text{Ar}$	(14)	$1.3 \times 10^{-12} \text{ }^a$	[30]
$\text{SiH}_3 + \text{SiH}_3 (+\text{Ar}) \rightarrow \text{Si}_2\text{H}_6 \text{ and } \text{SiH}_2 + \text{SiH}_4 (+\text{Ar})$	(15)	$1.2 \times 10^{-10} \text{ }^a$	[31]

^a Effective second-order rate constant at 0.67 kPa

Table 2, and considered the conditions $[\text{O}]_0 = 2.2 \times 10^{12} \text{ cm}^{-3}$, $[\text{SiH}_4] = 2.8 \times 10^{14} \text{ cm}^{-3}$, $P = 0.67 \text{ kPa}$ and $t = 25 \text{ ms}$ at 298 K. OH might consume O via reaction (9) but this is found to be negligible because of the removal of OH by SiH₄ in reaction (10). The reactivity of SiH₃ towards O has not been measured so we have assumed a nearly gas-kinetic value (Table 2) by

analogy with $O + CH_3$ [29]. This means that reaction (13) might lead to a doubling of the loss rate for O via (1) alone. However, SiH_3 is largely removed by recombination with NO (14), and the result is that for each O atom consumed in (1) on average another 0.21 are lost through the secondary chemistry. Inclusion of the $SiH_3 + SiH_3$ processes reduces this number to 0.18. The other reactions in Table 2 are included for completeness but have little effect. Thus we divide the measured k_1 by a stoichiometry factor of 1.18 to obtain $2.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at the 1σ level. The 2σ precision limits plus a $\pm 10\%$ allowance for any unrecognized sources of systematic error yield 95% confidence limits of $\pm 0.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

Nineteen FP-RF determinations of k_1 at $295 \pm 2 \text{ K}$ are listed in Table 3, together with experimental parameters such as the gas residence time τ_{res} and the discharge energy through the flashlamp F. The initial [O] formed by the flash is expected to be proportional to the product $F[SO_2]$ and we plotted k_1 vs. $F[SO_2]$ to test for any dependence of the measured k_1 on $[O]_0$. The data are consistent enough to pick out a slight trend of increasing k_1 with $F[SO_2]$: the correlation coefficient is 0.52 which is just significant at the 95% level [32]. Extrapolation of this graph to $[O]_0 = 0$ yields $k_1 = 2.96 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ with $\sigma = 0.21 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [27]. Other possible systematic errors in temperature, gas flow etc. are small compared to 2σ and thus k_1 and the 95% confidence limits are estimated to be $(3.0 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. This uncertainty includes a $\pm 5\%$ allowance for unrecognized inaccuracies.

4. DISCUSSION

Our DF-CL result for k_1 is compared to earlier measurements in Table 4. There is reasonable accord between the discharge-flow experiments of Horie *et al.* [10] which were

carried out with an excess of O over SiH₄, and the present work where an excess of SiH₄ was employed. The *ca.* 50% correction applied by Horie *et al.* [10], based on comparisons with literature values for other O-atom rate constants measured in their system, appears to be somewhat too large. Our FP-RF result is significantly below the measurement of Atkinson and Pitts [13] but otherwise agrees with the earlier measurements and our DF-CL result. The weighted mean [32] of all the data in Table 4 is $(3.26 \pm 0.20) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at the 1σ level. However, because the value of Atkinson and Pitts appears systematically high, possibly indicating unrecognized secondary chemistry, we have also derived the weighted mean of the other work which is $(3.12 \pm 0.21) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at the 1σ level. Our best estimate for k_1 is $3.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, with an accuracy of around $\pm 0.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at the 95% confidence level. The close agreement between four different techniques is consistent with the idea that any unrecognized systematic errors in the FP-RF apparatus are small.

Table 4. Literature data for the reaction $\text{O} + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{OH}$ at room temperature.

Method	$k_1, 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Authors	Ref.
FP-CL	4.8 ± 0.7	Atkinson and Pitts	[13]
DF-ESR	2.7 ± 0.5	Mkryan <i>et al.</i>	[14]
DF-MS	3.5 ± 0.3	Horie <i>et al.</i>	[10]
DF-CL	2.6 ± 0.5		this work
FP-RF	3.0 ± 0.5		this work

5. CONCLUSIONS

The rate constant k_1 for $O + SiH_4$ has been measured by two different methods, DF-CL and FP-RF, at room temperature, with careful attention to possible systematic errors. The results are in agreement and suggest any residual systematic errors are small. The results are also largely consistent with previous determinations and the best combined estimate of k_1 is $(3.2 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 295 K.

7. ACKNOWLEDGMENTS

This work was made possible with the help of Prof. L.A. Melton at U.T. Dallas and Prof. J.A. Roberts and Mr. R. Ramirez at U.N.T., and was supported by Texas Instruments, Inc., the Robert A. Welch Foundation (Grant B-1174) and the U.N.T. Organized Research Fund. We thank Prof. A. Fontijn at R.P.I. for valuable discussions.

REFERENCES

1. J. R. Hartman, J. Famil-Ghiriha, M. A. Ring and H. E. O'Neal, *Comb. Flame.*, **68**, 43 (1987).
2. C. J. Jachimowski and A. G. McLain, *NASA Tech. Paper*, **2129** (1983).
3. A. G. McLain, C.J. Jachimowski and R.C. Rogers, *NASA Tech. Paper*, **2415** (1985).
4. C. Cobianu and C. Pavelescu, *Thin Solid Films*, **102** 361 (1983).
5. S. Vepřek, *Thin Solid Films*, **130**, 135 (1985).
6. S. Yokoyama, D. W. Dong, D. J. DiMaria and S. K. Lai, *J. Appl. Phys.*, **54**, 7058 (1983).
7. J. M. Jasinski, B. S. Meyerson and B. A. Scott, *Ann. Rev. Phys. Chem.*, **38**, 109 (1987).
8. B. S. Agrawalla and D. W. Setser, *J. Chem. Phys.*, **86**, 5421 (1987).
9. C. R. Park, G. D. White and J. R. Wiesenfeld, *J. Phys. Chem.*, **92**, 152 (1988).
10. O. Horie, R. Taege, B. Reimann, N. L. Arthur and P. Potzinger, *J. Phys. Chem.*, **95**, 4393 (1991).
11. R. Withnall and L. Andrews, *J. Phys. Chem.*, **89**, 3251 (1985).
12. J. T. Herron, *J. Phys. Chem. Ref. Data*, **17**, 967 (1988).
13. R. Atkinson and J. N. Pitts, Jr., *Int. J. Chem. Kinet.*, **10**, 1151 (1978).
14. T. G. Mkryan, E. N. Sarkisyan and S. A. Arutyunyan, *Arm. Khim. Zh.*, **34**, 3 (1981).
15. L. Ding and P. Marshall, *J. Phys. Chem.*, **96**, 2197 (1992).
16. L. Ding and P. Marshall, *J. Am. Chem. Soc.*, in press.
17. Y. Shi and P. Marshall, *J. Phys. Chem.*, **95**, 1654 (1991).

18. We determined that the theoretical gas flow correction factor for Ar vs. N₂ supplied by MKS Instruments was in error by about 5%, which is a possible source of error for laboratories that do not carry out direct calibrations, although the recently released *empirical* correction factor is correct.
19. F. Kaufman, *Prog. React. Kinet.*, **1**, 1 (1961).
20. F. Kaufman, *Proc. Roy. Soc.*, **247**, 123 (1958).
21. G. R. Bradburn and H. V. Lilenfeld, *J. Phys. Chem.*, **92**, 5266 (1988).
22. M. A. A. Clyne and W. S. Nip, *Reactive Intermediates in the Gas Phase*, D. W. Setser, Ed. Academic, New York, 1979, Chap. 1.
23. A. Fontijn and W. Felder, *Reactive Intermediates in the Gas Phase*, D. W. Setser, Ed. Academic, New York, 1979, Chap. 2.
24. Atomic and molecular oxygen have similar Lennard-Jones parameters according to W. C. Gardiner, Jr., *Combustion Chemistry*, W. C. Gardiner, Jr., Ed. Springer-Verlag, New York, 1984, Chap. 1. D(Ar-O₂) is quoted by R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1958, p. 277.
25. C.J. Howard, *J. Phys. Chem.*, **83**, 3 (1979).
26. H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978.
27. J. A. Irvin and T. I. Quickenden, *J. Chem. Educ.*, **60**, 711 (1983).
28. W. Braun, J. T. Herron and D. K. Kahaner, *Int. J. Chem. Kinet.*, **22**, 51 (1988).
29. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr and J. Troe, *J. Phys. Chem. Ref. Data*, **18**, 881 (1989).
30. K. Sugawara, T. Nakanaga, H. Takeo and C. Matsumura, *Chem. Phys. Lett.*, **157**, 309 (1989).
31. M. Koshi, A. Miyoshi and M. Hiroyuki, *Chem. Phys. Lett.*, **184**, 442 (1991).

32. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969, Chap. 5 and 7.

Table 1. DF-CL measurements on $O + SiH_4 \rightarrow OH + SiH_3$

l , cm	v , cm s ⁻¹	$[Ar]$, 10 ¹⁷ cm ⁻³	P , kPa	$[O]_o$, 10 ¹² cm ⁻³	$[NO]$, 10 ¹⁴ cm ⁻³	$[SiH_4]_{max}$, 10 ¹⁴ cm ⁻³	k_1 , 10 ⁻¹³ cm ⁻³ s ⁻¹
10	457	2.25	0.93	2.2	2.91	2.80	2.64
10	380	0.80	0.33	3.9	3.16	3.06	2.84
10	388	0.78	0.32	4.5	2.33	3.07	3.18
10	458	2.42	0.99	2.4	2.84	2.40	3.60
10	441	1.59	0.65	3.1	2.10	2.85	3.05
10	392	0.56	0.23	5.0	1.55	2.93	3.04
10	454	2.43	1.00	2.2	2.78	2.90	3.06
10	435	1.41	0.58	3.8	2.20	3.03	3.27
10	401	0.48	0.20	5.5	1.43	2.65	3.22
10	403	1.09	0.45	2.8	3.24	3.12	2.73
10	417	1.05	0.43	4.0	1.81	3.13	2.84
10	429	1.02	0.42	7.5	3.13	3.14	2.55

Table 3. FP-RF measurements on $O + SiH_4 \rightarrow OH + SiH_3$

T, K	P, kPa	[M]=[Ar], 10^{18} cm^{-3}	τ_{res} , s	F, J	[SO ₂], 10^{15} cm^{-3}	[SiH ₄] _{max} , 10^{14} cm^{-3}	$k_1 \pm \sigma_{k_1}$, $10^{-13} \text{ cm}^3 \text{ s}^{-1}$
293	4.44	1.10	1.0	5.00	3.66	4.21	2.48 ± 0.12
297	6.67	1.63	1.0	4.05	7.20	4.12	3.34 ± 0.10
297	6.73	1.64	1.0	4.05	2.44	4.13	2.88 ± 0.23
297	6.80	1.66	1.0	4.05	4.90	4.21	3.41 ± 0.07
293	13.5	3.33	3.3	4.05	7.46	4.37	3.23 ± 0.15
293	13.5	3.33	3.3	2.45	7.50	4.36	2.50 ± 0.17
293	13.5	3.33	3.3	5.00	7.50	4.36	3.58 ± 0.04
296	13.5	3.30	1.0	5.00	7.26	3.40	3.60 ± 0.10
296	13.5	3.30	1.0	4.05	7.26	3.40	3.83 ± 0.08
296	13.5	3.30	1.0	2.45	7.26	3.41	2.62 ± 0.23
297	13.5	3.28	1.0	4.05	5.09	3.39	3.04 ± 0.07
297	13.5	3.28	1.0	4.05	2.57	3.40	3.03 ± 0.11
291	26.8	6.67	3.3	5.00	7.25	4.41	3.48 ± 0.01
291	26.8	6.67	3.3	2.45	7.25	4.42	3.30 ± 0.10
297	40.3	9.81	3.0	4.05	7.32	4.07	3.67 ± 0.06
297	40.3	9.80	3.0	4.05	4.91	4.07	3.34 ± 0.06
297	40.3	9.82	3.0	4.05	2.47	4.12	3.50 ± 0.14
297	40.7	9.92	3.0	5.00	7.41	4.20	4.25 ± 0.09
297	40.7	9.92	3.0	2.45	7.41	4.20	3.46 ± 0.12

FIGURE CAPTIONS

Fig. 1 Schematic diagram of the discharge-flow/chemiluminescence apparatus.

Fig. 2 Typical plot of $\ln(I)$ vs. $[\text{SiH}_4]$ to obtain k_1 from the slope.

Figure 1

Figure 2