

Experimental and theoretical studies of the reaction of atomic oxygen with silane

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The flash-photolysis resonance-fluorescence technique has been employed to measure the rate constant for $\text{O} + \text{SiH}_4 \rightarrow \text{products}$ from 295–565 K, and yielded $k_1 = 1.23 \times 10^{-10} \exp(-14.6 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1}$ with an accuracy of about $\pm 15\%$. The transition state for direct H-atom abstraction has been characterized at up to the Gaussian-2 *ab initio* level of theory. With small adjustments it is possible to model kinetic data for $\text{O} + \text{SiH}_4$ in terms of an abstraction channel leading to $\text{OH} + \text{SiH}_3$. This agreement does not rule out minor participation by addition or insertion channels, but there is no theoretical evidence for bound triplet intermediates in the potential energy surface. A transition state theory analysis suggests that k_1 at 1000 K is 16 times larger than previously thought.

I. INTRODUCTION

Knowledge of the rate constant k_1 for the reaction of ground state atomic oxygen, $\text{O}(2p)^3P_J$, with SiH_4 at elevated temperatures



is needed to model the chemistry of SiH_4 flames and explosions^{1–7} and silicon oxide chemical vapor deposition (CVD) from mixtures of SiH_4 with O_2 or N_2O .^{8–14} There are significant deficiencies and discrepancies in the existing data for reaction (1), especially at high temperatures, and part of the impetus for our work is to obtain a good description of the temperature dependence of k_1 . The first part of the present work describes experimental measurements of k_1 at up to 565 K carried out with the flash-photolysis resonance-fluorescence (FP-RF) technique, using an apparatus which has already been shown to give k_1 results at room temperature¹⁵ in accord with other techniques.^{16–18}

There have been two previous kinetic studies carried out above room temperature, one by Atkinson and Pitts who employed flash-photolysis with O/NO chemiluminescence detection of O atoms (FP-CL) and obtained $k_1 = 6.8 \times 10^{-12} \exp(-6.6 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1}$ over 297–438 K,¹⁶ while discharge-flow experiments by Mkryan *et al.* with ESR detection of O (DF-ESR) yielded $k_1 = 2.7 \times 10^{-11} \exp(-11.3 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1}$ over 280–549 K.¹⁷ The first of these Arrhenius expressions is recommended for use up to 1000 K,¹⁹ but the alternative expressions yield k_1 values that differ by a factor of 5 if extrapolated to 1000 K. The pre-exponential A factors, especially the former, seem unusually small when compared to those found for O+hydrocarbon reactions. For instance, $A \approx 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ over the range 400–700 K for the reaction of atomic oxygen with the SiH_4 analog, CH_4 .¹⁹ Another area of disagreement concerns the products of reaction (1). Chemiluminescence and laser-induced fluorescence studies of OH by Agrawalla and Setser²⁰ and Park *et al.*,²¹ as well as a mass-spectrometric product study by Horie *et al.*,¹⁸ suggest that the dominant channel is



Such a reaction is important in combustion because it increases the number of radicals, while SiH_3 is thought to be a major species in CVD.²² However, Withnall and Andrews²³ observed formation of (singlet) SiH_3OH in matrix isolation experiments and proposed that reaction (1) proceeds via an addition/insertion mechanism, which implies a bound triplet OSiH_4 intermediate and would be nonadiabatic with respect to spin. Herron¹⁹ instead suggested that SiH_3OH was formed from recombination of the products of reaction (1a) in the matrix.

There have been semiempirical theoretical studies of silane reactivity, but Horie *et al.* noted that the BEBO method “fails completely” for the reactions of O with silanes.¹⁸ The second part of this work describes the first *ab initio* study of the mechanism of reaction (1), the prototypical O+silane reaction. This was made to test whether the abstraction channel (1a) can account for the observed kinetics, and to search for possible triplet OSiH_4 intermediates. The theoretical work also checks the magnitude of the pre-exponential A factor, and permits reliable extrapolation of k_1 beyond the experimental temperature range.

II. EXPERIMENTAL MEASUREMENTS

A. Technique

Details of the variable-temperature reactor,²⁴ the general FP-RF method,²⁵ and modifications for the study of atomic O¹⁵ have been given elsewhere. A mixture of SO_2 and SiH_4 diluted in a large excess of Ar bath gas flowed through the reactor which operated pseudostatically. The bath gas maintained isothermal conditions and slowed diffusion of atomic oxygen to the reactor walls, and the temperature was measured with a thermocouple corrected for radiation errors.²⁶ O atoms were produced by flash-photolysis of SO_2 , in an initial concentration $[\text{O}]_0 \ll [\text{SiH}_4]$, so that

$$-\frac{d[\text{O}]}{dt} = k_1[\text{SiH}_4][\text{O}] + k_{\text{diff}}[\text{O}] = k_{\text{ps1}}[\text{O}], \quad (2)$$

TABLE I. Summary of rate constant measurements for O+SiH₄.

<i>T</i> (K)	<i>P</i> (mbar)	τ_{res} (s)	<i>F</i> (J)	[SO ₂] 10 ¹⁵ (cm ⁻³)	[SiH ₄] _{max} 10 ¹⁴ (cm ⁻³)	$k_1 \pm \sigma_{k_1}$ 10 ⁻¹³ (cm ³ s ⁻¹)
295						3.0 ± 0.2 ^{a,b}
333	52	2.4	4.05	4.41	1.55	6.08 ± 0.16
333	101	1.5	4.05	3.39	0.99	5.98 ± 0.25
333	103	2.9	4.05	6.71	1.97	7.19 ± 0.20
333	200	3.0	4.05	6.70	1.96	6.90 ± 0.17
333						6.5 ± 0.3 ^b
378	101	3.0	5.00	5.98	1.95	13.0 ± 0.3
378	101	3.0	2.45	5.98	1.95	10.0 ± 0.9
378	205	3.0	5.00	6.12	1.99	12.8 ± 0.3
378	205	3.0	2.45	6.12	1.99	14.2 ± 0.3
378						12.5 ± 0.9 ^b
466	133	1.0	5.00	2.70	1.01	27.5 ± 1.1
466	133	1.0	2.45	2.70	1.01	27.1 ± 1.2
466	133	1.0	5.00	4.77	1.01	25.7 ± 0.8
466	133	1.0	2.45	4.77	1.01	27.8 ± 1.4
466	133	3.0	5.00	4.87	1.48	25.7 ± 1.4
466	133	3.0	2.45	4.87	1.48	20.5 ± 2.9
466	135	1.0	5.00	2.31	0.35	28.5 ± 0.6
466	135	1.0	2.45	2.31	0.35	27.7 ± 0.7
466	135	3.0	5.00	3.87	0.69	24.4 ± 0.5
466	135	3.0	2.45	3.87	0.69	27.0 ± 1.8
466						26.2 ± 0.7 ^b
563	268	1.5	4.05	3.09	0.35	60.1 ± 1.4
564	272	3.0	4.05	2.03	0.35	45.1 ± 1.3
565	67	0.5	4.05	2.50	0.23	57.0 ± 1.4
566	69	1.0	4.05	3.88	0.35	68.4 ± 1.7
566	68	3.0	4.05	3.74	0.33	53.7 ± 1.3
565						56.9 ± 3.8 ^b

^aSee Ref. 15.^bMean and s.d. of mean.

where k_{ps1} is the pseudo-first-order rate constant and k_{diff} accounts for diffusional loss of O from the reaction zone and recombination of O with SO₂. [O]₀ was varied by changing [SO₂] or the energy of the flash-lamp discharge, *F*. A microwave-powered discharge lamp excited resonance fluorescence at 130 nm, O(3s)³S → O(2p)³P_J,²⁷ which was monitored by a solar-blind photomultiplier tube operated with pulse-counting and signal-averaging. k_{ps1} values were obtained by nonlinear least-squares fits to the exponential decays of fluorescence intensity,²⁸ and k_1 values as the slopes of weighted linear plots²⁹ of typically 5 or 6 k_{ps1} values as a function of [SiH₄] from 0 to [SiH₄]_{max}.

B. Results

Twenty-three k_1 determinations at four temperatures from 333 to 565 K are summarized in Table I, where the quoted uncertainties represent precision only. *P* was varied by a factor of 5, the average gas residence time within the reactor before photolysis, τ_{res} , by a factor of 6, *F* by a factor of 2 and [SO₂] by a factor of 3. There was no consistent variation of k_1 with τ_{res} , which demonstrates that thermal decomposition of SiH₄ was unimportant, nor a significant variation with the product *F*[SO₂], i.e., [O]₀, which is consistent with attainment of pseudo-first-order conditions and successful isolation of reaction (1) from secondary chemistry. We averaged the k_1 determinations at each temperature, weighting them equally, and derived

the standard deviation of the mean. This standard deviation reflects the reproducibility of the individual k_1 measurements. The value of k_1 obtained from 19 measurements at 295 K made earlier in the same apparatus¹⁵ is also shown in Table I.

The five averaged k_1 results are plotted in Fig. 1 in Arrhenius form. The weighted fit to $A \exp(-E_a/RT)$, which takes into account both the uncertainty in *T*, about 2%, and the averaged k_1 values, yields

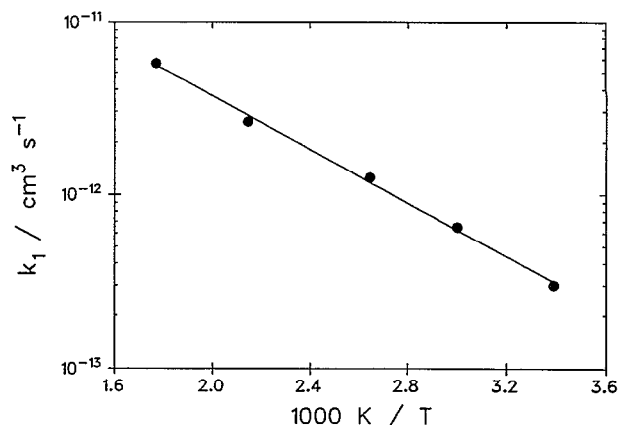


FIG. 1. Arrhenius plot summarizing 42 determinations of k_1 for O+SiH₄ at five temperatures.

TABLE II. HF/6-31G* and MP2/6-31G* geometries.^a

Species	Symmetry	HF/6-31G*		MP2/6-31G*	
SiH ₄	T _d	r _{Si-H} 1.475,	∠HSiH 109.47	r _{Si-H} 1.483,	∠HSiH 109.47
OSiH ₃ [‡]	C _s	r _{O-Ha} 1.205,	r _{Si-Ha} 1.747,	r _{O-Hb} 1.310,	r _{Si-Ha} 1.627,
		r _{Si-Hb} 1.473,	r _{Si-Hc} 1.473,	r _{Si-Hb} 1.481,	r _{Si-Hc} 1.481,
		∠OH _a Si 178.52,	∠H _a SiH _b 108.54,	∠OH _a Si 174.86,	∠H _a SiH _b 108.63,
		∠H _a SiH _c 107.62,	∠H _b SiH _c 111.03	∠H _a SiH _c 107.48,	∠H _b SiH _c 111.14
OH	C _{∞v}	r _{O-H} 0.959		r _{O-H} 0.979	
SiH ₃	C _{3v}	r _{Si-H} 1.476,	∠HSiH 110.88	r _{Si-H} 1.483,	∠HSiH 111.25

^aBond lengths in 10⁻¹⁰ m, and angles in degrees.

$$k_1 = (1.23 \pm 0.18) \times 10^{-10} \times \exp(-14.6 \pm 0.5 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (3)$$

for 295 K < T < 565 K. The uncertainties in *A* and *E_a* represent ±1σ. The uncertainty in *k₁* is smaller, because errors in *A* and *E_a* are coupled, and consideration of the covariance³⁰ yields 1σ for *k₁* that varies from 3.5% in the middle of the 1/*T* range up to about 6% at the ends. Comparison between different techniques at room temperature suggests that any systematic errors are small.¹⁵ Allowance of ±5% for possible but unrecognized systematic errors yields a 95% accuracy for *k₁* of about ±15%.

III. THEORETICAL ANALYSIS

Ab initio calculations were carried out with the GAUSSIAN90 program³¹ on a VAX 6310 and a Solbourne 5E/902 computer, using theoretical methods outlined by Hehre *et al.*³² The geometries of the species of reaction (1a) and the corresponding transition state (TS), SiH₄O[‡], were optimized with the 6-31G* atomic basis set at the self-consistent field or Hartree-Fock (HF) and MP2 levels of theory. The latter level makes a partial correction for electron correlation. Spin-unrestricted UHF wave functions were employed for open-shell species, and spin-restricted RHF wave functions for SiH₄. Next, vibrational frequencies were calculated at each stationary point on the potential energy surface (PES), to verify them as true minima, with all real frequencies, or the TS, with a single imaginary frequency. The HF and MP2 frequency results were scaled by factors of 0.893 and 0.95, respectively, before calculation of the zero-point vibrational energies (ZPE) of each species. The wavefunctions at the stationary points were verified to be HF stable.³³ The Gaussian-2 (G2) methodology of Pople and co-workers, a series of additive corrections to the MP4/6-311G**//MP2/6-31G* energy, was then applied to obtain approximate QCISD(T)/6-311+G** (3df,2p)//MP2/6-31G* energies.³⁴⁻³⁶ Combination of these electronic energies with the ZPE allows estimation of Δ*H*₀, the enthalpy change for reaction (1a) at 0 K, and *E*₀[‡], the enthalpy of the TS relative to O+SiH₄ at 0 K. The G2 method calls for use of the HF/6-31G* ZPE. We have also employed the MP2/6-31G* ZPE and denote the results as G2*. The G2 method makes no allowance for errors arising from spin contamination: here we define a spin-projected P-G2 energy as the G2 value plus a correction equal to the differ-

ence between the PMP4/6-311G** and MP4/6-311G** energies, where spin contamination has been projected out of the PMP4 energy using the algorithm of Schlegel.³⁷ An alternative approach to estimating *E*₀[‡] was also applied, the MP-SAC4 method of Gordon and Truhlar.^{38,39} In this approach, the MP4 correlation energy of the TS is scaled by a factor derived from comparison of MP4 and experimental dissociation energies *D_e* for SiH₃-H and O-H.

Simple transition state theory^{40,41} (TST) was employed to analyze the kinetics of channel (1a)

$$k_{\text{TST}} = \dot{f}^\ddagger \frac{k_B T}{h} \frac{Q^\ddagger}{Q_{\text{O}} Q_{\text{SiH}_4}} \exp\left(-\frac{E_0^\ddagger}{RT}\right), \quad (4)$$

where \dot{f}^\ddagger is the reaction path degeneracy, and the *Q*'s are the partition functions. Each *Q* is estimated from the MP2/6-31G* data with the usual assumption of the separability of vibrational and rotational motions.⁴² As argued by Cohen and Westberg, only six of the nine states of O(³*P_j*) correlate with the products; the experimental electronic partition function *Q_{el}* for O is 5+3 exp(-228 K/*T*) + exp(-326 K/*T*), *Q_{el}* for SiH₄ is 1, and a value of six was assumed for *Q_{el}* for the TS.⁴¹ Rotational symmetry factors were set equal to 1, and symmetry was taken into account via $\dot{f}^\ddagger=4$.

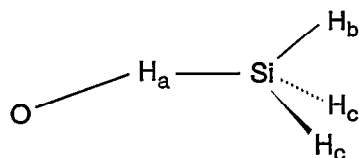
IV. DISCUSSION

A. Comparison between measured *k₁* values

Our data at 295 K have already been shown to be in accord with those from most other experimental techniques at room temperature.¹⁵⁻¹⁸ Figure 3 is an Arrhenius plot of Eq. (3) together with the best-fit rate constant expressions from the FP-CL work of Atkinson and Pitts¹⁶ and the DF-ESR work of Mkryan *et al.*¹⁷ It may be seen that while there is accord to within about a factor of 1.5 between the three expressions at *T* ≤ 400 K, above 400 K there are significant differences, with the present work lying higher than the earlier results. This reflects the different Arrhenius parameters measured here.

B. Comparison between theory and experiment for O, SiH₄, SiH₃, and OH

The *ab initio* geometries for minima in the PES shown in Table II and Fig. 2 are, of course, identical with previous

FIG. 2. Structure of the transition state for $O + SiH_4 \rightarrow OH + SiH_3$.

equivalent calculations where they exist.^{32,43} Typically MP2 theory leads to longer bonds than HF theory,³² and this can be seen in Table II. For OH and SiH_4 the MP2 bond lengths are closer to the experimental values⁴⁴ and we therefore employ results from MP2 theory in the kinetic calculations below.

Vibrational frequencies at stationary points in the $O + SiH_4$ PES are summarized in Table III. For SiH_4 the mean absolute error is 34 cm^{-1} at the HF level and 18 cm^{-1} at the MP2 level, relative to the measured frequencies.⁴⁴ For SiH_3 the lowest mode has been measured to be $\approx 724 \text{ cm}^{-1}$,⁴⁵ 57 and 41 cm^{-1} below the HF and MP2 estimates, respectively. For OH the errors at the scaled HF and MP2 levels are 0 and 16 cm^{-1} , respectively.⁴⁶ The similarity of the HF and MP2 frequencies means that the corresponding ZPE are essentially identical, and that there is a negligible difference between the G2 and G2* energies.

Ab initio energies for O, SiH_4 , SiH_3 , and OH have been listed elsewhere;³⁴⁻³⁶ new results for SiH_4O^\ddagger are shown in Table IV. The theoretical ΔH_0 for reaction (1a) listed in Table V can be tested against the experimental value derived from the measured $\Delta H_{f,298}(SiH_3)$ ⁴⁷ together with $H_{298} - H_0(SiH_3)$ calculated by Hudgens⁴⁸ and $\Delta H_{f,0}$ for O, SiH_4 , and OH.⁴⁴ As the size of the basis set is increased there is a monotonic improvement in ΔH_0 . Only the highest and computationally most demanding levels of theory, G1, G2, and MP-SAC4/6-311+G**//MP2/6-31G*, give results within 10 kJ mol^{-1} of experiment, probably because of the large changes in electron correlation for the O atom in the course of reaction. The small degree of spin-contamination in the UHF/6-311G** wave functions of the products OH and SiH_3 ($\langle S^2 \rangle = 0.755$ and 0.756 , respectively, versus the ideal value of 0.75 for doublets) is slightly greater than for the reactants ($\langle S^2 \rangle = 2.005$ for O vs the ideal value of 2 for a triplet), so that at the P-G2 level of theory ΔH_0 is slightly more negative and yields excellent accord with experiment.

TABLE III. HF/6-31G* and MP2/6-31G* frequencies.^a

Species	HF/6-31G*	MP2/6-31G*
SiH_4	907 (3), 939 (2), 2131 (3), 2138	909 (3), 955 (2), 2207, 2220 (3)
SiH_4O^\ddagger	2355i, 157, 223, 349, 794, 827, 850, 908, 910, 2134, 2143, 2147	1985i, 149, 238, 440, 820, 832, 867, 920, 927, 2211, 2235, 2238
OH	3569	3553
SiH_3	781, 906 (2), 2111, 2128 (2)	765, 922 (2), 2186, 2222 (2)

^aVibrational frequencies in cm^{-1} , scaled by 0.893 at the HF/6-31G* level and 0.95 at the MP2/6-31G* level. Degeneracies are shown in parentheses.

TABLE IV. Components of the G2 energy for the SiH_4O^\ddagger transition state.^a

Calculation	Energy
Zero-point energy	0.026 07 ^b
MP4/6-311G**	-366.314 48
PMP4/6-311G**	-366.317 49
MP4/6-311+G**	-366.321 24
MP4/6-311G**(2df)	-366.370 30
QCISD(T)/6-311G**	-366.320 10
MP2/6-311G**	-366.268 88
MP2/6-311+G**	-366.274 94
MP2/6-311G**(2df)	-366.318 25
MP2/6-311+G(3df,2p)	-366.331 74

^aAt the MP2/6-31G* optimized geometry. Electronic energies are quoted in atomic units: 1 hartree $\approx 2625 \text{ kJ mol}^{-1}$.

^bBased on HF/6-31G* frequencies at the HF/6-31G* optimized geometry, scaled by 0.893.

C. Properties of the transition state

The MP2 geometry of the TS, by comparison with the HF data, suggests that inclusion of electron correlation yields a TS earlier along the reaction coordinate, with a longer O-H partial bond and a shorter Si-H partial bond, although the vibrational frequencies at both levels of theory, especially the lower modes that contribute most strongly to Q^\ddagger , are very similar. The differences in geometry make only a small change in the rotational partition function. As seen from the discussion of ΔH_0 in the preceding section, values of E_0^\ddagger from levels of theory lower than G1, G2, and MP-SAC4/6-311+G**//MP2/6-31G* are unreliable, and the best purely *ab initio* estimate is $E_0^\ddagger \approx 11 \text{ kJ mol}^{-1}$ at the P-G2 level. This value is close to the measured E_a , although it should be noted that the G2 method has *not* been parameterized nor recommended for transition states,³⁴⁻³⁶ and that $E_a \neq E_0^\ddagger$.

A more accurate assessment of E_0^\ddagger is obtained by fitting Eq. (4) to our measured k_1 , on the assumption that $k_1 \approx k_{1a}$. Agreement between Eqs. (3) and (4) with a root-mean-square deviation of about 11% is obtained with $E_0^\ddagger = 11.8 \text{ kJ mol}^{-1}$. This estimate is somewhat dependent on the kind of TST employed, so a reasonable conservative estimate of the uncertainty is around 3 kJ mol^{-1} . The error in the P-G2 barrier height is only about 0.5 kJ mol^{-1} , which is probably fortuitously small, but certainly lies within the target accuracy for the G2 method.

TABLE V. Enthalpies of the transition state and products relative to reactants at 0 K, E_0^\ddagger and ΔH_0 , for $O + SiH_4 \rightarrow SiH_4O^\ddagger \rightarrow OH + SiH_3$.

Calculation	E_0^\ddagger (kJ mol ⁻¹)	ΔH_0 (kJ mol ⁻¹)
HF/6-31G**	119.0	50.7
MP2/6-31G*b	50.7	-26.6
MP4/6-31G*b	50.9	-16.4
MP-SAC4/6-31G*	5.6	-70.8
MP4/6-311G**b	43.2	-21.1
PMP4/6-311G**b	37.1	-22.4
MP-SAC4/6-311G**b	31.8	-32.6
MP4/6-311+G**b	36.4	-30.0
MP-SAC4/6-311+G**	25.9	-40.3
G1 ^c	18.4	-38.1
G2 ^c	17.4	-42.9
G2* ^b	17.7	-43.6
P-G2 ^c	11.3	-44.9
Expt. (see the text)	11.8 ± 3.0	-46.4 ± 2.0

^aAt the HF/6-31G* optimized geometry, including scaled zero-point energy (ZPE) at the HF/6-31G* level.

^bAt the MP2/6-31G* optimized geometry, including scaled ZPE at the MP2/6-31G* level.

^cAt the MP2/6-31G* optimized geometry, including scaled ZPE at the HF/6-31G* level.

D. Kinetic implications

Use of $E_0^\ddagger = 11.8$ kJ mol⁻¹ leads to the following TST expression for 295 K $\leq T \leq 2000$ K,

$$k_{1a} = 5.1 \times 10^{-17} (T/K)^{2.15} \exp(-1062 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1}, \quad (5)$$

which fits the measured k_1 to within the experimental uncertainty. This expression is plotted on Fig. 3 and the accord with Eq. (4) provides theoretical support to the A factor measured here. This A factor lies within a factor of 1.4 of that measured for $O + CH_4$ (Ref. 19) and those measured for $Cl + SiH_4$ and $Br + SiH_4$.²⁵ Equation (5) also provides a reasonable extrapolation of k_1 beyond the measured range. The k_1 values implied at higher temperatures are significantly greater than recommended earlier:¹⁹ for example, at 1000 K we suggest $k_1 \approx 5.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

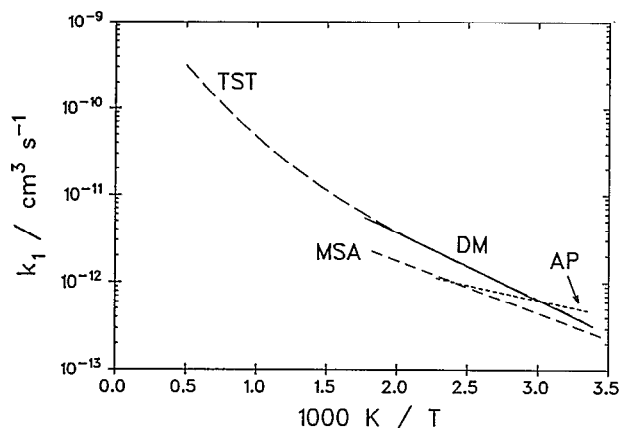


FIG. 3. Comparison of fits to k_1 : present measurements (DM); Atkinson and Pitts, Ref. 16 (AP); Mkyran *et al.*, Ref. 17 (MSA); transition state theory (TST).

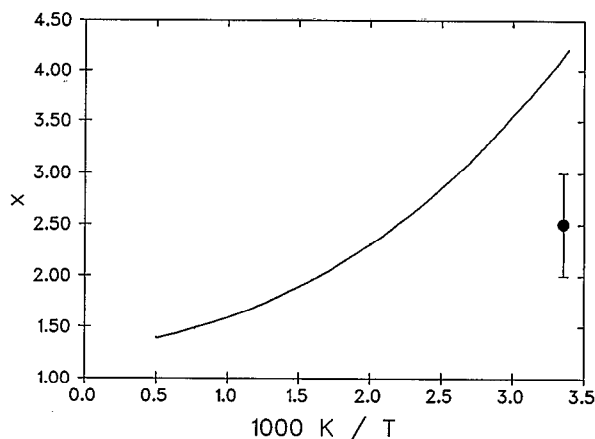


FIG. 4. Comparison of computed kinetic isotope effect $x = k_1(O + SiH_4) / k_1(O + SiD_4)$ (—) with the measurement of Horie *et al.*, Ref. 18 (●).

which is about 16 times greater than the recommendation. Thus reaction (1) may be more important in combustion and CVD chemistry than previously thought.

No explicit allowance for quantum mechanical tunneling has been made, because with the small E_0^\ddagger of around 10 kJ mol⁻¹ classical passage of reactants over the barrier dominates any tunneling contribution.⁴⁹ A sensitive test of the present application of simple TST is whether the kinetic isotope effect, quantified here as $x = k_1(O + SiH_4) / k_1(O + SiD_4)$, is correctly predicted. New moments of inertia, frequencies and ZPE for deuterated SiH_4 and SiH_4O^\ddagger and unchanged electronic energies were employed with Eq. (3). The results over the range 295–2000 K may be approximately summarized as

$$x \approx 0.30 (T/K)^{0.17} \exp(493 \text{ K}/T). \quad (6)$$

At the high temperature limit x approaches $\sqrt{2}$ as all the terms in the ratio of TST expressions cancel except for the ratios of the rotational partition functions. At room temperature $x \approx 4$ and is dominated by the higher effective barrier E_0^\ddagger in the deuterated case. This higher barrier arises from a smaller loss of ZPE going from the reactants to the TS for the deuterated species. Figure 4 shows a comparison of Eq. (6) with the experimental determination by Horie *et al.* at room temperature,¹⁸ where we have estimated approximate error limits for x of $\pm 20\%$. That value falls somewhat below the theoretical line. One possible interpretation is that the high frequencies in the TS are overestimated: if the three highest were reduced by about 200 cm^{-1} each then the experimental and theoretical x would agree while Q^\ddagger (and thus k_1) would be largely unaffected. Any role for tunneling would increase x and increase the divergence from experiment. Thus it is possible to rationalize *all* the kinetic data, with only minor modifications to the *ab initio* information, in terms of a single direct abstraction channel (1a) that leads to OH formation.

E. Addition or insertion channels

A search of the triplet $O + SiH_4$ PES was carried out at the correlated MP2/6-31G* level for possible adducts or stable insertion species. A C_{3v} van der Waals adduct be-

tween O and SiH₄ was found, with the O atom 3.6 Å from the Si, opposite from an Si-H bond, and with all real vibrational frequencies. G2* theory suggests this adduct is about 8 kJ mol⁻¹ endothermic with respect to O + SiH₄, so this adduct is not expected to influence the kinetics significantly. No other bound pentacoordinated ³OSiH₄ structures, or insertion products such as ³SiH₃OH, were located, so that at present *ab initio* theory supports abstraction as the main reaction mechanism in accord with the recommendation of Herron¹⁹ and the discussion of Horie *et al.*¹⁸ Insertion with a simultaneous spin-flip is possible, but would proceed with a reduced probability and is unlikely to make a major contribution to O(³P) consumption.

V. CONCLUSIONS

The rate constant k_1 for O + SiH₄ → products has been determined over the temperature range 295–565 K. Kinetic data for this reaction have been successfully modeled in terms of an abstraction mechanism to form OH + SiH₃, using *ab initio* information to characterize the transition state. Tunneling appears to be unimportant, and the G2 estimate of the energy barrier lies within about 6 kJ mol⁻¹ of the experimental value. Correction for spin-contamination yields essentially exact accord. Transition state theory permits extrapolation of k_1 to higher temperatures, and indicates that reaction (1) is faster than previously thought. No theoretical evidence was found for addition or insertion channels proceeding via triplet intermediates.

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