Dynamics of OH Production in the Reaction of $O({}^{3}P_{J})$ with SiH₄

Chan Ryang Park, Gary D. White, and John R. Wiesenfeld*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301 (Received: May 12, 1987; In Final Form: July 28, 1987)

Laser-induced fluorescence detection of the OH product following the reaction $O({}^{3}P_{J}) + SiH_{4} \rightarrow OH(X^{2}\Pi) + SiH_{3}$ reveals a strong vibrational population inversion, $P(1)/P(0) = 3.4 \pm 0.4$. The rotational distribution of the major product in v'' = 1 is thermal with $T_{rot} = 600 \pm 20$ K. The product distribution of OH in v'' = 0 cannot be simply characterized in terms of a temperature, nor does the population ratio for the Λ doublet components provide unambiguous evidence concerning the production mechanism, but it clearly differs from that responsible for production of the vibrationally excited products.

Introduction

Extensive study of oxygen atom chemistry has resulted in a large body of kinetic information that facilitates the modeling of such diverse systems as combustion flames, atmospheric composition, and chemical lasers. Reliable rate coefficients characterizing a broad range of elementary processes involving atomic oxygen in its ground electronic state $O({}^{3}P_{J})$ are known over an extensive temperature range.¹ Ongoing examination of the thermal kinetics of fundamental processes such as $O({}^{3}P_{J}) + H_{2} \rightarrow OH(X^{2}\Pi) +$ H provide ever more detailed information concerning the mechanism of oxidation reactions.²

One may contrast the copious available data concerning the kinetics of $O({}^{3}P_{J})$ reactivity with a relative dearth of information concerning the dynamics of such reactions. Selected studies of energy disposal of oxidation reactions resulting in the production of CO have been carried out using the technique of small signal laser gain spectroscopy,³ while laser-induced fluorescence (LIF) detection of $OH(X^2\Pi)$ has yielded information concerning the energetics of products following reaction of $O({}^{3}P_{J})$ with relatively large hydrocarbons.⁴⁻⁷ Together these experiments revealed that reaction of $O({}^{3}P_{J})$ with saturated substrates generally proceeds via a direct interaction, a conclusion that may be compared to the now well-documented observation that oxygen atoms in their lowest, optically metastable electronic state $O(^{1}D_{2})$ primarily insert into chemical bonds forming a relatively long-lived intermediate collision complex that then dissociates into product fragments.9-19

(1) Herron, J. T.; Huie, R. E. J. Phys. Chem. Ref. Data 1974, 2, 467. (2) Presser, N.; Gordon, R. J. J. Chem. Phys. 1985, 82, 1291.

- (3) Lin, M. C.; Umstead, M. E.; Djeu, N. Annu. Rev. Phys. Chem. 1983, 34, 557.
 - (4) Andresen, P.; Luntz, A. C. J. Chem. Phys. 1980, 72, 5842
- (5) Klerinermanns, K.; Luntz, A. C. J. Chem. Phys. 1982, 77, 3533.
- (6) Dutton, N. J.; Fletecher, I. W.; Whitehead, J. C. Mol. Phys. 1984, 52, 475.
- (7) Barry, N. J.; Fletcher, I. W.; Whitehead, J. C. J. Phys. Chem. 1986, 90, 4911.
- (8) Luntz, A. C.; Schinke, R.; Lester, Jr., W. A.; Gunthard, Hs. H. J. Chem. Phys. 1979, 70, 5908.
- (9) Smith, G. K.; Butler, J. E.; Lin, M. C. Chem. Phys. Lett. 1979, 65, 115. (10) Luntz, A. C. J. Chem. Phys. 1980, 73, 1143.
- (11) Smith, G. K.; Butler, J. E. J. Chem. Phys. 1980, 73, 2243.
- (12) Saunders, N. D.; Butler, J. E.; McDonald, J. R. J. Chem. Phys. 1980, 73, 5381.
- (13) Buss, R. J.; Cassavecchia, P.; Hirooka, T.; Sibener, S. J.; Lee, Y. T. Chem. Phys. Lett. 1981, 82, 386.
- (14) Cordova, J. E.; Rettner, C. T.; Kinsey, J. L. J. Chem. Phys. 1981, 75, 2742.
- (15) Butler, J. E.; MacDonald, R. G.; Donaldson, D. J.; Sloan, J. J. Chem. Phys. Lett. 1983, 95, 183.
- (16) Butler, J. E.; Jursich, G. M.; Watson, I. A.; Wiesenfeld, J. R. J. Chem. Phys. 1986, 84, 5363.
 - (17) Aker, P. M.; Sloan, J. J. J. Chem. Phys. 1986, 85, 1412.
- (18) Huang, Y.; Gu, Y.; Liu, C.; Yang, X.; Tao, Y. Chem. Phys. Lett. 1986, 127, 432

In this regard, $O({}^{3}P_{1})$ reacts with dynamics that are similar to those characterizing the chemistry of atomic fluorine. The product energetics of the HF resulting from $F(^{2}P_{J}) + RH \rightarrow HF + R$ have been extensively examined primarily because such reactions proceed with relatively large cross section to yield vibrationally excited HF, which may be detected in defined quantum states with good efficiency by observation of infrared emission.²⁰ Because OH luminescence is significantly weaker than that of HF and the reaction rate for hydrogen abstraction by thermal $O({}^{3}P_{J})$ significantly smaller than that by $F(^{2}P_{J})$, similar investigations of oxygen atom reaction dynamics are not generally feasible.

The present experiments probe the dynamics of the reaction

$$O(^{3}P_{J}) + SiH_{4} \rightarrow OH(X^{2}\Pi) + SiH_{3}$$
(1)

a process that is likely to be of considerable importance during the initial phase of plasma enhanced and photoinduced chemical vapor deposition of SiO_2 from $N_2O/SiH_4\,\text{mixtures}^{21\text{--}23}$. The rate coefficient characterizing reaction 1 has been measured²⁴ over the range 297–438 K, $k_1 = 6.84 \times 10^{-12} \exp[-(1580 \pm 300)/RT]$ cm^3 molecule⁻¹ s⁻¹. A more recent determination of the rate of the analogous reaction of atomic oxygen with trimethylsilane²⁵ $O(^{3}P_{J}) + (CH_{3})_{3}SiH \rightarrow OH(X^{2}\Pi) + (CH_{3})_{3}Si \text{ at } 297 \text{ K yielded}$ a value approximately 5 times larger than that measured for reaction 1, $k_1(297) = 4.8 \times 10^{-13}$. This result suggests that the reported value of k₁ may reflect a systematic error resulting from the prereaction of SiH_4 with the O atom precursor, NO₂. This discrepancy has not yet been resolved. The analogous reaction of atomic fluorine with silane

$$F(^{2}P_{J}) + SiH_{4} \rightarrow HF + SiH_{3}$$
(2)

is known to be fast,²⁶ $k_2 \approx 5 \times 10^{-10}$, and to yield HF in an inverted vibrational distribution.²⁷ Information theoretic analysis suggests that reaction 2 may be viewed as a three-body collision in which the SiH₃ radical plays the role of the isoelectronic chlorine atom in²⁰

$$F(^{2}P_{J}) + HCl \rightarrow HF + Cl$$
(3)

Experimental Section

The energetics of $OH(X^2\Pi)$ produced following reaction 1 were monitored shortly following the initial formation of $O({}^{3}P_{1})$ in the ultraviolet laser photodissociation of NO2. Observation of near-nascent OH population distributions was ensured by minimization of both the delay time prior to excitation of the LIF signal

- (19) Cleveland, C. B.; Jursich, G. M.; Trolier, M.; Wiesenfeld, J. R. J. Chem. Phys. 1987, 86, 3253.
- (20) Ding, A. M. G.; Kirsch, L. J.; Perry, D. S.; Polanyi, J. C.; Schreiber, J. L. Discuss. Faraday Soc. 1973, 55, 252. (21) Rand, R. J. J. Vac. Sci. Technol. 1979, 16, 420.
- (22) Boyer, P. K.; Roche, G. A.; Ritchie, W. H.; Collins, G. J. Appl. Phys. Lett. 1982, 40, 716.
- (23) Chen, J. Y.; Henderson, R. C.; Hall, J. T.; Peters, J. W. J. Electrochem. Soc. 1984, 131, 2146. (24) Atkinson, R.; Pitts, Jr., J. N. Int. J. Chem. Kinet. 1978, 10, 1151.

(25) Hoffmeyer, H.; Horie, O.; Potzinger, P.; Reimann, B. J. Phys. Chem. 1985, 89, 2901.

- (26) Smith, D. J.; Setser, D. W.; Kim, K. C.; Bogan, D. J. J. Phys. Chem. 1977, 81, 898.
- (27) Bogan, D. J.; Setser, D. W. J. Chem. Phys. 1976, 64, 586.

and the ambient gas pressure in a reaction chamber, the details of which have been previously published.¹⁶

1. Photolytic Production of Atomic Oxygen. Photodissociation of NO_2 below the threshold wavelength for predissociation yields atomic oxygen

$$NO_2 + h\nu(\lambda < 400 \text{ nm}) \rightarrow NO + O(^3P_J)$$
 (4)

In the present work, 350-nm photolysis of NO₂ is accomplished with a XeF excimer laser outfitted with unstable resonator optics. Less than 1% of the NO₂ in the reaction zone was decomposed with each laser pulse ($E_{\text{laser}} = 1.5 \text{ mJ cm}^{-2}$, $\tau \approx 20 \text{ ns}$, repetition rate = 20 Hz).

Photodissociation of NO₂ above the energetic threshold for (4) results in the production of translationally excited $O({}^{3}P_{J})$. Molecular beam studies²⁸ of reaction 4 reveal roughly equal populations of NO in v'' = 0 and 1 following photolysis at 347.1 nm. Assuming similar behavior following photodissociation at 350 nm, we calculate a collision energy of ca. 1200 cm⁻¹ in the center of mass frame of O/SiH₄. The energy arising in reaction 1 from thermal reagents as calculated from bond dissociation energies and the phenomenological activation energy, ²⁴ E_{a} ,

$$E = D_0^0(\text{O-H}) - D_0^0(\text{SiH}_3-\text{H}) + E_a + 3RT \approx 4670 \text{ cm}^{-1}$$
(5)

thus represents a lower bound on the total available energy. It includes neither the excess collision energy nor excitation energy associated with the possible production of the spin-orbit levels, $O(^{3}P_{1})$ and $O(^{3}P_{2})$ (158 and 226 cm⁻¹, respectively) from NO_{2} photolysis.

2. Detection of OH by LIF. Approximately 200 ns following the initiating XeF laser pulse, a XeCl-pumped, frequency-doubled, tunable dye laser (Lumonics Hyperdye, $\Delta\lambda \approx 0.002$ nm) probes the population of OH(X²\Pi, v'', N'', f'', \lambda'') by exciting the 0,0 and 1,1 bands of the A² $\Sigma \leftarrow X^2\Pi$ transition in the range 306-318 nm. The unresolved fluorescence is subsequently detected at right angles to the counterpropagating photolysis and probe laser beams with a high-gain photomultiplier (EMI 9558QB) viewing through a broad-band ultraviolet filter consisting of UG11 glass and 10 cm of 1 M NiSO₄. This combination significantly attenuates the scattered photolysis light at 350 nm. The electronic signal is then sampled with a boxcar detector and recorded in a laboratory microcomputer system.

Conversion of the measured LIF signal S to state-resolved OH(X² Π) population requires correction for variation in the intensities of both the XeF and probe lasers, I_{XeF} and I_{probe} , as well as accurate values of the Einstein coefficients for stimulated emission, $B_{\nu,T'}^{\nu,\mu}$

$$P(v'', N''f'', \lambda'') \propto \frac{S}{I_{\text{XeF}}I_{\text{probe}}B_{v'J''}^{v'J'}}$$
(6)

Laser intensities are monitored and recorded simultaneously with the LIF signal during spectral scans. Tabulated values of $B_{\nu'J''}^{v'J''}$ are used throughout.²⁹ Under the present experimental conditions, electronic quenching of OH(A² Σ) by ambient gases does not affect the derived populations of even the lowest lying rotational levels by more than 20%.^{30,31} The reported values of $P(v'',N'',f'',\lambda'')$ need not be corrected for predissociation of the excited state because the highest rotational levels formed are well below the crossing of the ⁴ Σ ⁻ state near 5300 cm⁻¹ of A² Σ , $v'' = 0.^{32}$ The linearity of the LIF measurements was confirmed by comparing the relative intensities of satellite and main branch transitions that probe the same level of OH; these were usually within a factor of 25% even though the $B_{\nu'J''}^{v'J'}$ differ by factors of 2–6.

3. Materials. Nitrogen dioxide (Matheson Gas) was purified of low-boiling impurities by multiple freeze-thaw cycles. Silane



Figure 1. Merged LIF spectrum of the OH product arising from $O({}^{3}P_{J})$ + SiH₄ \rightarrow OH(X²II) + SiH₃ obtained under the experimental conditions described in the text. The signal intensities have been corrected for variations in I_{XeF} and I_{probe} .

(Air Products) was used as supplied. These experiments were carried out at a total pressure of 180 mTorr (NO₂:SiH₄ = 2:1); the mixtures were prepared in a standard mercury- and grease-free high-vacuum line.

Results

The quality of the experimental data can best be judged from examination of the merged $OH(A^2\Sigma \leftarrow X^2\Pi)$ LIF spectrum presented in Figure 1. Extensive population of $OH(X^2\Pi, \nu''=1)$ can clearly be discerned. Conversion of the spectrum to micropopulations (the state populations divided by their rotational degeneracy, 2J'' + 1) yields the distributions displayed in Figure 2.

1. Electronic Populations. Analysis of the spectra reveals that the ratio of the fine structure state micropopulations summed over all of the accessible rotational levels differs for the two vibrational states, $P({}^{2}\Pi_{3/2})/P({}^{2}\Pi_{1/2}) = 1.1 \pm 0.1$ for OH(X ${}^{2}\Pi, v''=0$), and 1.5 ± 0.2 for OH(X ${}^{2}\Pi, v''=1$). Thus, there is no significant difference between the populations of the fine structure levels in the lowest vibrational state and a small difference favoring the production of the lower level in v'' = 1.

The relative populations of OH produced in the π^+ and π^- states, probed by the P/R and Q branches, respectively, display an exceptionally interesting and, to the best of our knowledge, unprecedented state-dependent behavior. Examination of Figure 3 reveals that the ratio of Λ doublet state population, $P(\pi^+)/P(\pi^-)$ for the OH product formed in v'' = 1 following reaction 1 is slightly greater than unity. By contrast, the $OH(X^2\Pi, v''=0)$ product does display (Figure 3) remarkable behavior not previously observed in the OH product of a bimolecular reaction. Although the populations of the lower $(2 \le J'' \le 6)$ rotational levels derived from the P and R branches appear to be larger than those derived from the Q branches, those obtained from all branches at higher rotational levels (where the angular momentum coupling most closely approximates that of Hund's case b) are equal within experimental error. Possible interpretations of the observed Λ doublet state populations in OH($X^2\Pi$, v''=0) are reserved for the Discussion; the data do appear to support different mechanisms for formation of the OH product in the two thermochemically accessible vibrational levels.

2. Rotational Populations. Just as the Λ doublet populations of OH in the v'' = 0 and 1 states differ, so do the rotational distributions. That of OH(v''=1) can be described (Figure 2b) quantitatively in terms of a thermal distribution characterized by a temperature $T_{\text{rot}}^{v'=1} = 600 \pm 20$ K. Description of the rotational distribution characterizing the OH($X^2\Pi, v''=0$) product of reaction 1 is clearly more complex (Figure 2a). Below N'' = 6, the distribution can be approximated by a rotational temperature $T_{\text{rot}}^{v''=0}$ = 750 ± 150 K. However at higher rotational energies, the

⁽²⁸⁾ Busch, G. E.; Wilson, K. R. J. Chem. Phys. 1972, 56, 3626.

⁽²⁹⁾ Chidsey, I. L.; Crosley, D. R. J. Quant. Spectrosc. Radiat. Transfer 1980, 23, 187.

⁽³⁰⁾ Copeland, R. A.; Crosley, D. R. Chem. Phys. Lett. 1984, 107, 295.
(31) Copeland, R. A.; Dyer, M. J.; Crosley, D. R. J. Chem. Phys. 1985, 82, 4022.

⁽³²⁾ Sutherland, R. A.; Anderson, R. A. J. Chem. Phys. 1973, 58, 1226.





Figure 2. Micropopulation distributions derived from experimental spectrum: (a) v'' = 0; (b) v'' = 1. These were obtained from the following transitions: $P_{11}(\Box)$, $P_{22}(\blacksquare)$, $Q_{11}(O)$, $Q_{22}(\bullet)$, $R_{11}(\Delta)$, $R_{22}(\blacktriangle)$. The solid line represents an RRHO prior distribution calculated assuming no internal excitation of the SiH₃ fragment. The dashed lines correspond to the values of T_{rot} referred to in the text.



Figure 3. Dependence of λ doublet population ratios $P(\pi^+)/P(\pi^-)$ upon rotational state in OH(X²II,v''=0) (O) and OH(X²II,v''=1) (\bullet).

observed distribution clearly inverts in a manner quite similar to product OH distributions arising from the reactions of electronically excited $O({}^{1}D_{2})$ with hydrogen-containing molecules.^{10,12,14}

Because neither observed rotational distribution corresponds to $T_{rot} \sim 300$ K, these almost certainly do not arise as the result of collisional relaxation of the nascent OH distribution. Furthermore, no a priori mechanism predicts a much larger efficiency for rotational relaxation in OH(X²\Pi, v''=1) than in the ground

vibrational state. Indeed were the observed thermal rotational distribution in v'' = 1 due to collisional relaxation, one would expect the collisionally metastable levels¹⁹ (for which $E_{J''} - E_{J''-1}$ > kT) to assume a different distribution than those at lower levels. The data of Figure 2b do not support such a bimodal distribution, strengthening the argument that the rotational distribution for OH in the ground vibrational state, which was obtained under the same conditions as were used in the determination of the OH rotational distribution in v'' = 1, actually approximates the nascent one. The observed rotational distributions appear to support the existence of two quite different mechanisms for reaction 1, the first leading to a largely (but we see here, not exclusively) inverted rotational distribution and some enhanced production of the π^+ component for OH molecules formed in v'' = 0, while the other leads to production of $OH(X^2\Pi, v''=1)$ with a relatively cool thermal rotational distribution and no significant propensity for formation of one or the other Λ doublet component.

3. Vibrational States. Summation of the observed rotational distributions in v'' = 0 and 1 leads directly to an estimate of the relative populations of OH product formed in these two vibrational levels, $P(1)/P(0) = 3.4 \pm 0.4$. The primary source of systematic error in this measurement arises from the need to correct the observed LIF emission signals for the wavelength dependent response of the filter-photomultiplier combination which strongly attenuates the $A^2\Sigma(v'=1) \rightarrow X^2\Pi(v''=0)$ bands. The product OH vibrational distribution resulting from reaction 1 is highly inverted, in good accord with the previously reported ratio of HF state populations deduced from an information theoretic treatment²⁷ of reaction 2, P(1)/P(0) = 3.1. In general, such strongly inverted vibrational population ratios can be associated with the early release of reaction exoergicity along the reaction coordinate.

Discussion

We begin by examining the overall energetics of reaction 1. The most highly excited observed states of $OH(X^2\Pi)$ are v'' =0, J'' = 15.5, $E_{\text{internal}} = 4400 \text{ cm}^{-1}$, and v'' = 1, J'' = 9.5, E_{internal} = 5200 cm^{-1} , the internal energies of which can be compared with the 4670 cm⁻¹ nominally available to the reaction of thermalized reagents at 300 K. In the case of OH(v''=1), the population of the rotational levels above 5000 cm⁻¹ is at least 2 orders of magnitude less than those in the lowest levels. Hence the signal quality of the data is significantly worse and the populations of the high-lying levels can only be regarded as estimates. The quantitative estimates of the population in the higher rotational levels of v'' = 0 are, by contrast, at least as good as those of the lower ones, because the observed population distribution does not vary by more than an order of magnitude over the entire observed manifold of states. Thus the value of maximum $E_{\text{internal}} = 4400$ cm^{-1} derived from the population in v'' = 0 can be regarded as being significantly more reliable and in sensible accord with both the SiH₃-H bond energy³³ and the reported activation energy E_a .²⁴ The observation of small populations in the higher rotational levels of $OH(^{2}\Pi, v''=1)$ may also reflect the coupling into OH product rotation of excess translational energy from incompletely thermalized oxygen atoms formed²⁸ in the photodissociation of NO₂.

Elegant experimental studies of $O({}^{3}P_{J})$ reaction with alkanes⁴

$$O(^{3}P_{J}) + RH \rightarrow OH(X^{2}\Pi) + R$$
(7)

revealed a strong preference for near-collinear encounters and subsequent direct hydrogen abstraction with little excitation of OH rotation. Consistent with this mechanism was the failure to observe any preference for π orbital orientation with respect to the rotation plane of the product diatomic. A slight preference for formation of OH(${}^{2}\Pi_{3/2}$) was observed, but nonadiabatic transitions between the ${}^{3}\Pi_{0}$ and ${}^{3}\Pi_{2}$ states of the ROH collision complexes scramble the expected correlations favoring production of the lower lying ${}^{3}\Pi_{2}$ state that correlates with O(${}^{3}P_{2}$) + RH.

Table I contains a brief qualitative description of the OH internal mode population distributions observed following reactions 1 and 7. Both reaction 7 and the channel of reaction 1 leading

⁽³³⁾ Doncaster, A. M.; Walsh, R. Int. J. Chem. Kinet. 1981, 13, 1981.

TABLE I: Characteristics of Observed OH Population Distributions following Reaction of $O({}^{3}P_{J})$ with Alkanes and SiH₄

internal mode	0 + RH (ref 4) $v'' = 0$	$O + SiH_4$ (this work)	
		v'' = 0	<i>v</i> ″ = 1
fine structure Λ doublet rotation	$^{2}\Pi_{3/2}$ favored no preference cool	no preference π^+ slightly favored inverted	$^{2}\Pi_{3/2}$ favored no preference cool

to OH(v''=1) display characteristics of a direct abstraction via a nearly collinear collision complex with steep barriers to Si-H-O bending. These include a relatively low degree of rotational excitation in OH and lack of Λ doublet specificity, the latter resulting from a failure to orient the nascent π orbital of the OH to the rotation plane during H-Si bond scission. The predominance of the vibrationally excited product in reaction 1 suggests that direct abstraction plays a major role during the course of the $O({}^{3}P_{J})$ -SiH₄ interaction. Further support of a mechanism involving abstraction comes from the observation that the rotational distribution characterizing $OH(^{2}\Pi, v''=1)$ closely approximates that of the HF product following reaction 3.20 Indeed, the average fraction of available energy in excess of vibrational energy which is deposited into rotation of the HF(v''=1) product of (3), 43%, closely approximates the 37% deposited into rotation of the OH-(v''=1) product of reaction 1.

Except for the lowest rotational levels for which a thermal distribution can be discerned, the product distribution of OH- $(^{2}\Pi.v''=0)$ differs significantly from that observed for molecules formed in v'' = 1 and from that expected to result from direct abstraction. Presumably, these low-lying levels arise as the result of direct abstraction as in the case of all observed levels of the v'' = 1 state. The relatively high degree of rotational excitation in the v'' = 0 product may be compared to similar observations made following reaction of $O({}^{1}D_{2})$ with alkanes¹⁰ and ammonia.^{12,14} Insertion of the excited oxygen atom into the R-H bond precedes dissociation to yield R + OH. Abstraction generally plays only a minor role. The observed rotational populations in the higher levels of the v'' = 0 state along with the transient propensity for π^+ component production appears to support a mechanism in which the product OH results from the dissociation of a relatively long-lived intermediate, perhaps an internally excited silanol intermediate formed following attack of $O({}^{3}P_{1})$ on the H-SiH₃ bond,

$$O(^{3}P_{J}) + SiH_{4} \rightarrow H_{3}Si-OH^{\dagger} \rightarrow SiH_{3} + OH(X^{2}\Pi, v''=0)$$
(8)

The insertion mechanism exemplified by reaction 8 cannot occur during the reaction of $O({}^{3}P_{J})$ with alkanes, because the energy of the lowest lying triplet state of the ROH collision complex lies above that of the reactants.

The existence of a bridged structure arising from interaction of the d orbitals of Si with O

could modify the critical configuration of the exit channel. Such

a bridged structure has been invoked³⁴ to explain seemingly anomalous rotational excitation following reaction 2. We cannot presently assess whether such an intermediate might account for the broad distribution of rotational energy in the v'' = 0 product of reaction 1, but its effect may be reflected in the limited propensity for π^+ component production observed in Figure 3. Such an interpretation provides for the intermediacy of a linear O-H-Si configuration which leads to the predominant production of vibrationally excited OH; the detailed energetics of the O(³P_J)/SiH₄ interaction control the relative vibrational populations and rotational distributions.

Whether the OH formed in v'' = 0 and v'' = 1 following reaction 1 arises either as the result of collisional encounters that proceed on different potential surfaces or in different regions of the same surface remains an open question. That the ratio of fine structure state populations differs for the two product vibrational states provides some support for a mechanism involving different surfaces which mediate collisions resulting in formation of OH in v'' =0 and v'' = 1. Certainly the value of $P({}^{2}\Pi_{3/2})/P({}^{2}\Pi_{1/2}) = 1.5$ \pm 0.2 observed for the product in v'' = 1 does not compare to that of 12 expected⁴ on the basis of a purely adiabatic reaction of $O({}^{3}P_{2})$ and $O({}^{3}P_{0})$ with SiH₄ via the $\Omega = 2$ and $\Omega = 0$ levels of the collision complex, thereby indicating that the channel of reaction 1 leading to production of vibrationally excited products cannot be described in terms of a pure adiabatic or diabatic interaction. By contrast, we observe no significant selectivity for production of either fine structure state in $OH(^{2}\Pi, v''=0)$. This suggests that the interaction of $O({}^{3}P_{I})$ with SiH₄ to produce OH in its vibrational ground state is accompanied by many nonadiabatic transitions between the spin-orbit states of the collision complex, an interpretation consistent with the existence of a relatively long-lived intermediate.

Future kinetic studies of reaction 1 and efforts to model the gas-phase chemistry controlling the plasma enhanced chemical vapor deposition of SiO_2 must account for the complications introduced by the predominant production of vibrationally excited hydroxyl radicals, which may abstract, with an enhanced rate, an additional hydrogen atom from ambient SiH_4 . The dynamics of the O/SiH₄ interaction leading to OH(v''=1) are similar to those governing the analogous reaction of O(³P_J) with alkanes, which can be characterized as a direct abstraction of hydrogen along a nearly collinear reaction coordinate. The details of reaction 1 differ, however, in the channel leading to production of OH in its ground vibrational state. Here, product distributions of both the rotational and electronic states suggest the intermediacy of a relatively long-lived complex with a nonlinear structure.

Acknowledgment. This work was supported under an NSF grant to the National Resource and Research Facility for Submicron Structures at Cornell University. Stimulating discussions with C. B. Cleveland and M. Trolier were important in the analysis of these results.

Registry No. O, 17778-80-2; SiH₄, 7803-62-5; OH, 3352-57-6.

(34) Duewer, W. H.; Setser, D. W. J. Chem. Phys. 1973, 58, 2310.