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Multiple dynamical pathways in the $O+SiH_4$ reaction studied by the crossed molecular beam method

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In this report, the $O+SiH_4$ reaction is investigated using crossed molecular beam techniques. Multiple pathways have been observed for this reaction. Angular resolved time-of-flight spectra have been measured for all reaction products in a single set of experiments. Different product angular distributions were measured for various product channels, indicating that multiple reaction pathways with distinctive dynamics are present. An intriguing triple product channel, $SiO+2H_2$, has also been clearly identified. However, the role of $O({}^3P)$ vs $O({}^1D)$ in the reactions remains to be clarified in further experimental investigations. This study provides a good example of multiple dynamical pathways in a complicated reaction, which opens enormous opportunities in investigating the dynamics of chemical reactions that are important in combustion and atmospheric chemistry. © 2000 American Institute of Physics. [S0021-9606(00)01129-6]

I. INTRODUCTION

Modern experimental studies of reaction dynamics have mainly focused on elementary chemical reactions during the last few decades. Chemical dynamics studies of complicated reactions of energetic species with multiple reaction channels have received little attention, even though a significant fraction of chemical reactions in atmospheric and combustion processes involve multiple reaction pathways. This is largely due to the lack of sensitive and low background universal detection techniques which can detect all chemical reaction products. Reliable full-fledged quantum mechanical dynamical calculations for complicated reactions are still lacking even though overall theoretical studies on chemical reactions are becoming more and more reliable. Therefore, experimental investigation still remains to be the most viable way to learn the detailed dynamics of complicated reactions with multiple reaction pathways.

The universal crossed molecular beam method based on electron impact ionization of chemical products has been essential in investigating the dynamics of bimolecular chemical reactions during the last few decades. Product angular and translational energy distributions can be measured using this powerful method. Electron impact ionization with quadrupole mass selection is, in principle, an ideal universal detection method for all reaction products. The detection efficiency of this method is, however, limited by the low ionization efficiency, the limited quadrupole transmission efficiency, and the high background in the detector. Recently, a

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new apparatus was set up in our laboratory with a much improved detection efficiency in order to investigate more complicated chemical reactions. A custom designed, larger sized quadrupole mass filter was installed in an effort to increase the transmission efficiency for product ions. A much lower background in the detector ($<10^{-12}$ Torr) was also achieved using multiple high vacuum pumps and cleaner vacuum conditions.¹ With these efforts, the detection efficiency is much improved for all reaction products. This much improved instrument opens an exciting new avenue for investigating the dynamics of more complex reactions with multiple pathways under single collision conditions. In this report, the O(${}^{3}P$, ${}^{1}D$) + SiH₄ reaction using this new apparatus will be presented, providing a good example of extremely complicated reactions with a clear dynamical picture.

The reactivity of $O({}^{3}P)$ and $O({}^{1}D)$ is very important because of their roles in combustion processes and chemical vapor deposition (CVD) processes. One of the methods to produce the SiO₂ layer over the Si is CVD using oxygen gas and silane gas.^{2–6} A number of relevant chemical processes have been investigated theoretically.^{7–17} However, very little is known about the detailed mechanism of this oxidation process even in the gas phase. In addition, this reaction is very important in the combustion and the explosion of silane.

The O(³*P*) reaction with SiH₄ has been quite extensively investigated in the gas phase. A few measurements have been carried out on the total reaction rate at room temperature for this reaction. Atkinson and Pitts¹⁸ used flash-photolysis with O/NO chemiluminescence detection of the O atoms and obtained $k=4.8 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$. Mkryan *et al.*¹⁹ measured the rate constant to be $2.8 \times 10^{-13} \text{ cm}^{3} \text{ s}^{-1}$

using a discharge-flow method with ESP detection of O atoms. A recent measurement by Ding and Marshall²⁰ determined the rate constant at the room temperature to be 3.5 $\times 10^{-13}$ cm³ s⁻¹. These measured rate constants are quite consistent with each other. At a temperature of 1000 K, the total reaction rate was measured to be about 4 $\times 10^{-11}$ cm³ s⁻¹.²¹ Clearly, the reaction rate increases as the temperature rises. A critical review is also provided for this reaction in that paper. At even higher temperature, no experimental data are available yet for this reaction. The dynamics of the OH+SiH₃ channel from this reaction has been investigated using the laser induced fluorescence (LIF) technique by Park et al.²² This work reveals that the OH vibrational population at v = 0 and 1 is strongly inverted, indicating that the abstraction mechanism is likely to play a significant role in the reaction. The rotational distributions for the v = 0 and 1 states are also quite different from each other. The only rate constant measurement for the OH channel for the $O({}^{3}P)$ reaction with silane was done by Setser et al.23 The rate constant k_{OH} was determined to be $1.2 \pm 0.4 \times 10^{-12} \,\text{cm}^3 \,\text{s}^{-1}$ at room temperature, which is actually a few times larger than that of the total rate constant measured at the room temperature. Obviously, there is no consensus yet on k_{OH} from previous studies. From the previous studies, 2^{2-24} the main reaction channel for the $O({}^{3}P)$ reaction with silane is determined to be the OH formation process likely through an abstraction channel and the insertion mechanism through the triplet surface is likely spin-forbidden. Therefore reaction channels occur through the insertion mechanism are likely not important in the $O({}^{3}P)$ reaction with silane.

The $O(^{1}D)$ reaction with SiH₄ has also been investigated extensively.²⁵⁻²⁹ The total reaction rate constant for this reaction was determined to be $3.0\pm0.3\times10^{-10}$ cm³ s⁻¹ at room temperature by Okuda et al.²⁹ From the same study, the relative yield of the OH channel was measured to be 36% with an inverted vibrational state distributions for the OH v=0 and 1 products. An interesting triple product channel SiO+2H₂ has also been observed by direct laser induced fluorescence of SiO, with the relative yield determined to be about 6%-13%. The H atom product channel has also been measured, with the yield measured to be 21%. The infrared diode laser spectroscopy study³⁰ of the same reaction measured the OH production rate k_{OH} to be 5 $\times 10^{-11} \,\mathrm{cm^3 \,molecule^{-1} \, s^{-1}}$, which is about half the value obtained by Okuda et al.²⁹ Many theoretical investigations³¹ suggest that the $O(^{1}D) + SiH_{4}$ reaction goes via an insertion mechanism similar to the analogous CH₄ reaction.^{32–34} Even though much experimental data are available, a clear and complete dynamical picture has still not been obtained. The relative importance of the $O({}^{3}P)$ and $O({}^{1}D)$ reactions with SiH₄ is also not exactly clear at the moment. Since the reaction rate of $O(^{1}D) + SiH_{4}$ is significantly larger than that of $O({}^{3}P) + SiH_{4}$ at room temperature, it is conceivable that even at high collision energies, the $O(^{1}D)$ reaction with SiH₄ might still be more important than the $O({}^{3}P)$ reaction with silane.

The heat formations for all the reactants and products involved in the pathways for both the $O(^{1}D)$ and $O(^{3}P)$ reactions have already been determined.^{35–37} Figure 1 shows



FIG. 1. Energy diagram for the possible channels of the $O({}^{3}P, {}^{1}D) + SiH_{4}$ reaction, based on previous *ab initio* calculations from Refs. 35, 36, and 37.

the possible pathways and the energy diagram. There are a total of ten different product channels that are energetically accessible for the $O(^{1}D) + SiH_{4}$ reaction, and eight different product pathways for the $O(^{3}P) + SiH_{4}$ reaction. For $O(^{1}D) + SiH_{4}$, the following channels are accessible:

$$O(^{1}D) + SiH_{4} \rightarrow SiH_{3} + OH$$
 (I)

$$\rightarrow$$
 H₃SiO+H/H₂SiOH+H (IIa/IIb)

$$\rightarrow$$
 H₂SiO+H₂/HSiOH+H₂ (IIIa/IIIb)

$$\rightarrow$$
 SiO+2H₂ (IV)

$$\rightarrow$$
 HSiO+H₂+H/SiOH+H₂+H (Va/Vb)

$$\rightarrow$$
 H₂SiO+2H/HSiOH+2H. (VIa/VIb)

For the $O({}^{3}P)$ + SiH₄ reaction, all channels listed above, except the H₂SiO+2H/HSiOH+2H channels, are energetically accessible.

II. EXPERIMENT

The apparatus used in this experiment is a recently built crossed molecular beam machine which has been described in detail elsewhere.¹ Briefly, the O atomic beam, generated using the photodissociation of O_2 at 157.6 nm in a skimmed O_2 pulsed beam, was crossed with a skimmed SiH₄ beam at a fixed angle of 90 deg. The O_2 beam was obtained by expanding a neat O_2 (99.99%) sample through a commercial pulsed valve (General Valve) with a rise time of about 50 μ s, at a stagnation pressure of about 5 atm. The expanded beam was then skimmed by a sharp edged skimmer (Beam Dynamics) with 2 mm diameter orifice. The O_2 beam was then intercepted by an unpolarized 157.6 nm laser beam, generated by a Lambda Physik LPX210I F₂ laser, with a pulse energy of about 30 mJ at a repetition rate of 50 Hz. The O

atomic beam was then skimmed once before entering the main chamber. In order to reduce the O_2 background, both in the main chamber and in the detector, the O₂ beam was rotated to an angle between 60° and 70° from the detector rotating plan The F2 laser beam was focused on a spot of 4 $mm(w) \times 2 mm(h)$ in the interaction region by a sphericalcylindrical MgF₂ shaping lens. Using the above focusing condition and laser power, the O₂ transition (cross-section $\sigma = 6.8 \times 10^{-18} \text{ cm}^2)^{38}$ at 157.6 nm can be easily saturated. The O_2 molecule breaks into one $O({}^3P)$ atom and one $O(^{1}D)$ atom at 157.6 nm photolysis, therefore the O atom beam contains both $O({}^{3}P)$ and $O({}^{1}D)$ with a ratio of 50:50.39 Because both types of O atoms react with silane, it will not be easy to differentiate the products from the two reactions. However, since the energetics of the $O({}^{3}P)$ and $O(^{1}D)$ reactions are significantly different, it is possible to make some conclusions in certain cases. The SiH₄ molecular beam was generated by expanding a neat SiH_4 (99.99%) sample at a stagnation pressure of 5 atm through a carefully adjusted pulsed valve (General Valve) with a rise time (10%-90%) of about 60 μ s, and then skimmed once by a 1.5 mm orifice skimmer before entering the main chamber. The $O({}^{3}P, {}^{1}D)$ beam, the SiH₄ molecular beam, and the detection axis are all in the same plane. The speed of the $O({}^{3}P, {}^{1}D)$ beam was 2367 m/s with less than $\pm 3\%$ velocity spread. The angular divergence of the O(${}^{3}P$, ${}^{1}D$) beam was about $\pm 2.5^{\circ}$. The speed of the SiH₄ beam was about 800 m/s with a speed ratio of about 10 and an angular divergence of about $\pm 2^{\circ}$. The collisional energy at which this work was carried out is about 8.0 kcal/mol.

The whole experiment was pulsed, and time zero was defined as the time when the two beams were crossed. After flying about 25 cm from the crossed region, the neutral reaction products were then ionized by a Brink's type electron impact ionizer with an electron energy of about 60 eV. The product ions were mass filtered by a quadrupole mass filter, and counted by a Daly ion detector. All time-of-flight (TOF) spectra were taken at 1 μ s per channel during the experiment. The TOF spectra shown in this work were all rebinned for a better S/N ratio without changing the shapes of the spectra. The total product angular distributions were measured by rotating the detector. During the experiments described above, the vacuum in the detector ionization region was maintained at about 1×10^{-12} Torr.

The time-of-flight spectra and angular distributions of the neutral products measured in the laboratory (LAB) frame were computer-simulated in order to obtain the translational energy distributions and angular distributions in the centerof-mass (CM) frame. In the simulation for a single reaction channel, normally a few initial CM translational energy distributions at several CM angles and an initial CM angular distribution were used as the starting point. If the product translational energy distribution for the channel is angular dependent, several CM translational energy distributions using linear interpolation. If the translational energy distribution is not angular dependent, however, a single distribution is normally used. The method to find out how many CM kinetic energy distributions are required is usually trial and error. Starting from the initial CM energy distributions and the initial CM angular distribution, the laboratory TOF spectra and the angular distribution for this channel can be simulated using the transformation from the CM frame to the LAB frame. By adjusting these CM translational energy distributions and the CM angular distribution, satisfactory fits to the measured TOF spectra and angular distribution are obtained. In this way, the CM translational energy distributions and the CM angular distribution can be obtained. Simulation of multiple channel processes can be done in a similar way by simply adding a few different channels together. Both the velocity spread (Δv) and the angular divergence of the two molecular beams have been incorporated in the simulation. Therefore the simulated TOF spectra reported in this work should have included the effects of the beam conditions, which were measured in situ experimentally.

III. RESULTS AND DISCUSSIONS

this work, signals $m/e = 17 (OH^+)$, In at $47(H_3SiO^+/H_2SiOH^+),$ $46(H_2SiO^+/HSiOH^+),$ $45(HSiO^+/SiOH^+)$, and $44(SiO^+)$ were detected from the O+SiH₄ reaction. TOF spectra at different laboratory angles and the total product angular distributions were measured for all above products. From detailed analysis of these results, a number of reaction channels have been identified. While it is clear that the $m/e = 17 (OH^+)$ product is coming from the OH+SiH₃ channel (channel I) and the m/e= $47 (H_3 SiO^+/H_2 SiOH^+)$ products are from reaction channels IIa and IIb, signals at other masses (mass 46, mass 45, and mass 44) products obviously contain original reaction products at these masses and various contributions cracking from higher mass products. Therefore analyses of these observed TOF spectra become quite complicated. Systematic analyses on these data are carried out, a reasonable picture is obtained from these analyses. In the following paragraphs, detailed analyses and results are described.

A. The OH+SiH₃ channel

OH products were detected at m/e = 17, indicating clearly the existence of the OH+SiH₃ channel. OH products are normally difficult to detect using conventional universal crossed beam apparatus because of the high background at mass 17 in the detector. This is especially true for reactions in which fast products are scattered into a large solid angle, such as O(¹D)+SiH₄ in which the OH products are scattered into the whole solid angle 4π (see Fig. 2 for the Newton diagram for this reaction). TOF spectra for the OH product were measured at 11 different angles. Figure 3 show six of these TOF spectra with TOF signals at different angles normalized. The signals observed are all due to reactive scattering since no other sources can contribute significantly to the mass 17 signal. The total product angular distribution for the OH product is shown in Fig. 4.

Reasonable fits to the TOF spectra of the OH product at different lab angles have been obtained using three different energy distributions at CM angles 0° , 25° , and 180° (see upper panel in Fig. 5). Kinetic energy distributions at other CM angles are obtained by linear interpolation using the above three distributions. Clearly, the translational energy



FIG. 2. Newton diagram for the $OH+SiH_3$ channel. The circle represents the OH product scattering Newton circle with 10 kcal/mol kinetic energy release.

distribution is coupled to the angular distribution, indicating that reaction products scattering into different CM angles obviously have different translational energy distributions, and thus different internal energy distributions. The OH



FIG. 3. The TOF flight spectra of mass 17 (OH) at six different laboratory angles. The empty circles are the experimental data, while the solid lines are the simulated results. These TOF spectra were taken by averaging signals over 200 000 laser shots.



FIG. 4. The total product angular distribution of the OH radical product. The solid squares are the experimental data, while the solid line is the simulation.

product CM angular distribution $P(\theta)$ used in the fitting is shown in the lower panel of Fig. 5. The CM velocity flux contour map (Fig. 6) of the OH product was also obtained from fitting the angular resolved TOF spectra (Fig. 3). From the results (Figs. 4, 5, and 6) described above, it is clear that



FIG. 5. The CM kinetic energy distributions of the OH product channels and the CM product angular distribution used in simulating the experimental TOF spectra and the laboratory angular distribution.

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FIG. 6. The product flux contour diagram of the OH product channel.

the OH products are scattered predominantly to the forward direction with respect to the O atom beam. This interesting observation provides important insight for the OH formation channel.

Since the long-lived complex mechanism normally produces forward and backward symmetric or isotropic angular distributions, it is quite obvious that the forward scattered OH products from the $O({}^{3}P, {}^{1}D)$ reaction with SiH₄ are formed with a totally different mechanism. These forward OH products are most likely produced from an abstraction type mechanism, in which the O atom comes in at a relative larger impact parameter and strips a hydrogen atom from the silane molecule directly; the intermediate reaction to produce the forward scattered OH products should be very shorted lived. In addition to the strongly forward scattered OH products, a significant portion of the OH products is backward scattered (see Fig. 5). These products are probably due to a long-lived complex mechanism. If the backward scattered products $(90^{\circ}-180^{\circ} \text{ in Fig. 5})$ are all due to this mechanism (the same amount of forward scattered products should also be included), the overall contribution to the OH channel from this mechanism should be about 36%. This is a rather significant contribution, implying that even though the abstraction mechanism is the most important for the OH formation, a mechanism involving a long-lived complex which is likely formed through the O atom insertion could also be significant.

The averaged product translational energy obtained from this experiment for this channel is about 16 kcal/mol for the fast forward scattered products ($\Theta_{CM}=0$). The available energy for the OH formation is about 64 kcal/mol for the $O(^{1}D)$ reaction, and 18 kcal/mol for the $O(^{3}P)$ reaction. Since it is not likely that all the available energy can be deposited into the product translational degree of freedom, especially for such a complicated reaction, the major forward scattered OH products observed in this study should mostly come from the $O(^{1}D)$ reaction. The high energy limit (all larger than 40 kcal/mol) in the translational energy distributions also supports this conclusion. Previous LIF measure-



FIG. 7. Newton diagram for the binary H and H_2 formation channels. The circles represents the Newton circles for heavy radicals from H and H_2 formation channels with different kinetic energy releases.

ments of the OH radical products^{22,29} from the $O({}^{3}P, {}^{1}D)$ reactions show inverted vibrational distributions, indicating that the OH radicals are internally hot. This is also consistent with the conclusion that main forwarded OH products observed are coming from the $O(^{1}D)$ reaction. For the backward scattered OH products ($\Theta_{CM} = 180^\circ$), averaged translational energy release is about 10.7 kcal/mol, which is significantly smaller than that for the forward scattered products. This is probably due to the long-lived intermediate formation mechanism in which energy is more randomized in the internal degrees of freedom of the products. It is possible that the $O({}^{3}P)$ reaction contributes more to this mechanism. The overall $O({}^{3}P)$ contribution should be minor in the OH production. In any case, the results presented above clearly show that an abstraction type reaction mechanism is largely responsible for the OH+SiH₃ pathway which is mainly due to the $O(^{1}D)$ reaction, while a more statistical long-lived intermediate mechanism is also significant. From the above investigations, it is also quite clear that the $O({}^{3}P)$ reaction is significantly less reactive than the $O(^{1}D)$ reaction at 8 kcal/ mol collisional energy. This is, nevertheless, not so surprising since $O({}^{3}P)$ is less reactive than $O({}^{1}D)$ at room temperature by almost two orders of magnitude. Even though the $O({}^{3}P)$ reaction cross section increases as temperature rises, it might still be less important than the $O(^{1}D)$ reaction at the collisional energy of this experiment.

B. The H+H₃SiO/H₂SiOH channel

The H₃SiO/H₂SiOH product was detected at $m/e = 47 (H_3SiO^+/H_2SiOH^+)$, which is clearly from the H+H₃SiO/H₂SiOH channel since no product at higher masses from this reaction is present. The Newton diagram for this channel is shown in Fig. 7. The CM direction for this



FIG. 8. The TOF flight spectra of mass $47 (H_3SiO^+/H_2SiOH^+)$ at four different laboratory angles. The empty circles are the experimental data, while the solid lines are the simulated results.

reaction is at about 34° laboratory angle. The experimental TOF spectra at four different laboratory angles are shown in Fig. 8. The total product angular distribution of the mass 47 product in the laboratory frame is shown in Fig. 9. The TOF spectra and the product angular distributions were simulated using two different CM kinetic energy distributions at 0° and 180°, shown in the upper panel of Fig. 10, and the CM product angular distribution shown in the lower panel of Fig. 10. CM kinetic energy distribution at other angles are obtained using linear interpolation from the distributions at 0° and 180°. The simulated results are also shown in Fig. 8 and Fig. 9 in comparison with the experimental results, which are in rather good agreement. It is interesting to point out that the product kinetic energy distributions at 0° and 180° degrees in the CM frame are apparently different from each other. At CM 180° degree (backward direction relative the O atom), the mass 47 product (H₃SiO/H₂SiOH) kinetic energy distribution is shifted toward higher energy in comparison with the 0° distribution. The product flux contour map for this reaction channel is constructed from the CM kinetic and angular distributions, and is presented in Fig. 11.



FIG. 9. The total product angular distribution of the H_3SiO/H_2SiOH product. The solid squares are the experimental data, while the solid line is the simulation.

From the CM angular distribution, it is obvious that the mass 47 product is essentially backward scattered relative to the O atom beam. This is quite interesting since the H atom formation are believed to come from an insertion mechanism from previous studies, which is unlikely to produce clearly backward scattered radical products. This indicates that the backward scattered products are likely from reaction mechanisms other than insertion type. The experimental results



FIG. 10. The CM kinetic energy distributions of the $H+H_3SiO/H_2SiOH$ product channels and the CM product angular distribution used in simulating the experimental TOF spectra and the laboratory angular distribution.

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FIG. 11. The product flux contour diagram for the $\rm H+H_3SiO/H_2SiOH$ product channel.

show that after the O atom attacks the SiH₄ molecule, some of the H₃SiO/H₂SiOH radical products bounces back while an H atom pops forward along the O atom beam. This backward scattered angular distribution suggests that this reaction pathway likely occurs at small impact parameters. Since SiH₄ is a tetrahedral molecule, the backward scattered radicals could come from a $S_N 2$ type mechanism in which the O(¹D) atom approaches directly at the Si atom along the departing H atom direction.

The product translational energy distribution peaks at about 11 kcal/mol with the maximum translational energy cut off at about 43 kcal/mol. Since the H atom product does not have any internal energy, the product internal energy for this channel should all be carried by the H₃SiO/H₂SiOH radicals, which should have about 55 kcal/mol internal energy if this reaction is due to the $O(^{1}D)$ reaction. Since the maximum available energy of the $O({}^{3}P)$ reaction with silane for the H formation channel (H₂SiOH+H) is about 49.8 kcal/ mol, it is certainly possible that some of these radical products observed are due to the $O({}^{3}P)$ reaction. There is, however, no documented observation of the H atom formation from the $O({}^{3}P)$ + SiH₄ reaction, while there are experimental evidences that the H formation processes are present in the $O(^{1}D)$ reaction. If the observed radical products at mass 47 are coming from the $O(^{1}D)$ reaction and the available energy is deposited into the vibrational degrees of freedom of the H₃SiO/H₂SiOH radicals, most of these radical products certainly will go through a secondary dissociation to form H₂SiO/HSiOH+H since the energetic H₃SiO/H₂SiOH radical products are clearly above the barriers to the triple product channels (see Fig. 1). Therefore if the products observed are from the $O(^{1}D)$ reaction, the majority of the H₃SiO/H₂SiOH products observed at m/e = 47 are likely electronically excited since these products clearly do not go through a secondary dissociation. Theoretical investigations of these radicals are desirable in order to better understand the sources of these processes.



FIG. 12. The neutral TOF spectra at m/e=47, 46, 45, 44 at lab angle $\Theta_L = 35^{\circ}$ which is close to the LAB angle of the center-of-mass velocity vector. Open circles: experimental data. Solid lines: fitting curves of various channels. Please see text for different assignments. All TOF signals have been normalized to the same number of laser shots. These spectra were typically taken by averaging signals over 100 000 laser shots.

C. The 2H+H₂SiO/HSiOH channel

In comparison with the TOF spectrum at mass 47 at 35° (the laboratory angle nearly along the CM direction), TOF spectra of ionized products at mass 46, 45, 44 at the same lab angle are shown together in Fig. 12. The TOF signals at these different masses have been normalized. From these TOF spectra it is quite obvious that the shapes of the lower mass products (m/e = 46, 45, and 44) are significantly different from the TOF spectrum at mass 47, indicating that extra neutral products at these lower masses are likely present in addition to the contribution from the dissociative ionization of mass 47 products. Furthermore, TOF spectra at 44, 45, and 46 are also substantially different from each other, implying that product channels to produce these lower mass neutral products are present with contributions from cracking of higher mass products. Since there are likely multiple contributions to the signals at masses 44. 45, 46, careful analyses have been carried out to show the least possible number of channels that are responsible to these signals. The analyses are done in the following way. For example, since the TOF spectra at mass 46 are significantly different from those at mass 47, a single component from dissociative ionization of mass 47 signals would not be sufficient to properly simulate the mass 46 TOF spectra. Therefore a new component is

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FIG. 13. The TOF flight spectra of mass $46 (H_2SiO^+/HSiOH^+)$ at four different laboratory angles. The empty circles are the experimental data, while the solid lines are the simulated results. Different contributions are labeled as in Fig. 12.

added to simulate the mass 46 TOF spectra. For the mass 45 signals, contributions from dissociative ionization of mass 46 and mass 47 are considered at first. Similarly, if the TOF spectra at mass 45 cannot be simulated using the dissociative ionization of mass 46 and mass 47 products, new contributions will be added to simulate the TOF spectra. TOF spectra at mass 44 are also analyzed in a similar way. From these analyses, a minimum number of reaction channels can be extracted from the data. These analyses provide at least a reasonable picture for the complicated dynamical processes which are hard to study by any other experimental method. During the analyses, dissociative ionization is assumed to be independent of internal energy excitation of the radical products. This should be a rather good approximation since high energy electrons ($\sim 60 \text{ eV}$) are normally used to ionize the reactive products with much less internal energy.

Four typical TOF spectra at $m/e = 46 (H_2SiO^+/HSiOH^+)$ are shown in Fig. 13. The total product angular distribution of mass 46 is also presented in Fig. 14. Since these TOF spectra are clearly different from those of mass 47, it is obvious that the observed products at mass 46 are not purely from the dissociative ionization of the

mass 47 products (H₃SiO/H₂SiOH). Therefore, the TOF spectra at mass 46 are simulated using two different contributions: the cracking contribution from the mass 47 product, and a neutral product channel at mass 46 with mass ratio of 46:2. A single CM kinetic energy distribution (the upper panel in Fig. 15) and a forward-backward symmetric product angular distribution (the lower panel in Fig. 15) are used to simulate the TOF spectra at different lab angles and the product laboratory angular distribution. The simulated TOF spectra and the laboratory angular distribution are shown in Fig. 13 and Fig. 14 along with the experimental results. The agreement between the experimental and simulated results is quite satisfactory. From this simulation, it is quite clear that the main product observed at mass 46 is the new channel of mass 46 neutral product, while there is some contribution from the cracking of the mass 47 product. The neutral mass 46 signals are most likely due to the neutral H₂SiO/HSiOH products. There are two possible sources for these radicals: the H₂+H₂SiO/HSiOH channel and the 2H+H₂SiO/HSiOH channel. The kinetic energy limit obtained from the above simulation is about 38 kcal/mol (Fig. 15). Since the energetic



FIG. 14. The total product angular distribution of the mass 46 ($H_2SiO^+/HSiOH^+$) product. The solid squares are the experimental data, while the solid lines are the simulations from two different contributions. Different contributions are labeled as in Fig. 12.

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FIG. 15. The CM translational energy distribution (upper panel) and CM angular distribution (lower panel) which are used to simulate the TOF spectra and the laboratory angular distribution of the extra contribution to the mass 46 signal using a 46:2 mass ratio. Some of the signals observed at mass 46 are from dissociative ionization of the mass 47 product.

limit of the 2H+H₂SiO/HSiOH channel from the O(¹D) reaction is about 40 kcal/mol, it is quite likely that the observed neutral products at mass 46 are due to this channel. The observed energy cutoff for this channel is much lower than that of the H₂ formation processes (~142 kcal/mol for H₂+H₂SiO/HSiOH), therefore it is not likely that the observed mass 46 signals are due to the H₂ formation processes. From the energy diagram in Fig. 1, it is quite obvious



FIG. 17. The total product angular distribution of the mass $45 (HSiO^+/SiOH^+)$ product. The solid squares are the experimental data, while the solid lines are the simulations from various contributions. Different contributions are labeled as in Fig. 12.

that the products observed are consistent with the $O({}^{1}D)$ reaction, not the $O({}^{3}P)$ reaction in which this triple product channel is not accessible energetically. The fact that the angular distribution for this channel obtained from the simulation is essentially forward–backward symmetric indicates that the products are likely produced through a long-lived intermediate which is possibly formed through the insertion of the O atom into the Si–H bond.

D. The H₂+H₂SiO/HSiOH channel

Signals at mass 45 have also been observed. Four typical TOF spectra at m/e = 45 (HSiO⁺/SiOH⁺) at different laboratory angles are shown in Fig. 16. The total product angular distribution of mass 45 is also presented in Fig. 17. The slower part of the signal at mass 45 can be simulated rather well using cracking contributions from the H formation (mass 47) and the 2H formation (mass 46) channels with slightly different ratio between the two channels from that at mass 46. This is likely due to the different cracking patterns of the original radicals. In addition, there is clearly some



FIG. 16. The TOF flight spectra of mass $45 (HSiO^+/SiOH^+)$ at six different laboratory angles. The empty circles are the experimental data, while the solid lines are the simulated from various contributions. Different contributions are labeled as in Fig. 12.

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FIG. 18. The translational energy distribution (with isotropic angular distribution) for the H_2 + H_2 SiO/HSiOH reaction channel used to simulate the fast contribution to the TOF spectra and the laboratory angular distribution of the mass 45 product using a 46:2 mass ratio.

extra fast feature in the TOF spectra of mass 45 in comparison with those of mass 46. This feature is assigned to the H₂+H₂SiO/HSiOH process. The kinetic energy distribution for this feature is obtained from simulation, and is shown in Fig. 18. The energetic limit (~120 kcal) of the distribution obtained is consistent with the available energy of the $H_2+H_2SiO/HSiOH$ process (~142 kcal/mol) of the O(¹D) reaction. This is rather significant evidence that these fast products at mass 45 are from the H₂SiO/HSiOH products which subsequently undergo dissociative ionization to become mass 45 ions (SiHO⁺/SiOH⁺). This observation is also very similar to that in the $O(^{1}D) + CH_{4}$ reaction, in which nearly all H₂CO/HCOH products from the H₂ formation channel were observed at mass 29 (HCO⁺).⁴⁰ The peak $(\sim 30 \text{ kcal/mol})$ of the kinetic energy distribution is also consistent with a typical reverse barrier height (20-30 kcal/mol) of a more statistical H₂ elimination process. An isotropic CM angular distribution fits well with the experimental results, implying that this process occurs also likely through a longlived complex which is possibly formed by the insertion mechanism.

E. The 2H₂+SiO channel

TOF spectra at mass 44 (SiO⁺) have also been measured. Figure 19 shows TOF spectra of mass 44 at four different laboratory angles. The measured product angular distribution of mass 44 is presented in Fig. 20. The main feature of the TOF spectra of mass 44 can be simulated using the contributions from dissociative ionization of higher mass products. An extra fast feature is required to simulate the TOF spectra of this mass in addition to the dissociative ionization contributions of higher mass products. Since this feature only exists at mass 44, it is most likely due to the neutral SiO products. There are two sources of generating SiO products: $SiO+H_2+2H$ and $SiO+2H_2$. It is known that the SiO+H₂+2H channel is not accessible energetically in this reaction. Therefore this new feature at mass 44 is likely from the $SiO+2H_2$ pathway. A reasonable fit to the TOF spectra and the laboratory angular distribution of mass 44 can be obtained by adding the SiO+2H₂ channel using a mass ratio of 44:4. The simulated results (see Figs. 19 and 20) including other contributions are in good agreement with the experimental data. Once again, an isotropic angular distribution in the CM frame for the $SiO+2H_2$ channel fits best to the experimental data, implying this product channel also likely goes through a long-lived reaction intermediate which is possibly formed through an insertion mechanism. The CM kinetic energy distribution used in the simulation is shown in Fig. 21. The energy cutoff (\sim 125 kcal/mol) of this distribution is quite consistent with that of the $SiO+2H_2$ channel, ~145 kcal/mol, from the O(^{1}D) reaction. This triple product channel has also been observed previously using laser induced fluorescence technique.²⁹ It has to be noted that because of the complicated nature of this reaction and the relative contributions of different channels are somewhat correlated, the analyses provided above should be regarded as qualitative only.



FIG. 19. The TOF flight spectra of mass 44 (SiO⁺) at four different laboratory angles. The empty circles are the experimental data, while the solid lines are the simulated from various contributions. Different contributions are labeled as in Fig. 12.

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FIG. 20. The total product angular distribution of the mass 44 (SiO⁺) product. The solid squares are the experimental data, while the solid lines are the simulations from various contributions. Different contributions are labeled as in Fig. 12.

F. Relative branching ratios

From the above analyses of the different product channels, relative branching ratios can also be estimated. Assuming the transmission efficiencies for all different ions are the same, and ionization efficiencies for masses 44–48 are twice that of mass 17 (OH),⁴¹ the OH channel should count about 48%, while other channels count the rest 52%. Among the other channels, the $2H_2$ +SiO channel is estimated to be 11%, the H₂+H₂SiO/HSiOH channel counts about 15%, the 2H+H₂SiO/HSiOH triple product channel is about 21%, and the H+H₃SiO/H₂SiOH channel (mass 47) is about 5%. These branching ratios are only roughly estimated numbers. It is interesting to point out that triple product processes are quite important in the title reaction, and the most important channel is the OH formation channel, similar to the O atom reactions with hydrocarbon molecules.

IV. CONCLUSIONS

From the above investigations, a total of six different channels have been observed in the $O+SiH_4$ reaction in this



Three binary product channels, SiH_3+OH , study. H₂SiO/HSiOH+H₂, H₃SiO/H₂SiOH+H, have been observed. Each of these three channels shows distinctive dynamical behaviors. The OH products are largely forward scattered, implying an abstraction type reaction mechanism is responsible for this channel. The H₃SiO/H₂SiOH products are scattered backward relative to the O atom beam, which is probably due to a SN₂ type reaction mechanism to this channel is possible. An H₂ formation channel has also been also observed. Since the 2H+H₂SiO/HSiOH channel shows a forward and backward symmetric distribution, it is likely that this channel goes through a long-lived (H₃SiOH)* reaction intermediate formed by O insertion to a S-H bond in SiH₄. An intriguing 2H₂+SiO channel is also clearly present. From the above analyses, the $O(^{1}D)$ reaction seems to be more important than the $O({}^{3}P)$ reaction in most of the channels.

Even though this study is qualitative in nature, it, nevertheless, provides a good experimental case of a complicated reaction with multiple pathways and triple product channels. With improved crossed molecular beam methods, it is now possible to study the dynamics of these complicated reactions under molecular beam conditions. More experimental studies on this reaction using either pure $O({}^{1}D)$ or $O({}^{3}P)$ beam are certainly desirable in order to clear some of the experimental facts. Further theoretical investigations are also in need in order to better understand this complicated reaction.

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