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ARTICLE

Crossed Beams Study on the Dynamics of Cl Atom Reaction with Silane

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The dynamics of the Cl+SiH_4 reaction has been studied using the universal crossed molecular beam method. Angular resolved time-of-flight spectra have been measured for the channel SiH_3Cl+H. Product angular distributions as well as energy distributions in the center-of-mass frame were determined for the channel. Experimental results show that the SiH_3Cl product is mainly backward scattered relative to the Cl atom beam direction, suggesting that the channel takes place via a typical S_N2 type reaction mechanism.

Key words: Chlorine atom, Silane, S_N2 mechanism, Universal crossed molecular beam

I. INTRODUCTION

Silane is one of the most important gases in the modern electronic industry. Its reactions with different species are related to many industrial related processes. The reaction dynamics of silane with the O atom has recently been investigated using the crossed molecular beam method [1]. Multiple channel dynamics were observed in this reaction. An intriguing triple product channel, SiO+$2H_2$, has been identified. The reaction dynamics of silane with F atom also has recently been investigated using the crossed molecular beam method [2]. The dynamics of the chlorine atom reaction is also interesting because of the rich dynamics involved in related reactions and its importance in the etching processes. Dynamics of Cl atom reactions with different species vary substantially. The Cl atom reaction with hydrogen is slightly endothermic. It has played a seminal role in the development of transition state theory and also serves as a textbook example of the kinetic isotope effect. The reaction is the abstractive type with a collinear barrier of about 22.99 kJ/mol. Spin orbit effect of the reaction had been much studied [3−5]. In the Cl atom reaction with methane [6], the very interesting state-to-state correlated dynamical picture has been observed, in which the methyl radical product at different quantum state correlate with a very dramatically different scattering picture of the HCl products at various vibrational states. The reactions of Cl atom and saturated hydrocarbons have been studied by Zare's [7] and Dagdigian's [8] groups. This is a photoinitiated reaction study using a single molecular beam. The angular distribution of the products was determined through the product speed distribution measurements using the core extraction technique in the ion-TOF (time-of-flight) measurement. The changing dynamics of these Cl atom reactions present a colorful picture of how chemical reactions occur for this important atom with different species.

Cl+SiH_4 reaction has two channels as following:

$$\mathrm{Cl} + \mathrm{SiH_4} = \mathrm{SiH_3} + \mathrm{HCl} \tag{1}$$

$$\mathrm{Cl} + \mathrm{SiH_4} = \mathrm{SiH_3Cl} + \mathrm{H} \tag{2}$$

Channel (1) has been widely studied in the past several decades by kinetic and dynamical experiment and theory [9−12]. But channel (2) has little been investigated by kinetic experiment and theory [13, 14]. And to our best knowledge, Only one dynamical experiment on channel (2) has been studied [15]. Figure 1 shows the energy diagram for the channel (2) of the Cl+SiH_4 reaction [16]. Infrared luminescence in the vicinity of 4.5 μm has been detected in SiH_4/Cl_2 mixtures under pulsed ultraviolet initiation of chemical reactions by Chesnokov and Panfilov [15], and they has attributed this infrared luminescence from vibrationally excited SiH_3Cl molecules generated by SiH_4 chlorination.

In this work, crossed molecular beam studies of the

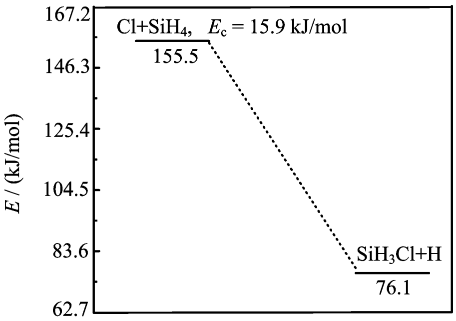

FIG. 1 Energy diagram for the SiH_3Cl formation channel from the Cl+SiH_4 reaction [16].

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Cl+SiH_4 reaction have been carried out using the universal crossed molecular beam technique. By careful measurements and detailed analyses of the TOF spectra and angular distributions of different products from the Cl+SiH_4 reaction, the SiH_3Cl+H channel has been observed. The detailed dynamics of the channel has also been analyzed.

II. EXPERIMENTS

The reaction of the Cl atom with silane has been studied recently in our laboratory using the crossed molecular beam technique based on electron impact ionization detection. The apparatus used in this experiment is a universal crossed molecular beam machine which has been described in detail elsewhere [17]. In brief, the Cl atom beam, generated using the double-stage pulsed dc discharge of Cl_2 in He [18], was crossed with another skimmed beam at a fixed angle of 90°. The 5%Cl_2 in He sample was expanded through a commercial pulsed valve (general valves) with a gas pulse width of about 150 μs, going through a pulsed discharge region, which is a 2 mm long channel before the discharged products re-expand out to vacuum. The high voltage discharge pulse is about 2 μs long and it is normally set to discharge on the peak of the gas pulse. From the TOF measurement of the beam, the pulse width of the Cl-atom beam pulse is determined to be about 10 μs. The expanded Cl atom beam was skimmed by a skimmer (beam dynamics) with 2 mm diameter orifice. The another molecular beam was generated by expanding a neat SiH_4 sample at about 303 kPa stagnation pressure through a carefully adjusted pulsed valve (general valve) with a rise time of about 50 μs and a pulse width of about 100 μs. The expansion was then skimmed by a 1.5 mm orifice skimmer before entering the main chamber. The Cl atom beam, the other beam and the detection axis are all in the same plane. The speed of the Cl atom beam is about 1.3 km/s with a speed ratio ($v/\Delta v$) of about 5. The speed of the other beam is about 420 m/s with a speed ratio of about 6 and an angular divergence of about ±3°. The collision energy in this experiment is about 22.99 kJ/mol. To measure the reactive scattering signals from the Cl atom reaction, signals were measured normally with the discharge pulse on and off so that background subtraction can be done properly.

Reaction products from the crossed region are detected by an ultrahigh vacuum mass elective, electron impact ionization detector. The whole experiment was carried out in a pulsed mode. Time zero was defined as the time when the two beams were crossed. After flying about 18.7 cm from the crossed region, the neutral reaction products were then ionized by Brink-type electron impact ionizer with electron energy of about 60 eV. The product ions were mass filtered by a quadrupole mass filter, and counted by MCP. All TOF spectra were taken at 10 μs/channel during the experiment. The product angular distribution can also be measured by rotating the detector. The experimental angular distribution is measured by taking the TOF spectra at different laboratory angles back and forth many times in order to reduce the measurement errors. Typically, the error bars for the experimental angular distribution should be about ±5%. During the experiments, the vacuum in the detector ionization region was maintained at 1.33 nPa. The TOF spectra and angular distributions of the neutral products measured in the laboratory frame were converted to the kinetic energy distributions and the angular distributions in the center-of-mass (CM) frame by using a forward convolution program.

III. RESULTS AND DISCUSSION

Reaction products at masses 66 and 65 from the title reaction have been detected. The shapes of the TOF signals at these masses are very similar at every laboratory detection angle. The parent mass is clearly at mass 66. The ion mass 65 resulted from the dissociative ionization of the SiH_3Cl product in the SiH_3Cl+H reaction channel.

Figure 2 shows the Newton diagram for the H formation channel of the title reaction for the SiH_3Cl products. From this diagram, it is clear that the SiH_3Cl fragments are scattered into a narrow laboratory angle range. Figure 3 shows the TOF spectra at mass 65 (SiH_2Cl^+) at four laboratory angles. In the laboratory frame, the Cl atom beam is defined at 0° while the silane atom beam is at 90°. To obtain the product kinetic energy distributions and angular distribution in the CM frame for the observed channels, a WINDOWS-based forward convolution program is used in the simulation. After simulations to these TOF spectra by iteratively adjusting one set of kinetic energy distributions and a single CM product angular distribution, CM product angular distributions as well as kinetic distributions have been determined for the SiH_3Cl formation process. The simulated TOF spectra for signals at mass 65 are shown together with the measured TOF spectra in Fig.3. The overall agreement between the experimental and the simulated TOF spectra is good at both shapes and intensities. Since the kinetic energy release is normally angular dependent, four different kinetic energy distributions at four CM angles were used in fitting the

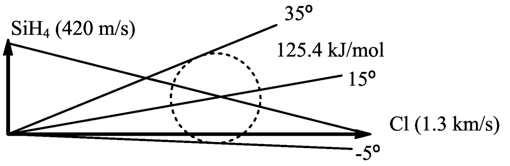

FIG. 2 Newton diagram for the H formation channel from the Cl+SiH_4 reaction.

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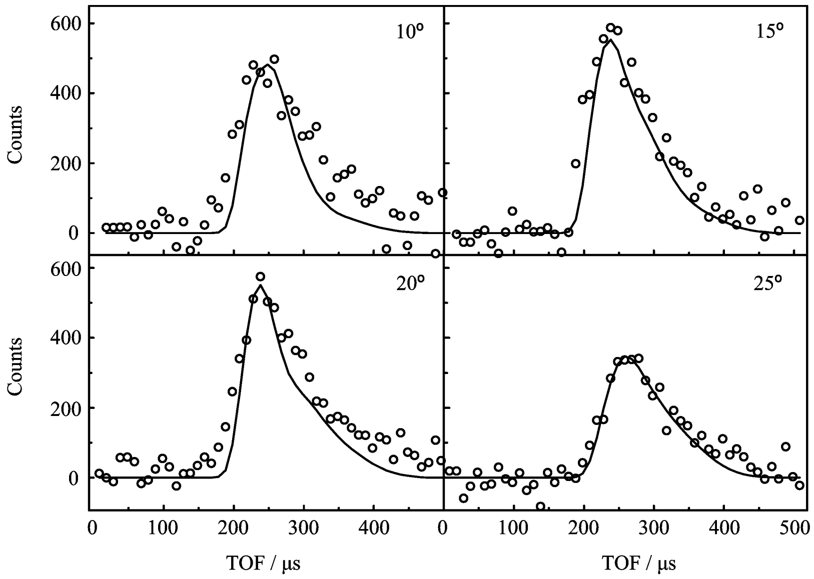

FIG. 3 TOF spectra measured at mass 65 at four different laboratory angle. The open circles are the experimental data, whereas the solid lines are the simulated results. The experimental results were taken by averaging over 3×10^4 pulses with discharge on and off.

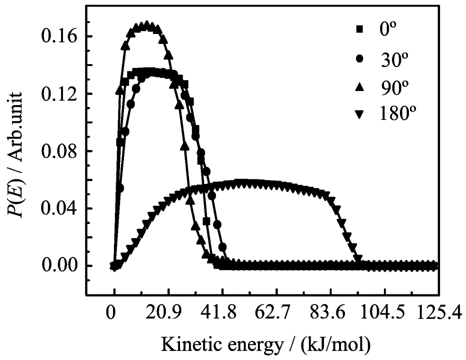

FIG. 4 The product CM kinetic energy distributions at four CM angles for the SiH_3Cl product obtained from the simulations. Kinetic energy distributions at other CM angles are obtained from the linear interpolations of these four distributions.

SiH_3Cl product signal in the TOF spectra at mass 65.

Figure 4 shows the four kinetic energy distributions at CM angles of 0°, 30°, 90°, and 180° used in modeling the SiH_3Cl formation channel. Figure 5 shows the CM product angular distribution used in the simulation. From these distributions, a three dimensional product flux contour diagram can be determined for this reaction channel (Fig.6). From the product flux diagram and the CM product angular distribution, it is quite clear that the SiH_3Cl product from this reaction channel is dominantly backward scattered relative to the Cl atom beam direction, suggesting that the reaction channel occurs mainly through an S_N2 type reaction.

In this mechanism, the Cl atom attacks the silane molecule, the SiH_3Cl product is backward scattered relative to the Cl atom beam direction while an H atom pops out along the Cl atom beam direction. This mechanism has been observed previously in other reactions, such as the O atom reactions with methane [9] and silane [20]. However, the picture has never been as clear as in this reaction in which predominantly backward scattered products are observed.

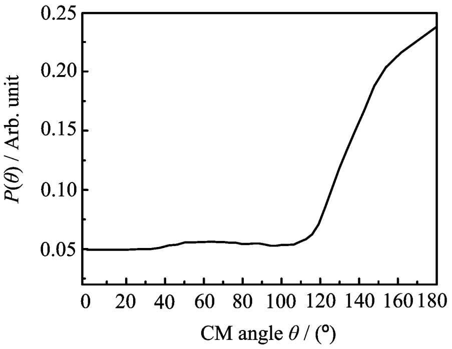

FIG. 5 The product CM angular distribution for the SiH_3Cl product obtained from the simulations.

IV. CONCLUSION

In this work, the dynamics of the $Cl+SiH_4$ reaction has been studied using the universal crossed molecular beam method. Angular resolved TOF spectra have been measured for the channel SiH_3Cl+H. Product angular distributions as well as energy distributions in the CM frame were determined for the channel. Experimen-

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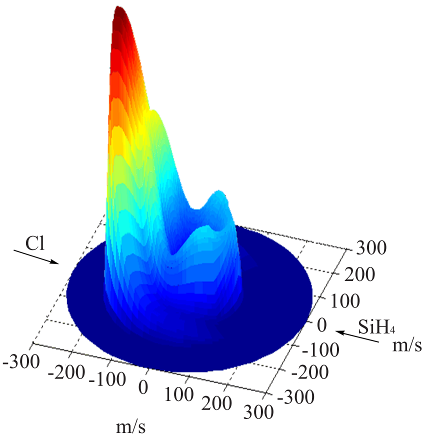

FIG. 6 The three dimensional product flux diagram for the SiH_3Cl product in the $Cl+SiH_4$ reaction.

tal results show that the SiH_3Cl product is backward scattered relative to the Cl atom beam direction, suggesting that the channel takes place via a typical S_N2 type reaction mechanism.

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