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Crossed Beams Study on the Dynamics of F Atom Reaction with 1,2-Butadiene

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(Dated: Received on May 25, 2010; Accepted on October 9, 2010)

We have investigated the dynamics of the $F+C_4H_6$ reaction using the universal crossed molecular beam method. The C_4H_5F+H reaction channel was observed in this experiment. Angular resolved time-of-flight spectra have been measured for the C_4H_5F product. Product angular distributions as well as kinetic energy distributions were determined for this product channel. Experimental results show that the C_4H_5F product is largely backward scattered with considerable forward scattering signal, relative to the F atom beam direction. This suggests that the reaction channel mainly proceeds via a long-lived complex formation mechanism, with possible contribution from a direct S_N2 type mechanism.

Key words: Fluorine atom, 1,2-Butadiene, S_N2 mechanism, Universal crossed molecular beam

I. INTRODUCTION

1,2-butadiene, as the simplest polyene, has been investigated quite extensively in both theory and experiment, such as mercury photosensitization [1], vacuum ultraviolet (VUV) photolysis [2–7], and shock tube pyrolysis [8–12]. All these studies were carried out at relatively high pressure, such that multiple collisions are very significant in the measurement. Extensive *ab initio* calculations have also been performed [13–15]. Calculations on the minimum energy path for the isomerization process, 1,2-butadiene \leftrightarrow 1,3-butadiene \leftrightarrow 1-butyne \leftrightarrow 2-butyne, indicate that there are multiple transition states along the reaction coordinate. Recently, Robison and co-workers have investigated photodissociation of 1,2-butadiene by the 193 nm [16] and 157 nm [17] laser, multiple product channels have been observed.

Dynamics of the F atom reactions with different species vary substantially. In the F atom reaction with hydrogen, a collinear abstraction mechanism is mainly responsible. At energy below the reaction barrier, however, the reaction resonances are extremely important [18–22]. In the F atom reaction with methane [23–26], a 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 HF products at various vibrational states. Possible resonance at low collision energy has also been observed.

In the F atom reaction with silane, the HF formation channel mainly occurs through abstraction at large impact parameters, producing forward scattering products. The F atom reaction with ethylene has also been investigated [27, 28]. The HF reaction channel mainly goes through a long-lived complex formation process through the F atom addition to the double bond as suggested from the experimental results. Clear site specific dynamics has been observed in the F atom reaction with propyne [29], in which the abstraction of H atoms by the F atom is clearly dependent on specific sites. The dynamics of the F atom reaction with propene has also been investigated recently [30]. The F atom reaction with aromatic and heterocyclic molecules as well as chloroethylenes have also been investigated previously using the crossed molecular beam method [31–33]. From previous experimental studies, the competing nature of different reaction channels in the F atom reactions with hydrocarbon molecules has not been investigated in great details. Therefore, it would be interesting to further study systematically the reaction dynamics of F atom with hydrocarbon molecules with both single and double/triple bonds, in which reactions through both direct abstraction and long lived complex formation mechanisms are possible.

Universal crossed molecular beam techniques based on electron impact ionization have been essential in investigating the dynamics of bimolecular chemical reactions during the last few decades. Product angular and transitional energy distributions can be measured using this powerful method. Electron impact ionization with quadrupole mass selection is an ideal universal detection method for all reaction products. Reaction of the F atom with 1,3-butadiene has been studied using this

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method [34].

In this work, crossed molecular beam studies of the F+1,2-butadiene (C_4H_6) reaction have been carried out using the universal crossed molecular beam technique. By careful measurements and detailed analyses of the time-of-flight (TOF) spectra and angular distributions of different products from the F+ C_4H_6 reaction, the C_4H_5F+H channel has been observed. The detailed dynamics of the channel has also been analyzed.

II. EXPERIMENTS

The reaction of F atom with C_4H_6 in this work 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 [35]. Briefly, the F atom beam, generated using the double-stage pulsed dc discharge of F_2 in He [36], was crossed with another skimmed beam at a fixed angle of 90° . The 5% F_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 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 F atom beam pulse is determined to be about 10 μs . The expanded F atom beam was skimmed by a skimmer (beam dynamics) with 2 mm diameter orifice. The another molecular beam was generated by expanding a neat C_4H_6 sample at a stagnation pressure of 303 kPa 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 F atom beam, the other beam and the detection axis are all in the same plane. The speed of the F atom beam is about 1.2 km/s with a speed ratio ($v/\Delta v$) of about 5. The speed of the C_4H_6 beam is about 350 m/s with a speed ratio of about 5 and an angular divergence of about $\pm 3^\circ$. The collision energy in this experiment is about 11.3 J/mol. In order to measure the reactive scattering signals from the F 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 selective, electron impact ionization detector. The whole experiment was carried out in a pulsed mode. Time zero (τ_0) 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

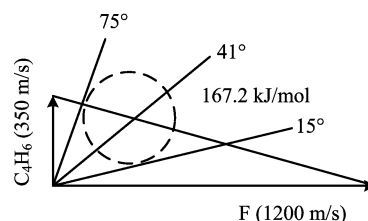


FIG. 1 Newton diagram for the C_4H_5F formation channel from the F+ C_4H_6 reaction.

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 $\pm 5\%$. 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 product at mass 72 from the title reaction has been detected, and can be clearly assigned to the C_4H_5F product from the C_4H_5F+H reaction channel. Figure 1 shows the Newton diagram for the H formation channel of the title reaction for the C_4H_5F products. From this diagram, it is clear that the C_4H_5F fragments are scattered between 15° and 75° laboratory angle range. TOF spectra at about ten laboratory angles were measured in this work. Figure 2 shows the TOF spectra at mass 72 ($C_4H_5F^+$) at six laboratory angles. In the laboratory frame, the F atom beam is defined at 0° while the C_4H_6 atom beam is at 90° . In order to obtain the product kinetic energy distributions and angular distribution in the CM frame for the observed channel, a WINDOWS-based forward convolution program is used in the simulation. By iteratively adjusting a set of kinetic energy distributions and a single CM product angular distribution until satisfactory fits to the TOF spectra are obtained, product angular distributions as well as kinetic distributions can be determined for the C_4H_5F reaction channel. The simulated TOF spectra for signals at mass 72 were also shown together with the experimental TOF spectra in Fig.2. Since the kinetic energy release is normally angular dependent, four different kinetic energy distributions at four CM angles were used in fitting the TOF spectra of the C_4H_5F product. Figure 3 shows the four

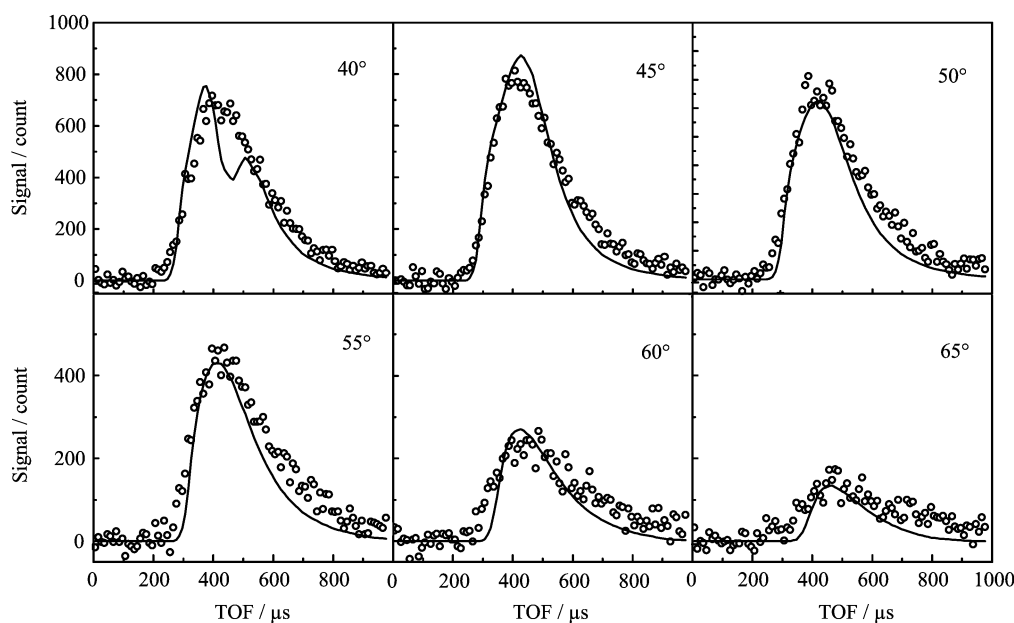


FIG. 2 Time-of-flight spectra measured at mass 72 at six different laboratory angle. The open circles are the experimental data, while the solid lines are the simulated results. The experimental results were taken by averaging over 3×10^4 pulses with discharge on and off.

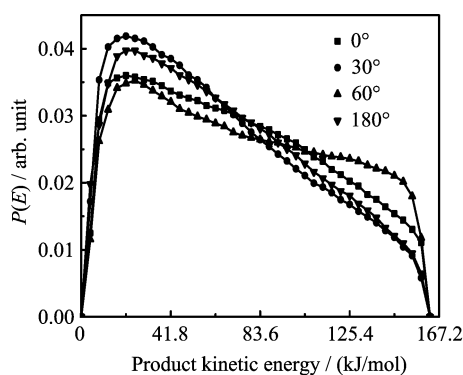


FIG. 3 The product CM kinetic energy distributions at four CM angles for the C_4H_5F product obtained from the simulations. Kinetic energy distributions at other CM angles are obtained from the linear interpolations of these four distributions.

kinetic energy distributions at the CM angles of 0° , 30° , 60° , and 180° used in modeling the C_4H_5F formation channel, whereas Fig.4 shows the CM product angular distribution used in the simulation. From these distributions, a three dimensional (3D) product flux contour diagram can be constructed for this reaction channel, which is shown in Fig.5.

From the product flux diagram and the CM product angular distribution, it is quite obvious that the C_4H_5F radical product from the H elimination channel is largely backward scattered relative to the F atom beam, but with considerable forward scattered signal.

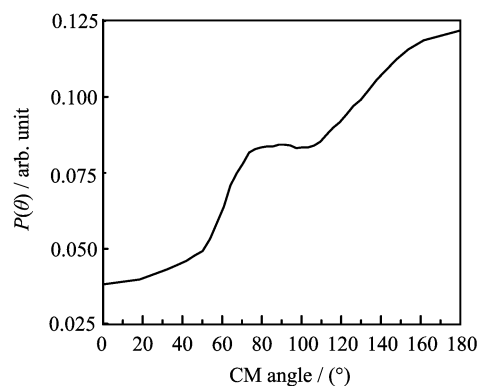


FIG. 4 The product CM angular distribution for the C_4H_5F product obtained from the simulations.

This scattering pattern suggests that the main mechanism of the reaction is likely due to a long-lived formation mechanism, which is similar to the previous results on similar systems [37]. However, relatively larger scattering product signal at the backward direction suggests a possible S_N2 type reaction mechanism is present, in which the F atom collides with C_4H_6 molecule, a hydrogen atom pops out from the C_4H_6 molecule along the F beam direction, while the C_4H_5F product scattered backward. Therefore, it is possible that this reaction occurs via multiple mechanisms.

In the experiment, we know that the reaction product is C_4H_5F . It is, however, not possible to determine which isomers of C_4H_5F is formed in the title reaction.

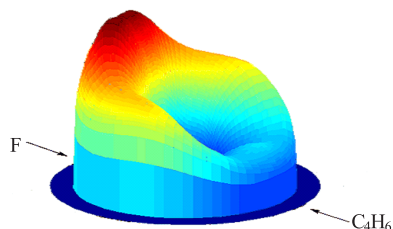


FIG. 5 The three-dimensional product flux diagram for the C_4H_5F product constructed from the CM kinetic energy distributions and the CM angular distribution.

There are three possible isomers for the C_4H_5F product: $CH_3CFCCCH_2$, $CH_3CHCCHF$, and $CH_2FCHCCH_2$. Energetically, all three channels could occur based on *ab initio* calculations [38] at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level. Dynamically, the first two microchannels is quite differently from the third microchannel. The first two microchannels ($CH_3CFCCCH_2$, $CH_3CHCCHF$) occurs more likely via a long-lived complex channels because there are two rather stable complexes for the two, while the third microchannel ($CH_2FCHCCH_2$) reacts more likely via a direct reaction mechanism because no stable complex was found in the theoretical calculations.

IV. CONCLUSION

In this work, we have investigated the dynamics of the $F+C_4H_6$ reaction using the universal crossed beam method. Angular resolved time-of-flight spectra have been measured for the channel C_4H_5F+H . Product angular distributions as well as energy distributions were determined for the channel. Experimental results show that the C_4H_5F product is largely backward scattered with considerable forward scattering signal, relative to the F atom beam direction. This implies that the reaction channel mainly proceeds via a long-lived complex formation mechanism, with significant contribution from a direct S_N2 type reaction mechanism. Two product ($CH_3CFCCCH_2$ and $CH_3CHCCHF$) are more likely to form through a long-lived complex formation channel, while the product $CH_2FCHCCH_2$ is more likely to form through a direct S_N2 type reaction mechanism.

V. ACKNOWLEDGMENTS

This work is supported by the Chinese Academy of Sciences, the National Natural Science Foundation of China and the Ministry of Science and Technology. Chong-fa Xiao also very acknowledge experimental help of Dr. Jin-dou Huang.

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