CHINESE JOURNAL OF CHEMICAL PHYSICS

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Crossed Molecular Beam Studies of the Fluorine

Atom Reaction with *Trans*-1 3-butadiene[*]

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Abstract　The fluorine atom reaction with *trans*-1 3-butadiene has been investigated by using the crossed molecular beam method. Signals at mass 72　46 and 33 have been observed. A single reaction channel $C_4H_5F + H$ is observed for this reaction channel. Product angular distributions and velocity distributions are determined. The experimental results indicate that the channel mainly proceeds via a long-lived complex at a collisional energy of 23. 8 kJ/mol. The collision complex is likely formed with the F atom attacking the delocalized electrons in the direction perpendicular to the molecular plane of *trans*-1 3-butadiene molecule.

Keywords　Crossed molecular beam　*trans*-1 3-butadiene　Fluorine atom

1   Introduction

The reactivity of the fluorine atom is an interesting research topic because of the complicated nature of the reaction mechanism involved in these reactions and its importance in the etching processes. In the F atom reaction with H_2 the reaction mainly proceeds through collinear abstraction mechanism with significant contribution of dynamical resonances in the transition state at low collisional energies [1 2] . In the F atom reaction with methane [3-7] however the reaction mainly occurs through an abstraction mechanism to produce an HF molecule and a methyl radical CH_3 in which the CH_3 part is largely a spectator during the reaction process. In contrast the F atom reaction with ethylene however mainly goes through a long-lived complex formation process through the F atom addition to the double bond as suggested from previous experimental results [8 9] . The F atom reaction with aromatic and heterocyclic molecules as well as chloroethylenes has also been investigated using the crossed molecular beam method [10-12] . 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 look systematically at 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 translational 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 [13] . The simplest of all conjugated polyenes 1 3-butadiene as a very interesting organic molecule has been studied using many experimental and theoretical techniques [14 15] . Recently the photodissociation dynamics of 1 3-butadiene at 193 nm has been investigated with photofrag-

ment translational spectroscopy coupled with product photoionization using tunable VUV synchrotron radiation by Neumark and co-workes [16] . Five product channels are evident from his study $C_4H_5 + H$ $C_3H_3 + CH_3$ $C_2H_3 + C_2H_3$ $C_4H_4 + H_2$ and $C_2H_4 + C_2H_2$. The production of $C_3H_3 + CH_3$ is found to be dominant channel followed by $C_4H_5 + H$ and $C_2H_3 + C_2H_3$ for which the yields are approximately equal. However the dynamics of the $F + C_4H_6$ reaction has never been investigated previously. In this paper we report the results of crossed molecular beam studies on the fluorine atom reaction with the *trans*-1 3-butadiene molecule.

2   Exprimenatl methods

The reaction fluorine atom with *trans*-1 3-butadiene has been studied in our lab using the universal crossed molecular beam technique. The apparatus used in this experiment is a newly built crossed molecular beam machine which has been described in great detail elsewhere. Briefly the F ^2P atomic beam generated by using the dc discharge method in a skimmed F_2 pulsed beam was crossed with a skimmed C_4H_6 molecular beam at a fixed angle of $90°$. A schematic of the F-atom source is depicted in Fig. 1 similar to the scheme used in previous experimental studies [17] . A Teflon insulator 1 mm long was firstly closely contacted by the pulsed valve general valve with a rise time of about 30 μs then a pair of electrodes was mounted further downstream and a teflon insulating piece was mounted between two electrodes and a DC negative high voltage typically -1 kV was applied to the front electrode. As the pulsed valve opened the gas inside the extended channel 1 mm diameter 2 mm long initiated the discharge duration time 1. 5 μs and sustained it until the gas expanded out of the channel. Typically 5% F_2 in He total pressure at 454 kPa was used in this work. It is known that discharge of F_2 can also generate a spin-orbit excited F^* atom. The spin-orbit excited $^2P_{1/2}$ state lies 404 cm^{-1} above the $^2P_{3/2}$ ground state. Unfortunately our F-atom source is with unknown spin-orbit contents in our setup. The expanded pulsed F-atom beam was then

skimmed by a sharp edged skimmer Beam Dynamics with 2 mm diameter then skimmed once again before entering the main chamber. The 1 3-butadiene molecular beam was generated by expanding a neat 1 3-butadiene 9% sample total pressure at 303 kPa obtained from Scott USA through a carefully adjusted pulsed valve General Valve with a rise time of about 40 μs and then skimmed once by a 1.5 orifice skimmer before entering the main chamber. The F ^2P atom beam 1 3-butadiene molecular beam and the detection axis were all in the same plane. The speed of the F ^2P atom beam was 1650 m/s with an angular divergence of ±3° and a speed ratio of about 13. The speed of the 1 3-butadiene molecular beam was about 752 m/s with a speed ratio of about 9.2 and an angular divergence of about ± 2°. The collisional energy at which this work was carried out is about 23.8 kJ/mol.
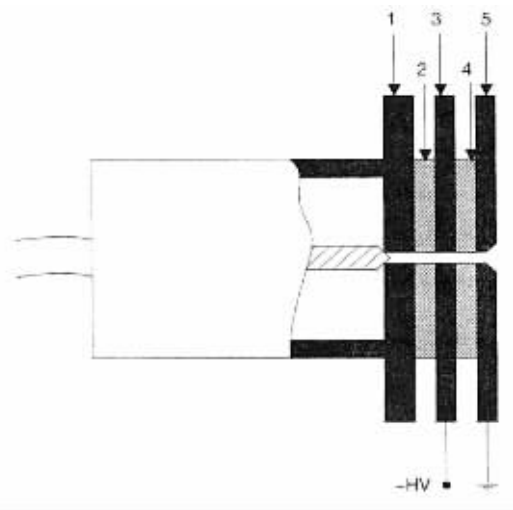

Fig. 1　F atom discharge source
1 Nozzle 2 4 Teflon insulator plate 3 5 Electrode

The whole experiment was pulsed at a frequency of 50 Hz 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-type ion detector. All time-of-flight TOF spectra were taken at 1 μs per channel during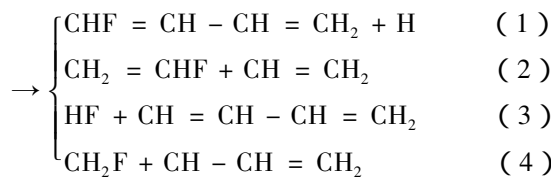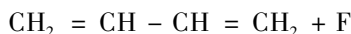 the experiment. The TOF spectra shown in this work were all rebinned to 3 μs for a better S/N ratio without distorting the shape of the TOF spectra. The product angular distributions can also be measured by rotating the detector. During the experiments described above the vacuum in the detector ionization region was maintained at about 0.13 μPa.

The TOF 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 center-of-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 dependent were used as the starting point. If the product translational energy distribution for the channel is angular dependent several CM translational energy distributions are necessary to describe the angular dependent energy distributions using linear interpolation. If the translational energy distribution is angular independent 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 distributions were 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 $\triangle V$ 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.

3　Results and analysis

The possible multiple pathways of this reaction are

as follows

$$CH_2 = CH - CH = CH_2 + F$$

$$\rightarrow \begin{cases} CHF = CH - CH = CH_2 + H & 1 \\ CH_2 = CHF + CH = CH_2 & 2 \\ HF + CH = CH - CH = CH_2 & 3 \\ CH_2F + CH - CH = CH_2 & 4 \end{cases}$$

The exothermicity of channel 1 is not well enough known but referring to Lee's past similar work [18-20] it should be 46 ± 16 kJ/mol. 2-F-*trans*-1 3-butadiene lies 1.7 kJ/mol below 1-F-*trans*-1 3-butadiene [21]. So available energy of channel 1 should be about 83.6kJ/mol. The exoergicity of the channel 2 is about 25kJ/mol [22] available energy is 49kJ/mol. Channel 3 is likely energetically [18-20] but in present work the product of HF was not detected even though the background of HF was very small. Channel 4 process is very unlikely energetically. In this work signals at $m/e = 72$ $C_4H_5F^+$ 46 $C_2H_3F^+$

33 CH_2F^+ are detected from the fluorine atom reaction with *trans*-1 3-butadiene. Because the angular distributions and TOF spectra shapes of all of the fragments have almost the same profile it is implied that two peaks of $m/e = 46$ $C_2H_3F^+$ and 33 CH_2F^+ come from dissociative ionization of the $C_4H_5F^+$ $m/e = 72$. Any signals of channel 2 are not observed in this experiment. In the following paragraphs detailed analyses and results of channel 1 are described.

From the experimental results the reaction F ^2P $+ C_4H_6$ has only a single reaction channel. The observed signals at mass 72 C_4H_5F could only come from the H atom elimination process from the reaction intermediate. Fig. 2 shows TOF spectra at mass 72 at six different laboratory angles. The total product angular distribution for C_4H_5F product is shown in Fig. 3. Reasonable fits to the TOF spectra of the C_4H_5F product in Fig. 2 at different lab angles have been obtained
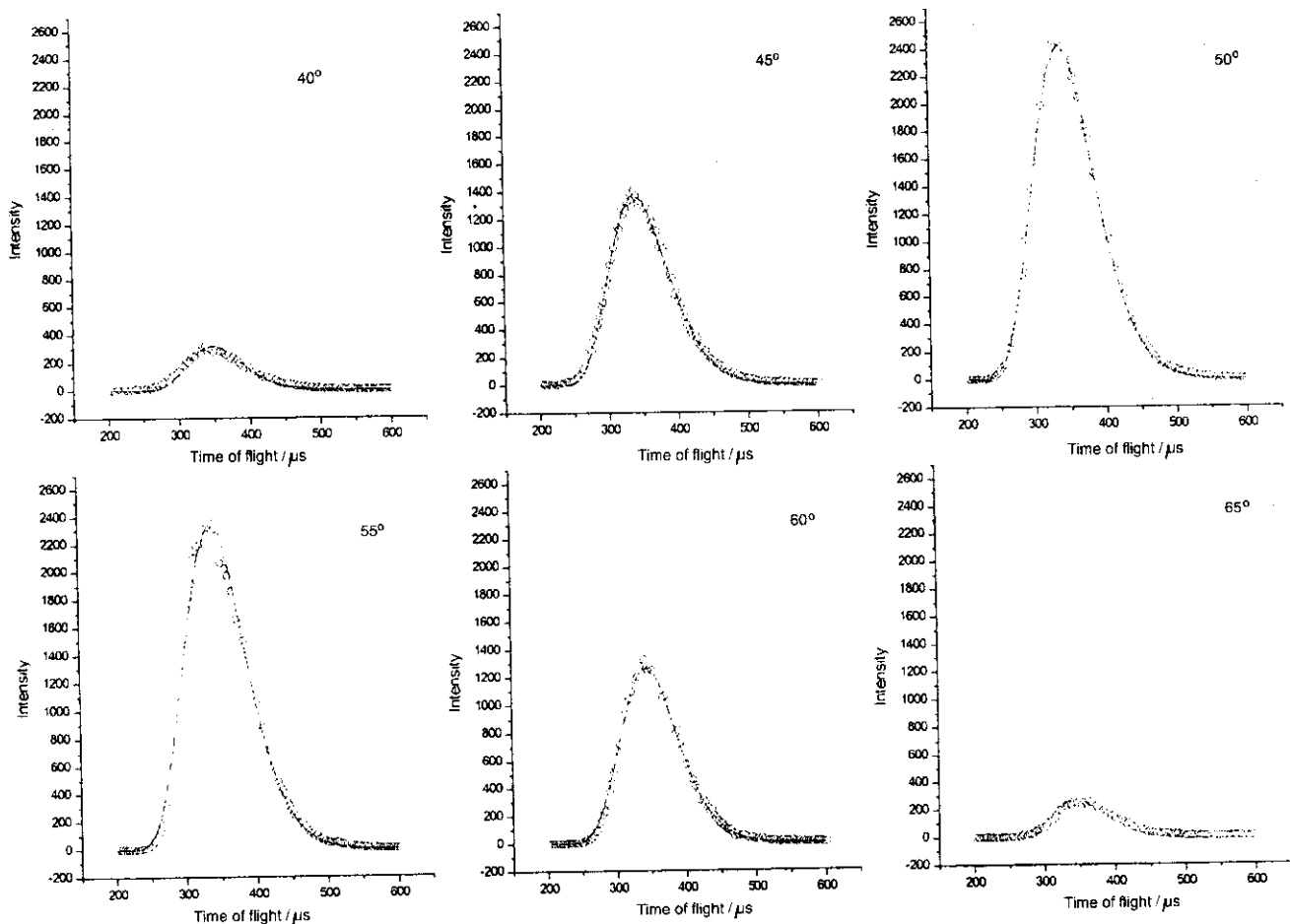

Fig. 2   TOF spectra at mass 72 at six different laboratory angles from the F atom reaction with *trans*-1 3-butadiene

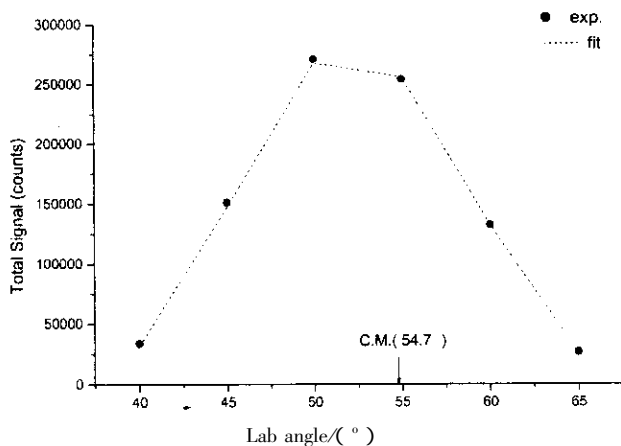The empty circles represent the experimental data while the solid lines are the simulated results.

Fig. 3   The laboratory angular distribution of product at mass 72
Solid circles are the experimental data while
the dashed line is the simulated result.

Fig. 5   The CM angular distribution of product at mass 72 also
used in simulating the TOF spectra shown in Fig. 2
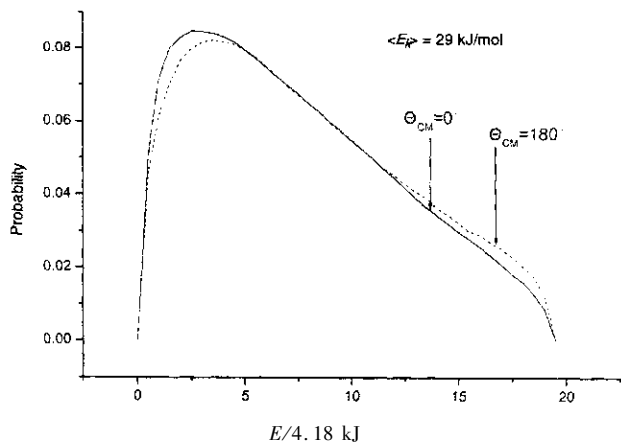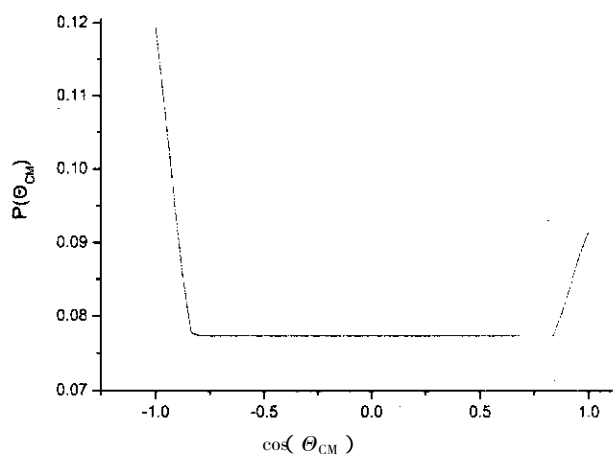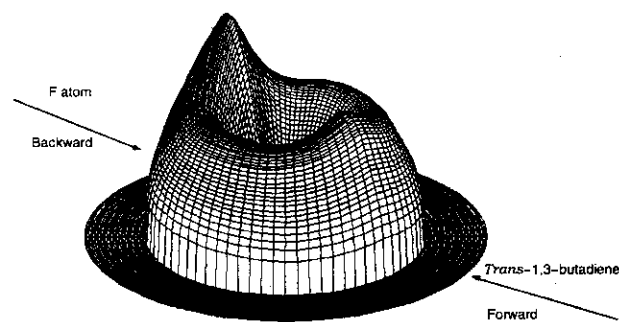from six different laboratory angles

Fig. 4   The CM product at mass 72 kinetic energy distributions
used in simulating the TOF spectra shown in Fig. 2
from six different laboratory angles. Total two
distributions are used at two CM angles.

Fig. 6   The 3D product flux diagram for H emission channel
constructed from the CM product kinetic energy
distributions Fig. 4 and the CM angular
distribution Fig. 5

using two different energy distributions at CM angles $0°$ $180°$ which are shown in Fig. 4. Kinetic energy distributions at other CM angles are obtained by linear interpolation using the above two distributions. The C_4H_5F product CM angular distribution P Θ_{CM} used in the fitting process is shown in Fig. 5. The three dimensional CM velocity flux contour map Fig. 6 of the C_4H_5F product was also obtained from the CM product kinetic energy distribution Fig. 4 and the CM angular distribution Fig. 5 . It is quite obvious that overall the radical product from the H emission channel is roughly backward-forward symmetric consistent with a

long-lived complex mechanism also similar to previous results on similar systems [18-20] . The slightly backward-scattered products could be from a minor direct reaction mechanism. However no particular argument could be found for why the asymmetry is tilted to the backward direction in this case. From Fig. 4 the cutoff of the CM kinetic energy distributions is about 79 kJ/mol which is quite close to the available energy of H atom elimination channel. The average kinetic energy released from the observed product is about 29 kJ/mol indicating that majority of the available energy is deposited into the internal degrees of freedom of the radical product.

4 Conclusions

The F atom reaction with *trans*-1 3-butadiene has been investigated by using the crossed molecular beam method. Signals at mass 72 46 and 33 have been observed. These signals are attributed to the $C_4H_5F + H$ reaction. Product angular distributions and velocity distributions are determined which indicate that the H atom elimination channel mainly proceeds via a long-lived complex.

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