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## $O(^{1}D)$ reaction with cyclopropane: Evidence of O atom insertion into the C–C bond

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The O(<sup>1</sup>D)+C<sub>3</sub>H<sub>5</sub> reaction has been investigated using the universal crossed molecular beam method. A number of reaction pathways have been observed. One of the most interesting channels is the H<sub>2</sub>CO/HCOH+C<sub>2</sub>H<sub>4</sub> process, in which H<sub>2</sub>CO products are clearly identified. Experimental results indicate that the H<sub>2</sub>CO products are likely produced through a long-lived complex formation process, for which insertion of O(<sup>1</sup>D) into the C–C bond should be responsible. © 2001 American Institute of Physics. [DOI: 10.1063/1.1383792]

The reactions of  $O(^{1}D)$  with small alkane molecules, such as methane, ethane, propane etc., have been investigated extensively during the last few decades.<sup>1-20</sup> Among these reactions, the reaction of  $O(^{1}D)$  with methane is the most important since methane is the most abundant hydrocarbon species in the atmosphere. The OH radical generated from this source partly determines the chemistry of the earth's ozone layer through the HO<sub>x</sub> cycles.<sup>21,22</sup> Recently, we have studied the  $O(^{1}D)$  reaction with various hydrocarbon molecules, including methane.<sup>23-25</sup> In addition to the CH<sub>3</sub>+OH channel, there are also other significant channels in the  $O(^{1}D)$  reaction with methane, such as the atomic hydrogen formation channel and the molecular hydrogen formation channel. While CH<sub>2</sub>OH is found to be the dominant radical product for the H formation channel, both H<sub>2</sub>CO and HCOH products are present in the H<sub>2</sub> elimination channel in almost equal amount. The reactions of  $O(^{1}D)$  with other small hydrocarbon molecules, such as ethane, propane, etc., have also been investigated using the same experimental technique.<sup>26,27</sup> It appears that insertion into a C-H bond in these small alkanes is the most important pathway for these reactions. The reactions of  $O(^{1}D)$  with these normal alkanes provide a rather complete set of experimental results to show how the reaction dynamics change in these systems. However, the reactivity of  $O(^{1}D)$  with cyclic alkanes has not been well understood. Since the electronic structure of cyclic alkane is significantly different from normal alkane, it would be interesting to know how the reaction dynamics of the  $O(^{1}D)$  reaction with cyclic alkane differs from that with normal alkanes.

The reaction of  $O(^{1}D)$  with cyclopropane has been studied in this work using the crossed molecular beam method. Through both careful measurements and detailed analyses of the time-of flight (TOF) spectra and the angular distribution of the total reaction products from the crossed molecular beam study of the  $O(^{1}D) + C_{3}H_{6}$  reaction, detailed dynamics of this reaction can be understood. The energetics of some related reaction pathways are shown in Fig. 1, and are obtained through ab initio calculations. We used the hybrid density functional B3LYP/6-311G(d,p) method<sup>28</sup> to obtain optimized geometries and vibrational frequencies, and the coupled cluster single double triple [CCSD(T)]/6-311+G(3df,2p) approach<sup>29</sup> to compute relative energies of various reactants, products, intermediates and transition states. The CCSD(T)/6-311+G(3df,2p)||B3LYP/6-311+G(d,p)+ZPE[B3LYP/6-311G(d,p)] calculational scheme is expected to provide accuracies of 1-2 kcal/mol for the energetic parameters.<sup>30</sup> The GAUSSIAN 98<sup>31</sup> and MOLPRO 200032 program packages were employed for the calculations.

The apparatus used in this experiment is a newly built crossed molecular beam machine, which has been described in detail elsewhere. Briefly, the O atomic beam, generated using the photodissociation of O<sub>2</sub> at 157.6 nm in a skimmed O<sub>2</sub> pulsed beam, was crossed with a skimmed C<sub>3</sub>H<sub>6</sub> beam at a fixed angle of 90°. The <sup>18</sup>O<sub>2</sub> beam was used here instead of the normal O<sub>2</sub> beam in order to avoid the higher background at mass 17 in the detector. The <sup>18</sup>O<sub>2</sub> beam was obtained by expanding a neat <sup>18</sup>O<sub>2</sub> sample through a commercial pulsed valve with a rise time of about 50  $\mu$ s, at a stagnation pressure of about 5 atm. The molecular beam was then skimmed by a sharp-edged skimmer with a 2 mm diameter orifice. The molecular oxygen beam was then intercepted by an unpolarized

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FIG. 1. Energy diagram for possible reaction channels of the bimolecular reaction of  $O(^{1}D) + C_{3}H_{6}$  as calculated at the CCSD(T)/6-311 + G(3*df*,2*p*)//B3LYP/6-311G(*d*,*p*) + ZPE[B3LYP/6-311G(*d*,*p*)] level.

157.6 nm laser beam, generated by a Lambda Physik LPX210IF<sub>2</sub> laser, with a pulse energy of about 30 mJ at a repetition rate of 50 Hz. The O atomic beam generated from the 157 nm photolysis was skimmed once before entering the main chamber. In order to reduce the detector background related to the  ${}^{18}O_2$  beam, the  ${}^{18}O_2$  beam was rotated to an angle between 60 and 70° from the detector-rotating plan. The  $F_2$  laser beam was focused on a spot of 4 mm(w) $\times 4$  mm (h) in the interaction region by a sphericalcylindrical MgF<sub>2</sub> lens. Using the above focusing condition and laser power, the  ${}^{18}O_2$  transition at 157.6 nm can be easily saturated. The C<sub>3</sub>H<sub>6</sub> beam was obtained by expanding a neat C<sub>3</sub>H<sub>6</sub> sample at a stagnation pressure of about 5 atm through a carefully adjusted pulsed valve with a rise time of about 60  $\mu$ s and then skimmed once by a 1.5 mm orifice before entering the main chamber. The <sup>18</sup>O atomic beam, the  $C_3H_6$ molecular beam, and the detection axis are all in the same plane. The velocity spread of the <sup>18</sup>O atomic beam is less than 2% according to our measurement. The collisional energy of the title reaction is about 9 kcal/mol in this experiment. The angular divergence of the <sup>18</sup>O atomic beam was about  $\pm 3^{\circ}$ . The speed of the C<sub>3</sub>H<sub>6</sub> beam was about 840 m/s with a speed ratio of about nine and an angular divergence of about  $\pm 2^{\circ}$ . Reaction products scattered from the crossed region are detected by a mass-selective electron impact ionization detector. The whole experiment was pulsed, and the time zero was defined as the time when the beams were crossed. After flying about 25 cm from the crossed region, the neutral reaction products were 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. 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  $1 \times 10^{-12}$  torr or below.

the neutral products measured in the laboratory (LAB) frame were simulated in order to obtain the product kinetic energy distribution (PKED) and product angular distribution (PAD) in the center-of-mass (CM) frame using a computer program. The simulation is an iterative forward convolution program to use the initially guessed CM kinetic energy distributions and angular distribution to calculate the laboratory TOF spectra and angular distribution. By comparing the calculated TOF spectra and the experimental TOF spectra, the initially guessed PKED is adjusted iteratively so that satisfactory fits to the TOF spectra are obtained. In the same simulation, the initially guessed CMPAD is also iteratively adjusted so that good agreement between the experimental and simulated PADs is reached. The relative ratio of each channel can be adjusted interactively. The effects of the velocity spread  $(\Delta \nu)$  and the angular divergence of the two molecular beams are incorporated in the simulation.

In this experiment, signals at m/e = 19, 31, and 57 were detected from the  $O(^{1}D) + C_{3}H_{6}$  reaction. TOF spectra at mass  $31(HC^{18}O^+)$  were measured at 11 different lab angles. Nine of these TOF spectra are shown in Fig. 2. From the TOF spectra, there are apparently three distinctive peaks, indicating three different channels are contributing to the signal at mass 31. The slowest peak in some of the TOF spectra is due to the dissociative ionization signal  $(HC^{18}O^+)$  of the radical product (C<sub>3</sub>H<sub>5</sub><sup>18</sup>O) from the H atom elimination channel. The two faster peaks should come from reaction channels with comparable product masses. Therefore, these fast products are unlikely from H and H<sub>2</sub> elimination processes. Because the HCO<sup>+</sup> ion is very stable, it is likely produced from dissociative ionization of some unstable parent product. Since no product has been detected in the mass range between mass 31 and mass 56, the HCO<sup>+</sup> ion is quite possibly coming from either HC<sup>18</sup>OH and/or H<sub>2</sub>C<sup>18</sup>O products. There are two probable reaction pathways to produce the two species:  $HCOH+C_2H_4$  and  $H_2CO+C_2H_4$ . These two channels also have a comparable product mass ratio, 32

The time-of-flight spectra and angular distributions of

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FIG. 2. TOF spectra at m/e=31 at nine different laboratory angles. The open circles represent the experimental data, while the solid lines are the simulated results.

(HCOH or  $H_2CO$ ): 28(C<sub>2</sub>H<sub>4</sub>), which agrees with the experimental observation. From the energetic diagram, these two channels are also likely to occur. Therefore, we believe that the observed fast signals are due to the  $H_2CO/HCOH+C_2H_4$ channel. A single POE and a single CM angular distribution have been tried to simulate both fast features in the TOF spectra, but the results are less than satisfactory. The main reason is that the two fast features appear to have somewhat different angular distributions. Therefore, two distinctive contributions with different CM angular distributions are used to fit the two fast features in the TOF spectra. Since the two features are overlapped, there are clearly some serious correlations between the two contributions in the overlapped region. The kinetic energy distributions obtained from simulating the two fast TOF features at mass 31 are shown in Fig. 3. From Fig. 2, the simulated TOF spectra are in good agreement with the experimental spectra. Using the product CM kinetic energy distributions and CM angular distributions obtained, 3D product flux contour diagrams can be constructed



FIG. 3. The two CM product kinetic energy distributions used in simulating the TOF spectra shown in Fig. 2.

for the two observed processes. Figure 4 shows the 3D product flux diagrams for the observed reaction products of the two contributions. It is clear that the two new features have somewhat different angular distributions, implying different dynamical natures of the two observed features. The faster feature [(b) in Fig. 4] shows a rather forward–backward symmetric angular distribution, while the slower feature [(a) in Fig. 4] shows a somewhat backward angular distribution.



FIG. 4. 3D product flux diagram (mass 31) constructed from the CM kinetic energy distributions (Fig. 3), and the CM angular distributions obtained from the simulation. (a) the slower process; (b) the faster process.

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As pointed above, two dynamical features are observed. The nature of these two features is a more interesting issue. According to the above analysis, the two features are likely to come from the following two channels:  $HCOH+C_2H_4$  and  $H_2CO+C_2H_4$ . From the energetic diagram, the available energy for the H<sub>2</sub>CO+C<sub>2</sub>H<sub>4</sub> channel is about 136 kcal/mol, while that for the HCOH+ $C_2H_4$  channel is about 84 kcal/ mol. From the CM kinetic energy distributions shown in Fig. 3, the energetic limit of the faster component of the two contributions is about 130 kcal/mol, which agrees quite well with the available energy of the  $H_2CO+C_2H_4$  channel. Therefore, it is reasonable to assign the faster contribution to the  $H_2CO+C_2H_4$  channel. The nature of the slower contribution observed at mass 31 is, however, more ambiguous. Obviously this slower contribution is quite different from the faster one because of its distinctive angular distribution. From the simulation, the energetic limit of the slower contribution is about 40 kcal/mol. However, there is a rather large uncertainty in this limit due to the correlations in simulating the two features. Nevertheless, this limit appears to be significantly lower than the available energy of the HCOH+C<sub>2</sub>H<sub>4</sub> channel. Therefore, it is somewhat questionable to assign this slower feature to the HCOH+ $C_2H_4$  channel. It is still possible that this channel is from the  $HCOH+C_2H_4$  pathway since the mismatch between the energetic limit and the available energy could be due to the fact that available energy is distributed into the internal degrees of freedom of the two molecular products. This feature could also come from the other sources, such as excited product channels of  $H_2CO+C_2H_4$  or even  $HCOH+C_2H_4$ . Mention that the adiabatic excitation energy for the first excited state of H<sub>2</sub>CO is 80.7 kcal/mol,<sup>33</sup> which leaves 55.6 kcal/mol of available energy for the  $H_2CO(S_1) + C_2H_4$  products. More detailed theoretical study on this issue is desirable in order to clarify this point.

The implications of an  $H_2CO+C_2H_4$  reaction is even more interesting. From the energetic diagram, this reaction channel should be a direct product from the oxetane complex formed through the  $O(^{1}D)$  insertion into the C-C bond (see Fig. 1). Therefore, we believe that the observation of this channel is a clear experimental evidence of the  $O(^{1}D)$ atom insertion into a C-C bond, which is normally quite difficult to achieve. From our previously studies of the  $O(^{1}D)$  reactions with small alkanes,  $O(^{1}D)$  normally inserts into a C-H bond, which is somewhat less difficult because the H atom is lighter and that makes it easier to displace. It is reasonable to believe that the insertion of  $O(^{1}D)$  into the C-C bond in cyclopropane is made easier due to the banana type character of the C–C bond, in which the electronic cloud of the C-C bond is more accessible than for normal alkanes because of its banana shape. An interesting question regarding this process is whether the breaking up of the C-C and C-O bonds in the "hot" oxetane complex is simultaneous or one that is stepwise and involves a ring-opening process. Our present calculations show that this reaction occurs in one step with simultaneous rupture of two bonds in the ring.

In addition to the above observed channel, three additional channels H formation, H<sub>2</sub> formation, and OH formation, have also been observed in the  $O(^{1}D) + C_{3}H_{6}$  reaction. Final analysis of all reaction channels will be reported in a future full paper.

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