AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **115**, 1742 (2001); doi: 10.1063/1.1382814
View online: http://dx.doi.org/10.1063/1.1382814
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/115/4?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 4 22 JULY 2001

The gaseous reaction of vinyl radical with oxygen

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(Received 9 March 2001; accepted 9 May 2001)

The gaseous reaction of vinyl radical with oxygen has been experimentally investigated. C_2H_3 radical was produced by laser photolysis of C_2H_3Br at 248 nm. The vibrationally excited products of the reaction were detected by time-resolved Fourier transform infrared emission spectroscopy. $H_2CO(\nu_1)$, $HCO(\nu_1,\nu_3)$, and $CO_2(\nu_3)$ are ascertained as the main emitters. The most favorable product channel is HCO and H_2CO. The reaction channel leading to CO_2+CH_3 has been found for the first time. The minor reactions leading to $C_2H_2+HO_2$, C_2H_3O+O, and $C_2H_2O_2+H$ may also occur. A secondary reaction product of CO is observed, which is generated from the primary reaction product HCO. Combining theoretical analysis with the present experimental results, the reaction pathways are clarified. The results are of importance for understanding the combustion processes of hydrocarbon. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1382814]

I. INTRODUCTION

Vinyl radical is the simplest alkene radical. The reaction of C_2H_3 with molecular oxygen is thus of basic importance in fundamental chemistry. For example, vinyl radical is recognized as an important intermediate in hydrocarbon combustion processes. The reaction of C_2H_3 with oxygen plays a significant role either in saturated or unsaturated hydrocarbon fuel/oxygen flames.[1,2] Furthermore, the reaction is important for the acetylene formation, and may be the source of polycyclic aromatic hydrocarbons and soot.[3] In addition, it is also believed to play a role in the hydrocarbon chemistry of Jovian atmosphere.[4,5] Because of high exothermicity, many reaction channels are thermodynamically accessible:[6,7]

$$\Delta H_0^\circ \ \text{(kcal/mol)}$$

$$C_2H_3(^2A')+O_2(^3\Sigma_g)\rightarrow H_2CO(^1A_1)+HCO(^2A') \quad -87.5, \quad (1)$$

$$\rightarrow H_2C_2O_2(^1A_g)+H \quad -77.1, \quad (2)$$

$$\rightarrow CO_2(^1\Sigma_g)+CH_3(^2A_2'') \quad -131.1, \quad (3)$$

$$\rightarrow C_2H_2(^1\Sigma_g)+HO_2(^2A'') \quad -13.4, \quad (4)$$

$$\rightarrow C_2H_3OO(^2A') \quad -46.4, \quad (5)$$

$$\rightarrow C_2H_3O(^2A'')+O \quad -9.0, \quad (6)$$

$$\rightarrow H_2C_2O(^3A'')+OH \quad -0.6. \quad (7)$$

Using mass spectroscopy, Gutman and co-workers[8,9] measured the rate constant of the overall reaction as $6.6(\pm1.3)\times10^{-12}\exp(250\pm100\ \text{cal}/RT)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ between 297 and 602 K. Krueger and Weitz[10] obtained the rate constant as $(1.0\pm0.4)\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ at room temperature by tunable diode laser. Using vacuum ultraviolet (UV) flash photolysis spectroscopy, Fahr and Laufer[6] measured the rate constant as $(6.7\pm2.7)\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^1$. Recently, Slagle and co-workers[11] obtained the Arrhenius expression $k=(6.92\pm0.17)\times10^{-12}\exp[(120\pm12\ \text{K})/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^1$ for this reaction at higher temperatures (299–1005 K) using laser photolysis/photoionization mass spectrometry.

Some theoretical studies have also been performed for this significant reaction. Based on *ab initio* molecular orbital calculations, Westmoreland,[7] Bozzelli and Dean[12] individually applied the energized complex/QRRK theory to estimate the rate constants of several possible channels in the temperature range of 300–2500 K. Carpenter[13,14] computed the overall rate constants and activation parameters between 297 and 602 K using semi-empirical and *ab initio* calculations. A detailed *ab initio* and density functional theory (DFT) study on the potential energy surface and a careful energetic analysis of the reaction mechanism were carried out by Morokuma *et al.*[15] recently. They predicted that the most favorable reaction channel is $HCO+H_2CO$ and that at $T\geqslant900\ \text{K}$, C_2H_3O+O are the major products. At very high temperatures, the channel producing $C_2H_2+HO_2$ becomes competitive. These theoretical investigations discuss the complicated reaction mechanism, proposing many possible reaction channels. However, the studies lack evidence to determine which product channels really exist. A comprehensive experimental investigation on the reaction products is thus invoked.

Compared to the theoretical studies, detailed experimental studies on this reaction are insufficient. Only the products of HCO and H_2CO have been found by mass spectroscopy.[9] In this paper, we report our experimental investigation on all the reaction channels. The study is performed by using time-resolved Fourier transform infrared (TR-FTIR) emission spectroscopy. TR-FTIR spectroscopy is a powerful tool for detecting various primary products of bimolecular reactions. It has been successfully used to study free radical reactions in recent years.[16–18] In this work, several new primary and secondary products of the $C_2H_3+O_2$ reaction are found.

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Some possible reaction channels are verified, except for channel (1); channel (3) is identified for the first time. Minor reaction channels (2), (4), and (6) also possibly occur. In light of the previous theoretical analysis, the reaction mechanism is discussed.

II. EXPERIMENT

The experiment is performed in a laser photolytic reaction chamber. Infrared (IR) emission is recorded by a time-resolved FTIR spectroscope. Details of the experimental apparatus have been described in a previous work.[16] Vinyl radical is produced by pulsed laser photolysis of vinyl bromide at 248 nm (KrF laser, Lambda Physik LPX305I, ~200 mJ/pulse):

$$C_2H_3Br \xrightarrow{248\ \text{nm}} C_2H_3+Br+48.3\ \text{kcal/mol}. \quad (8)$$

A gas mixture consisting of 66 Pa C_2H_3Br (Aldrich, 98%) and 265 Pa O_2 (99.99%) flows through the reaction chamber. A gas flow rate of 20 ml/min ensures that the reactive gas is refreshed between two laser pulses. The IR emission from the vibrationally excited products is collected by a pair of gold-coated, confocal spherical mirrors and is collimated to an InSb detector. The IR emission spectrum between 1800 and 4000 cm^{-1} is recorded by a TR-FTIR spectrometer (Nicolet, 800) with the spectral resolution at 16 cm^{-1}. In order to improve signal to noise ratio, each spectrum is accumulated 64 times.

III. RESULTS AND DISCUSSION

A. Reaction products

1. Major products

Dai *et al.* performed a photolytic experiment of vinyl bromide at 193 nm very recently.[19] They recorded the IR emission spectrum of vinyl radical. However, no IR emission is observed in our experiment of laser photolysis of pure C_2H_3Br at 248 nm. Furthermore, the photolysis does not produce excited precursor molecules which may contribute to the emission spectra.[19] Therefore, it provides a neat IR emission background for the spectroscopic investigation of the $C_2H_3+O_2$ reaction. When we add the gas mixture of oxygen and vinyl bromide into the reaction chamber, a transient IR emission is recorded after the laser pulse. Figure 1 shows the IR emission spectra at different delay times. The spectra are obtained by subtracting the background emission from the total emission.

The first few spectra after the laser shot are more informative than the later ones. At the pressure of 265 Pa, about 170 collisions take place in 5 μs for each species. In this period, the chemical reaction of nascent vinyl radical has almost been accomplished, while the vibrational quenching of the reaction products is not serious. The intense IR emissions from the vibrationally excited products are clearly observed. Four major reaction products, $H_2CO(\nu_1)$, $HCO(\nu_1,\nu_3)$, $CO_2(\nu_3)$, and CO have strong emissions in the spectra. An intense emission between 2362 cm^{-1} and 3000 cm^{-1} is recorded. The emission is assigned to the overlapping of HCO (ν_1, fundamental vibrational frequency being 2483 cm^{-1}) and H_2CO (ν_1, fundamental vibrational frequencies being 2780 cm^{-1}) bands. The peak is mainly attributed to the emission of the H_2CO ν_1 band. The shoulder on the left side is attributed to the transitions of high vibrational levels in the ν_1 mode of HCO. The vibrational excitation of these modes rapidly quenches. But the cooled H_2CO can still be seen at 17 μs.

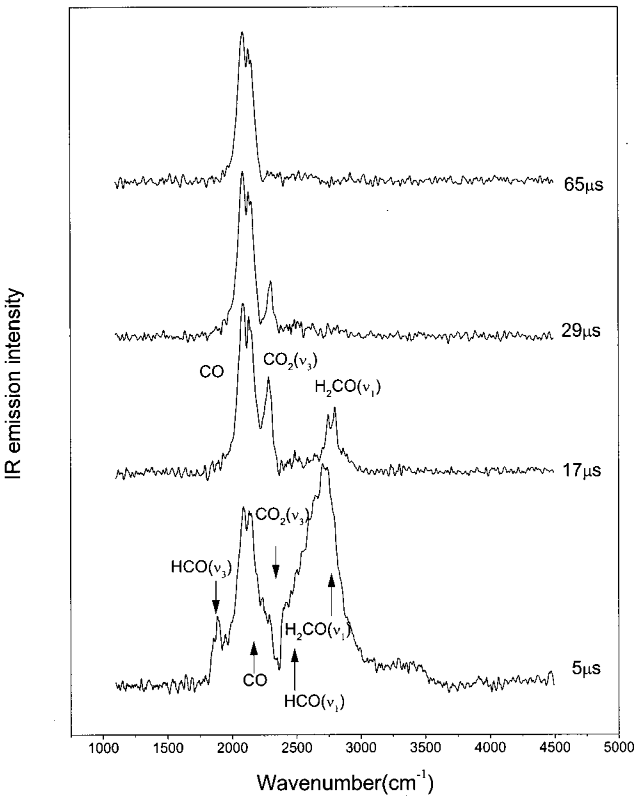

FIG. 1. The time-resolved infrared emission spectra of the $C_2H_3+O_2$ reaction. The spectra are taken at 5, 17, 29, and 65 μs respectively, after the KrF laser pulse. The arrows indicate the spectral positions of the relevant band origins.

The occurrence of HCO can also be identified by the appearance of its ν_3 band between 1803 and 1940 cm^{-1} (fundamental vibrational frequency being 1863 cm^{-1}) in the 5 μs spectrum. The actual emission could be much stronger than the recorded intensity, since the responsibility of the InSb detector has a sharp cutoff at 1840 cm^{-1}.

Another intense emission between 1914 cm^{-1} and 2362 cm^{-1} is attributed to the overlapping of the ν_3 band of CO_2 (fundamental vibrational frequency being 2349 cm^{-1}) and CO (fundamental vibrational frequency being 2143 cm^{-1}). The overlapped band splits into two components at 17 μs. Since then, the $CO_2(\nu_3)$ emission decays and eventually disappears in 65 μs. In contrast, the CO emission does not decay in this period and even lasts for 3 milliseconds.

2. Possible products

Since the photolysis of C_2H_3Br releases 48.3 kcal/mol, the nascent C_2H_3 radical possesses an energy of about 30 kcal/mol. Many "high-temperature" reactions with high barriers thus may take place. However, the yields of these prod-

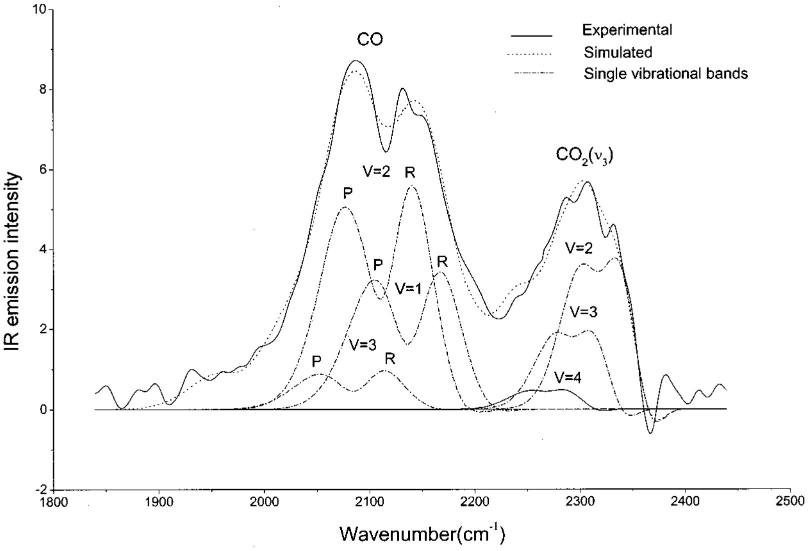

FIG. 2. The experimental (solid line) and the simulated (dashed line) infrared spectra of $CO_2(\nu_3)$ and the CO emission at a 17 μs delay after the KrF laser firing. In the simulation, a rotational temperature of 460 K is used. The contributions of some individual $v \rightarrow v-1$ bands are also shown as dashed–dotted lines in the figure. Other bands are not plotted for clarity of the figure.

ucts are relatively low. Some weak IR emissions in a plateau region between 3000 cm^{-1} and 3500 cm^{-1} have been recorded in the 5 μs spectrum. Possible products are CH_3 (ν_3 band, fundamental vibrational frequency being 3150 cm^{-1}), C_2H_3O (ν_1 band, fundamental vibrational frequency of 3208 cm^{-1} calculated by the GAUSSIAN 94 program in UMP2/6-311G(*d*) level[20]), C_2H_2 (ν_3 band, fundamental vibrational frequency being 3287 cm^{-1}), and HO_2 (ν_1 band, (fundamental vibrational frequency being 3415 cm^{-1}). Furthermore, on the right shoulder of the intense hump between 2362 cm^{-1} and 3000 cm^{-1}, there is possibly a ν_1 band of $C_2H_2O_2$ (fundamental vibrational frequency being 2844 cm^{-1}) and a ν_4 band of H_2CO (fundamental vibrational frequency being 2874 cm^{-1}).

B. Product channels

(1) $HCO+H_2CO$ channel. Reaction channel (1) has already been known as the major route of the $C_2H_3+O_2$ reaction.[9] This point is further proved by this work. The IR emission mainly originates from the primary reaction products of the channel (1), HCO and H_2CO, and from its secondary reaction product CO via HCO. Since channel (1) releases a large amount of energy (87.5 kcal/mol), the products should be highly excited. It is consistent with the fact that in the 5 μs spectrum, both HCO(ν_1) and $H_2CO(\nu_1)$ humps are very broad. Each hump emission covers almost 150 cm^{-1}, consisting of several ($v \rightarrow v-1$) vibrational transition bands.

(2) Secondary product CO. The observed CO is generated from two secondary reactions of HCO. As indicated above, the primary product HCO possesses rich internal energy. The available energy in HCO radicals is sufficient to overcome its low dissociation energy barrier (23.5 kcal/mol[21]), resulting in decomposition:

$$HCO \rightarrow CO+H-14.1\ \text{kcal/mol}. \tag{9}$$

The secondary product CO still retains a large amount of vibrational energy. Figure 2 shows the observed spectrum of the 17 μs delay and its spectral simulation. The simulation of $CO(v \rightarrow v-1)$ and $CO_2(\nu_3, v \rightarrow v-1)$ indicates that the excitation attains to the vibrational levels $v \leqslant 5$ for CO. The simulated relative vibrational populations are listed in Table I. The simulation is performed on the least squares iteration program.[17]

CO may also be produced by a bimolecular reaction

$$HCO+O_2 \rightarrow CO+HO_2+24.9\ \text{kcal/mol}. \tag{10}$$

The rate constant of this secondary $HCO+O_2$ reaction is $5\times10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$, comparable with that of the primary $C_2H_3+O_2$ reaction, $6.7\times10^{-12}\,\text{cm}^{-3}\,\text{molecule}^{-1}\,\text{s}^{-1}$.[8,11] Both reactions may be accomplished in a few microseconds in the present condition.

(3) CO_2+CH_3 channel. The observation of the nascent product CO_2 undoubtedly verifies the occurrence of channel (3). The spectral simulation of CO_2 ν_3 band (Fig. 2 and Table I) shows that CO_2 molecules are highly excited. The vibrational population of CO_2 is inverse with a maximum at $v=4$ or $v=2$ after a delay of 10 μs or 17 μs, respectively. The fact is consistent with the thermochemical data, which show that the exothermicity is as high as 131.1 kcal/mol in this reaction channel.

(4) C_2H_3O+O and $C_2H_2+HO_2$ channels. According to the kinetic evaluation[12] and to the energetic calculation,[7] the reaction channels (4) and (6) occur only at high temperatures. The products C_2H_3O, C_2H_2, and HO_2 are thus not observable in the previous investigations. In the present experiment, however, the nascent C_2H_3 radical generated from the UV photolysis is very "hot." The emission of

TABLE I. The relative vibrational population of CO_2 and CO.

Delay time		Vibrational level				
	(μs)	1	2	3	4	5
CO_2	10	0.04	0.06	0.06	0.1	0.1
	17	0.02	0.5	0.2	0.2	
CO	10	16.6	12.0	3.0	2.8	
	17	14.9	9.5	2.2	1.9	0.3

the 3000 cm^{-1}–3500 cm^{-1} plateau in the 5 μs spectrum shows that $C_2H_3O(\nu_1)$, $C_2H_2(\nu_3)$, or $HO_2(\nu_1)$ may occur. The emission of 3000 cm^{-1} to 3250 cm^{-1} may refer to $CH_3(\nu_3)$ or $C_2H_3O(\nu_1)$, the product of channel (6). While in the high frequency region of the plateau, from 3250 cm^{-1} to 3526 cm^{-1}, the emission may be generated from the ν_3 band of C_2H_2 or the ν_1 band of HO_2. Either case supports the occurrence of reaction channel (4). Since the emissions are weak, they must be the minor reaction channels.

(5) $H_2C_2O_2+H$ channel. The shoulder on the right side of the $H_2CO(\nu_1)$ hump extends to ~3000 cm^{-1}. The emission probably comes from the $H_2C_2O_2$ ν_1 band. Therefore, the $H_2C_2O_2+H$ channel possibly occurs.

C. Reaction mechanism

Comparing our experimental observations to the theoretical calculations,[13–15] we are able to gain insight into the dynamic mechanism. Since Carpenter's calculation is not complete and is less accurate, we compare our experimental observations to Morokuma's G2M (RCC, MP2) calculation results. Based on their calculated energy data, Morokuma *et al.* also evaluated the Rice-Rampsberger-Kassel Marcus RRKM rate constants for some reaction channels. From the rate constants, they predict that at low pressure and at the temperature below 900 K, the reaction is dominated by the $HCO+H_2CO$ channel. This prediction has been verified by our experiment. Although the temperature of the reactant O_2 is 300 K in our experiment, the C_2H_3 radical produced in the laser photolysis is a hot species, possessing rich translational and internal energies.

On the other hand, we do observe a large amount of CO_2, which no doubt verifies that channel (3) is one of the main reaction channels. Furthermore, the energy released in channel (3) is enormously high, causing the inversion of the vibrational population of $CO_2(\nu_3)$ at $v=4$.

Figure 3 shows a concise diagram of the reaction paths referred to as the observed channel. The energies of the intermediates (IM) and the transition states (TS) are adapted from Ref. 15. The feasible reaction paths involve ring-structured intermediates, where the O=O double bond is weakened to a single bond. Since the energy barrier in forming a three-membered ring is lower than that in forming a four-membered ring,[15] all the major products, HCO, H_2CO, and CO_2 are derived from intermediate V, which has a three-membered CCO ring. It is quite easy to form key intermediate V, since there are only two lower barriers between the reactants and V.

Either the C–O or the C–C bond in the ring of intermediate V breaks with a very low barrier. When the C–C bond breaks, two intermediates, VII and VIII, are formed. A subsequent C–O bond-breaking in intermediate VIII will directly lead to $HCO+H_2CO$, the products of channel (1). The barrier height of the related transition state, TS8, is the lowest. Channel (1) is thus the main reaction path 1,3-hydrogen shifting in VII followed by a C–O bond cleavage

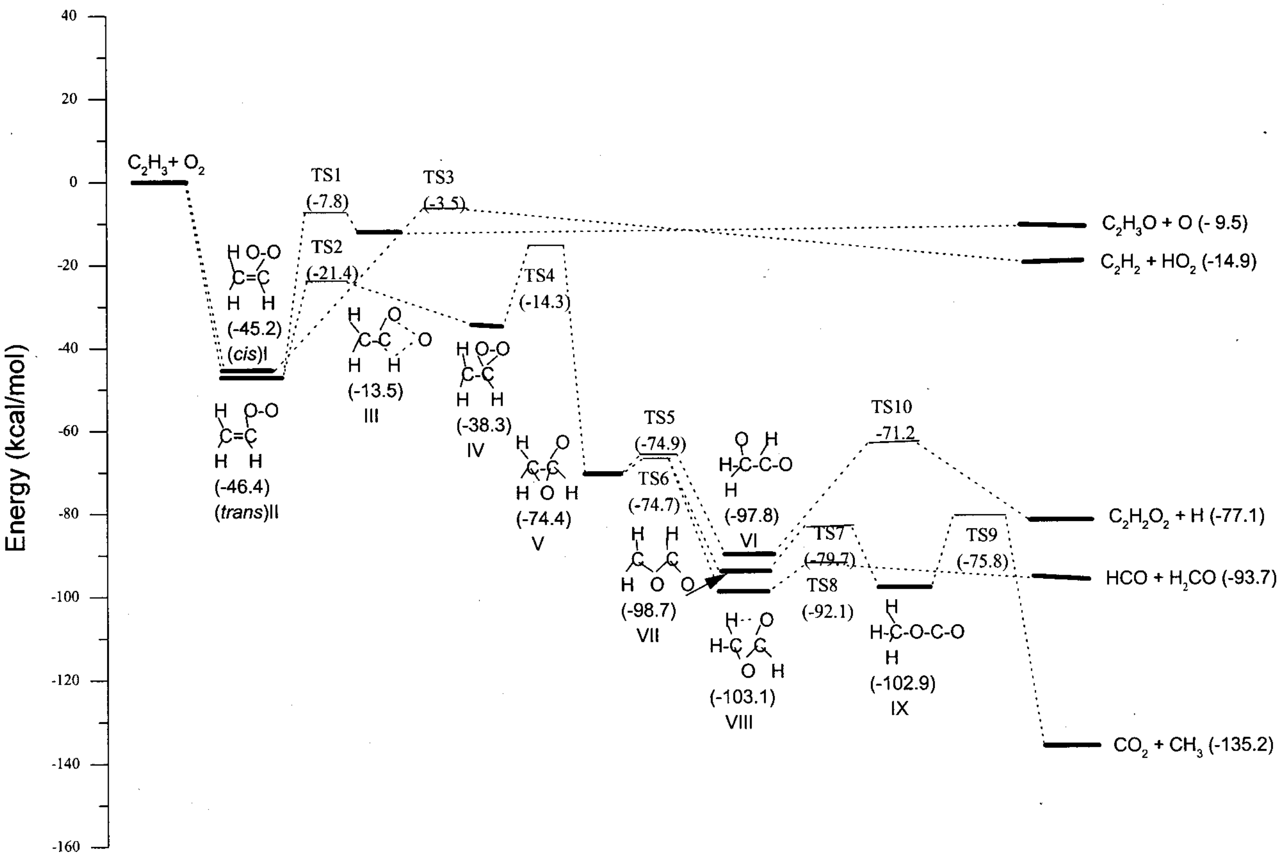

FIG. 3. Energy diagram of the $C_2H_3+O_2$ reaction. The energy data of the intermediates (IM) and transition states (TS) are adapted from Ref. 15.

will lead to CO_2+CH_3, channel (3). As shown in Fig. 3, two barriers, TS7 and TS9, in channel (3) are also lower. Channel (3) is therefore the second most significant reaction channel. The C–O band cleavage of the ring in V followed by an H atom elimination will result in the $H_2C_2O_2+H$ channel.

The reaction routes of channels (4) and (6) are relatively simple. Because the O–O bond still remains in the final product HO_2 of channel (4), the intermediates are not necessary to be ring-structures. The 1,4-hydrogen shifting in intermediate I via TS3 accompanied by the cleavage of the C–O bond leads to the final products $C_2H_2+HO_2$. Channel (6) is obtained by O elimination in intermediate III via TS1. However, the high barriers (TS3, 41.7 kcal/mol and TS1, 38.6 kcal/mol) cause channels (4) and (6) to occur only in high temperatures. Furthermore, because the total energy released in both reactions is only 14.9 kcal/mol and 9.5 kcal/mol respectively, the small amount of the exothermicity is insufficient to extensively excite the vibrations of the products. The mechanism explains why we can only record very weak IR emission signals for these species.

IV. CONCLUDING REMARKS

(1) Strong transient IR emissions from the vibrationally excited products $H_2CO(\nu_1)$, $HCO(\nu_1,\nu_3)$, and $CO_2(\nu_3)$ are observed by the TR-FTIR spectroscope.

(2) The predominant reaction pathway is confirmed as channel (1), which has been experimentally verified and theoretically predicted already. The second most important reaction route is channel (3), which has not been experimentally observed.

(3) Weak IR signals may refer to $C_2H_2O_2(\nu_1)$, $C_2H_2(\nu_3)$, $HO_2(\nu_1)$, or $C_2H_3O(\nu_1)$. These are the products of the reaction channels (2), (4), and (6).

(4) CO is the secondary reaction product. The CO source is either the decomposition of hot HCO or the subsequent reaction of $HCO+O_2\rightarrow CO+HO_2$.

(5) The favorable reaction routes are via intermediate V. The decomposition of the three-membered ring in V will lead to the reaction channels (1), (2), and (3).

ACKNOWLEDGMENTS

This work is supported by the China National Science Foundation and by the Department of Science and Technology of China. The authors deeply appreciate Professor Qi-He Zhu for reviewing the manuscript.

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