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# Reaction of $C_2H$ with NO and $O_2$ studied by TR-FTIR emission spectroscopy

Hongmei Su [a], Jixin Yang [a], Yihong Ding [b], Wenhui Feng [a], Fanao Kong [a,*]

[a] *Center for Molecular Science, Institute of Chemistry, Academia Sinica, Beijing 100080, China*
[b] *Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun, Jilin 130023, China*

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## Abstract

Vibrationally excited CO ($v$), HCO ($\nu_1$, $\nu_2$), HNC ($\nu_3$) and HCN ($\nu_3$) were observed as products of the reaction of $C_2H$ with NO by using time-resolved FTIR emission spectroscopy. Three exothermic reaction channels leading to HCN + CO, HNC + CO and CN + HCO are identified, verifying an association-elimination reaction mechanism. The nascent products of CO ($v \leqslant 10$) and $CO_2$ ($\nu_3$, $v \leqslant 3$) were observed for the reaction of $C_2H$ with $O_2$. A yield ratio of $CO/CO_2$ is estimated as 9. The experimental observations suggest that reaction is rapid and forms CO and HCO. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Well known for its great importance in hydrocarbon combustion [1], and the existence in planetary atmosphere [2] and interstellar space [3], $C_2H$ has evoked considerable interest in the past decades. Among the ethynyl radical reactions with $O_2$, NO, $H_2$ and $C_2H_2$, etc., relatively less efforts were made to investigate the reaction of $C_2H + NO$, which is believed to play an important role in NO re-burning combustion chemistry [4]. The reaction of $C_2H$ with $O_2$ consumes the ethynyl radical in lean and moderately rich flames preventing the initiation of soot formation [5].

Two groups reported their kinetic studies on the overall reaction of $C_2H$ with NO. Monitoring the decay of the $C_2H$ concentration by infrared absorption, Curl's group obtained a rate constant of $3.5 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at room temperature [6]. Peeters et al. [7] indirectly determined the rate constant as $k(T) = (1.0 \pm 0.2) \times 10^{-10} \exp[-(287 \pm 65)/T]$ $cm^3$ $molecule^{-1}$ $s^{-1}$ by CH(A → X) chemiluminescence over a temperature range of 295–440 K. Moreover, Peeters et al. performed an ab initio study on this reaction [8]. The most favorable reaction channel leads to the formation of HCN + CO. The other two channels leading to HNC + CO or HCO + CN have higher barriers and are accessible only at high temperature. However, no direct observation of the reaction products has been reported up to now. Thus, the possible reaction channels have not been verified. In the first part of the present paper, we report our observation of nascent products arisen from the $C_2H$ + NO reaction. The three proposed reaction channels by Peeters [8] have been identified.

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[*] Corresponding author. Fax: +86-10-6256-3167; e-mail: kong@mrdlab.icas.ac.cn

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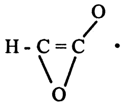
The reaction of $C_2H + O_2$ has been studied by many groups, mostly on measuring the rate constant of overall reaction [9–20]. The measured constants are between $5 \times 10^{-12}$ to $4.2 \times 10^{-11}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ with an average value of $3.3 \times 10^{-11}$ $cm^3$ molecule$^{-1}$ $s^{-1}$. The products of CH ($A^2\Delta$), CO ($a'^3\Sigma^+$), CO ($v = 0$–6), $CO_2$ ($v = 0, 1$), and HCCO have been detected [11,13,15]. A few earlier ab initio calculations explored the possible intermediates [21–23]. Very recently, an overall theoretical investigation on reaction surface has been carried out by Sumathi et al. using both ab initio and density function theories [24]. According to their calculation, the main reaction path consists of sequential ring-forming and ring-opening processes. There exist two competitive dissociation pathways for the key intermediate, oxyrenyloxy,



Simultaneously breaking both the C=C and C–O bonds of the three-membered ring will directly lead the intermediate to the products $CH + CO_2$. The other pathway is forming oxo-ketene, HC(O)CO, and then producing HCO + CO. Sumathi et al. suggest that the fate of the oxyrenyloxy is dynamically controlled and that the dominant reaction channel is forming HCO + CO. The verification of above hypothesis is of course important. The key is to clarify the competition between the two reaction channels referring to the $CO_2$ or CO formation. In the second part of this report, we concentrate our study on the energy disposal and the yield ratio of the $CO_2$ and CO products. The result is of benefit for elucidating the $C_2H + O_2$ reaction mechanism.

## 2. Experimental

The ethynyl radical $C_2H$ was produced via laser photolysis of bromoacetylene ($C_2HBr$) at 248 nm (KrF laser, Lambda Physik LPX305i, ~ 100 mJ/pulse). The experiment was conducted in a laser photolysis/time-resolved FTIR spectroscope set-up which was described in detail previously [25]. Gaseous mixtures of $C_2HBr$ and NO (99.9%) or $O_2$ (99.9%) flowed into the reaction chamber. The partial pressures of $C_2HBr$ and NO were maintained at 50 Pa and 150 Pa, respectively. For the oxygen reaction, the partial pressures were 40 Pa and 160 Pa, respectively. The IR emission from the reaction products was collected by a pair of gold-coated spherical mirrors and was leaded to a FTIR spectrometer (Nicolet 800). An InSb IR detector was used. The spectral resolution was set at 16 $cm^{-1}$. The data acquisition system provided 10 time-sequenced interferograms. The spacing time between each two adjacent interferograms is 18 μs.

Bromoacetylene was synthesized by the dehydrobromination of acetylene dibromide with molten, moist potassium hydroxide and was purified by trap-to-trap method [26].

## 3. Results and discussions

### 3.1. $C_2H$ production

The ethynyl radical was produced by photolysis of bromoacetylene at 248 nm [26]. The available energy is 24 kcal/mol for this reaction. According to our estimation based on the information theory [27,28], approximately 18 kcal/mol is distributed to the internal freedoms of $C_2H$. The first electronically excited state $A^2\Pi$ of $C_2H$ is only 12 kcal/mol above the ground $X^2\Pi$ state [29]. Therefore, the $C_2H$ produced might be a mixture of $A^2\Pi$ and $X^2\Pi$ states. No quenching gas was added to ensure the $C_2H$ being its ground state.

### 3.2. Spectral simulation

The contour line of the CO and $CO_2$ emission spectrum has been simulated. The simulation needs Einstein spontaneous coefficients $A(v, J)$. The $A(v, J)$ values for CO are calculated by the formula

$$A(s^{-1}) = \frac{64\pi^4}{3h}\nu^3\frac{|m|}{2J'+1}\langle \nu J|m|\nu' J'\rangle^2$$

where the $\langle vJ|m|v'J'\rangle$ is the dipole transition matrix elements in Debye; $m$ is equal to $J+1$ for the $R$ lines and to $J$ for the $P$ lines [30].

For $CO_2$ molecules, the $A(v, J)$ coefficients are calculated by the formula [31]

$$A(s^{-1}) = \frac{64\pi^4}{3h}\nu^3 \frac{|m|}{2J'+1}\left|R_{\nu_3' \to \nu_3}\right|^2 F(m)$$

The vibrational transition moment $|R_{\nu_3' \to \nu_3}|^2 = \nu_3'|R_{1\to 0}|^2$ have a precise approximation of $|R_{1\to 0}|^2 = 0.1032$ (Debye$^2$). The Herman–Wallis factor is $F(m) = (1 - 0.000143m)^2$.

### 3.3. $C_2H + NO$ reaction

Fig. 1 presents the IR emission spectra of $C_2HBr/NO$ system recorded at different delay time after laser photolysis. In the 5 μs spectrum, the emission between 1960–2360 $cm^{-1}$ is assigned to the vibrationally excited CO ($v \to v-1$). The sharp band centered at 1867 $cm^{-1}$ is assigned to the CO stretching mode of HCO radical (fundamental vibrational frequency being 1868 $cm^{-1}$). The band centered at 2487 $cm^{-1}$ is obviously the CH stretching mode of HCO (2483 $cm^{-1}$). The broad band of 3150–3680 $cm^{-1}$ is attributed to the overlapping of the NH stretching of HNC (3653 $cm^{-1}$) and the CH stretching of HCN (3314 $cm^{-1}$). The time evolution of the emission bands shows that the CH stretching and the NH stretching relax much faster than the CO

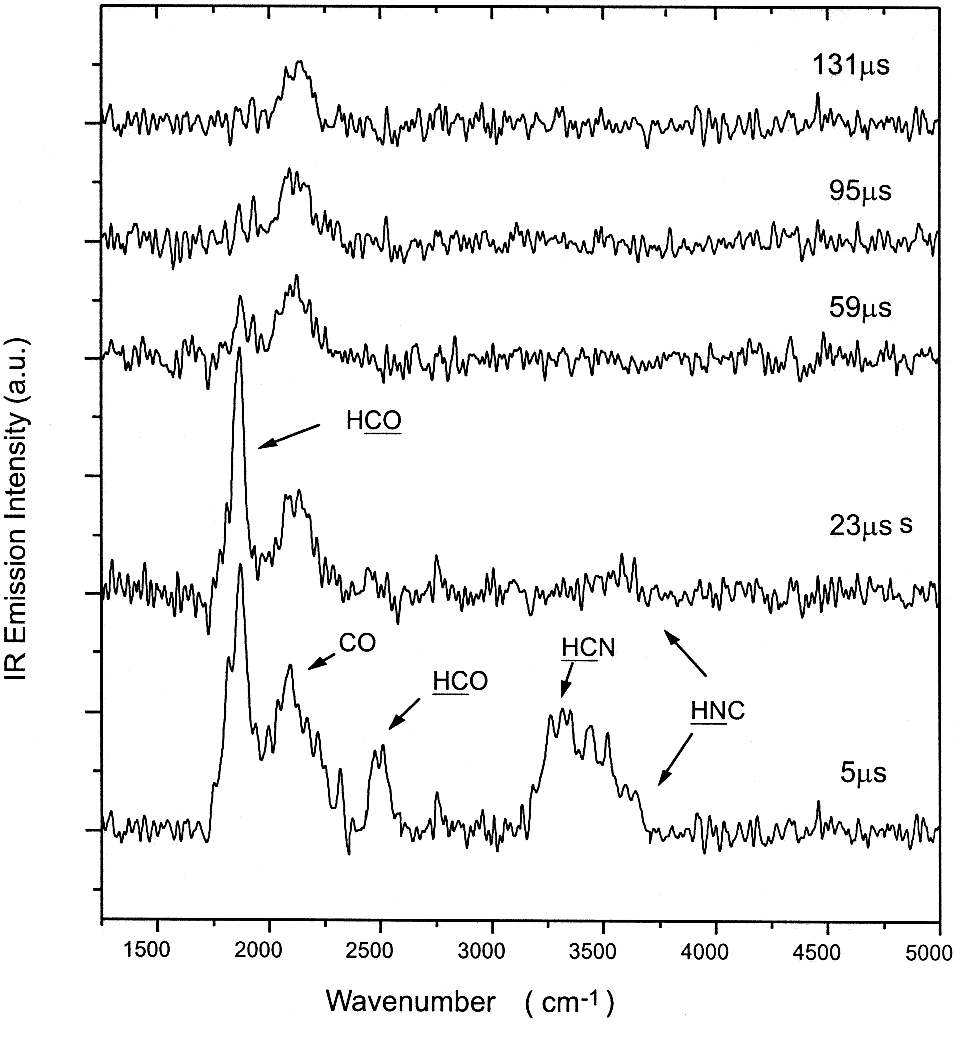


Fig. 1. The infrared emission spectra of $C_2HBr/NO$ system at different delay time after the 248 nm laser firing. The assignment of the products is indicated in the figure. The active vibrational modes are the stretching modes underlined in the figure.

Table 1
The vibrational populations of CO at 59 μs and 131 μs delays for the $C_2H+NO$ reaction

| | $v=1$ | $v=2$ | $v=3$ | $v=4$ |
|---|---|---|---|---|
| 59 μs | 1.0 ± 0.15 | 0.34 ± 0.09 | 0.32 ± 0.06 | 0.06 ± 0.04 |
| 131 μs | 1.0 ± 0.13 | 0.61 ± 0.08 | 0.16 ± 0.05 | |

stretching, probably due to the near-resonant $v$–$v$ energy transfer to the precursor molecule $C_2HBr$ (CH stretching at 3320 $cm^{-1}$).

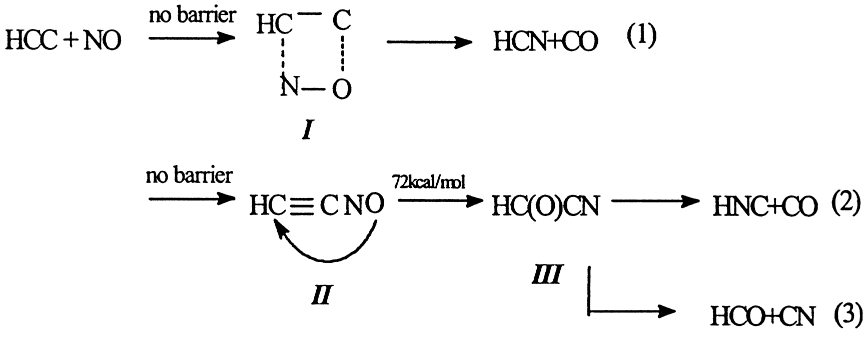
We performed spectral simulations for the CO ($v$) spectra of 59 μs and 131 μs.The vibrational populations of CO are listed in Table 1. After 131 μs, the vibration has almost been thermalized and can be expressed by a temperature of $T_v = 3400$ K. The vibrational excitation of the nascent CO ($v$) product must be much higher. Such large amount of the vibrational energy should be released from highly exothermal reactions.

Table 2

| | | $\Delta H_0°$(kcal/mol) |
|---|---|---|
| (1) | $C_2H(X^2\Sigma)+NO \rightarrow \underline{HCN}+\underline{CO}$ | −151 |
| (2) | $C_2H(X^2\Sigma)+NO \rightarrow \underline{HNC}+\underline{CO}$ | −136 |
| (3) | $C_2H(X^2\Sigma)+NO \rightarrow \underline{CN}+\underline{HCO}$ | −43 |

The thermodynamically allowed channels for the reaction are listed in Table 2. The underlined products have been observed by us, indicating that all the above reaction channels exist. The channels (1) and (2) are highly exothermic. Our observation of the highly excited CO ($v$) supports the occurrence of these two reaction channels. The existence of channel (3) is verified by the direct observation of HCO. Furthermore, the ground-state HCO ($X^2A'$) is unstable with a dissociation barrier of 23.5 kcal/mol [32]. Our observation of HCO implies that this product was arisen from a less exothemic channel. The fact also indirectly supports the existence of channel (3).

Recently, Peeters et al. suggest an association–elimination reaction mechanism on the base of their ab initio calculation [8]:



Via a four-membered cyclic intermediate ***I***, the channel (1) is suggested to be most favorable. They point out that channels (2) and (3) are only accessible at high temperature, because the energy barrier from the intermediate ***II*** to ***III*** is 9 kcal/mol higher than the reactants and thus can not be overcome at room temperature.

In our experiment, all of the three channels were verified to exist. The $C_2H$ radical holds about 18 kcal/mol internal energy estimated by the information theory [27,28]. With this amount of energy, the energy barrier from intermediate ***II*** to ***III*** can be overcome.

Using Gaussian 98 program, we performed an ab initio calculation at the B3LYP/6-311 + + G(d,p) level, the same level employed by Peeters et al., to explore another reaction mechanism. A H-atom migration to N atom in ***I*** might lead to HNC + CO. But the energy of the transition state is calculated as 17.3 kcal/mol higher than that of the reactants $C_2H+NO$. Obviously, this pathway could not occur in our experiment.

### 3.4. $C_2H+O_2$ reaction

When oxygen and bromoacetylene were added to the reaction chamber, strong IR emission was recorded after 248 nm laser firing. Fig. 2 shows emission spectra recorded at different delay times. At 5 μs, the emissions between 1800–2200 $cm^{-1}$ and 2220–2370 $cm^{-1}$ are assigned to the vibrationally excited CO $(v \rightarrow v-1)$ and $CO_2$ $(\nu_3, v \rightarrow v-1)$, respectively.

The simulation of IR emission spectra provides vibrational energy distribution of the CO and $CO_2$. Fig. 3 shows the experimental and simulated spectra. There are two humps appeared in the spectrum. Each hump consists of individual CO and $CO_2$ emission bands. Some $v \rightarrow v-1$ bands are shown by the dashed lines in the figure. The best-fitted rotational temperature is found to be 350 ± 50 K, indicating that rotational thermalization has almost been accomplished within 5 μs.

The relative vibrational population of CO and $CO_2$ at 5 μs is listed in Table 3. The data are obtained from the spectral simulations. The CO product is highly vibrationally excited up to $v = 10$, whereas the $\nu_3$ mode of $CO_2$ is only moderately excited up to $v = 3$. Both CO and $CO_2$ $(\nu_3)$ show inverse population distribution.

The ratio of the vibrational excited CO $(v)$ to the $CO_2$ ($\nu_3$, v) can be evaluated by the summation of population. In the evaluation, the vibrational

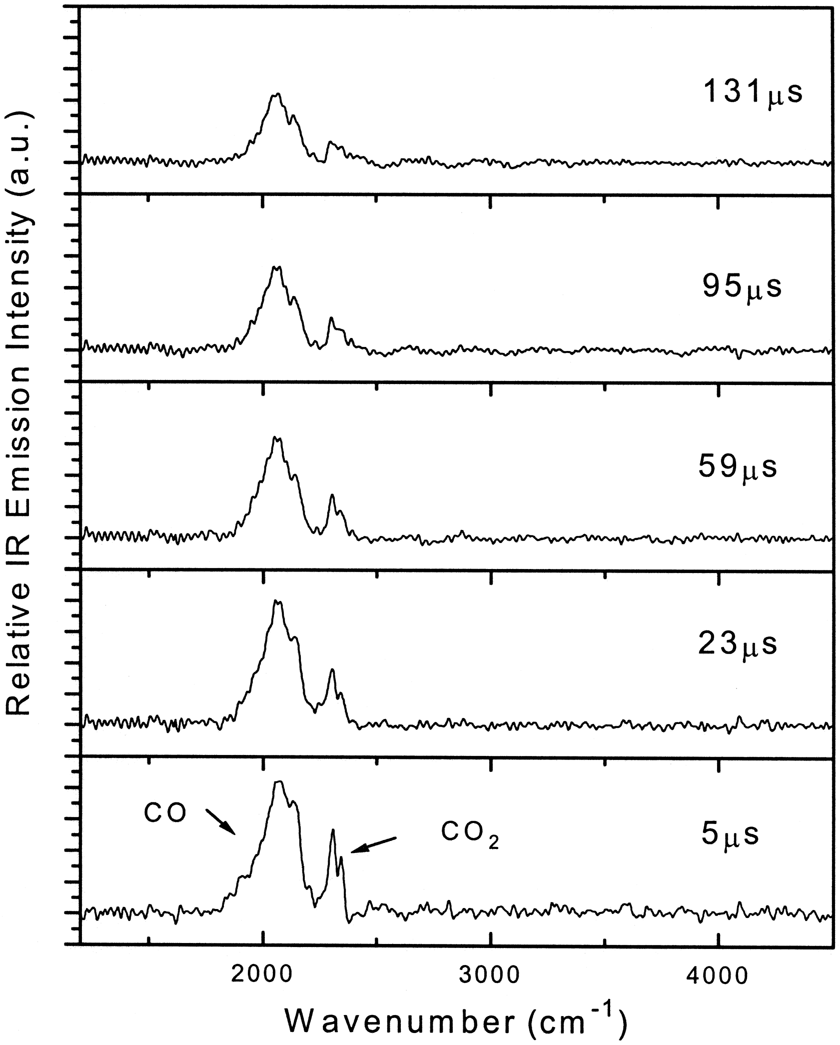


Fig. 2. The infrared emission spectra of $C_2HBr/O_2$ system taken at different delay time after 248 nm laser firing.

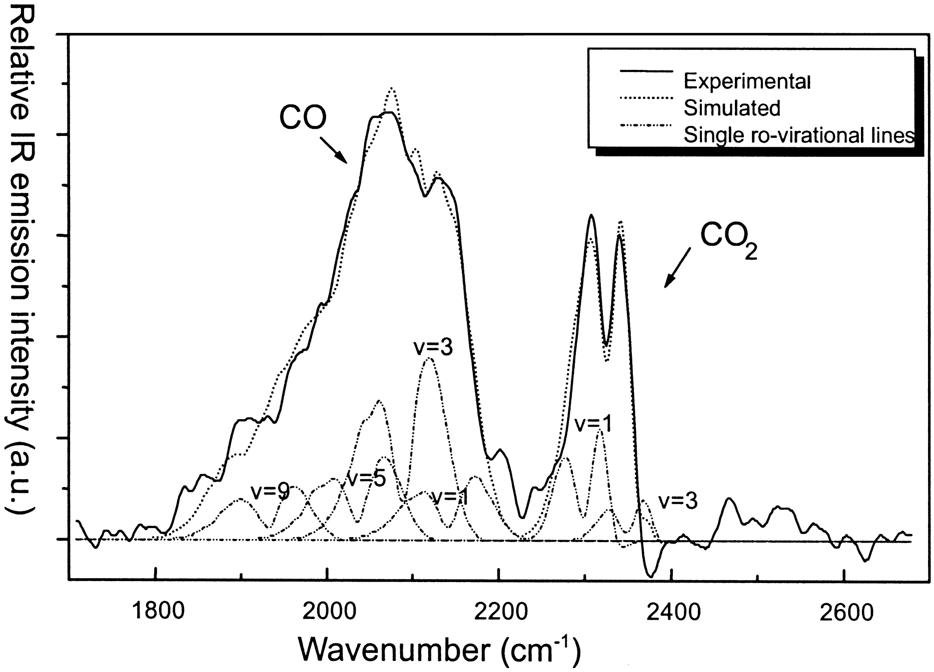


Fig. 3. The simulation of the CO and $CO_2$ spectrum for the $C_2H + O_2$ reaction at 5 μs. The solid line is the experimental spectrum. The dotted lines are the simulated results. Some simulated individual ro-vibrational transitions are also shown. The best-fitted rotational temperature is of 350 K.

ground-state species are not included. Because the population is inverted, it is anticipated that the ground-state molecules only hold a small population. As the population are normalized by Einstein $A(v, J)$ coefficients, the absolute values can be comparable. The ratio of the CO $(v)/CO_2$ $(\nu_3, v)$ populations is 80.1/2.2, or 36, reflecting their relative yields arisen from the reaction. The ratio only refers to the $CO_2$ molecules being excited in $\nu_3$ mode. For each $CO_2$ molecule, there are four vibrational degrees of freedom $(\nu_1, 2\nu_2, \nu_3)$. Assuming the internal energy is equivalently distributed in the $CO_2$ molecule, the overall $CO/CO_2$ ratio should be four time less than that of the $CO(v)/CO_2(\nu_3, v)$, or 9.

It is suggested by Peeters et al. that the initial process is a barrierless combination reaction of $C_2H + O_2$, yielding ethylylperoxy HCCOO radical [33]. The radical undergoes a series of isomerizations forming the key intermediate, oxisenyloxy. The energized oxisenyloxy has two parallel dissociation channels leading to the products of $CH + CO_2$ $(\Delta H_0° = -80$ kcal/mol) or $HCO + CO$ $(\Delta H_0° = -157$ kcal/mol), respectively. Because the reactions are highly exothermic, all the above processes must take place fiercely in a very short time, which is not sufficient long for the molecule to statistically distribute the internal energy. The observation of highly vibrational excitation of the products supports the

Table 3
The vibrational population of CO and $CO_2$ at 5 μs delay for the $C_2H + O_2$ reaction

| | $v = 1$ | $v = 2$ | $v = 3$ | $v = 4$ | $v = 5$ | $v = 6$ | $v = 7$ | $v = 8$ | $v = 9$ | $v = 10$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CO | 12.43 | 27.32 | 18.25 | 6.29 | 4.79 | 2.91 | 2.17 | 2.01 | 2.28 | 1.69 | 80.14 |
| $CO_2$ | 0.27 | 1.55 | 0.39 | | | | | | | | 2.21 |

above exothermic reaction mechanism. The population inverse of both CO $(v)$ and $CO_2$ $(\nu_3, v)$ implies a non-statistical energy distribution after a very fast dissociation process.

According to Sumathi's calculation, the ring-opening of oxisenyloxy leading to the HCO + CO formation has a low barrier of 10.6 kcal/mol. In contrast, another channel forming $CH + CO_2$ has a barrier height of 37.2 kcal/mol. The formation of HCO + CO is thus the dominant channel. A possible decomposition of the energized HCO even produces another CO molecule. Our estimation of $CO/CO_2$ ratio (9) supports the above hypothesis.

## 4. Concluding remarks

(1) The nascent products of CO, HCO, HNC and HCN have been observed in the $C_2H + NO$ reaction. The elementary reaction channels of (1), (2) and (3) are therefore verified. The CO $(v)$ is extremely vibrationally energized and should be produced via the highly exothermic channels (1) and (2). The reaction via channel (3) is mild so that the unstable product HCO still remains.

(2) The nascent products of the reaction of $C_2H$ with $O_2$ are vibrationally excited up to $v = 10$ for CO $(v)$ and up to $v = 3$ for $CO_2$ $(\nu_3, v)$, respectively. The branching ratio of the $CO/CO_2$ formation is 9. The preference of the CO formation can be explained by Peeters's calculation. Starting from the key intermediate, oxisenyloxy the energy barrier is 37.2 kcal/mol for the reaction forming $CH + CO_2$, while only 10.6 kcal/mol for the HCO + CO reaction.

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