*J. Phys. Chem. A* **2002,** *106,* 9499−9501

# Reaction of CH with $NO_2$ Studied by Time-Resolved FTIR Spectroscopy

**Li Ren and Fanao Kong***

*Institute of Chemistry, Chinese Academy of Sciences, Beijng, China 100080*

*Received: February 18, 2002; In Final Form: July 3, 2002*

The gaseous reaction of CH + $NO_2$ has been investigated by using time-resolved FTIR spectroscopy. The CH radical was generated by the laser photolysis of $CHBr_3$ at 248 nm. All of the reaction products, NO, CO, HNO ($v_1$), $CO_2$ ($v_3$), and OH, in their vibrationally excited states were observed. The reaction leading to CO + HNO is identified as the most favorable channel. Producing HCO + NO is a minor reaction channel. A much less competitive channel leading to OH + CNO may also occur. The observed $CO_2$ species may come from the secondary reaction HCO + $NO_2$. The observation agrees with the recent theoretical prediction based on ab initio calculations.

## 1. Introduction

The methylidyne radical, CH, is an important reactive intermediate in hydrocarbon combustion.[1,2] The reaction of CH with $NO_x$ is believed as one of the main reactions involved in the reburning process.[3] The reduction of nitric oxides by the CH radical is a key process for modeling nitrogen chemistry in a flame.[4]

Two groups report their kinetic studies on the reaction of CH + $NO_2$ and find that the reaction is very fast. Wagal et al. measured the total rate constant for the reaction by laser induced fluorescence, obtaining $k = (1.67 \pm 0.12) \times 10^{-10}$ $cm^3$ $molec^{-1}$ $s^{-1}$ at 298 K.[5] Mehlmann and co-workers[6] found that the rate constant for the removal of CH ($v = 0$) by $NO_2$ is $(1.99 \pm 0.34) \times 10^{-10}$ $cm^3$ $molec^{-1}$ $s^{-1}$.

Rim and Hershberger[7] studied the product ratio of the CH + $NO_2$ reaction. By using time-resolved infrared diode laser, the absorption of the CO, NO, and $CO_2$ was observed. On the basis of consideration of product yields and secondary reactions, a branching ratio of 92 ± 4% for the major channel to H + CO + NO or HNO + CO and 8 ± 4% for the minor channel to HCO + NO were obtained.

Because the enthalpy of formation of the CH radical is extremely high ($\Delta H_f^0 = 593.04$ kJ/mol),[8] many possible product channels are thermodynamically accessible for the reactants CH + $NO_2$:

$$CH + NO_2 \rightarrow NH + CO_2 \qquad \Delta H^0_{298} = -644.2 \text{ kJ/mol} \quad (1)$$

$$\rightarrow HNO + CO \qquad \Delta H^0_{298} = -638.2 \text{ kJ/mol} \quad (2)$$

$$\rightarrow HCO + NO \qquad \Delta H^0_{298} = -493.4 \text{ kJ/mol} \quad (3)$$

$$\rightarrow HCN + O_2 \qquad \Delta H^0_{298} = -492.1 \text{ kJ/mol} \quad (4)$$

$$\rightarrow H + CO + NO \qquad \Delta H^0_{298} = -429.5 \text{ kJ/mol} \quad (5)$$

$$\rightarrow NCO + OH \qquad \Delta H^0_{298} = -456.9 \text{ kJ/mol} \quad (6)$$

$$\rightarrow CNO + OH \qquad \Delta H^0_{298} = -194.8 \text{ kJ/mol} \quad (7)$$

Tao et al. performed an ab initio study for the reaction.[9] They obtained a detailed potential energy surface (PES) referred to the reaction system. Their prediction is in contradiction with the branching ratio observed by Rim and Hershberger.[7] According to their calculation, the most favorable reaction channel leads to products HCO + NO. The product channels leading to HNO + CO and HON + CO are less feasible channels. The other pathways leading to NH + $CO_2$, OH + CNO, and HCN + $O_2$ are much less competitive.

To understand which reaction channels really occur and to determine the main reaction channel, we carried out an extensive investigation on the reaction of CH + $NO_2$ by using time-resolved FTIR spectrometry. The method has the advantage of simultaneously recording the emissions from many reaction products. In this experiment, various products arisen from the reaction are observed, so that the related reaction channels are identified. Upon comparison with the PES of the CH + $NO_2$ reaction system, the reaction mechanism is clarified.

## 2. Experimental Section

The details of the TR−FTIR spectrometer and the reaction chamber have been described previously.[10] CH radicals were produced via multiple photon photolysis of $CHBr_3$ at 248 nm (KrF laser, Lambda Physik, LPX305i, ~400 mJ/pulse). The excimer laser beam was slightly focused into the reaction chamber by a cylinder lens ($f = 380$ mm), forming a spot of 0.2 × 10 $mm^2$. The intensity of the laser beam was about $10^8$ $W/cm^2$. In this experiment, a gas mixture of $CHBr_3$ (Shanghai reagent, Ltd. 99%) and $NO_2$ (Beifen Gas, Ltd. 99.9%) flowed through the reaction chamber. The partial pressures of $CHBr_3$ and $NO_2$ were maintained at 20 and 90 Pa, respectively. The IR emissions were collected by a pair of gold-coated confocal spherical mirrors and collimated to the FTIR spectrometer (Nicolet 800). An InSb (77 K) detector was used to record the IR emission, and the detectable spectral range is from 1800 to 4000 $cm^{-1}$. The spectral resolution was set at 16 $cm^{-1}$.

## 3. Results and Discussion

**3.1. Reaction Products.** CH radicals were produced via multiple photon photolysis of $CHBr_3$ at 248 nm. The photodissociation of $CHBr_3$ affords a high CH yield in the experiment.[11] A three-step sequential fragmentation mechanism, where each photon removes one bromine atom from the precursor molecule, was proposed by Lindner et al.[12]

None of the IR emission was observed in the photolysis of 20 Pa of pure $CHBr_3$ with the TR−FTIR spectroscope (Figure

---

* To whom correspondence should be addressed. Fax: +86-10-6256-3167. E-mail: kong@mrdlab.icas.ac.cn.

10.1021/jp0204408 CCC: $22.00

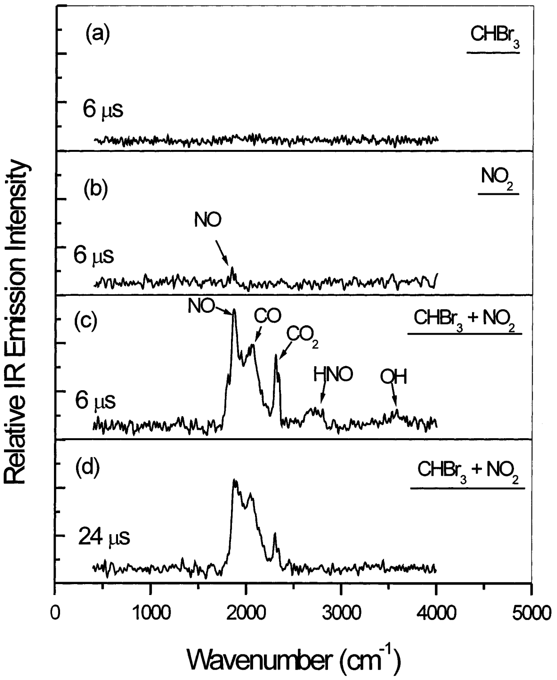

**Figure 1.** Time-resolved infrared emission spectra of the CH + $NO_2$ reaction recorded at different delay times after 248 nm laser firing. The spectra of the photolysis of (a) pure $CHBr_3$ (20 Pa) and (b) pure $NO_2$ (90 Pa) at 6 μs after the laser firing are shown. The spectra of the photolysis of a mixture of $CHBr_3$ (20 Pa) and $NO_2$ (90 Pa) recorded at 6 (c) and and 24 μs (d) are also shown in the bottom of the figure.

1a). There was a very weak emission (1844 $cm^{-1}$) at 6 μs after the photolysis of 90 Pa of $NO_2$ by 248 nm laser (Figure 1b). The emission was attributed to the vibrational transition of NO. However, when the reaction of the gas mixture of $CHBr_3$ and $NO_2$ was initialized by the laser, strong IR emissions were recorded. Figure 1, parts c and d, shows the IR emission spectra recorded at two different delay times after the laser firing. Product yields reach their maximum at 6 μs. The IR emissions decay in 24 μs. In the present case, each CH radical collides about 24 times with $NO_2$ in 6 μs. The rise time of the products is consistent with the overall reaction rate constant of (1.67∼1.99) × $10^{-10}$ $cm^3$ $molec^{-1}$ $s^{-1}$ reported by Wagal[5] and Mehlmann.[6]

A wealth of knowledge can be obtained from the IR spectrum at 6 μs. There is a strong emission centered at 1860 $cm^{-1}$ in the spectrum. Both the vibrational transitions of NO ($v = 1 \rightarrow 0$) and HCO ($v = 1 \rightarrow 0$, $v_3$) are around 1870 $cm^{-1}$. It is difficult to distinguish each other in the spectrum. However, the HCO immediately undergoes a rapid secondary reaction with $NO_2$[13,14] once it is formed (see section 3.3). So, this emission is assigned to NO. Another strong emission band between 1961 and 2151 $cm^{-1}$ is assigned to the transitions of vibrationally excited CO ($v \rightarrow v - 1$). A sharp band centered at 2325 $cm^{-1}$ is assigned to the unsymmetric stretching of $CO_2$ ($v_3$ mode, fundamental frequency being 2349 $cm^{-1}$). The emission between 2596 and 2812 $cm^{-1}$ is attributed to the N−H stretching of HNO ($v_1$ mode, fundamental frequency being 2684 $cm^{-1}$). Finally, a weak band of 3488−3676 $cm^{-1}$ probably refers to the emission from the vibrationally excited OH (fundamental frequency being 3569 $cm^{-1}$).

**3.2. The Primary Reactions.** Both the IR emissions of CO and HNO have been observed in this experiment, the reaction of CH + $NO_2$ → HNO + CO, channel 2, can thus be verified. Because the emission from CO is very strong, channel 2 is considered as the major pathway for the CH + $NO_2$ reaction. The conclusion confirms the Rim's observation.[7] In the formation of HNO + CO, a tunneling effect of H-atom shifting accelerates the reaction (see section 3.4).

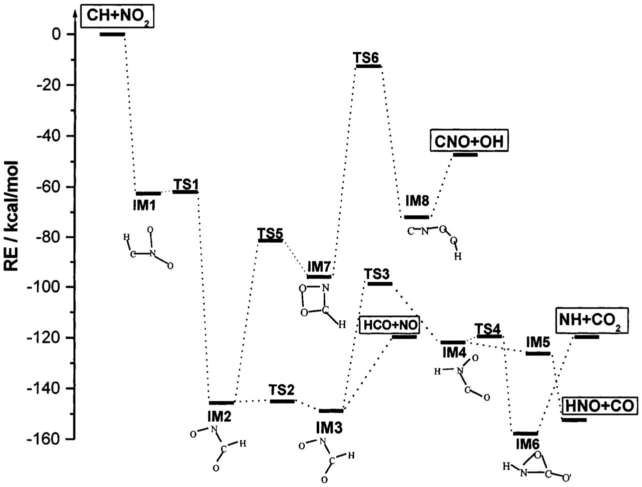

**Figure 2.** Schematic pathways of the CH+$NO_2$ reaction. The reaction route leading to the products HCO + NO, HNO + CO, NH + $CO_2$, and OH + CNO are shown. The energy data of the intermediates and transition states are adapted from ref 9.

Product NO emits the same intensity of IR light as that from CO. However, the Einstein spontaneous coefficient of NO is about 10 times greater than that of CO.[15,16] In other words, the yield of CO is 10 times than that of NO. Channel 3, which leads to HCO + NO, should be a minor reaction pathway. In Rim and Hershberger's study, the reactions leading to H + CO + NO or HNO + CO are also considered as the major product channels, whereas HCO + NO is a minor product channel. The branching ratio is estimated as (0.92 ± 0.04)/(0.08 ± 0.04). This result well agrees with our observation.

As shown in the spectrum of Figure 1c, the emission intensity of product CO is about 3 times greater than that of $CO_2$. Taking the Einstein spontaneous emission coefficient[16,17] into account, the amount of $CO_2$ is only about 3% of that of CO molecules. The weak signal represents a very small amount of $CO_2$. The fact indicates that even if $CO_2$ was a primary product, the reaction CH + $NO_2$ → NH + $CO_2$ should be a minor channel.

To ascertain the source of the $CO_2$, we further performed a reference experiment, studying the reaction of HCO + NO by TR−FTIR spectroscope also.[18] This reaction has the same intermediates IM3 and IM4 as those in the CH + $NO_2$ reaction (plotted in Figure 2). Figure 2 shows that a common pathway leads the intermediates to two product channels, forming NH + $CO_2$ and HNO + CO, respectively. Vibrationally excited HNO and CO were found as the major products in the reference experiment. The interesting thing is that $CO_2$ emission was not observed. The reference experiment indicates that the $CO_2$ observed in the present study is unlike a primary product of the CH + $NO_2$ reaction.

Because a weak emission may be attributed to OH ($v \rightarrow v -$ 1), the pathway forming products OH and CNO as a much less competitive channel may also exist.

**3.3. The Secondary Reactions.** On the other hand, te HCO radical, as a primary product of the reaction, can react fast with $NO_2$[13,14]

$$HCO + NO_2 \rightarrow CO_2 + H + NO + 160\ \text{kJ/mol} \quad (8)$$

$$HCO + NO_2 \rightarrow CO + OH + NO + 57\ \text{kJ/mol} \quad (9)$$

producing $CO_2$ in (8) and OH in (9) also. The reaction rate constant was about 5 × $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$. So the emission

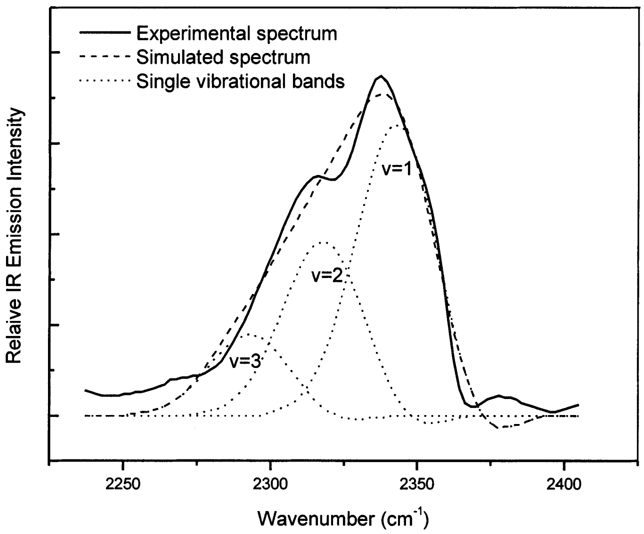

**Figure 3.** Simulation of $CO_2$ emission spectrum at 6 $\mu$s for the HCO + $NO_2$ reaction. The solid line is the experimental spectrum. The dashed line is the simulated results. The simulated individual vibrational transitions are also shown with the dotted lines. The best-fitted rotational temperature is of 300 K.

observed from $CO_2$ molecules and OH radicals in the present study may come from these secondary reactions.

In another auxiliary experiment, we investigated the IR emission from the reaction of HCO + $NO_2$. The emission from OH radicals were not founded, but a moderate emission of $CO_2$ ($v \rightarrow v - 1$) has been observed in the TR−FTIR spectrum of 23 $\mu$s delay.

The above facts support that the $CO_2$ should be yielded from the secondary reaction 8 but not from the primary reaction 1. In contrast, OH might be produced in the primary reaction 7, because we did not observe it in the IR emission of the secondary reaction.

The recorded emission spectrum of vibrationally excited $CO_2$ ($v_3$) has been simulated. The simulation provides the vibrational energy distributions of $CO_2$ in the unsymmetric stretching mode (Figure 3). The $CO_2$ populates up to $v = 3$. The relative population of $CO_2$ at $v = 1-3$ is 0.706, 0.222, and 0.07, respectively. The best fitted rotational temperature is 300 K.

The rate of reaction 9 is 1.7 times faster than that of the reaction 8.[14] In Figure 1c, the emission intensity of $CO_2$ is just 3% of that of the observed product CO. Then the amount of CO from the secondary reaction 9 is about 5% of that from the primary reaction 2 CH + $NO_2 \rightarrow$ CO + HNO. Therefore, the contribution of the secondary reaction to the product CO is limited.

**3.4. Reaction Mechanism.** Combining our experimental observations with the theoretical calculation, we are able to gain insight into the dynamic mechanism. Figure 2 plots the potential energy surface of the reaction paths. The energy data of the intermediates and the transition states are adapted from ref 9. It can be seen that the reaction starts with a recombination of the radicals CH and $NO_2$, forming an adduct of $HCNO_2$ (IM1). The recombination is a barrierless process, releasing an energy of 67.7 kcal/mol. The adduct converts to *cis*-OC(H)NO (IM2) with a shifting of the oxygen atom from the nitrogen atom to the carbon atom. There is a very low barrier (0.5 kcal/mol) between the *cis*-OC(H)NO (IM2) and *trans*-OC(H)NO (IM3). Dissociation of IM3 directly leads to the most feasible products of HCO and NO.

One of the key intermediates, IM4, is formed because of a 2,3-hydrogen shifting in IM3. From IM4 to IM5, the C−N bond stretches. The cleavage of the C−N bond in IM5 yields the products HNO and CO. Although the barrier height in forming HNO + CO is about 22 kcal/mol higher than that in forming HCO + NO, however, reaction 2 leading to HNO + CO is the major channel. It can be explained with the tunneling effect of the H atom. Considering the H-atom tunneling in the isomerization process from IM3 to IM4, the difference between the two barrier heights reduces to only 7 kcal/mol estimated by us on the basis of the WKB approximation.[19]

As a possible reaction route, ring closure of NOC in IM4 leads to another intermediate IM6, which dissociates into the products NH and $CO_2$. A pathway leading to OH + CNO is also considered. However, there are three high barriers involved in the reaction pathway. The occurrence of channel 6 is thus unlikely but possible.

In conclusion, we have studied the reaction of CH + $NO_2$ by TR−FTIR spectroscopy. Vibrationally excited species NO, CO, $CO_2$ ($v_3$), HNO ($v_1$), and OH are observed. Channel 2 leading to HNO + CO is the most favorable reaction pathway. It can be reasonably explained by the H-atom tunneling effect. Channel 3 to HCO + NO is a minor pathway. The reaction channel forming products OH + CNO may also exist. The $CO_2$ observed in this experiment is not the primary product but comes from the secondary reaction of HCO + $NO_2$. In light of the previous theoretical analysis, the reaction mechanism is well elucidated.

**Acknowledgment.** This work was supported financially by NSFC and MOST of China with the research Project No. 973. We thank Mr. Fong Dong for helping in the performance of the auxiliary experiments.

## References and Notes

(1) Strobel, D. F. *Planet Space Sci.* **1982**, *30*, 839.

(2) Becker, K. H.; Geiger, H.; Wiesen, P. Int. *J. Chem. Kinet.* **1996**, *28*, 115.

(3) Warnatz, J. *Combustion*, 2nd ed.; Springer: Berlin, 1999; p 253.

(4) Dean, A. J.; Hanson, R. K.; Bowman, C. T. *J. Phys. Chem.* **1991**, *95*, 3180.

(5) Wagal, S. S.; Carrington, T.; Filseth, S. V.; Sadowski, C. M. *Chem. Phys.* **1982**, *69*, 61.

(6) Mehlmann, C.; Frost, M. J.; Heard, D. E.; Orr, B. J.; Neson, P. F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2335.

(7) Rim, K. T.; Hershberger, J. F. *J. Phys. Chem. A* **1998**, *102*, 4592.

(8) Okabe, H. *Photochemistry of small molecules*; Wiley-Interscience: New York, 1978; p 376.

(9) Tao, Y.-G.; Ding, Y.-H.; Li, Z.-S.; Huang, X.-R.; Sun, C.-C. *J. Phys. Chem. A* **2001**, *105*, 3388.

(10) Zhu, Q.; Huang, S.; Wang, X.; et al. *Chin. J. Chem. Phys.* **1993**, *6*, 87.

(11) Fleming, J. W.; Fujimoto, G. T.; Lin, M. C.; Harvey, A. B. *Proc. Int. Conf. Lasers* **1979**, *63*, 104.

(12) Lindner, J.; Ermisch, K.; Wilhelm, R. *Chem. Phys.* **1998**, *238*, 329.

(13) Guo, Y.; Smith, S. C.; Moore, C. B. *J. Phys. Chem.* **1995**, *99*, 7473.

(14) Rim, K. T.; Hershberger, J. F. *J. Phys. Chem. A* **1998**, *102*, 5898.

(15) Billingsley, F. P. *J. Mol. Spec.* **1976**, *61*, 53.

(16) Chackerian, C., Jr.; Tipping, R. H. *J. Mol. Spec.* **1983**, *99*, 431.

(17) Johns, J. W. C. *J. Mol. Spec.* **1989**, *134*, 433.

(18) Dong, F.; Kong, F. A. *J. Phys Chem. A* Submitted.

(19) Bell, R. P. *The tunnel effect in chemistry*, 1st ed.; Chapman and Hall: New York, 1980; p 63.