



# The reaction of $\text{CH}_2(^3\text{B}_1) + \text{N}_2\text{O}$ studied by time-resolved Fourier transform infrared spectroscopy

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## Abstract

The reaction dynamics of methylene radical  $\text{CH}_2(\tilde{\text{X}}^3\text{B}_1)$  with  $\text{N}_2\text{O}$  was investigated by time-resolved Fourier transform infrared spectroscopy. Pure  $\text{CH}_2(\tilde{\text{X}}^3\text{B}_1)$  radical was produced via laser photolysis of ketene at 351 nm. Nascent vibrationally excited products CO, NO and HCN were observed. Five reaction pathways and three possible reaction intermediates are proposed. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Methylene radical plays an important role in combustion process and atmospheric chemistry [1].  $\text{CH}_2$  is formed from the pyrolysis of hydrocarbons or in the oxidation of acetylene in combustion flames. As a highly reactive species,  $\text{CH}_2$  radical can react with nitrous oxide, which also exists in flame. Therefore, the investigation of  $\text{CH}_2 + \text{N}_2\text{O}$  reaction is of importance for understanding  $\text{NO}_x$  emission processes in combustion.

Bell et al. [2] studied the reaction of singlet  $\text{CH}_2(\tilde{\text{a}}^1\text{A}_1)$  with  $\text{N}_2\text{O}$  molecule by gas chromatography and mass spectroscopy. However, they concluded that there is no evidence showing that  $\text{CH}_2$  reacted with  $\text{N}_2\text{O}$ . Using time-resolved IR diode laser absorption spectroscopy, Darwin and Moore [3] recently studied the reaction kinetics of  $\text{CH}_2(\tilde{\text{X}}^3\text{B}_1) + \text{N}_2\text{O}$ . They reported an upper bound of the rate constant of  $1.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the overall reaction. However, no reaction product has been reported.

Actually, the  $\text{CH}_2 + \text{N}_2\text{O}$  reaction has several routines. At least five pathways are energetically allowed. The reaction mechanisms are varied. A detailed study of the product formation and the reaction mechanism is thus invoked. In this work, the reaction dynamics of  $\text{CH}_2(\tilde{\text{X}}^3\text{B}_1)$  with  $\text{N}_2\text{O}$  studied by time-resolved Fourier transform infrared (TR-FTIR) spectroscopy is reported. According to the Ref. [4], the pure triplet state of methylene  $\text{CH}_2(\tilde{\text{X}}^3\text{B}_1)$  was produced via laser photolysis of ketene at 351 nm. After laser pulse, some nascent vibrationally excited products were observed. The reaction pathways leading to these products are identified. Three possible reaction processes were proposed.

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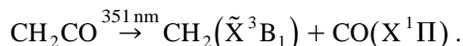
## 2. Experimental

The reaction chamber and the TR-FTIR spectrometer has been described in detail elsewhere [5]. Pure triplet state radical  $\text{CH}_2(\tilde{X}^3\text{B}_1)$  was produced via laser photolysis of ketene at 351 nm (XeF laser, Lambda Physik LPX305i,  $\sim 170$  mJ/pulse). Ketene was synthesized by pyrolysis of acetone and purified by trap-to-trap method [6]. During the experiment, a gas mixture of ketene and  $\text{N}_2\text{O}$  (99%) flowed into the reaction chamber. The partial pressure of ketene or  $\text{N}_2\text{O}$  was maintained at 70 and 180 Pa, respectively. The excimer laser beam was slightly focused by a cylinder lens ( $f=380$  mm) and was led to the chamber. The IR emission from reaction products was collected by a pair of gold-coated spherical mirrors to the FTIR spectrometer (Nicolet 800). An InSb IR detector was used. The spectral resolution was set at  $16\text{ cm}^{-1}$ . The data acquisition system provided 10 time-sequenced interferograms. The spacing time between each two adjacent interferograms is  $18\ \mu\text{s}$ .

## 3. Results and discussion

### 3.1. Nascent products

The  $\text{CH}_2$  radical generated from the photolysis of ketene at 351 nm has been ascertained to be the ground electronic state  $\tilde{X}^3\text{B}_1$  [4]. The photolysis reaction is:



A small amount of available energy (21 kJ/mol) of the above reaction is distributed to translation, rotation and vibration freedom of the products. The products thus are almost not expected to be vibrationally excited. In fact, no IR emission was observed after the photolysis of pure ketene. Therefore, the 351 nm photolysis of ketene at this wavelength provides a neat ground state  $\text{CH}_2(\tilde{X}^3\text{B}_1)$  source as well as a clean IR emission background.

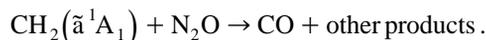
Due to the absence of absorption at 351 nm [7], the  $\text{N}_2\text{O}$  molecules are not expected to be photodissociated. Neither was any IR emission observed from the pure  $\text{N}_2\text{O}$  when it was irradiated by 351 nm laser. Therefore there is no side reaction between  $\text{CH}_2(\tilde{X}^3\text{B}_1)$  radicals and photofragments of  $\text{N}_2\text{O}$ .

Intense IR emission was recorded when the  $\text{CH}_2\text{CO}/\text{N}_2\text{O}$  mixture was irradiated by 351 nm laser. Fig. 1 shows the IR emission spectra at different delay time after laser firing. The emission between 1950 and 2260  $\text{cm}^{-1}$  at  $5\ \mu\text{s}$  is assigned to the vibrationally excited  $\text{CO}(v \rightarrow v-1)$ . The  $\text{CO}(v)$  emission decreases very fast due to vibrational relaxation. The vibrationally excited state  $\text{CO}(v)$  are nearly completely deactivated to the ground state after  $23\ \mu\text{s}$ . The fast quenching rate can be explained as that a near-resonant  $V-V$  transfer to the parent molecules  $\text{CH}_2\text{CO}(v_2 = 2152\ \text{cm}^{-1}$ , C–O stretching mode) takes place. The  $V-V$  quenching rate constant of this process is  $3 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$  [8].

Another spectral band around 2100  $\text{cm}^{-1}$  overlaps the strong IR emission of  $\text{CO}(v)$ . After  $\text{CO}(v)$  is almost quenched, the band from 1950 to 2260  $\text{cm}^{-1}$  appears. It is assigned to the  $\nu_1$  mode of HCN (2089  $\text{cm}^{-1}$ ).

Two other emission bands centered at 1880 and 3270  $\text{cm}^{-1}$  grew up in the first 40  $\mu\text{s}$ . The 1880  $\text{cm}^{-1}$  band is assigned to  $\text{NO}(v)$  emission. It is difficult to identify the 3270  $\text{cm}^{-1}$  band. The emission may be either from  $\text{N}_2\text{H}(\nu_3)$  or from  $\text{HCN}(\nu_3)$ .

Questionably, Bell et al. [2] believed that no chemical reaction of  $\text{CH}_2(\tilde{a}^1\text{A}_1)$  with  $\text{N}_2\text{O}$  occurred based on the fact that they did not observe the product of  $\text{N}_2$  as they expected. However, they disregarded another possible reaction channel with the formation of CO:



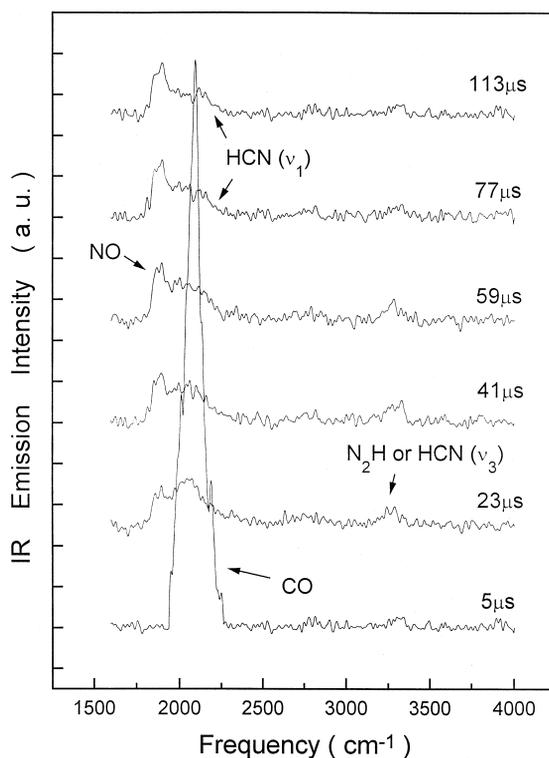


Fig. 1. The IR emission spectra of  $\text{CH}_2\text{CO}/\text{N}_2\text{O}$  system taken at different delay time after laser firing.

In another investigation of  $\text{CH}_2(\tilde{a}^1\text{A}_1) + \text{N}_2\text{O}$  reaction, we did observe the CO emission. This evidence can explain Bell's observation of the increasing ratio of  $\text{CO}/\text{C}_2\text{H}_4$  with increasing  $\text{N}_2\text{O}$  pressure. Therefore, their conclusion of no chemical reaction of  $\text{CH}_2(\tilde{a}^1\text{A}_1)$  with  $\text{N}_2\text{O}$  is doubtful.

### 3.2. Reaction pathways

The thermodynamically allowed pathways of the  $\text{CH}_2(\tilde{\text{X}}^3\text{B}_1) + \text{N}_2\text{O}$  reaction are as follows:

		$\Delta H$ (kJ/mol)	
$\text{CH}_2(\tilde{\text{X}}^3\text{B}_1) + \text{N}_2\text{O}$	$\rightarrow \text{CO} + \text{eH}_2 + \text{N}_2$	-588	(1)
	$\rightarrow \text{HCO} + \text{N}_2\text{H}$	-227	(2)
	$\rightarrow \text{H} + \text{CO} + \text{N}_2\text{H}$	-113	(3)
	$\rightarrow \text{HCN} + \text{HNO}$	-235	(4)
	$\rightarrow \text{HCN} + \text{H} + \text{NO}$	-71	(5)

As mentioned above, the IR emissions from the nascent vibrationally excited products  $\text{CO}(v)$ ,  $\text{NO}(v)$  and  $\text{HCN}(v_1)$  have been explicitly observed by the TR-FTIR spectrometer. The  $3270\text{ cm}^{-1}$  band may refer to the product  $\text{N}_2\text{H}$ . Thus, most of the IR active species of the possible products have been observed.



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