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The Reaction of CH_3 + NO in Gaseous Phase

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Abstract: Time-resolved Fourier transform infrared emission spectroscopy is employed for studing gaseous reaction of CH_3 with NO. The CH_3 radical was produced by laser photolysis of CH_3Br at 248 nm. The infrared emissions of vibrationally excited nascent products HCO (ν_3), HCN (ν_1, ν_3), NH_2 (ν_3), secondary product HNO (ν_1) and possible product HNCO (ν_1) were observed. It verifies that the reaction channels of HCO + NH_2 and HCN+H_2O exist, and that one other channel HNCO + H may also occur.

Keywords: CH_3, NO, TR-FTIR, reaction channel.

NOx is a major pollutant product from combustion processes. In hydrocarbon combustion there are a number of radicals as CH_2, C_2H, CH_3 and C_2H_3 can react with NO[1-3]. A large amount of CH_3 exists in natural gas combustion flame. Therefore the reaction of CH_3 with NO is very important.

A rate constant ($k_\infty = 1.5\times10^{-11}\exp(-60k/T)$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$) of the overall CH_3+NO reaction was measured with laser flash photolysis/absorption spectroscopy over the temperature range 296-509 K and at pressure of 25-600 Torr by Davies *et al*.[4]. Lifshitz *et al*.[5] evaluated a rate expression for the reaction $CH_3+NO\rightarrow HCN+H_2O$ as $10^{11.8}\exp(-15.0\times10^3/RT)$ $cm^3\cdot mol^{-1}\cdot s^{-1}$ in shock tube. Kaiser[6] measured pressure dependence of the rate constant for the reaction CH_3+NO. Theoretically, Nguyen *et al*.[7] employed *ab initio* molecular orbital method to calculate the potential energy surface of the reaction $CH_3+NO\rightarrow HCN+H_2O$. Obviously the studies of this important reaction is insufficient. Even the possible reaction channels are not clear.

In this paper, we report our experimental investigation on the CH_3+NO reaction using time-resolved Fourier transform infrared (TR-FTIR) emission spectroscopy. Several primary products have been observed in the IR spectrum and some possible reaction channels are found. .

Experimental

Details of the experiment apparatus of time-resolved FTIR spectroscope have been described in previous work[8]. In the experiment a gas mixture consisted of 80 Pa CH_3Br (99%) and 206 Pa NO (99%) flows through the reaction chamber. Methyl radical was

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produced by laser photolysis of methyl bromide at 248 nm (KrF laser, Lambda Physik LPX305I, 200 mJ/pulse). The IR emission from the vibrationally excited products was detected by TR-FTIR spectrometer (Nicolet, 800). The spectrum between 1800 cm^{-1} and 4000 cm^{-1} was recorded with a spectral resolution at 16 cm^{-1}. In order to improve signal to noise ratio, each spectrum was accumulated 10 times.

Result and Discussion

Nascent Products

The photolytic reaction of CH_3Br is :

$$CH_3Br \xrightarrow{248nm} CH_3+Br+46.6\ kcal/mol$$

No IR emission signal was observed in the 248 nm laser photolysis of pure CH_3Br. Therefore, it provides a neat IR emission background for the spectroscopic investigation of CH_3+NO reaction.

When CH_3Br was mixed with NO and led into the reaction chamber, then fired by the laser, a transient IR emission was recorded. The IR emitters are the nascent products of CH_3+NO reaction. **Figure 1** shows the IR emission spectrum at 5 μs after the laser ignition. A sharp peak between 1750 cm^{-1} and 1941 cm^{-1} corresponds to the C-O stretching of HCO (ν_3 1863 cm^{-1}) was observed. This peak increases with time but attenuates gradually after 23 μs. The weak band between 1941 cm^{-1} and 2126 cm^{-1} could be attributed to the emission of vibrationally excited HCN (ν_1 2089 cm^{-1}). A strong emission between 3170 cm^{-1} and 3611 cm^{-1} is recorded. The emission possibly can be assigned to the N-H stretching of NH_2 (ν_3 3301 cm^{-1}), HNCO (ν_1 3538 cm^{-1}) and the C-H stretching of HCN (ν_3 3312 cm^{-1}). The spectrum between 2370 cm^{-1} and 2570 cm^{-1} is HNO (200)–(100) band origin and between 2570 cm^{-1} and 2870 cm^{-1} is HNO (100)–(000) band origin. The secondary product HNO is generated from HCO+NO→ HNO+CO.

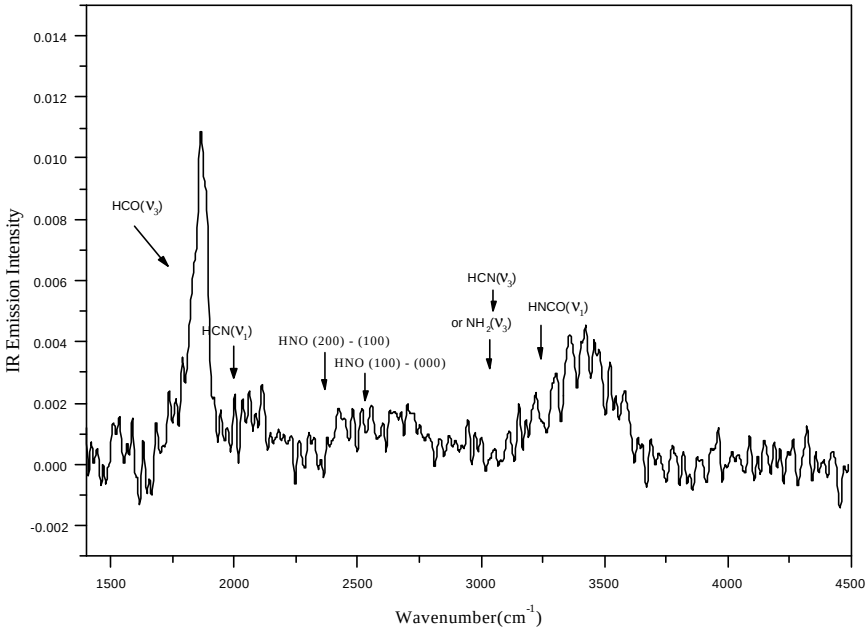
Reaction channels

These products observed are possibly produced from several thermodynamically accessible channels as follows:

		ΔH^o/kcal·mol^{-1}
CH_3+NO	→ $HNCO+H_2$	-81.1
	→ $HCN+H_2O$	-81.8
	→ $HCO+NH_2$	-6.0

From IR emission spectra it is known that $HCO+NH_2$ and $HCN+H_2O$ channels exist and $HNCO+H_2$ channels may occur.

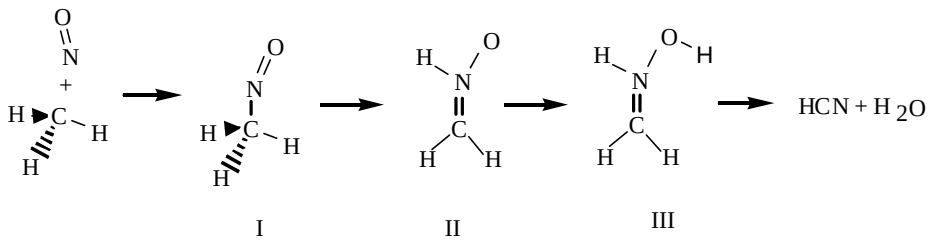
Figure 1 The IR emission spectrum at 5 μs in CH_3 + NO reaction system



Reaction mechanism

For the CH_3+NO → HCN+H_2O channel, with the consideration of the factors on symmetry-forbiddenness and energetics, the reaction CH_3+NO starts possibly through the formation of intermediate I, when NO molecule of linear ground state attaches to carbon possessing an unpaired electron in the CH_3 radical. The formation of intermediate II is 1, 2-hydrogen shift *via* intermediate I. This intermediate II can further undergo a 1, 2-hydrogen migration and forms intermediate III. Intermediate III rearranges and produces HCN and H_2O.

In brief, the intense emission of HCO (ν_3) and possible primary products HCN (ν_1, ν_3), HNCO (ν_1) and NH_2 (ν_3) have been observed for CH_3+NO reaction. Three reaction channels are suggested with experimental evidences. Further studies on the reaction mechanism employing *ab initio* molecular orbitial theory is invoked.



Acknowledgments

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