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A Diode Laser Study of the Product Branching Ratios of the CH + NO_2 Reaction

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The reaction of CH radicals with NO_2 was studied at 296 K using multiphoton photolysis of $CHBr_3$ at 248 nm, followed by time-resolved infrared diode laser detection of reaction products. CO, CO_2, and NO were detected in significant yield, while DCN (from $CDBr_3$), N_2O, HCNO, and HNCO were formed in undetectably low yields. On the basis of consideration of product yields and secondary chemistry, we find that the major product channel is H + CO + NO or HNO + CO, which together account for 92 ± 4% of the total rate constant. HCO + NO is a minor product channel, accounting for 8 ± 4%. Upper limits are estimated for several other product channels.

Introduction

Reactions of hydrocarbon fragments are of great interest in the kinetic modeling of flames. The methylidyne radical (CH), for example, is believed to play a crucial role in the prompt-NO formation mechanism[1] as well as the NO-reburning process in which NO_x-containing exhaust gases produced in fossil fuel combustion are recycled into a hydrocarbon-rich zone.[2,3] Previous kinetic investigations of CH radical reactions have concentrated primarily on total rate constant measurements, with comparatively few product studies. The CH + NO reaction has been the subject of several kinetic studies[4−10] as well as recent ab initio calculations.[11] This reaction is very fast with a virtually temperature-independent rate constant of $(1.6-2.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. A previous study of the deuterated CD + NO reaction in our laboratory indicated that the DCN + O channel accounts for the largest fraction of 48% of the total rate, and that minor product channels include NCO + H, CO + NH, and possibly HCO + N.[12] The observation of DCN + O as the major channel is in qualitative agreement with other studies.[7,13] Reactions with other nitrogen oxides include CH + N_2O and CH + NO_2. The CH + N_2O has a rate constant of $(6.9-8.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, with a small negative activation energy,[4,14−16] and produces primarily HCN + NO as well as smaller amounts of H + N_2 + CO.[17]

In this study we report measurements of the product branching ratios (defined as $\phi_{1a} = k_{1a}/k_{total}$, etc.) of the CH + NO_2 reaction. Only one previous study of this reaction has been reported. Wagal et al. measured the total rate constant of this reaction, obtaining $k = 1.67 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[5] No temperature-dependent kinetic studies have been reported, but if this reaction behaves similarly to the CH + NO and CH + N_2O reactions, a zero or small negative activation energy is expected. Numerous possible product channels are thermodynamically accessible:

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

$$\mathrm{\rightarrow HNO + CO} \qquad \Delta H^\circ_{298} = -638.2\ \mathrm{kJ/mol} \qquad \text{(1b)}$$

$$\mathrm{\rightarrow HCO + NO} \qquad \Delta H^\circ_{298} = -493.4\ \mathrm{kJ/mol} \qquad \text{(1c)}$$

$$\mathrm{\rightarrow HCN + O_2} \qquad \Delta H^\circ_{298} = -492.1\ \mathrm{kJ/mol} \qquad \text{(1d)}$$

$$\mathrm{\rightarrow H + NO + CO} \qquad \Delta H^\circ_{298} = -429.5\ \mathrm{kJ/mol} \qquad \text{(1e)}$$

$$\mathrm{\rightarrow NCO + OH} \qquad \Delta H^\circ_{298} = -456.86\ \mathrm{kJ/mol} \qquad \text{(1f)}$$

$$\mathrm{\rightarrow HCNO + O} \qquad \Delta H^\circ_{298} = -203.7\ \mathrm{kJ/mol} \qquad \text{(1g)}$$

$$\mathrm{\rightarrow HNCO + O} \qquad \Delta H^\circ_{298} = -479.7\ \mathrm{kJ/mol} \qquad \text{(1h)}$$

$$\mathrm{\rightarrow CN + HO_2} \qquad \Delta H^\circ_{298} = -190.0\ \mathrm{kJ/mol} \qquad \text{(1i)}$$

where JANAF values for heats of formation were used,[18] except for NCO, for which $\Delta H_f = 131.38$ kJ/mol was used.[19] To our knowledge, no direct measurements of the products of this reaction have been reported.

In this study, we use infrared diode laser detection of NO, CO, CO_2, HCNO, HNCO, DCN, and N_2O (produced by secondary chemistry) product molecules. $CHBr_3$ or $CDBr_3$ were used as CH radical precursors via multiphoton absorption of near-UV light:

$$\mathrm{CHBr_3} + h\nu\ (248\ \mathrm{nm}) \rightarrow \mathrm{CH + Br + Br_2\ or\ CH + 3Br}$$

$$\mathrm{CDBr_3} + h\nu\ (248\ \mathrm{nm}) \rightarrow \mathrm{CD + Br + Br_2\ or\ CH + 3Br}$$

Deuterated precursor molecules were used in some of the experiments because one of the possible products, HCN, lies outside the range of our laser diodes. $CHBr_3$ has been used as a CH radical precursor in numerous previous studies.[6,12,15,20−22]

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Excited-state CH($a^4\Sigma$) radicals may also be produced in this system, although previous studies have shown that they are relatively unreactive toward NO and N_2O.[23] In this study, we use xenon buffer gas to relax electronically excited states of CH to the $^2\Pi$ ground state. Although no direct measurements of the rate of this relaxation process have been reported, xenon is known to efficiently relax NH($^1\Delta$) to ground-state NH($^3\Sigma$),[24,25] and our previous studies of the CH + NO reaction suggested that similar processes are active for excited states of CH as well.[12]

Experimental Section

The experimental methods have been described in previous publications.[12,26−27] Briefly, ultraviolet light from an excimer laser (Lambda Physik Compex 200) operating on the KrF line at 248 nm was weakly focused by a 1-m focal length CaF_2 lens into the center of a 1.46-m Pyrex reaction cell. Infrared probe light from a lead-salt diode laser (Laser Photonics) was collimated and made collinear with the UV beam by means of a dichroic beam splitter. Both beams were copropagated through the cell, after which the UV beam was removed by a second beam splitter. The infrared light then passed through a $^1/_4$-m monochromator and was focused onto an InSb detector (1 μs response time). Transient absorption signals were collected on a LeCroy 9310A digital oscilloscope and stored on a personal computer.

Typical reaction conditions were 0.1 Torr $CHBr_3$, 0.1−0.5 Torr NO_2, 1.0 Torr Xe, and 1.0 Torr SF_6 or CF_4 buffer gas. $CHBr_3$ and $CDBr_3$ (Aldrich) were purified by repeated freeze−pump−thaw cycles to remove dissolved air. Other reagents (Matheson) were purified by vacuum distillation, primarily to remove traces of CO and NO from CF_4 and NO_2, respectively. The NO impurity levels in the NO_2 samples were estimated at ~0.1% by infrared diode laser absorption.

The HITRAN database[28] was used as an aid in the identification of spectral lines for CO, CO_2, N_2O, and NO. Other literature data were used to locate HNCO and HCNO line positions near 2270 and 2200 cm^{-1}, respectively.[29,30] For DCN, a 0.25 cm^{-1} resolution FTIR scan was used to identify with sufficient accuracy the line positions of the (00°0) → (00°1) band near 2600 cm^{-1}. Calibration of infrared absorption coefficients of DCN was performed by measuring the fractional absorption of the diode laser radiation as a function of DCN pressure, as reported earlier.[12]

Results

Typical time-resolved absorption signals are shown in Figure 1. To obtain these signals, transient signals were obtained with the diode laser tuned on resonance with a desired spectral line as well as detuned ~0.02 cm^{-1} off resonance. The off-resonance signals are due to thermal deflection of the infrared beam upon transient heating of the reagent gas by the photolysis laser. Because of the focused photolysis beam required, these artifacts are quite large in these experiments and are highly sensitive to beam alignment. By fine adjustment of the infrared beam alignment the long-time component of the off-resonant signal was adjustable to acceptable levels, although a large short-time component (~30 μs) remained. The absorption signals shown were obtained by subtraction of the off-resonant signal from the on-resonant signal.

Absorption signals were converted to absolute number densities using equations described in earlier publications.[12,26−27] We assume that the probed molecules are relaxed to a room-temperature Boltzmann distribution of rotational and vibrational states on the time scale of these experiments. Previous work has shown that this is the case for most molecules provided SF_6 buffer gas is included in the reaction mixture.[26,27] The one exception is CO, which is not vibrationally relaxed by SF_6. CF_4 buffer gas, which is more efficient at relaxing vibrationally excited CO, was therefore used whenever CO products were probed. Total pressures were low enough so that pressure broadening effects were negligible. Furthermore, we probed only low rotational levels near the maximum in the rotational Boltzmann distribution, so effects from transient heating of the reaction mixture are minimized.

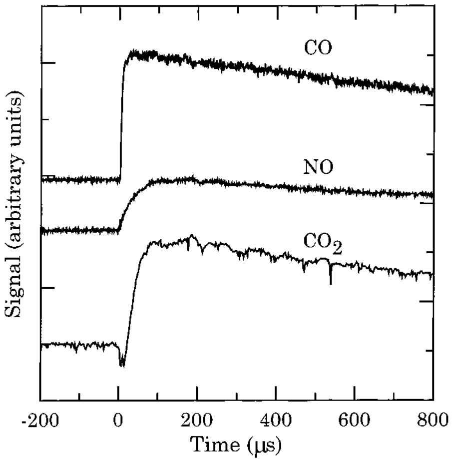

Figure 1. Transient absorption signals from the CH + NO_2 reaction. Lines probed: CO (0 → 1), P(5) at 2123.699 cm^{-1}, CO_2 (00°0 → 00°1), P(16) at 2335.920 cm^{-1}, NO (0 → 1), R(8.5) at 1906.141 cm^{-1}. Reaction conditions: $P_{CHBr_3} = 0.1$ Torr, $P_{NO_2} = 0.5$ Torr, $P_{Xe} = 1.0$ Torr, $P_{CF_4} = 1.0$ Torr (CO transient only), and $P_{SF_6} = 1.0$ Torr (NO and CO_2 transients).

Several control experiments were performed in order to verify the origin of the observed signals. Transient signals were collected upon photolysis of NO_2/Xe/SF_6 and NO_2/Xe/CF_4 mixtures, i.e., with the bromoform precursor omitted. No CO or CO_2 transients were observed, but a significant NO transient was observed under these conditions, presumably due to direct photolysis of NO_2. The number density of NO produced in this manner was subtracted from the number density of NO obtained with the full reaction mixture. The magnitude of this correction depends on the NO_2 pressure used but is about ~25% at 0.3 Torr NO_2.

The measured product yields of CO, CO_2, and NO from the CH + NO_2 reaction are shown as a function of reagent NO_2 pressure in Figure 2. As shown, only a very small yield of CO_2 was observed, but the large infrared absorption coefficient of CO_2 permitted a reasonably accurate measurement of [CO_2] nevertheless. In general, CO and CO_2 product yields were observed to increase slightly with increasing [NO_2] and level off at about 0.3 Torr of NO_2. This effect is probably caused by the competition of reaction 1 with other CH removal routes at low [NO_2]. These routes may include self-reaction, reaction with Br, Br_2, or $CHBr_3$, and diffusion out of the probed region. The observed NO yield is somewhat more dependent on [NO_2], probably due to some additional secondary chemistry resulting in NO formation, as is discussed below. The measured ratio of [CO]/[CO_2] did not depend significantly on [NO_2], indicating that CH removal by processes other than reaction 1 are sufficiently suppressed at these NO_2 pressures so as to not significantly affect the measured branching ratios.

In addition to CO, CO_2, and NO, attempts were made to detect the following molecules: N_2O, DCN (using $CDBr_3$ precursor

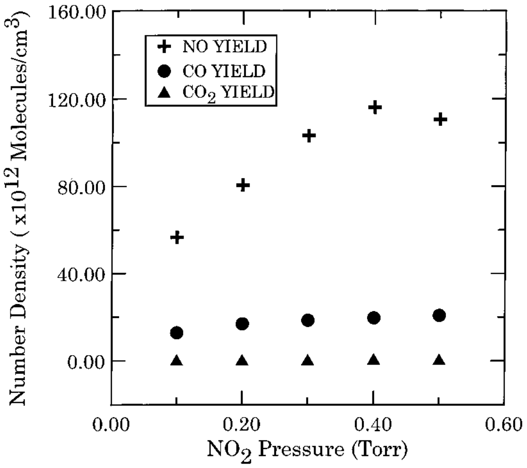

Figure 2. Product yields of the CH + NO_2 reaction as a function of NO_2 pressure. Reaction conditions: $P_{CHBr_3} = 0.1$ Torr, $P_{NO_2} = 0.1-0.5$ Torr, $P_{CF_4} = 1.0$ Torr (CO detection), and $P_{SF_6} = 1.0$ Torr (NO and CO_2 detection).

molecules), HNCO, and HCNO. No transient signals due to any of these species were observed. For N_2O and DCN, line strength data are available, and we estimate the following upper limits: $[CO]/[N_2O] > 120$; $[CO]/[DCN] > 7$. In the case of HCNO and HNCO, infrared line strengths are unknown, preventing an absolute calibration. It is apparent, however, that reaction channels (1g) and (1h) represent very minor or negligible contributions to the title reaction.

Discussion

Numerous secondary reactions are possible in this system, as almost any radical formed by the title reaction also reacts with NO_2:

$$H + NO_2 \rightarrow NO + OH \tag{2}$$

$$NH + NO_2 \rightarrow N_2O + OH \tag{3a}$$

$$\rightarrow NO + HNO \tag{3b}$$

$$HCO + NO_2 \rightarrow CO + OH + NO \tag{4a}$$

$$\rightarrow H + NO + CO_2 \tag{4b}$$

$$NCO + NO_2 \rightarrow N_2O + CO_2 \tag{5a}$$

$$\rightarrow 2\,NO + CO \tag{5b}$$

$$CN + NO_2 \rightarrow NCO + NO \tag{6}$$

At 298 K, the following rate constants (in $cm^3\ molecule^{-1}\ s^{-1}$) and branching ratios are applicable: $k_2 = 1.4 \times 10^{-10}$,[31] $k_3 = (3.8-5.8) \times 10^{-11}$,[32-34] with $\phi_{3a} = 0.41$ and $\phi_{3b} = 0.59$,[35] $k_4 = (5.1-5.7) \times 10^{-11}$,[36,37] with $\phi_{4a} = 0.63$ and $\phi_{4b} = 0.37$,[38] $k_5 = (1.8-2.8) \times 10^{-11}$,[39,40] with $\phi_{5a} = 0.92$ and $\phi_{5b} = 0.08$,[39] and $k_6 = (7.4-9.3) \times 10^{-11}$.[41,42]

On the basis of the above data, any H, NH, HCO, or NCO radicals produced in the title reaction are expected to quickly react with NO_2 in the limit of high $[NO_2]$, although, at very low NO_2 concentrations, other removal routes for these radicals may compete with reactions 2−6. Two radicals which do not react quickly with NO_2 are OH and HNO. The OH + NO_2 reaction is termolecular and is therefore expected to be slow at the pressures used in this study.[31,43] No direct measurements of the HNO + NO_2 rate constant have been reported, but a recent estimate of a very small value of 3.5×10^{-14} $cm^3\ molecule^{-1}\ s^{-1}$ at 298 K has been suggested.[31]

TABLE 1: Branching Ratios of the CH + NO_2 Reaction

product channel	branching ratio
NH + CO_2	<0.02[a]
HNO + CO and H + NO + CO	0.92 ± 0.04
HCO + NO	0.08 ± 0.04
HCN + O_2	<0.15[b]
NCO + OH	<0.01[a]
CN + HO_2	<0.01[a]

[a] Based on upper limit of N_2O yield from expected secondary chemistry. See text for details. [b] Based on upper limit of DCN yield from CD + NO_2 reaction.

Upon consideration of the above secondary reactions, the lack of N_2O production in these experiments is extremely significant, providing strong evidence that channels (1a), (1f), and (1i) do not represent significant contributions to the title reaction, as any NH or NCO radicals produced would be expected to produce large amounts of N_2O via reactions 3 and 5. Similarly, any CN produced in channel (1i) would react via (6) to form NCO, which would then react further, producing N_2O. As a result, we can state that little or no CO_2 is formed by reactions 1a or 5a and that the only significant source of CO_2 in this system is reaction 4b. Using our estimate of $\phi_{4b} = 0.37 \pm 0.05$,[38] and assuming that all the HCO molecules produced in channel (1c) react with NO_2 via reaction 4, we can write:

$$[CO_2] = 0.37[1c] \tag{7}$$

where [1c] represent the concentration of HCO produced in reaction 1c. Several sources of CO are present: the primary channels (1b) and (1e) and the secondary reaction 4a:

$$[CO] = [1b] + [1e] + 0.63[1c] \tag{8}$$

Sources of NO include primary channels (1c) and (1e), secondary reaction 4, and the secondary reaction 2 due to H atoms produced in channels (1e) and (4b). Summing these together gives

$$[NO] = [1c] + [1e] + [1c] + 0.37[1c] + [1e] = 2.37[1c] + 2[1e] \tag{9}$$

Equation 7 and the experimentally measured CO_2 yields were used to calculate [1c], the product yield of channel (1c). Equation 8, along with the measured CO yield, was then used to calculate [1b] + [1e]. Since (1b), (1c), and (1e) are the only observed product channels, we can then immediately determine branching ratios $\phi_{1c} = [1c]/([1c] + [1b] + [1e])$ and $\phi_{1b+1e} = [1b] + [1e]/([1c] + [1b] + [1e])$. These results are shown in Table 1, along with upper limits on other product channels.

Note that the above branching ratio determination was made without use of the measured product yields for NO. The experimental NO yields, however, were found to be inconsistent with the prediction of eq 9. Even if we assumed [1b] = 0 and that therefore [1e] = [1e] + [1b], values of [NO] calculated from eq 9 are only approximately half of the observed NO yield. If one assumes that [1b] > 0, the discrepancy becomes even larger. We therefore believe that there are additional secondary reactions that form NO in this system. Some possibilities include reactions of photolysis byproducts with NO_2:

$$Br + NO_2 + M \rightarrow BrNO_2 + M \rightarrow BrO + NO + M \tag{10}$$

$$CHBr + NO_2 \rightarrow CHOBr + NO \tag{11}$$

The bimolecular rate constant of reaction 10 is pressure dependent[43] and is probably quite slow at the experimental pressures used. Nevertheless, if this is the only removal route for bromine atoms in this system, it may represent a significant source of NO, especially considering the fact that up to three Br atoms are formed per CH radical in the photolysis of $CHBr_3$. No literature data are available on the rate of reaction 11, and we do not know how much CHBr is formed in the photolysis of $CHBr_3$, although $[CHBr]_0$ is probably less than $[CH]_0$. It is therefore unfortunately not feasible to quantify all the sources of nitric oxide products in this experiment. As a result, we are unable to distinguish between product channels (1b) and (1e) in the title reaction, because both produce one CO molecule for every CH radical consumed.

No ab initio calculations have been reported for the CH + NO_2 reaction, but we can make qualitative suggestions about possible reaction mechanisms on the basis of our results. In principle, CH can bind to NO_2 via either the nitrogen atom or an oxygen atom, forming an $HCNO_2$ or HCONO complex, respectively. The HCONO complex can dissociate to HCO + NO products or it can rearrange to a four-center transition state via hydrogen atom migration to the nitrogen atom. This structure can then dissociate to HNO + CO by breaking C−H and N−O bonds. Either of these product channels contains enough energy to further dissociate to H + CO + NO. Formation of NCO + OH or HCN + O_2, however, would require unlikely three-center cyclic intermediates or transition states. Our failure to observe these product channels suggests that these routes are not significant in the CH + NO_2 reaction. What is somewhat surprising is that dissociation of the $HCNO_2$ complex to form O + HCNO is not observed. One possible explanation is that this $HCNO_2$ complex might rearrange to the HCONO complex via CH migration from the nitrogen to a terminal oxygen atom. Transition states in which the CH group bridges the N−O bond have been shown to be important in the CH + NO reaction[11] and are likely to be present in the CH + NO_2 system as well. Clearly, detailed ab initio calculations are needed to better characterize these reaction pathways.

Conclusions

The CH + NO_2 reaction was studied at room temperature by infrared diode laser spectroscopic detection of products. CO, NO, and CO_2 product yields were measured. After consideration of likely secondary reactions, the CO and CO_2 yields were found to be consistent with the formation of H + CO + NO or HNO + CO as the major product channel. A minor channel into HCO + NO is also present. The observed NO yield in these experiments was higher than can be accounted for by the title reaction, suggesting the existence of additional secondary chemistry for NO formation.

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