

Temperature Dependence of the Product Branching Ratio of the CN + O₂ Reaction

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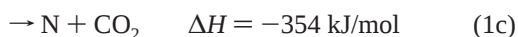
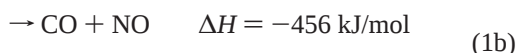
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The reaction of CN radicals with O₂ was studied using infrared diode laser absorption spectroscopy. CO and CO₂ products were detected directly, while the yield of NCO products was inferred by measuring the N₂O yield upon addition of excess NO. Experiments and kinetic modeling calculations were performed to examine the extent of secondary chemistry in this system. The following branching ratios of the CN + O₂ reaction at 296 K were determined: $\phi(\text{N}+\text{CO}_2) = 0.02 \pm 0.01$ and $\phi(\text{CO}+\text{NO}) = 0.22 \pm 0.02$. The branching ratio into the CO + NO channel has a strong negative temperature dependence over the range 239–643 K.

Introduction

The chemical kinetics of the CN radical are of substantial importance because of the role this species plays in combustion chemistry. For example, CN radicals are intermediates in the oxidation of HCN by OH radicals, which is an important part of NO_x formation mechanisms in both fuel-rich hydrocarbon flames (the prompt-NO mechanism) and flames containing fuel nitrogen.¹ The CN + O₂ reaction has been widely studied previously by both experimental^{2–17} and computational^{18–20} methods. Part of the interest is due to the fact that this is one of the simplest radical–radical reactions known, proceeding over an attractive potential energy surface without a barrier in the entrance channel.^{17,21–22} The total rate constant has been measured by numerous groups,^{5–16} which together span the temperature range 13–3800 K, wider than any other reaction. Recent reviews of this kinetic data may be found in refs 17 and 23. The Baulch review recommends $k = (1.20 \times 10^{-11}) \exp(-210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–4500 K.²³ Agreement between different groups is good although not perfect.

In contrast to the wealth of total rate constant data, much less information is available regarding product branching ratios of this reaction. This is an important question, leading to significant uncertainties in modeling. For example, the temperature dependence of the branching ratio is a crucial parameter in recent attempts to evaluate empirical rate laws of the low-temperature kinetics of this reaction.²² Three exothermic product channels are possible:

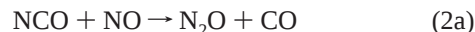


where the thermochemical data from ref 17 was used. Channel 1a has generally been considered the most important product channel even though it is least exothermic because only an O–O bond breaking of an initially formed NCOO collision complex is required.

Several reports of the existence of channel 1b as a minor pathway have appeared. In an early report, Schmatjko and Wolfrum used CO laser absorption spectroscopy to estimate that

channel 1b contributes ~6% of the total reaction at 298 K.³ More recently, in our laboratory, we used infrared diode laser absorption to estimate $\phi_{1b} = 0.23 \pm 0.10$ at 298 K, with a very significant temperature dependence.²⁴ Mohammad et al. used infrared emission spectroscopy and reported $\phi_{1b} = 0.29 \pm 0.02$,²⁵ in reasonable agreement with our results. The most obvious route to channel 1b involves a four-centered transition state. MP2 calculations of Mohammad et al. indicated that such a transition state is energetically unfavorable, and they proposed a dynamic mechanism for CO + NO formation in which NCO + O are initially formed with a high degree of NCO rotational excitation followed by N-atom abstraction as the complex dissociates.²⁵ No report of any contribution by channel 1c has previously appeared.

Our earlier work²⁴ on this reaction suffered from large uncertainties. That study was primarily concerned with a measurement of the branching ratio of NCO + NO:



where NCO was formed in reaction 1a by photolyzing a CN-radical precursor in the presence of O₂. The existence of channel 1b was inferred by the observation of a modest excess of CO yields over N₂O yields in this system. Determination of ϕ_{1b} in this way required subtracting two comparable product yields, leading to large error bars. The observation of a large temperature dependence in ϕ_{1b} was therefore tentative. In addition, all previous experimental reports of ϕ_{1b} , both in our laboratory and in others, have suffered from the possibility that some of the observed CO may have been formed by secondary chemistry, of which the most serious is the NCO + O reaction:



The experiments reported here are similar but not identical to our previous approach. First, we obtain ϕ_{1b} without the subtraction of two comparable numbers inherent in our previous determination and therefore obtain substantially improved precision. Second, we investigate in greater detail the possible role of secondary chemistry and, in particular, demonstrate that our results are not affected by reaction 3. These improvements

permit a more precise determination of the temperature dependence of the branching ratio.

Experimental Section

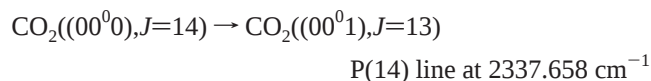
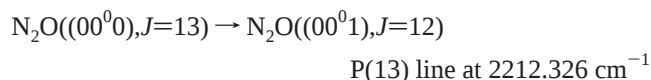
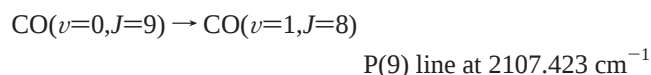
The experimental procedure is similar to that described in previous publications.^{24,26} A schematic of the experimental apparatus is shown in Figure 1. Photolysis light of 248 or 193 nm was provided by an excimer laser (Lambda Physik, Compex 200). Several lead salt diode lasers (Laser Photonics) operating in the 80–110 K temperature range were used to provide tunable infrared probe laser light. The IR beam was collimated by a lens and combined with the UV light by means of a dichroic mirror, and both beams were copropagated through an absorption cell. After the UV light was removed by a second dichroic mirror, the infrared beam was then passed into a 1/4 m monochromator and focused onto a 1 mm InSb detector (Cincinnati Electronics, $\sim 1 \mu\text{s}$ response time). Transient infrared absorption signals were recorded on a LeCroy 9310A digital oscilloscope and transferred to a computer for analysis.

A 1.46 m static absorption cell was used for experiments at room temperature and above. Resistive heating was used to achieve elevated temperatures. For measurements at $T < 296$ K, a 1.21 m jacketed cell was used. Cooling was achieved by pumping chilled solvent through the outer jacket. For CO_2 product measurements, the infrared laser beam path was purged with N_2 to remove atmospheric CO_2 .

Two different CN precursors were used in these experiments. For room temperature and elevated temperatures, ICN dissociation at 248 nm was used. ICN did not have sufficient vapor pressure for reliable measurements at temperatures below ambient, however. C_2N_2 photolysis at 193 nm was therefore used for experiments at these temperatures. Typical photolysis laser pulse energies were $\sim 5\text{--}15$ mJ/pulse, producing CN number densities of $\sim 10^{13} \text{ cm}^{-3}$.

SF_6 and CF_4 (Matheson) were purified by repeated freeze–pump–thaw cycles at 77 K. NO (Matheson) were purified by repeated freeze–pump–thaw cycles at 163 K to remove NO_2 and N_2O . ICN (Aldrich) was purified by vacuum sublimation to remove dissolved air. C_2N_2 was synthesized by the reaction of copper sulfate with aqueous sodium cyanide²⁷ and purified by freeze–pump–thaw cycles at 77 K. Traces of CO_2 were removed from O_2 (Matheson, Research Grade) and SF_6 by the use of an ascarite trap.

CO , N_2O , and CO_2 product molecules were probed by observing the following absorption lines:



In some of the experiments at elevated temperatures, higher rovibrational transition lines P(10) at 2103.270 cm^{-1} and P(24) at 2201.749 cm^{-1} were probed for CO and N_2O product molecules, respectively. The HITRAN molecular database was used to locate and identify the spectral lines of product molecules.²⁸

Typical experimental conditions were P_{ICN} or $P_{\text{C}_2\text{N}_2} = 0.05$ Torr, $P_{\text{O}_2} = 2.0$ Torr, P_{SF_6} or $P_{\text{CF}_4} = 1.5$ Torr, and $P_{\text{NO}} = 0\text{--}0.4$

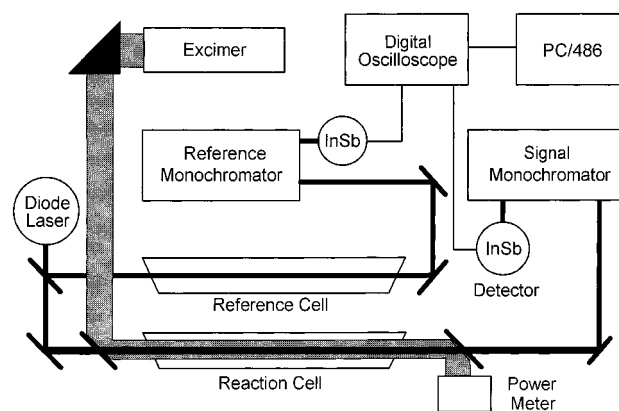


Figure 1. Schematic of the experimental apparatus.

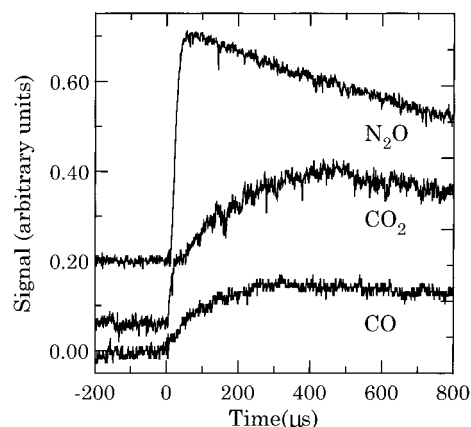


Figure 2. Transient infrared absorption signals for N_2O , CO , and CO_2 product molecules. Each transient was obtained from a single photolysis laser shot. Reaction conditions: $P_{\text{ICN}} = 0.05$ Torr (CO and N_2O signals only), $P_{\text{ICN}} = 0.08$ Torr (CO_2 signal only), $P_{\text{O}_2} = 2.0$ Torr, $P_{\text{SF}_6} = 1.5$ Torr (N_2O and CO_2 signals only), $P_{\text{CF}_4} = 1.5$ Torr (CO signal only), $P_{\text{NO}} = 0.2$ Torr (N_2O signal only).

Torr. To prevent signal degradation due to buildup of product molecules, the reaction cell was evacuated and refilled after only a few (two to five) excimer laser shots.

Results

Time-resolved transient absorption signals of product molecules at 296 K are shown in Figure 2. The lower and middle traces show the CO and CO_2 transient signals produced by the photolysis of ICN in the presence of O_2 and buffer gas. The upper trace shows an N_2O transient signal obtained when NO reagent is included in the reaction mixture. Given the fast rate constant of the title reaction, one expects the reaction to occur on a time scale of a few microseconds under the experimental condition of 2.0 Torr of O_2 . The slower rise time observed in the transient absorption signals is due to the fact that products are produced in excited vibrational and rotational states and that vibrational relaxation to the probed ground state is significantly slower than the reaction rate. Previous experiments in our laboratory²⁹ as well as measurements of vibrational relaxation rates^{30–33} have demonstrated that SF_6 is an effective buffer gas for the relaxation of CO_2 and N_2O vibrational excitation. For CO , CF_4 is a more efficient relaxer of vibrational excitation and was therefore used as the buffer gas whenever CO was probed. Under the experimental conditions used (1–2 Torr buffer gas), relaxation of the nascent vibrational distribution to a Boltzmann distribution occurs on a time scale of $\sim 20\text{--}40 \mu\text{s}$ for CO_2 and N_2O , and $\sim 200 \mu\text{s}$ for CO . In all cases this

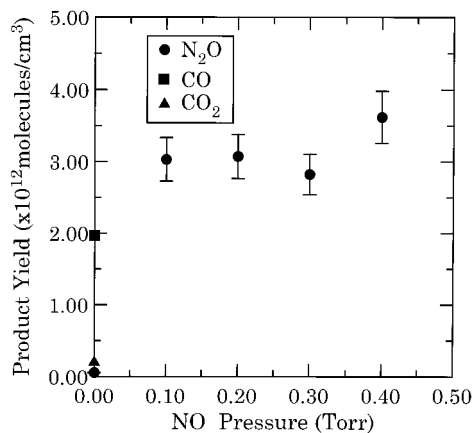


Figure 3. Product yields of CO, CO₂, and N₂O. N₂O yields are shown as a function of NO pressure. ICN, SF₆, CF₄, and O₂ pressures are identical to those in Figure 2.

relaxation was fast compared to the ~ 1 ms time scale for diffusion of product molecules out of the probed beam volume, which appears in Figure 2 as a slow decay.

A. Branching Ratio Determination. Absorption signals were converted to number densities using tabulated line strengths²⁸ and equations described previously.²⁴ Calibration experiments in our laboratory have demonstrated that these line strengths are accurate to better than 10% (and probably better than 5%) for the molecules probed in these experiments. For CO and N₂O, peak amplitudes were used to calculate number densities. The CO₂ transient signals displayed both a fast and a slow rise component, with rise times of ~ 30 and ~ 300 μ s, respectively. For reasons described below in section B, only the fast rise components were used to calculate branching ratios. Figure 3 shows the resulting product yields. As shown, the N₂O yield in the absence of added NO is essentially zero, as expected. When NO is included in the reaction mixture, N₂O formation is expected via reaction 2a, which has a branching ratio of $\phi_{2a} = 0.44 \pm 0.07$ over the temperature range 296–623 K.²⁴ In the limit of high NO pressure, every NCO radical formed in channel 1a reacts with NO. As shown in Figure 3, this occurs at ~ 0.1 Torr, beyond which the N₂O yield is essentially constant. Note that an excess of 2.0 Torr of O₂ was used and that CN reacts only very slowly with NO at low total pressures, with a rate constant of 4.3×10^{-13} cm³ molecule⁻¹ s⁻¹ at 296 K and 5 Torr.³⁴ Since k_1 is ~ 50 times greater than this and [O₂] > [NO], essentially all of the photolytically created CN radicals are removed by reaction 1.

The branching ratio can be obtained from our data in two different ways. The first method is the less accurate approach and was only applied in $T = 296$ K experiments. In this approach, we calculate the initial radical yield [CN]₀ from the measured photolysis laser pulse energy and the 248 nm absorption coefficient of ICN ($\alpha = 0.009$ cm⁻¹ Torr⁻¹).²⁴ A dissociation quantum yield of unity is assumed. If secondary chemistry is insignificant, then ϕ_{1b} is simply [CO]/[CN]₀. Using this method, we obtain $\phi_{1b} = 0.22 \pm 0.02$ at 296 K, where the uncertainty represents two standard deviations.

The second approach, which we believe is potentially more accurate, is to measure the product yields of all active channels. Unfortunately, quantification of channel 1a by direct NCO detection is difficult, even though infrared transition wavelengths near 1900 cm⁻¹ are known,³⁵ because these transitions are quite weak and precise absorption coefficients are unknown. The addition of excess NO to the reaction mixture, however, efficiently converts any NCO into N₂O via reaction 2, as

TABLE 1: Product Branching Ratios of the CN + O₂ Reaction at 296 K

product channel	branching ratio
NCO + O	$\phi_{1a} = 0.76 \pm 0.02$
CO + NO	$\phi_{1b} = 0.22 \pm 0.02$
CO ₂ + N	$\phi_{1c} = 0.02 \pm 0.01$

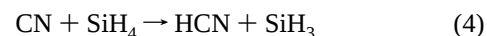
described above. Since ϕ_{2a} is accurately known, the NCO concentration is then readily calculated as [NCO] = [N₂O]/ ϕ_{2a} . The branching ratio ϕ_{1b} is then [CO]/([CO] + [CO₂] + [NCO]), where CO and CO₂ yields are measured without the addition of NO, as shown in Figure 3. Similarly, $\phi_{1c} = [\text{CO}_2]/([\text{CO}] + [\text{CO}_2] + [\text{NCO}])$ and $\phi_{1a} = 1.0 - \phi_{1b} - \phi_{1c}$. Table 1 shows the resulting branching ratios obtained at 296 K in this way upon averaging of four separate experimental runs. The uncertainties quoted represent two standard deviations. Note that both methods produce the same result for ϕ_{1b} , indicating that our estimate of [CN]₀ was reliable.

By use of the second method, the branching ratio between channels 1a and 1b was investigated as a function of temperature. Channel 1c, which was only a very minor contribution at 296 K, was ignored during these variable temperature measurements. Figure 4 shows the resulting branching ratio into channel 1b vs T over the range 239–643 K.

B. Secondary Chemistry. The branching ratio measurements described above depend on the assumption that most or all of the observed CO is formed by reaction 1b and that contributions to the CO yield by secondary reactions are small. The most serious potential secondary reaction is that between the products of channel 1a:



In addition, reaction 2 may occur to some extent even in the absence of added NO reagent, since NO is formed in channels 1b and 3a. To examine these possibilities, we performed experiments in which an additional reagent was included to remove any NCO formed in channel 1a, effectively quenching reactions 2 and 3. Among possible NCO quenching reagents, saturated hydrocarbons are not ideal because NCO + alkane reactions are generally rather slow except at elevated temperatures.^{36,37} As a result, we chose silane (SiH₄) as a quencher. SiH₄ reacts quickly with both NCO and CN without forming CO:



Measurements in our laboratory indicate that $k_4 = 2.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and $k_5 = 7.0 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 296 K.³⁸ Reaction 5 effectively competes with reaction 3 when even a small amount of SiH₄ is present. For example, if [SiH₄] = 0.1 Torr $\approx 3 \times 10^{15}$ molecules cm⁻³, most NCO radicals formed will react via reaction 5 rather than reaction 3, since [O] $\approx 10^{13}$ molecules cm⁻³ under typical experimental conditions. As a result, any CO formed via reactions 2 or 3 is expected to be almost completely suppressed by the addition of small amounts of SiH₄. CO formed by the title reaction 1b will also be suppressed by the competition for CN radicals (reactions 1b vs reaction 4); however, this requires higher SiH₄ concentrations, since [O₂] $\approx 10^{16}$ molecules cm⁻³.

The squares of Figure 5 show the experimentally measured CO yield as a function of added silane reagent. As shown, the

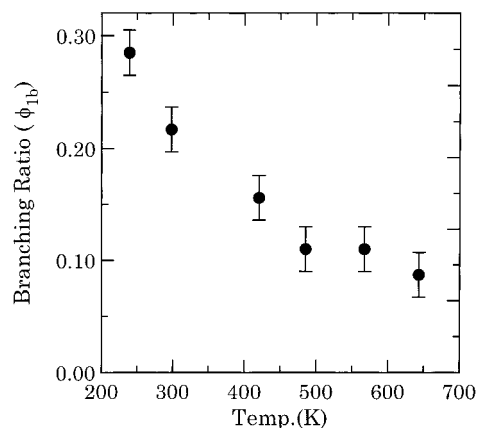


Figure 4. Temperature dependence of the branching ratio into channel 1b, CO + NO.

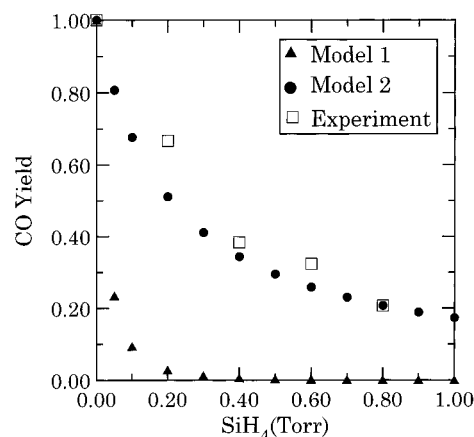


Figure 5. Experimental and modeled dependence of CO yield on added SiH_4 reagent. Experimental results are represented by open squares. Model 1 (triangles) assumes that all CO originated from secondary chemistry. Model 2 (circles) assumes that all CO originated from channel 1b. See text for details. $P_{\text{ICN}} = 0.05$ Torr. $P_{\text{O}_2} = 2.0$ Torr. $P_{\text{CF}_4} = 1.0$ Torr.

TABLE 2: Reactions Used in Kinetic Quenching Modeling Simulations of CO and CO_2 Yields

reaction	$k(298\text{K})$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	ref
$\text{CN} + \text{O}_2 \rightarrow \text{products}$	2.3×10^{-11}	23 ^a
$\text{NCO} + \text{O} \rightarrow \text{CO} + \text{NO}$	7.0×10^{-11}	43
$\text{NCO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO}$	1.50×10^{-11}	24
$\text{NCO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$	1.90×10^{-11}	24
$\text{CN} + \text{SiH}_4 \rightarrow \text{HCN} + \text{SiH}_3$	2.2×10^{-10}	38
$\text{NCO} + \text{SiH}_4 \rightarrow \text{HCN} + \text{SiH}_3$	7.0×10^{-12}	38

^a This work used for the branching ratio

product yield declines to nearly zero only as the SiH_4 pressure exceeds 1.0 Torr. Comparison of these data to the argument above suggests that little of the observed CO could have been formed from any secondary reaction involving NCO because such CO should have been suppressed by a silane pressure as low as 0.1 Torr.

To quantitatively test these arguments, kinetic modeling simulations were performed on this system. Table 2 shows the reactions included in the kinetic model. The ACUCHEM kinetic modeling program³⁹ was used to predict the CO yield under two contrasting assumptions: that all CO was formed by the title reaction 1b and that all CO was formed by secondary reactions 2a and 3a. These modeling predictions are shown in Figure 5 as circles and triangles, respectively. As expected, any CO produced by the secondary reactions is predicted by the

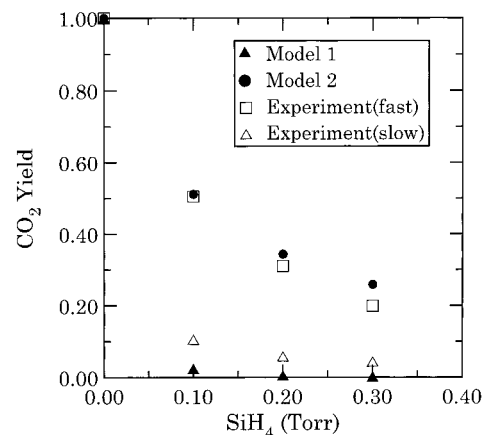


Figure 6. Experimental and modeled dependence of CO_2 yield on added SiH_4 reagent. See text for details. $P_{\text{ICN}} = 0.08$ Torr. $P_{\text{O}_2} = 2.0$ Torr. $P_{\text{SF}_6} = 1.5$ Torr.

model to be suppressed by 0.1–0.2 Torr SiH_4 , in sharp contrast to the experimental data. As shown, a satisfactory agreement between the model and the experimental data is obtained only on the assumption that essentially all of the observed CO did indeed originate from reaction 1b.

Similar modeling calculations were performed for the CO_2 products. A slight complication is that the CO_2 transient signals displayed both a fast and a slow rise, as shown in Figure 2. The fast rise time scale of $\sim 30 \mu\text{s}$ is comparable to that apparent in previous measurements of CO_2 reaction products in our laboratory^{24,29} and is attributed to rapid vibrational relaxation of nascent CO_2 produced by channel 1c to the probed ground vibrational state. The slow rise occurs on a longer time scale than can be attributed to vibrational relaxation, and this rise time was unaffected by the SF_6 buffer gas pressure. We attribute this slow component of the signal to formation of CO_2 by secondary chemistry such as reaction 2b and possibly reaction 3b. The silane quenching experiments shown in Figure 6 support this hypothesis. The fast rise component of the CO_2 signal (open squares) decays only gradually with increasing $[\text{SiH}_4]$, as predicted by the modeling calculations (filled circles) for CO_2 originating from channel 1c. The slow rise components, however (open triangles), are greatly affected by the addition of small quantities of SiH_4 , in fair but not perfect agreement with modeling predictions for CO_2 originating from channel 2b (filled triangles). Part of the disagreement between the experiment and the model for the slow rise component may be due to the difficulty in distinguishing the slow and fast components on small, noisy signals. On the basis of these observations, we used only the fast rise components of the CO_2 signals in determining the branching ratio ϕ_{1c} listed in Table 1. We note that these CO_2 signals are significantly affected by secondary chemistry only because ϕ_{1c} is so small.

Discussion

Our value of $\phi_{1b} = 0.22 \pm 0.02$ at 296 K is in excellent agreement with our previous measurement,²⁴ which was obtained in a somewhat less direct manner by measuring the excess of CO over N_2O yields in the $\text{NCO} + \text{NO}$ reaction, where NCO was formed by the $\text{CN} + \text{O}_2$ reaction. Our result is in fair although not perfect agreement with the value of $\phi_{1b} = 0.29 \pm 0.02$ obtained by Mohammed et al. using infrared emission.²⁵ In general, we believe that absorption spectroscopy has fewer uncertainties in the determination of absolute concentrations than emission spectroscopy. For example, our experiment is not

sensitive to the nascent vibrational distribution of product molecules because our use of polyatomic buffer gases relaxes the detected products to an ambient Boltzmann distribution. In any case, both techniques are in qualitative agreement that channel 1b represents a significant but not dominant pathway of the CN + O₂ reaction at room temperature.

The temperature dependence of ϕ_{1b} is an important result of this experiment. Comparison with our earlier work²⁴ shows that the decrease in ϕ_{1b} as T increases is slightly less pronounced than previously thought (Figure 4 of this work shows $\phi_{1b} = 0.07$ at $T = 640$ K, while Figure 7 of ref 24 shows $\phi_{1b} \approx 0.02$ at a similar temperature). Our uncertainties of ± 0.02 , however, are much improved compared to ref 24, which reported ± 0.10 error bars. Furthermore, our newer data show that at temperatures below 296 K, ϕ_{1b} increases quite dramatically. Although extremely low temperatures are not attainable in our experiments, it appears quite likely that channel 1b is in fact the dominant channel as $T \rightarrow 0$. In any case, it is remarkable that the branching ratio changes so much over a modest temperature range. This is in contrast to many other radical-radical reactions in combustion chemistry, such as NCO + NO^{24,40} and NH₂ + NO,^{41,42} in which significant changes in branching ratio are observable only when comparing experiments performed over a much wider temperature range.

In principle, ab initio and RRKM calculations should be able to predict the temperature dependence of the branching ratio. Unfortunately, all the high-level calculations to date have essentially ignored channel 1b and instead concentrated on either the entrance channel to the NCOO collision complex or the transition state leading to NCO + O products.^{18–20} In addition, Phillips has suggested that this system may be too small for a statistical treatment of the NCOO complex decay kinetics.²⁰ Prediction of our results thus represents a substantial challenge for ab initio calculations. Our observation of a dramatic temperature dependence in ϕ_{1b} suggests that the transition states leading to product formation have energies fairly close to that of the initial CN + O₂ reactants. Thus, it is somewhat surprising that a recent G2 calculation indicates that the transition state to NCO + O lies 71.5 kJ/mol below the reactants.¹⁸ It is clear that more computational work on this system, especially in regard to transition states leading to CO + NO, are needed.

Conclusion

Infrared absorption spectroscopy was used to determine the product branching ratios of the CN + O₂ reaction. CO₂ + N is a very minor channel, as expected. CO + NO is a significant channel with a surprisingly large temperature dependence, becoming more important at lower temperatures.

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