# **Product Channel Dynamics of the NCO + NO Reaction**

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The NCO + NO reaction was studied by time-resolved infrared diode laser spectroscopy. The CO<sub>2</sub> + N<sub>2</sub> channel was found to account for 56 ± 7% of the total reaction rate, with N<sub>2</sub>O + CO accounting for the remaining  $44 \pm 7\%$ . These branching ratios were found to be independent of temperature in the range 296-623 K. Furthermore, the CN + O<sub>2</sub> reaction at room temperature produces CO + NO products with a yield of 23 ± 10% in addition to the NCO + O channel, with a significant negative temperature dependence. Product energy disposal studies were also performed. CO vibration and the  $\nu_3$  mode of CO<sub>2</sub> were found to account for only 0.55% and 3.4% of the available energy, respectively. These results are discussed in terms of statistical models and simple ab initio computations.

# Introduction

The combustion chemistry of nitrogen-containing compounds is a topic of great importance.<sup>1</sup> Much of this interest is due to the role of nitrogen oxide pollutants in combustion exhaust. One of many exhaust gas treatment approaches to  $NO_x$  removal is the RAPRENO<sub>x</sub> process, which involves the addition of cyanuric acid, (HOCN)<sub>3</sub>, to the exhaust gases.<sup>2</sup> The detailed mechanism of this process has been studied using kinetic modeling techniques.<sup>3</sup> Current understanding is that cyanuric acid thermally decomposes into HNCO, followed by reaction with H and OH radicals to produce the NCO radical. One of the primary steps responsible for NO<sub>x</sub> removal is then:<sup>3</sup>

$$NCO + NO \rightarrow N_2O + CO \Delta H^{\circ}_{300} = -278 \text{ kJ/mol}$$
 (1a)

$$\rightarrow CO_2 + N_2 \qquad \Delta H^{\circ}_{300} = -643 \text{ kJ/mol} \qquad (1b)$$

$$\rightarrow$$
 CO + O + N<sub>2</sub>  $\Delta H^{\circ}_{300} = -111 \text{ kJ/mol}$  (1c)

The laser-induced fluorescence spectroscopy of the NCO radical has recently been characterized.<sup>4-6</sup> This has resulted in several kinetic<sup>7-9</sup> and quantum state-resolved studies<sup>10,11</sup> of NCO reactions. In particular, several groups have measured the total rate constant of the NCO + NO reaction.<sup>7-9</sup> Agreement is good, with  $k_1 = (3.2-3.4) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. A negative temperature dependence has been observed, suggesting that an NCONO collision complex is initially formed, followed by possible rearrangement and subsequent decomposition.

The branching ratio of reaction 1 has been less thoroughly studied. The above three product channels were proposed by Perry.<sup>7</sup> Previous kinetic modeling studies have used channel 1a as the only product channel in this reaction. In general, branching ratio determinations require the measurement of absolute concentrations of product species. Many time-resolved techniques can accomplish this only after an instrument-dependent calibration. Traditional chemical analysis of final products is useful, but interpretation is often complicated by secondary reactions and heterogeneous chemistry.

We have recently initiated a series of measurements to determine product branching ratios in chemical reactions of interest in combustion and atmospheric chemistry.<sup>12-14</sup> In a previous paper, we reported the first direct measurement of the branching ratio of the NCO + NO reaction.<sup>13</sup> Time-resolved infrared spectroscopy was used to provide absolute product



Figure 1. Diagram of the experimental apparatus.

concentrations. In that paper, we reported preliminary results of  $k_{1a}/k_1 = 0.33$ ,  $k_{1b}/k_1 = 0.44$ , and  $k_{1c}/k_1 = 0.23$  at room temperature. Several aspects of this reaction are investigated in this paper. We reinvestigate the branching ratio at room temperature, with a more detailed analysis of competing secondary reactions. The conclusion that both channels 1a and 1b represent major contributions remains unaltered, but a moderate adjustment of the quantitative branching ratios results. In addition, we extend the measurements to a temperature range of 296–623 K. Finally, we report results of energy disposal studies for this reaction and compare these results to a simple statistical model.

### **Experimental Section**

The experimental apparatus has been described previously.<sup>13,14</sup> Only a brief description will be given here. A diagram of the apparatus is shown in Figure 1. A frequency-quadrupled Nd: YAG laser (Lumonics JK750) was used as the photolysis source. In most of the experiments NCO radicals were generated by dissociation of ICN followed by reaction with O<sub>2</sub>:

$$ICN + h\nu (266 \text{ nm}) \rightarrow I + CN$$
 (2)

$$CN + O_2 \rightarrow NCO + O$$
 (3a)

The CN + O<sub>2</sub> reaction is fast, with  $k_3 = (1.8-3.0) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K.<sup>15-17</sup> In some of the experiments, bromine isocyanate was used as an alternate precursor, producing NCO directly:

$$BrNCO + h\nu (266 nm) \rightarrow Br + NCO$$
 (4)

Light from an infrared diode laser was copropagated with the

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**Figure 2.** Transient absorption signals for CO<sub>2</sub>(00<sup>0</sup>0) R(6) line. Reaction conditions for trace A:  $P_{\rm ICN} = 0.05$  Torr,  $P_{\rm O_2} = 0.30$  Torr,  $P_{\rm NO} = 0.30$  Torr,  $P_{\rm SF_0} = 1.50$  Torr, YAG laser energy = 9 mJ. Trace B: same conditions as trace A except  $P_{\rm O_2} = 0.0$  Torr. Trace C: same conditions as trace A except  $P_{\rm NO} = 0.0$  Torr.

photolysis light through the reaction cell. Transient infrared absorption signals were detected using an InSb detector (Cinncinatti Electronics), averaged on a digital oscilloscope (Hitachi 6065), and stored on a personal computer. Only 2–8 laser shots (1-Hz repetition rate) were needed for each transient, so depletion of reactants and buildup of reaction products during the experiment were negligible. The reaction cell was evacuated and refilled before each transient signal. Gases were then allowed to stand for 5 min before signal collection in order to ensure complete mixing.

Room temperature experiments were performed using a 145cm single-pass Pyrex absorption cell with  $CaF_2$  windows. Experiments at elevated temperatures used a 86-cm heated Pyrex cell. Experiments that probed vibrationally excited states of CO or CO<sub>2</sub> made use of a high-voltage dc discharge in the reference cell in order to locate excited-state spectral lines. The HITRAN and AFGL databases were used for diode laser wavelength calibration.<sup>18,19</sup>

Bromine isocyanate was synthesized as described in the literature<sup>20</sup> by passing  $Br_2$  through a column of AgNCO at 420 K. The AgNCO had been preheated for 24 h under vacuum at 420 K. Products were collected at 77 K and vacuum distilled at 210 K. The sample was stored in a Pyrex bulb at 77 K. BrNCO was introduced into the reaction cell by briefly warming the storage bulb until a sufficient vapor pressure of sample had entered the cell.

NO, SF<sub>6</sub>, CF<sub>4</sub>, and CO<sub>2</sub> (Matheson) were purified by repeated freeze-pump-thaw cycles and stored in Pyrex bulbs. NO was purified by repeated vacuum distillation at 113 K to remove trace amounts of  $N_2O$  impurity. ICN (Fluka) was purified by vacuum sublimation to remove dissolved air.

## Results

A. Branching Ratio Experiments. Transient absorption signals for CO<sub>2</sub>, CO, and N<sub>2</sub>O in the ground vibrational state were detected when a mixture of ICN, O<sub>2</sub>, NO, and SF<sub>6</sub> buffer gas was photolyzed at 266 nm. A typical signal is shown in Figure 2. We attribute these signals to rapid formation of reaction products. Before transient signals can be converted into product branching ratios, several criteria must be met. First, the probed species must be in a thermal Boltzmann distribution of quantum states at a known temperature. This is necessary because it is not practical to explicitly probe each possible product state. Instead, we probe one rotation-vibration state and assume a Boltzmann distribution to obtain a total concentration. The second requirement is that competing secondary reactions either



Signal

Absorption

100

time ( $\mu$ s) Figure 3. Transient absorption signals for CO( $\nu$ =0) P(10) line. Reaction conditions for trace A:  $P_{ICN} = 0.05$  Torr,  $P_{O_2} = 0.30$  Torr,  $P_{NO} = 0.30$ Torr,  $P_{CF_2} = 2.0$  Torr, YAG laser energy = 5 mJ. Trace B: same as trace A except  $P_{CF_4} = 0.0$  Torr,  $P_{SF_6} = 2.0$  Torr. Trace C: same as trace A except  $P_{NO} = 0.0$  Torr. Trace D: same as trace B except  $P_{NO} = 0.0$  Torr. be eliminated or be at least understood. We consider each of these criteria.

200

300

100

The relaxation of the nascent quantum state distribution of reaction products is accomplished by the addition of 0.5-3.0 Torr of buffer gas to the reaction mixture. As described in an earlier publication,<sup>13</sup> SF<sub>6</sub> is efficient at relaxing vibrational excitation of  $CO_2$  and  $N_2O$  but is extremely inefficient at relaxing CO.  $CF_4$ , however, relaxes carbon monoxide reasonably quickly.<sup>21</sup> Therefore, we used SF<sub>6</sub> buffer gas when probing N<sub>2</sub>O and CO<sub>2</sub> products and CF<sub>4</sub> buffer gas when probing CO products. Figure 3 illustrates this effect: using  $SF_6$  buffer gas, the transient signal for CO consists of a fast rise followed by a very slow decay due to diffusion of products out of the probed volume. Because vibrational relaxation in  $SF_6$  is slow, the transient signal detects only carbon monoxide created in the vibrational ground state. Using CF<sub>4</sub> buffer gas, however, we observe a fast rise of equal amplitude, followed by a slower rise which roughly corresponds to the literature value<sup>21</sup> of the relaxation rate for

$$CO(v=1) + CF_4 \rightarrow CO(v=0) + CF_4^*$$
 (5)

where  $k_5 = 2.5 \times 10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. Thus, the fast rise amplitude represents nascent CO produced in the vibrational ground state, and the slow rise amplitude represents additional CO cascading down from excited vibrational states.

The transient absorption signals were analyzed by fitting the slow diffusional decay to a convenient mathematical function (a single exponential was a sufficiently good approximation for our purposes) and extrapolating to zero time. The resulting amplitude was converted into an absolute molecular concentration  $N_{\nu J}$  in the probed ro-vibrational quantum state by

$$N_{vJ} = \ln [I_0/(I_0 - \Delta I)] f_v^0 f_J^0 N_0/\alpha l$$

where  $\Delta I$  and  $I_0$  are the transient signal amplitude and incident probe laser intensity, respectively.  $f_v^{0}$  and  $f_J^{0}$  are the fraction of molecules in the probed v and J state in a  $T_0 = 296$  K Boltzmann distribution,  $N_0$  is Loschmidt's number =  $3.24 \times 10^{16}$  molecules cm<sup>-3</sup> Torr<sup>-1</sup>,  $\alpha$  is the absorption coefficient, and l is the absorption path length. The absorption coefficient at line center was obtained from tabulated<sup>15,16</sup> line strength  $S_{vJ}$  by

$$\alpha = (1/\Delta v_{\rm D})(\ln 2/\pi)^{1/2} N_0 S_{vJ}$$

where  $\Delta \nu_D$  is the Doppler half-width at half-maximum. The total number density N was obtained from

$$N = N_c / f_v = N_{vJ} / f_v f_J$$

Since we assume that all product quantum states are quickly

D

400

500

**TABLE I: Summary of Relevant Reactions** 

eq	reaction	$\Delta H^{\circ}_{300}{}^{a}$	ref	k <sup>b</sup>	ref
la	$NCO + NO \rightarrow CO + N_2O$	-644	9	$1.45 \times 10^{-11}$	d
16	$NCO + NO \rightarrow CO_2 + N_2$	-272	9	1.85 × 10 <sup>-11</sup>	d
3a	$CN + O_2 \rightarrow NCO + O$	-29	10	$\phi_{3a}(2.5 \times 10^{-11})^{c}$	17
3b	$CN + O_2 \rightarrow CO + NO$	-460	10	$\phi_{3b}(2.5 \times 10^{-11})^{\circ}$	17
6	$NCO + O \rightarrow CO + NO$	-427	31	$3.3 \times 10^{-11}$	3
7	$CN + NO \rightarrow CO + N_2$	-640	23	$1.2 \times 10^{-13}$	1
8a	$NCO + O_2 \rightarrow NO + CO_2$	-436	9	5 × 10 <sup>-15</sup>	9
8b	$NCO + O_2 \rightarrow NO_2 + CO$	-226	9	5 × 10 <sup>-15</sup>	9

<sup>*a*</sup> Reaction enthalpies are in kJ/mol. <sup>*b*</sup> Rate constants are in cm<sup>3</sup> molecule <sup>1</sup> s<sup>-1</sup>. <sup>*c*</sup>  $\phi_{3a}$  and  $\phi_{3b}$  were varied in the modeling calculations. <sup>*d*</sup> This work.

relaxed,  $f_v$  and  $f_J$  are calculated from a Boltzmann distribution at the experimental temperature T.

The product yields obtained as describe above were found to be independent of NO and O<sub>2</sub> pressure over the range 0.1–0.5 Torr. In addition, yields scaled linearly with ICN pressure and photolysis laser pulse energy. Experiments performed using a variety of probed rotational states resulted in identical results to within 10%. The ratio of CO<sub>2</sub>:N<sub>2</sub>O:CO yields, averaged over numerous experiments, was found to be 1.00:0.79:1.34. Thus CO<sub>2</sub>, N<sub>2</sub>O, and CO are all produced with significant yields. Note that the CO yield exceeds the N<sub>2</sub>O yield. This would be impossible if reaction 1a were the only source of CO and N<sub>2</sub>O. Thus, either reaction 1c or some competing secondary reaction must be responsible for the additional CO.

We now consider possible secondary reactions. A secondary source of carbon monoxide is a minor channel of the  $CN + O_2$  reaction:

$$CN + O_2 \rightarrow CO + NO$$
 (3b)

This channel has been estimated to account for approximately 6% of the total CN + O<sub>2</sub> reaction.<sup>22</sup> Other possible secondary reactions include

$$NCO + O \rightarrow CO + NO$$
 (6)

$$CN + NO \rightarrow CO + N_2$$
 (7)

$$NCO + O_2 \rightarrow NO + CO_2$$
 (8a)

$$\rightarrow$$
 NO, + CO (8b)

Table I lists the important reactions relevant to this system. Reaction 8 is very slow, with  $k_8 < 5.0 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature.9 Reaction 7 has a pressure-dependent rate constant.<sup>23</sup> Under pressure conditions roughly similar to ours, this reaction is quite slow, with  $k_7 = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$  $s^{-1}$ .<sup>24</sup> This is ca. 100 times smaller than  $k_3$ , and we use comparable NO and O<sub>2</sub> concentrations in these experiments. Thus, reaction 7 should not represent a significant contribution to our signals when both  $O_2$  and NO are present. To test this assumption, we performed the experiment with  $[O_2] = 0$ . As shown in trace B of Figure 2,  $CO_2$  product yields are small under these conditions. The slight amount of product observed is probably due to dissolved O<sub>2</sub> impurity in the solid ICN sample. Similar results were obtained when probing CO or  $N_2O$  in the absence of  $O_2$  reactant, indicating that reaction 7 is not significant under our experimental conditions.

Reactions 3b and 6 represent possible significant sources of CO in addition to the title reaction. To test for these, we photolyzed  $ICN/O_2/SF_6$  and  $ICN/O_2/CF_4$  mixtures. In the absence of NO, only reactions 3b and 6 can contribute to the product yields, as the amount of NO formed in channel 3b is much too small for the NCO + NO reaction to proceed at a significant rate. (We also neglect reaction 8, as it is extremely

slow). The results of these experiments are shown in traces C and D of Figure 3. As shown, we observed negligible CO yield when the experiment was performed using SF<sub>6</sub> buffer gas but quite significant CO yield in CF<sub>4</sub> buffer gas. This result indicates that vibrationally hot CO is produced via reaction 3b or 6 and is relaxed to the ground vibrational state by CF<sub>4</sub>. CO produced by secondary reactions thus contributes to the signal shown in trace A of Figure 3. This point is discussed further in the Discussion section, but to a good approximation, the carbon monoxide yield from the title reaction 1 can be obtained by subtracting the signal obtained with a ICN/O<sub>2</sub>/CF<sub>4</sub> mixture from the signal obtained with the full ICN/O<sub>2</sub>/NO/CF<sub>4</sub> mixture. This results in a correction of roughly 40% to the CO product yield.

After making this correction, we find that the CO and  $N_2O$  yields from reaction 1 are equal to within 10%. This suggests that channel 1c is not active, although we cannot exclude the possibility of a small (<10%) contribution. The resulting branching ratios for channels 1a and 1b are then calculated using

$$\phi_{1a} = [N_2O]/([CO_2] + [N_2O])$$
  
$$\phi_{1b} = [CO_2]/([CO_2] + [N_2O])$$

The branching ratios obtained are shown in Table II for a variety of experiment conditions. As can be seen, these results are essentially independent of  $[O_2]$ , [NO], [ICN], and YAG laser pulse energy. Table III shows a summary of the room temperature branching ratios and rate constants. We estimate an uncertainty of 0.07 (=1.5  $\sigma$ ) for each of the branching ratios.

As a test of some of the above assumptions, some product yield experiments were performed using BrNCO as a direct photolytic NCO precursor. This involves photolysis of BrNCO/NO/SF<sub>6</sub> and BrNCO/NO/CF<sub>4</sub> mixtures. Reactions 3 and 6 are unimportant since no  $O_2$  is necessary in the reaction mixture. Unfortunately, the BrNCO synthesis procedure produces a substantial  $CO_2$  impurity which we were unable to remove by vacuum distillation. As a result, we could not probe  $CO_2$  in the ground vibrational state when using this precursor because most of the infrared probe light was absorbed by this static  $CO_2$ . This prevents measurement of the full branching ratio using BrNCO precursor. We could, however, measure the CO and N<sub>2</sub>O yields after photolysis of a BrNCO/NO/CF4 or BrNCO/NO/SF6 mixture. We find the CO and  $N_2O$  yields to be equal to within 10% under these conditions, confirming that reaction 1c is not significant.

The temperature dependence of the branching ratio of the NCO + NO reaction was also investigated. Using a resistively heated absorption cell, experiments at elevated temperatures were performed using ICN precursor. As described earlier for the room temperature experiments, the CO<sub>2</sub> and N<sub>2</sub>O yields in the absence of NO or O<sub>2</sub> were negligible. Figure 4 shows the results of these experiments. To within the precision of the measurement, the branching ratio did not change over the range 296–623 K. At temperatures above 650 K, transient signal levels for all probed species were observed to rapidly decrease to unacceptably low levels. It is likely that that thermal decomposition and/or dark reactions become significant at these temperatures.

**B.** Energy Disposal Experiments. Experiments were performed to examine the disposal of reaction excergicity into product vibrational degrees of freedom. Given the large exothermicity associated with both channels of the NCO + NO reaction, a very large number of vibrational states of linear triatomic molecules such as  $N_2O$  and  $CO_2$  are energetically accessible. Measurement of the full vibrational distributions into  $N_2O$  or  $CO_2$  would therefore be an extremely arduous task. Preliminary experiments using Ar buffer gas to relax rotational but not vibrational motion in  $N_2O$  and  $CO_2$  proved unsuccessful because of this problem. It is possible, however, to obtain useful information by allowing

	-						
YAG power	PICN	P <sub>NO</sub>	<b>P</b> O <sub>2</sub>	P <sub>SFe</sub>	φia	<b>Ф</b> 1ь	Фзь
6.0	0.05	0.30	0.10	1.5	0.35	0.65	0.27
6.0	0.05	0.30	0.30	1.5	0.48	0.52	0.47
6.0	0.05	0.30	0.50	1.5	0.40	0.60	0.24
6.0	0.05	0.10	0.30	1.5	0.47	0.53	0.31
6.0	0.05	0.30	0.30	1.5	0.48	0.52	0.27
6.0	0.05	0.50	0.30	1.5	0.43	0.57	0.24
10.0	0.05	0.30	0.30	0.5	0.44	0.56	0.21
10.0	0.05	0.30	0.30	1.5	0.43	0.57	0.20
10.0	0.05	0.30	0.30	3.0	0.34	0.66	0.20
1.8	0.10	0.30	0.30	1.0	0.35	0.65	0.23
9.6	0.05	0.30	0.30	0.5	0.44	0.56	0.18
9.6	0.05	0.30	0.30	1.5	0.50	0.50	0.23
9.6	0.05	0.30	0.30	3.0	0.50	0.50	0.11
7.6	0.05	0.30	0.30	1.2	0.45	0.55	0.22
7.6	0.10	0.30	0.30	1.2	0.43	0.57	0.21
3.5	0.10	0.20	0.25	1.0	0.43	0.57	0.23
3.5	0.10	0.40	0.40	2.0	0.47	0.53	0.22
3.5	0.10	0.40	0.40	2.0	0.48	0.52	0.24

"YAG power is in mJ/pulse. Reagent pressures are in Torr. Product branching ratios are defined as  $\phi_{1a} = k_{1a}/(k_{1a} + k_{1b})$  etc.

TABLE III: Branching Ratios of the NCO + NO Reaction

product channel	branching ratio <sup>a</sup>	rate const <sup>b</sup>	
$N_2O + CO$	0.44	1.45 × 10 <sup>-11</sup>	
$CO_2 + N_2$	0.56	$1.85 \times 10^{-11}$	

<sup>a</sup> The branching ratio is defined as  $\phi_{1a} = k_{1a}/(k_{1a} + k_{1b})$  for channel 1a, etc. Data shown are at room temperature. <sup>b</sup> In units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Assuming that  $k_{1a} + k_{1b} = 3.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.



Figure 4. Temperature dependence of branching ratio of the NCO + NO reaction into the CO<sub>2</sub> + N<sub>2</sub> product channel, defined as  $\phi_{1b} = k_{1b}/k_1$ . All measurements at elevated temperature were performed using ICN precursor.

a partial, selective relaxation via the quantum harvesting technique of Flynn and co-workers.<sup>28,29</sup> The basic idea is to probe a vibrationally excited fundamental of  $CO_2$  using  $CO_2$  as the buffer gas. Nascent overtone and combination bands of  $CO_2$  relax via nearly energy resonant intramode processes such as

$$CO_2(002) + CO_2(000) \rightarrow CO_2(001) + CO_2(001)$$
 (9)

Intermode V–V processes and V–T,R relaxation processes such as

$$CO_2(001) + CO_2(000) \rightarrow CO_2(010) + CO_2(000)$$
 (10)

$$CO_2(001) + CO_2(000) \rightarrow CO_2(000) + CO_2(000)$$
 (11)

occur much more slowly because of the large vibrational energy mismatch. The vibrational fundamentals, especially (001), are therefore metastable, lasting thousands of gas kinetic collisions in a  $CO_2$  bath.<sup>29</sup> We can then estimate the average number of



**Figure 5.** Transient absorption signals for CO<sub>2</sub>(00<sup>0</sup>1) P(27) line under harvesting conditions. Top trace:  $P_{BrNCO} = 0.1$  Torr,  $P_{NO} = 0.4$  Torr,  $P_{CO_2} = 2.0$  Torr, YAG laser energy = 2.0 mJ. Bottom trace shows transient signal under identical conditions except for omission of NO.

 $CO_2 \nu_3$  quanta produced in reaction 1 by probing a  $CO_2(00^01)$  spectral line.

The harvesting experiments were performed using BrNCO precursor molecules. This approach is preferred over the ICN/ $O_2$  route because NCO produced by the CN +  $O_2$  reaction has been shown to contain a substantial degree of vibrational excitation,<sup>10</sup> which could complicate the interpretation of energy disposal data. NCO produced by BrNCO photolysis has been observed to contain relatively little vibrational excitation,<sup>25</sup> although quantitative studies of the NCO quantum state distribution have yet to be performed.

Figure 5 shows an absorption signal for the CO<sub>2</sub>(00<sup>0</sup>1) P(27) spectral line obtained under harvesting conditions in which a BrNCO/NO/CO<sub>2</sub> mixture is photolyzed with CO<sub>2</sub> buffer gas in excess. The rise in this signal represents the accumulation of CO<sub>2</sub> in the (00<sup>0</sup>1) state by harvesting collisions such as reaction 9. The decay of the transient signal represents the relaxation of CO<sub>2</sub> out of the (00<sup>0</sup>1) state. The decay rate of the transient signal was found to depend on BrNCO pressure. This indicates that BrNCO is an efficient relaxer of CO<sub>2</sub>  $\nu_3$  vibrational excitation. True harvesting conditions are best approximated when the amount of CO<sub>2</sub> buffer gas far exceeds [NO] or [BrNCO].

Before the transient signal in Figure 5 can be used, we must check for nonreactive excitation sources. Figure 5 also shows the signal for  $CO_2(00^{0}1)$  P(27) obtained in the absence of NO reactant. The resulting signal is probably due to energy-transfer processes from vibrationally excited NCO or spin-orbit excited bromine:

$$NCO^* + CO_2(00^00) \rightarrow NCO + CO_2(00^01)$$
 (12)

$$Br(^{2}P_{1/2}) + CO_{2}(00^{0}0) \rightarrow Br(^{2}P_{3/2}) + CO_{2}(10^{0}1)$$
 (13)

As described earlier, the BrNCO precursor produces relatively cold NCO,<sup>25</sup> but quantitative data are currently insufficient to completely rule out reaction 12. The bromine atom spin-orbit energy-transfer process shown in reaction 13 has been previously observed in studies of IBr photolysis and bromine chemical lasers.<sup>26,27</sup> In our experiments, we account for reactions 12 and 13 by simply subtracting the transients in Figure 5. As is shown, this results in a small (ca. 15%) correction.

After correcting for nonreactive excitation mechanisms, the transient signal amplitude was converted into an absolute number density of CO<sub>2</sub> molecules in the (00°1) vibrational state. N<sub>2</sub>O absorption signals were collected under identical [BrNCO] and [NO] conditions, but using SF<sub>6</sub> buffer gas to obtain the total N<sub>2</sub>O yield. Using the branching ratios measured above, the number of CO<sub>2</sub> product molecules was calculated. (Note that we cannot measure this directly using BrNCO precursor, because of a CO<sub>2</sub> impurity in the BrNCO sample.) The number of nascent  $\nu_3$  quanta per CO<sub>2</sub> product molecule was then calculated. We obtain the result that 0.79 ± 0.20  $\nu_3$  quanta are excited per CO<sub>2</sub> molecule produced by reaction 1b.

The nascent vibrational distribution of carbon monoxide products was also measured. For these experiments, BrNCO was photolyzed in the presence of NO and argon buffer gas. The buffer gas quickly relaxes rotational motion to a Boltzmann distribution but is extremely slow at relaxing vibrational motion. Thus, the signals for v = 0, v = 1, and v = 2 lines may be directly converted into  $N_v$ , the number density of CO molecules in a specific vibrational state. We find that 94% of the CO products are formed in the v = 0 vibrational ground state;  $6 \pm 2\%$  are formed in v = 1, and a negligible amount (<2%) are formed in v = 2.

#### Discussion

A. Branching Ratios. The most important results of the product yield studies are that both the  $CO_2 + N_2$  and the  $N_2O + CO$  channels represent significant contributions to the NCO + NO reaction and that the branching ratios are essentially independent of reaction temperature. This may require a significant revision to the overall mechanism of the RAPRENO<sub>x</sub> process, because previous modeling studies have accounted for N<sub>2</sub>O production by assuming  $\phi_{1a} = 1.00$ . We cannot approach actual combustion temperatures in our experiments, but the observed flat temperature dependence suggests that our results may apply at least qualitatively to RAPRENO<sub>x</sub> conditions.

The NCO produced by the  $CN + O_2$  reaction contains a substantial amount of vibrational excitation. Patel-Misra et al. have used laser-induced fluorescence to measure the nascent vibronic populations of this product.<sup>10</sup> They found a large amount of excitation of the  $\nu_2$  bending mode of NCO, with significant population up to  $v_2 = 6$ .  $v_1$  and  $v_3$  stretching excitation was also observed. We do not expect this excitation to significantly affect our experiments, however. Although no detailed V-V rate constants are known, vibrational excitation in open-shell molecules tends to relax more quickly than in closed-shell molecules. The experiments of ref 10 show that excited vibrational states of NCO relax on a ~50- $\mu$ s time scale in a mixture of 20 mTorr of C<sub>2</sub>N<sub>2</sub> and 120 mTorr of  $O_2$ . The CF<sub>4</sub> and SF<sub>6</sub> buffer gases used in our experiments almost certainly relax nascent vibrational excitation in NCO more efficiently than  $O_2$ . Furthermore, we use buffer gas pressures of 0.5-3.0 Torr. Thus, it is likely that NCO is relaxed to a Boltzmann distribution within a few microseconds in our experiments. In any case, the branching ratios observed

were independent of buffer gas pressure over the range 0.5-3.0Torr, indicating that our results are not significantly affected by NCO vibrational excitation.

When calculating the CO yield due to reaction 1a, it was necessary to subtract a background signal obtained in the absence of NO. This procedure is clearly appropriate if reaction 3b is primarily responsible for the background CO. This reaction has been previously estimated by other authors to contribute 6% to reaction 3.22 We must also consider the possibility, however, that reaction 6 plays a role. Since this is a radical-radical reaction, it has a large rate constant. Nevertheless, it is expected to be quite slow under our experimental conditions, since both transient species are present in small concentrations. Thus, reaction 6 is expected to occur to a significant degree only in the absence of alternate CN removal channels, i.e., only in the absence of NO. If reaction 6 produces the background CO, it is not appropriate to simply subtract the two transients. This is a crucial issue, because the presence or absence of channel 1c can only be inferred in our experiments by a comparison of the CO and  $N_2O$  yields.

To investigate the source of the background CO produced by photolysis of ICN/O<sub>2</sub>/CF<sub>4</sub> mixtures, we measured the dependence of the CO signal on [ICN]. If the CO originates from reaction 3b, we expect a linear dependence on the number of CN radicals initially produced. Since we are using an optically thin sample, this implies a linear dependence on laser pulse energy or initial ICN concentration. The CO yield from reaction 6, however, is expected to be quadratic in transient radical concentration. We observe a linear dependence of CO yield versus [ICN] over the pressure range  $p_{\rm ICN} = 0.05-0.6$  Torr. This suggests that reaction 3b dominates over reaction 6 under our conditions, although we cannot completely exclude the possibility that both reactions contribute.

The experiments using BrNCO/NO/CF<sub>4</sub> and BrNCO/NO/SF<sub>6</sub> reaction mixtures are more conclusive. Under these conditions, neither reaction 3b nor reaction 6 can occur. Our observation that  $[CO] = [N_2O]$  under these conditions provides convincing evidence that reaction 1c is not a significant product channel and that the excess CO observed in the experiments with ICN precursor is due to secondary reactions.

An interesting consequence of our results is that if the CO produced in the photolysis of an  $ICN/O_2/CF_4$  mixture (i.e.,  $p_{NO} = 0$ ) is due primarily to reaction 3b, then the previously published<sup>22</sup> branching ratio of 6% for  $k_{3b}/k_3$  must be underestimated. To show this, let  $[CO]_{tot}$ ,  $[N_2O]_{1a}$ , and  $[CO_2]_{1b}$  be the total CO,  $N_2O$ , and CO<sub>2</sub> yields obtained in the  $ICN/O_2/NO/CF_4$  experiment. Let  $[CN]_0$  be the number of CN radicals initially produced by the ICN photolysis. If we neglect reactions 6, 7, and 8, then the CO yield originates solely from reactions 3b and 1a.

$$[CO]_{tot} = [CO]_{1a} + [CO]_{3b} = [N_2O]_{1a} + [CO]_{3b}$$

where we have used the fact that channel 1c is not significant, so that the CO and  $N_2O$  yields from reaction 1a are equal. Since we are only considering reactions 3 and 1, we can write

$$[CN]_0 = [NCO]_{3a} + [CO]_{3b} = [CO_2]_{1b} + [CO]_{1a} + [CO]_{3b}$$

where  $[NCO]_{3a}$  is the total amount of NCO radicals produced by reaction 3a after all CN radicals have reacted. Therefore

$$[CN]_0 = [CO]_{tot} + [CO_2]_{1b}$$

Defining the branching ratio of reaction 3b to be  $\phi_{3b} = k_{3b}/k_3$ , we have

$$\phi_{3b} = [CO]_{3b} / [CN]_0$$

$$\phi_{3b} = ([CO]_{tot} - [N_2O]_{1a})/([CO]_{tot} + [CO_2]_{1b})$$

Therefore, we can measure the branching ratio of channel 3b by



**Figure 6.**  $[CO]_{tot}$   $[N_2O]$  yield as a function of  $[CO_2] + [CO]_{tot}$  yield (molecules cm<sup>-3</sup>). Circles are experimental data. Lines are predictions of kinetic model assuming  $\phi_{3b} = 0.06$  and  $\phi_{3b} = 0.23$ . See discussion in text for details.

using the observed yields  $[CO]_{101}$ ,  $[N_2O]_{1a}$ , and  $[CO_2]_{1b}$ . Using our data, we find that  $\phi_{3b}$  calculated in this way is 0.23 ± 0.10 for all reaction conditions used, as shown in Table II.

An additional test of these ideas is to calculate  $[CN]_0$  from the incident photolysis laser energy and compare it with our measured value of  $[CO]_{tot} + [CO_2]_{1b}$ . These quantities should be equal if our kinetic model is valid. We have measured the absorption coefficient of ICN at 266 nm to be 0.009 cm<sup>-1</sup> Torr<sup>-1</sup> (base e). This is in reasonable agreement with previously reported values.<sup>30,31</sup> Assuming a quantum yield for ICN dissociation of unity, we find that  $[CN]_0$  calculated in this way agrees to within ~20% with values of  $[CN]_0$  calculated from our observed CO and CO<sub>2</sub> yields.

We have also performed kinetic modeling calculations using the ACUCHEM modeling program<sup>32</sup> to examine the importance of secondary reactions 6, 7, and 8. Table I shows the reactions that were included in the kinetic model. Calculations were performed by varying the value of  $[CN]_0$  and tabulating the resulting [CO]<sub>tot</sub>, which includes all possible sources of carbon monoxide. The calculation was performed using two assumed values of  $\phi_{3b}$ :  $\phi_{3b} = 0.06$  as reported in ref 22 and  $\phi_{3b} = 0.23$  as suggested by our simplified model, which includes only reactions 1 and 3. The results of this calculation are shown in Figure 6. As can be seen, the calculation fits the experimental data best for  $\phi_{3h} = 0.23$ , as obtained above. Essentially, this demonstrates that we were justified in ignoring the NCO + O and CN + NOreactions. The NCO + O reaction can become significant, but only at substantially greater CN concentrations than used in these experiments.

In our discussion above, we have ignored reactions of  $NO_2$ , which is a product of the third-order reaction

$$2NO + O_2 \rightarrow 2NO_2 \tag{14}$$

where  $k_{14} = 1.96 \times 10^{-37}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> at room temperature and decreases as *T* increases in the range 298–600 K.<sup>33</sup> At our typical reaction conditions of  $p_{NO} = p_{O_2} = 0.4$  Torr, the rate of NO<sub>2</sub> formation by this dark reaction is less than 5 mTorr h<sup>-1</sup> or less than 0.5 mTorr in the ~5-min mixing time before each transient signal.

We have also used the temperature-dependent data to obtain  $\phi_{3b}$  at elevated temperatures, as is shown in Figure 7. As can be seen, the CO + NO product channel represents a significant fraction of the CN + O<sub>2</sub> reaction only near room temperature but becomes insignificant at T > 600 K.

It is useful to compare our results with previous work. As discussed in the Introduction, our preliminary study<sup>13</sup> of the NCO + NO reaction at room temperature included a  $\sim 20\%$  contri-



Figure 7. Temperature dependence of the branching ratio of the CN +  $O_2$  reaction into the CO + NO product channel, defined as  $\phi_{3b} = k_{3b}/k_3$ .

TABLE IV: Energy Disposal in the NCO + NO Reaction

	prior distribution		experiment		
	no. of quanta	% of E <sub>avail</sub>	no. of quanta	% of $E_{\text{avail}}$	
CO vibration	1.28	11.8	0.06	0.55	
CO <sub>2</sub> v <sub>3</sub> vibration	2.71	11.8	0.79	3.4	

bution from reaction 1c. That conclusion was based on an excess of the CO yield over the N<sub>2</sub>O yield which we now believe to originate from the secondary reaction 3b. The relative branching fraction between channels 1a and 1b remains essentially unchanged. The branching ratio of this reaction has also very recently been studied by Becker et al. using FTIR spectroscopy.<sup>34</sup> They report room temperature branching ratios of  $0.35 \pm 0.06$ for the N<sub>2</sub>O + CO channel and  $0.65 \pm 0.06$  for the CO<sub>2</sub> + N<sub>2</sub> channel, in reasonable agreement with our results.

B. Energy Disposal. The energy disposal data show that only a small fraction of the reaction excergicity is deposited into highfrequency stretching modes of CO and CO<sub>2</sub>. For a simple comparison, we can calculate the fraction of energy expected by a statistical prior model of Muckerman.<sup>35</sup> Reaction 1b corresponds to the case of a linear triatomic and diatomic products. The statistical fraction of energy deposited into the  $\nu_3$  mode of the linear triatomic is 2/17 = 11.8%. As shown in Table IV, our experimental data indicate that only 3.4% of the available energy is deposited into the  $v_3$  mode of CO<sub>2</sub>. Similarly, vibrational excitation in CO accounts for only 0.55% of the available energy in channel 1a, in contrast to a statistical prediction of 11.8%. Most of the energy is apparently deposited into translation, rotation, and/or low-frequency vibrational modes. Collisions of NCO with NO are almost certainly dominated by long-range attractive forces and involve a deep potential well. Complete randomization of energy is quite likely. The lower than statistical energy yields are therefore somewhat surprising. Exit channel effects in the dissociating collision complex may favor the excitation of low-frequency modes over high-frequency modes, but it is also very likely that translational energy release dominates the energy disposal dynamics of this reaction.

Further insight into the NCO + NO reaction may be obtained by the use of ab initio calculations. An accurate theoretical description of this reaction would entail a detailed study using multiconfigurational methods to obtain accurate energies of all critical points on the potential energy surface. Our objectives here are far more modest: we have performed computations on the ground-state potential surface at the restricted Hartree–Fock level in order to estimate the structures of collision complexes and saddle points for the NCO + NO reaction system. In addition to neglecting correlation energy, we are also ignoring possible



Figure 8. Calculated (RHF 6-31G(d)) local minima on the NCONO ground-state potential surface. Bond lengths are in angstroms, and bond angles are in degrees.



Figure 9. Calculated (RHF 6-31G(d)) saddle points on the NCONO ground-state potential surface: (A) saddle point connecting structure A in Figure 9 with  $CO_2 + N_2$  products; (B) saddle point connecting structure B in Figure 9 with  $CO + N_2O$  products.

effects of excited-state potential surfaces. It is hoped that these computations will provide a base line for more accurate studies.

Geometry optimization calculations were performed using the GAMESS ab initio electronic structure package,<sup>36</sup> using the 6-31G(d) basis set<sup>37</sup> at the restricted Hartree-Fock level. The primary result of these calculations is that we find two local minima on the potential energy surface. One minimum is the cyclic structure shown in Figure 8a, while the lowest energy complex is the bent structure shown in Figure 8b. Both of these structures had positive definite curvature as determined by a calculation of the Hessian matrix. Several saddle points were also found; two of these are shown in Figure 9. The intrinsic reaction coordinate (IRC) feature of the GAMESS package was used to follow each saddle point by a path of steepest descent down to a local minimum structure of product channel. This leads to a qualitative picture of the NCO + NO reaction shown schematically in Figure 10. The bent complex can either dissociate into  $N_2O + CO$  or isomerize to the cyclic structure. The cyclic



Figure 10. Qualitative potential energy diagram for the NCO + NO reaction.

structure then has a dissociation pathway via a four-center transition state into  $CO_2 + N_2$ . While these calculations are not of sufficient accuracy to make a quantitative comparison with experiment, they do qualitatively predict the existence of both  $N_2O + CO$  and  $CO_2 + N_2$  as accessible product channels, in agreement with our results.

#### Conclusions

The product channel dynamics of the NCO + NO reaction was studied. Two product channels are found:  $56 \pm 7\%$  of the reaction produces  $CO_2 + N_2$ , while  $44 \pm 7\%$  produces  $N_2O +$ CO. These branching ratios are independent of temperature in the range 296-623 K. Furthermore, the CN +  $O_2$  reaction was found to have a significant CO + NO product channel in addition to the better known NCO + O channel. The energy disposal dynamics of NCO + NO was also studied. The fractions of energy deposited into the CO vibration and the  $\nu_3$  mode of CO<sub>2</sub> were found to be much less than predicted by a statistical model.

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