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Photochemistry of ClNCO

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The gas phase chemistry that occurs after the photolysis of ClNCO at 248 nm is characterized by the action of two excited intermediates, $N(^2D)$ and $N_2(A)$. Each of these reacts with ClNCO to generate $NCO(A\,^2\Sigma^+)$, and blue emission from the $NCO(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ transition is observed. The time profile of the NCO emission consists of two distinct components, a fast component arising from the $N(^2D)$ + ClNCO reaction and a slow component arising from the $N_2(A)$ + ClNCO reaction. The $N(^2D)$ is an initial photofragment and the $N_2(A)$ is generated in the $N(^2D)$ + ClNCO reaction. The value of the rate constant for $N(^2D)$ + ClNCO is determined to be $7.0 \pm 0.8 \times 10^{-11}$ cm^3 s^{-1}. The rate constant measured from the decay of the NCO emission in a previous work ($2.1 \pm 0.2 \times 10^{-11}$ cm^3 s^{-1}) is assigned to the $N_2(A)$ + ClNCO reaction.

INTRODUCTION

In previous experiments performed in our laboratory by Bell and Coombe,[1] the photolysis of ClNCO at 248 nm was found to produce bright blue emission identified as the $A\,^2\Sigma^+ \rightarrow X\,^2\Pi$ transition in NCO. From the time profile of the emission, it was determined that the excited NCO was not a direct photofragment, but rather was the product of a reaction of an excited species with the parent ClNCO. In addition, the apparent second order rate constant for the reaction of ClNCO with this excited species was obtained by analyzing the decay profile of the NCO emission. The presence of $N(^2D)$ was detected in the photolysis system by the addition of N_2O, which quenched the NCO $A \rightarrow X$ emission and produced NO $B \rightarrow X$ emission. From this, it was concluded that $N(^2D)$ was the excited species responsible for the formation of excited NCO. The following mechanism was postulated to explain these results:

$$\mathrm{ClNCO} + h\nu \rightarrow \mathrm{N}(^2D) + \mathrm{Cl} + \mathrm{CO}, \tag{1}$$

$$\mathrm{N}(^2D) + \mathrm{ClNCO} \rightarrow \mathrm{NCl} + \mathrm{NCO}(A), \tag{2}$$

$$\mathrm{N}(^2D) + \mathrm{N_2O} \rightarrow \mathrm{N_2} + \mathrm{NO}(B). \tag{3}$$

The ground electronic state for the halogen isocyanates (and for the isoelectronic halogen azides) is $^1A'$ and excited $^1A''$ states are accessible via optical transitions. Conservation of spin angular momentum predicts that these excited singlet states may dissociate to two singlet, two doublet, or two triplet fragments:

$$\begin{aligned} &\rightarrow \mathrm{NX^*}\ (\text{singlets}) + \mathrm{CO}(X\,^1\Sigma^+), &\text{(4a)}\\ \mathrm{XNCO^*}(^1A'') &\rightarrow \mathrm{X}(^2P_J) + \mathrm{NCO}\ (\text{doublets}), &\text{(4b)}\\ &\rightarrow \mathrm{NX}(X\,^3\Sigma^-) + \mathrm{CO^*}\ (\text{triplets}). &\text{(4c)}\end{aligned}$$

For the halogen azides FN_3,[2] ClN_3,[3] and BrN_3,[4,5] the primary dissociation channels for photolysis at $\lambda \geqslant 193$ nm are analogous to reactions (4a) and (4c), forming singlet and triplet fragments, respectively. In the ClNCO experiments noted above, no evidence of the production of excited singlets ($a\,^1\Delta$ or $b\,^1\Sigma^+$) of NCl or excited triplets of CO was found. These results were interpreted as indicative of the operation of the doublet channel with ClNCO dissociating to $\mathrm{Cl}(^2P) + \mathrm{N}(^2D) + \mathrm{CO}(^1\Sigma^+)$. This mechanism is distinctly different from that operating in the azides and may be attributed to the much stronger XN–CO bond in the isocyanates relative to the weak XN–N_2 bond in the azides.

One potentially useful aspect of the ClNCO photolysis system was that it appeared to be a relatively clean pulsed source of $N(^2D)$. Since the $N(^2D)$ decay should track the time profile of the observed NCO $A \rightarrow X$ emission, a straightforward method should exist for measuring the rates of $N(^2D)$ quenching by various added molecular species. However, upon reexamining the time profiles of the NCO emission in the low density regime, two distinct components were discovered, indicating the chemistry to be more complex than the mechanism shown in reactions (1), (2), and (3) above. This paper describes the results of experiments which were performed to elucidate this complex chemistry. From these experiments, strong evidence was obtained showing that, in fact, two different excited species are present in the photolysis system, each of which reacts with ClNCO to form NCO(A).

EXPERIMENTAL DETAILS

The synthesis of ClNCO as well as the photolysis and data collection systems have already been described in detail,[1] and will only be briefly outlined here. ClNCO was synthesized by passing a 3.5% mixture of Cl_2 in N_2 or He over solid AgNCO that was suspended on glass wool and heated to 160 °C. The presence of ClNCO in the effluent from the generator was detected by monitoring the asymmetric stretching vibration of NCO at 2200 cm^{-1} with a Perkin-Elmer 337 IR spectrometer. The gas stream passed through a stainless steel cell where it was photolyzed at 248 nm with a pulse from an excimer laser. The subsequent emission was observed at right angles to the photolysis pulse with a 0.25 m monochromator and a cooled GaAs photomultiplier tube (RCA C31034). The amplified output from the PMT was sent to a Stanford Research Systems gated integrator interfaced to an IBM-PC for collection and storage of spectra, or

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to a Nicolet 1270 data aquisition instrument for collection of time profiles. The time profiles were transferred to a VAX 780 computer and analyzed with curve fitting routines from an RS/1 statistical package.

Several experiments were carried out with a discharge/flow reactor similar to the system described in Ref. 6. N_2 (A) was produced in the reactor by generating $Ar(^3P_{0,2})$ metastables in a microwave discharge cavity and adding N_2 immediately downstream. ClNCO was admitted further downstream through an injector.

RESULTS

An example of the time profile of the blue NCO emission collected at 438 nm following the pulsed photolysis of ClNCO at 248 nm is shown in Fig. 1(A). Two components are apparent in the profile, a short-lived component (component I) which displays an electronics limited rise (0.3 μs) and a fast decay (a few μs), and a long-lived component (component II) which rises to a maximum at about 7 μs followed by a decay over about 14 μs. Only a single component with a decay that extended over about 20 μs had been observed by Bell and Coombe. By varying the ClNCO concentration, the reason for the disagreement became apparent. As the ClNCO concentration was increased, the slower component was partially quenched and the time profile began to assume the appearance of a single decay. The previous experiments had been carried out at ClNCO concentrations that were high enough to mask the two component nature of the time profile.

We obtained spectra of both components by choosing a time gate on the boxcar integrator that would allow us to collect the integrated intensity of each component separately. The spectrum of component I was collected with a 1 ns delay and a 2 μs gate width, and the spectrum of component II was collected with a 9 μs delay and a 15 μs gate width. The spectra, shown in Fig. 2, are both NCO $A \rightarrow X$ emission, although the spectrum of component I indicates somewhat greater vibrational excitation in the NCO(A) state than component II. Fluence dependence experiments performed in the earlier work by Bell and Coombe showed that the intensity of the entire time profile varies linearly with the laser fluence.

Bell and Coombe's experiments had shown that $N(^2D)$ atoms were present in the photolysis system since the addition of N_2O resulted in NO β band emission. This result was readily reproduced in the present experiments. Other known quenchers of $N(^2D)$ were added as further verification of the presence of these excited atoms. For example, the addition of CF_3Br quenched component II of the NCO emission and weak $NBr(b\,^1\Sigma^+ \rightarrow X\,^3\Sigma^-)$ emission was observed, as would be expected in the presence of $N(^2D)$.[7]

Figure 1(B) shows the NCO emission time profile when 1.10 Torr of N_2O was added to the system. Most of component II is quenched, and the profile consists primarily of component I. Based on this result it would seem that compo-

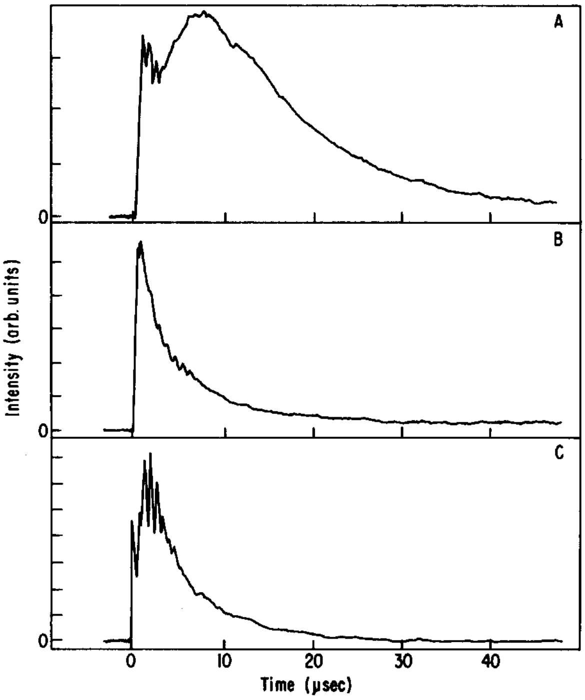

FIG. 1. (A) Time profile of the NCO emission collected at 438 nm following the photolysis of ClNCO at 248 nm. (B) Time profile of the NCO emission with 1.10 Torr of N_2O added. (C) Time profile of the NO β emission at 320 nm in the ClNCO photolysis system. Note: the oscillations appearing at short times are due to electronic noise generated by the signal amplifier.

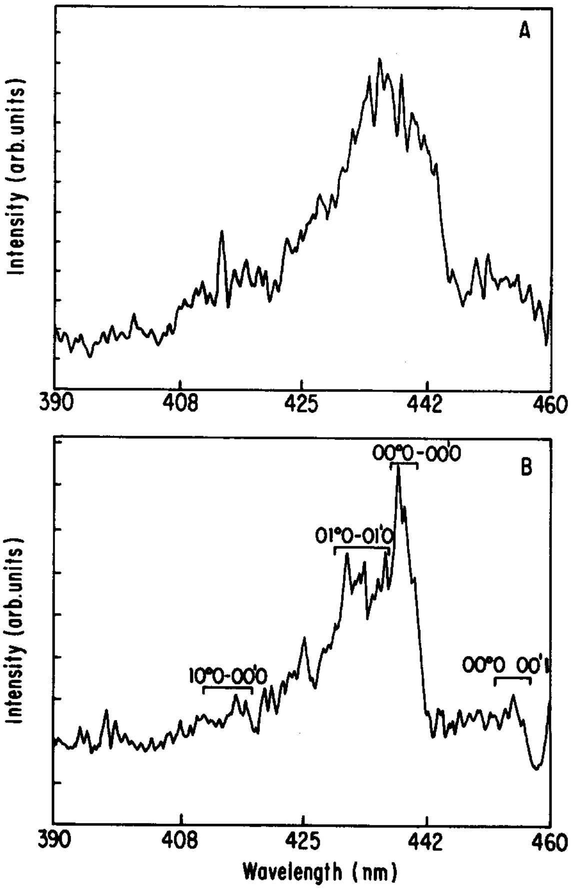

FIG. 2. Spectra of (A) component I and (B) component II of the NCO emission time profile.

nent II of the NCO emission should correspond to formation of NCO(A) by the N(^2D) + ClNCO reaction. If this were the case, the time profile of the NO β band emission should track the decay of component II. A representative NO $B\rightarrow X$ time profile is shown in Fig. 1(C). Clearly, the intensity of the β bands tracks component I rather than component II. The rise of the NO $B\rightarrow X$ emission is somewhat slower than the time constant of the data collection electronics, reflecting the 3 μs radiative lifetime of the NO(B) state, and is followed by a decay which matches the decay of component I. Hence, this decay must correspond to the removal of N(^2D) from the system, in collisions with either ClNCO, producing NCO(A), or N_2O, producing NO(B).

A series of experiments was performed to determine the rate constants for quenching of N(^2D) by ClNCO and N_2O. For this purpose, the decay of the NO $B\rightarrow X$ emission was analyzed for various ClNCO and N_2O densities. The rate law for the formation of NO(B) can be expressed as

$$R = r/\rho = k_2 + (k_3 - k_2)X_{N_2O},$$

where k_2 and k_3 are the rate constants for reactions (2) and (3), respectively, r is the decay rate (s^{-1}) of the NO β emission, ρ is the sum of the ClNCO and N_2O densities, and $X_{N_2O} = [N_2O]/([N_2O] + [ClNCO])$. The quenching of NO($B$) by N_2, the buffer gas in these studies, is negligible.[8] A linear least squares analysis of the plot of R vs X_{N_2O}, shown in Fig. 3 gives $7.0 \pm 0.8\times 10^{-11}$ and $2 \pm 1\times 10^{-12}$ $cm^3\,s^{-1}$ for k_2 and k_3, respectively. The error reported for k_2 is the standard deviation of the intercept obtained from the least squares analysis, and the error in k_3 is obtained from the propagation of the intercept and slope errors. Our value for k_3 is in agreement with the value reported by Husain *et al.*, $1.6 \pm 0.1\times 10^{-12}$ for N(^2D) + N_2O.[9]

It would seem that component II of the NCO $A\rightarrow X$ emission must be due to the presence of a second energy carrier which is also quenched by N_2O, but unlike N(^2D), does not give rise to the NO β bands. In order to ascertain the nature of this second energy carrier, the effects of other added quenchers were tested. Upon addition of NO to the photolysis system, NO γ band emission ($A\,^2\Sigma^+ \rightarrow X\,^2\Pi$) was observed, with no accompanying β bands. The time profile of the γ band emission tracked component II of the NCO emission, showing the characteristic slow rise and decay as in Fig. 3(A). Since the radiative lifetime of the NO(A) state is 178 ns,[10] the observed time profile of the γ bands maps the time profile of the second energy carrier. It is well known that NO is efficiently pumped to its $A\,^2\Sigma^+$ state in collisions with N_2 ($A\,^3\Sigma_u^+$) metastables. If these N_2 metastables were in fact the second energy carrier in the ClNCO system, they must react with ClNCO to produce NCO(A). To test this possibility, a number of discharge-flow experiments were performed in which ClNCO was admitted to a flowing stream of N_2 (A) metastables. A faint blue emission was produced, requiring the presence of both N_2 (A) and ClNCO. From its spectrum, the emission was identified as NCO $A\rightarrow X$.

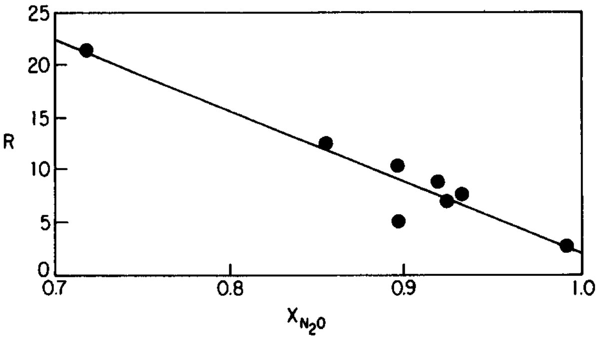

FIG. 3. Plot of R vs X_{N_2O} where R is the decay rate of the NO β emission divided by the sum of the ClNCO and N_2O densities and X_{N_2O} is the mole fraction of N_2O.

DISCUSSION

The results of these experiments, and those previously reported by Bell and Coombe, suggest the following overall mechanism for the observed ClNCO photochemistry:

$$\mathrm{ClNCO} + h\nu \rightarrow \mathrm{N}(^2D) + \mathrm{Cl} + \mathrm{CO}, \quad (1)$$

$$\mathrm{N}(^2D) + \mathrm{ClNCO} \rightarrow \mathrm{NCl} + \mathrm{NCO}(A) \quad (2)$$

$$\rightarrow \mathrm{N_2}(A) + \mathrm{Cl} + \mathrm{CO}, \quad (2')$$

$$\mathrm{N_2}(A) + \mathrm{ClNCO} \rightarrow \mathrm{N_2} + \mathrm{Cl} + \mathrm{NCO}(A). \quad (5)$$

N(^2D) is an initial photofragment. It subsequently reacts with the parent ClNCO by either path (2) or (2′), producing NCl + NCO(A) or N_2 (A) + Cl + CO, respectively. Process (2) is responsible for component I of the observed NCO $A\rightarrow X$ emission, and the rate constant for N(^2D) quenching by ClNCO [paths (2) and (2′)] is $7.0 \pm 0.8\times 10^{-11}$ $cm^3\,s^{-1}$, determined as described above. The N_2 (A) metastables produced in reaction (2′) suffer collisions with ClNCO (present in very large excess over all other species except the diluent), generating NCO(A) as in reaction (5). The rise of this NCO $A\rightarrow X$ emission will represent the rate of formation of N_2 (A), and hence will track the N(^2D) decay. The rise of component II should therefore track the decay of component I, as was indeed found experimentally (see Fig. 3). The decay of component II should correspond to the rate of process (5). The rate constant measured by Bell and Coombe in the previous experiments, $2.1 \pm 0.2\times 10^{-11}$ $cm^3\,s^{-1}$, corresponds to this process.

The identification of the principal energy carriers as N(^2D) and N_2 (A) seems firm. The production of NO β bands upon the addition of N_2O is a well-known diagnostic for the presence of N(^2D),[11,12] as is the production of NO γ bands from energy transfer between N_2 (A) and NO.[13] By analogy with previous results from the photolysis of halogen azides, excited triplet CO might also be considered as a possible energy carrier [see for example reaction (4c) above]. Energy transfer from excited CO($a\,^3\Pi$) to NO produces both NO(A) and NO(B), however, and the ratio of the intensities of the γ and β band systems has been reported to be 2.3:1.0.[14] Energy transfer from N_2 (A) to NO produces almost exclusively NO(A), with a γ:β ratio of 71:1.[13] Since no evidence of β bands was found when NO was added to the photolysis system, it seems apparent that $N_2(A)$ rather than $CO(a)$ is the energy carrier. From the lower limit on the heat of formation of ClNCO reported by Bell and Coombe ($\Delta H_f \geqslant 52.9$ kcal mol^{-1}), the energy liberated by the $N(^2D)$ + ClNCO reaction is easily sufficient for the production of $N_2(A)$ [process (2')]. Further, the production of NCO(A) by the interaction of ClNCO with $N_2(A)$ [reaction (5)] was verified by the discharge-flow experiments described above.

When N_2O, NO, or CF_3Br were added to the photolysis system, component II of the NCO emission was quenched because all of these species quench $N_2(A)$. The rate constants for $N_2(A)$ quenching by N_2O, NO and CF_3Br are 7.7×10^{-12}, 1.5×10^{-10}, and 5.0×10^{-11} cm^3 s^{-1}, respectively.[13,7] Although the rate constant for quenching by N_2O is considerably smaller than that for quenching by ClNCO ($k_5 = 2.1\times10^{-11}$ cm^3 s^{-1}), the present experiments involved very large excesses of N_2O over ClNCO such that the $N_2(A)$ (i.e., component II of the NCO $A \rightarrow X$ emission) was effectively removed.

The work by Bell and Coombe suggested that the photodissociation channel leading to the doublet manifold of fragments [reaction (4b)] is dominant in ClNCO. This conclusion is reaffirmed by the present experiments, the primary excited photofragment being $N(^2D)$ atoms. No evidence of excited singlet NCl or excited triplet CO was found. Since a number of electronic states of the NCO radical correlate to $N(^2D) + CO(^1\Sigma^+)$, the initial dissociation event may proceed to Cl + NCO, the excited NCO dissociating to $N(^2D)$ + CO. Hence, the actual quantum yield of $N(^2D)$ may well be low, with a much higher yield of ground state (perhaps vibrationally excited) NCO being generated. LIF experiments are planned to test this possibility. Further, the present results show that ClNCO can release energy upon collisions with excited metastables like $N(^2D)$ or $N_2(A)$. Such collisions may excite the molecule to a different manifold of dissociative states than does photolysis, and hence may represent a different way of extracting energy from metastable XNCO systems.

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