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Citation: The Journal of Chemical Physics **82**, 1317 (1985); doi: 10.1063/1.448962 View online: http://dx.doi.org/10.1063/1.448962 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/82/3?ver=pdfcov Published by the AIP Publishing

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# Photodissociation of chlorine isocyanate

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(Received 13 August 1984; accepted 25 October 1984)

Gaseous CINCO exhibits a continuous ultraviolet absorption feature peaked near 250 nm. Photolysis of this compound at 249 nm produces bright blue emission identified as the  $A^{2}\Sigma^{+} \rightarrow X^{2}\Pi$  transition in NCO. The excited NCO arises from a collisional process in which N(<sup>2</sup>D) atoms, produced directly by the photodissociation, react with the parent CINCO. The rate constant for this process is  $k = (2.1 \pm 0.2) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. From production of N(<sup>2</sup>D) by the 249 nm photolysis, the heat of formation of gaseous CINCO is inferred to be  $\Delta H_f(\text{CINCO}) \ge 52.9$  kcal mol<sup>-1</sup>. CINCO is metastable with respect to the ground electronic states of NCl and CO by 8.2 kcal mol<sup>-1</sup>.

#### INTRODUCTION

Recent work in our laboratory<sup>1-4</sup> has shown that the halogen azides  $(XN_3, X = halogen)$  are a group of molecules capable of unique chemical reactivity and photochemical behavior. The strong perturbation exerted by the halogen atom on the N<sub>3</sub> chain tends to destabilize these compounds, which are metastable with respect to the ground states of the nitrenes and N<sub>2</sub>.<sup>1,2</sup> In comparison, better known azides like HN3 or CH3N3 are thermodynamically stable. Apparently, interaction with the filled porbitals of the halogen atom results in a greater distortion of the  $\pi$  cloud on the azide chain, weakening the XN- $N_2$  bond.<sup>5</sup> The energy borne by the halogen azides has a significant effect on the photochemistry of these species. Since the energy available to photodissociation products is the sum of the photon energy plus the metastability of the molecules, a number of higher energy dissociation channels are accessible at relatively long photolysis wavelengths. Assuming the excited dissociative states pumped by the photolysis to be singlets (the ground states are  $X^{1}A'$ ), spin allowed dissociation processes could generate singlet (ground state) N<sub>2</sub> and excited singlet states of the nitrenes, or triplet (ground state) nitrenes and excited triplet states of N<sub>2</sub>. For the more common azides, triplet products are produced only by photolysis in the vacuum UV,<sup>6</sup> since the lowest energy triplet state of N<sub>2</sub> lies more than 143 kcal  $mol^{-1}$  above the ground state. In the halogen azides, however, the extra energy carried by the molecules allows the generation of N<sub>2</sub>  $A^{-3}\Sigma_{u}^{+}$  from photolysis of ClN<sub>3</sub> at wavelengths as long as 249 nm,<sup>1</sup> and from  $BrN_3$  at wavelengths as long as 308 nm.<sup>2</sup> The generation of significant quantities of triplet N<sub>2</sub> in these systems results in the occurrence of a number of unique chemical reactions subsequent to the photolysis, including reactions with the parent azides,<sup>2</sup> energy pooling processes among the excited states of  $N_2$ ,<sup>1</sup> and processes generating the excited  $D'({}^{3}\Pi 2_{\rm g})$  states of the molecular halogens.<sup>4</sup>

Although the halogen isocyanates (XNCO) are isoelectronic with the halogen azides, they exhibit much greater chemical stability. Presumably, this behavior arises from the greater strength of the XN-CO and X-NCO bonds relative to their counterparts in the azides. Although some information on the bond lengths in these molecules is available from microwave spectroscopy,<sup>7,8</sup> large differences in bond strengths cannot necessarily be inferred. In the molecules HNCO and HN<sub>3</sub>, however, the HN-CO bond has a strength<sup>9</sup> of about 55 kcal  $mol^{-1}$  (relative to the ground states of NH and CO), whereas the strength<sup>10</sup> of the HN-N<sub>2</sub> bond is only 10.8 kcal mol<sup>-1</sup>. If, in the halogen isocyanates, the XN-CO bonds are similarly stronger than the XN-N<sub>2</sub> bonds in the analogous azides, the perturbation by the halogen atom may have a significantly smaller effect on the overall chemical behavior of these molecules. For example, the photochemistry CINCO might well be expected to more strongly parallel that of HNCO rather than ClN<sub>3</sub>. The photodissociation of HNCO has been studied by a number of research groups.<sup>10,12-14</sup> Drozdoski et al.<sup>13</sup> have observed that the major path for photolysis of HNCO at 193 nm (in its longest wavelength absorption band) is dissociation to NH ( $a^{-1}\Delta$ ) and CO  $(X^{1}\Sigma^{+})$ . This result is similar to that found for photolysis of HN<sub>3</sub> in an analogous band.<sup>15</sup> For photolysis at 206 nm, dissociation to H + NCO has been reported to be as important as dissociation to NH + CO.<sup>12</sup> Excited triplets of NH and electronically excited NCO have been observed from vacuum UV photolysis of HNCO.<sup>10</sup>

In this paper, we present results of our investigation of the photodissociation of CINCO. The objective of this work was to establish the stability of the molecule relative to possible fragments NCl + CO or Cl + NCO, and to determine whether any additional energy made available via perturbation by the chlorine atom significantly affects the nature of the fragments or the chemistry of the postphotolysis environment. The data obtained indicate that CINCO is in fact a unique species whose behavior is quite different from that of either ClN<sub>3</sub> or HNCO.

## EXPERIMENTAL DETAILS

A flowing stream of gaseous CINCO was produced by the method outlined by Frost and co-workers.<sup>5</sup> In brief, a stream of  $Cl_2$  heavily diluted with  $N_2$  ( $Cl_2: N_2$ = 1:28) was passed slowly over solid AgNCO suspended

J. Chem. Phys. 82 (3) 1 February 1985

0021-9606/85/031317-06\$02.10

on glass wool, in an oven held at 423 K. The total pressure in the generator was typically about 60 Torr. The effluent from the generator was analyzed via infrared spectroscopy, which indicated that no significant IR active impurities were present. During photolysis experiments, relative amounts of CINCO in the flow were monitored by on-line measurement of the absorption intensity of the NCO asymmetric stretching vibration<sup>16</sup> near 2200 cm<sup>-1</sup>. UV and vacuum UV absorption spectra were also measured on line with the generator flow, by using a Heath 0.5 m spectrometer or an Acton Research Model 502V UV-VUV spectrometer. The ultraviolet absorption was also used as a convenient monitor of the CINCO flow. For the conditions employed, continuous absorption<sup>17</sup> by Cl<sub>2</sub> was not evident in the UV spectra recorded, suggesting a high yield of CINCO as was found by Frost et al.<sup>5</sup>

The apparatus used for pulsed photolysis experiments has been described previously.<sup>24</sup> The flowing gases were passed through a 10 cm long stainless steel cell where they were exposed to pulsed radiation from a KrF excimer laser (249 nm) at a repetition rate of 1 Hz. The incident laser fluence was typically between  $50-100 \text{ mJ cm}^{-2}$ . Emission produced subsequent to the photolysis was viewed at 90° to the axis of the laser beam by using the combination of a 0.25 m monochromator and a cooled GaAs photomultiplier tube. For detection in the near IR region, a grating blazed at 1.0  $\mu$ m was used in the monochromator and the PMT was replaced by an intrinsic germanium detector (North Coast Optics 817P) cooled to 77 K. The monochromator was calibrated by using Ar, Hg, and N<sub>2</sub> lamp sources as well as the output of a HeNe laser. Time resolved spectra of emissions produced by the photolysis were measured by using gated integration methods, as described previously.2,4 Time profiles of particular spectral features were measured by digitally storing the amplified output of the detectors, and signal averaging over a number of photolysis pulses. The instrument used for this purpose was a Nicolet 1270 data acquistion and analysis system equipped with a 20 MHz digitizer. For emissions in the visible and UV regions (detected by the PMT), the overall time constant of the data collection system was approximately 0.4 µs, limited primarily by the pulse amplifier. For infrared detection, the germanium detector limited the time constant of the system to about 10  $\mu$ s.

A premixed sample of  $Cl_2$  diluted in  $N_2$ , obtained from Matheson Gas Products, was used in the CINCO generator.  $N_2O$  (Matheson, U.H.P., 99.99%) was used without further purification. Solid AgNCO was prepared by precipitation from aqueous mixtures of AgNO<sub>3</sub> and KOCN, and was thoroughly dried prior to use in the CINCO generator.

#### RESULTS

#### UV-VUV absorption spectrum of CINCO

As noted above, the ultraviolet absorption spectrum of CINCO for wavelengths above 200 nm was measured

by using a Heath 0.5 m spectrometer in conjunction with an absorption cell on line with the generator effluent. The absorption cell had a path length of 20 cm. Only a single absorption feature was evident in this region as shown in Fig. 1. The feature appears to be continuous in nature, within the 0.1 nm spectral resolution of the spectrometer, and is peaked near 250 nm. The intensity of the 250 nm band varied in proportion to the CINCO density, as monitored by the IR absorption intensity. If it is assumed that the Cl<sub>2</sub> flow was completely converted to CINCO on a 1:1 basis, an extinction coefficient can be assigned to this feature. This treatment yields  $\epsilon_{250}$  $(\text{decadic}) = 460 \text{ 1 mol}^{-1} \text{ cm}^{-1}$ . The continuous nature of the absorption suggests that photodissociation of CINCO can be conveniently accomplished by irradiation with a KrF laser at 249 nm.

Absorption spectra in the range from 120 to 300 nm were recorded by replacing the Heath spectrometer by an Acton Research 502V system. In this case, the absorption cell used was equipped with MgF<sub>2</sub> windows and had a path length of 4 cm. The spectrum obtained, with a resolution of about 5 nm, is also shown in Fig. 1. A second strong absorption was observed to begin near 210 nm, monotonically increasing in strength to below 160 nm. The extinction coefficient at 149 nm was determined to be  $\epsilon_{149}$  (decadic) =  $5.2 \times 10^3 1 \text{ mol}^{-1} \text{ cm}^{-1}$ , assuming unity yield of CINCO from the generator as noted above.

#### UV-visible emission from photolysis at 249 nm

KrF laser photolysis of the ClNCO/N<sub>2</sub> flow at a pressure of 4.0 Torr produced a deep blue emission easily visible to the eye. A preliminary observation of the time profile of the emission indicated it to have a duration of about 20  $\mu$ s after the laser pulse. Consequently, spectra were recorded for a time gate extending from 0.5 to 50  $\mu$ s after the pulse. The most intense portion of the spectrum measured is shown in Fig. 2. For the data shown, the spectral bandwidth of the monochromator was 1.0 nm. The observed features are easily identified as



FIG. 1. Absorption spectrum of gaseous CINCO. The extinction coefficients shown were calculated by assuming complete conversion of Cl<sub>2</sub> to CINCO in the generator. This assumption is supported by the fact that no Cl<sub>2</sub> absorption ( $\lambda_{max} = 330$  nm) was observed in the spectrum.



FIG. 2. Spectrum of NCO  $A^{2}\Sigma^{+} \rightarrow X^{2}\Pi$  emissions produced by 249 nm photolysis of a ClNCO/N<sub>2</sub> mixture. The data shown were taken for a time gate extending from 0.5 to 20  $\mu$ s after the laser pulse, and a ClNCO density of  $5 \times 10^{15}$  cm<sup>-3</sup>.

bands of the  $A^{2}\Sigma^{+} \rightarrow X^{2}\Pi$  transition in the NCO radical.<sup>18</sup> From the relative intensities of the bands, the  $A^{2}\Sigma^{+}$  excited state is populated primarily in very low vibrational levels.

No emission was found at wavelengths greater than 500 nm. In particular, no NCl  $b^{1}\Sigma^{+} \rightarrow X^{3}\Sigma^{-}$  emission in the visible region<sup>19</sup> was found. Similarly, bands of the  $B^{2}\Pi \rightarrow X^{2}\Pi$  transition in NCO<sup>20</sup> were unsuccessfully sought in the region of 300 nm. We note, however, that the gated integrator was not sensitive to emission occurring in the first 0.5  $\mu$ s after the laser pulse. Consequently, direct photofragments capable of relaxation by allowed radiative routes (such as the  $B^{2}\Pi$  state of NCO) would not have been observed.

Changes in the intensity of the NCO emission with variation of the incident laser fluence were investigated at  $\lambda = 438$  nm, near the  $00^{0}0 \rightarrow 00^{1}0$  band of the  $A^{2}\Sigma^{+} \rightarrow X^{2}\Pi$  spectrum. The data were recorded for a time gate from 0.5 to 50  $\mu$ s after the laser pulse. The laser fluence was varied over the range from 0.125 to 0.025 J cm<sup>-2</sup>. The data, shown in Fig. 3, indicate that the intensity varies linearly with the fluence. This behavior suggests that the excited NCO is produced by a process involving one photon, i.e., it may be generated directly by the photodissociation or by reaction of a photofragment with the parent CINCO.

The observed temporal profile of the NCO emission excludes the first of these two possibilities. A typical intensity vs time trace ( $\lambda = 438$  nm) is shown in Fig. 4. The trace indicates a very short rise followed by a decay over about 20  $\mu$ s. In view of the fact that the radiative rate of the  $A^{2}\Sigma^{+} \rightarrow X^{2}\Pi$  transition is  $2.71 \times 10^{6}$  s<sup>-1,21</sup> this long decay time is indicative of a collisional formation process. From the linear variation of the  $A \rightarrow X$  intensity



FIG. 3. Variation of the NCO  $A \rightarrow X$  intensity with the incident fluence of the KrF laser. The line shown is a linear least squares fit to the data.

with the laser fluence, a likely mechanism would be reaction of a photofragment with the parent CINCO. This hypothesis is further supported by the fact that, for a fixed CINCO density, the  $A \rightarrow X$  decay time was found to be invariant with the laser fluence. The rise of the NCO emission is then identified as reflecting a combination of collisional and radiative relaxation of NCO  $(A^{2}\Sigma^{+})$ , distorted by the finite risetime of the detection electronics (0.4  $\mu$ s).

The decay rate of the emission (i.e., the formation rate of excited NCO) was found to vary in proportion to the ClNCO density, which was controlled by variation of the Cl<sub>2</sub> flow through the generator and monitored by online measurement of the UV absorption at 250 nm. Figure 5 shows a plot of the decay rate vs the ClNCO density. The linearity of the plot and the intercept near the origin are indicative of a process which is pseudofirst order in ClNCO. The slope of the plot yields a rate constant  $k = 2.1 \pm 0.2 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

This rate constant corresponds to a process in which a photolysis fragment reacts with the parent CINCO, generating NCO ( $A^{2}\Sigma^{+}$ ) as a product. Hence, the fragment in question must carry sufficient energy for this process



FIG. 4. Time profile of the NCO  $A \rightarrow X$  emission produced by 249 nm photolysis of a CINCO/N<sub>2</sub> mixture. The density of CINCO for the data shown was 5.1  $\times$  10<sup>15</sup> cm<sup>-3</sup>.



FIG. 5. Plot of the decay rate of the NCO  $A \rightarrow X$  emission vs the density of CINCO. The line shown was obtained from a linear least squares fit to the data, yielding a pseudofirst order rate constant k = 2.1 $\pm 0.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

to be thermodynamically allowed and, further, it must have a lifetime long enough for collisions with CINCO to take place. The NCO  $A \rightarrow X$  time profile should in fact track the density of the photolysis product. The identity of the fragment was indicated by a series of experiments in which  $N_2O$  was added to the CINCO/ $N_2$  flow upstream of the photolysis cell. Admission of only small flows of N<sub>2</sub>O completely quenched the NCO  $A \rightarrow X$  emission. In its place, an intense spectrum of the well known NO  $\beta$ bands  $(B^{2}\Pi \rightarrow X^{2}\Pi)$  was found. Figure 6 shows a portion of the NO spectrum measured. The spectrum is dominated by an intense progression out of v' = 0 in the  $B^{2}\Pi$  state, with weaker bands from v' = 1 and v' = 2also being evident. The time profile of the NO emission indicated a short rise (close to the risetime of the electronics), followed by a decay over about 5  $\mu$ s for an N<sub>2</sub>O



FIG. 6. Spectrum of NO B  ${}^{2}\Pi \rightarrow X {}^{2}\Pi$  emission produced by 249 nm photolysis of a CINCO/N<sub>2</sub>/N<sub>2</sub>O mixture, for a time gate from 0.5 to 20  $\mu$ s after the laser pulse.

partial pressure on the order of 1.0 Torr. From these data, it can be inferred that the photofragment precursor of the NCO  $A \rightarrow X$  emission is electronically excited  $N(^{2}D)$  atoms. It is well known that reaction of  $N(^{2}D)$ atoms with N<sub>2</sub>O produces NO in the  $B^{2}\Pi$  state, followed by characteristic  $\beta$  band emission.<sup>22-24</sup> Addition of N<sub>2</sub>O to the CINCO system would thus result in quenching of the NCO  $A \rightarrow X$  emission, as observed, by removal of the  $N(^{2}D)$  precursor.  $N(^{2}D)$  atoms are metastable and hence can suffer many collisions with the CINCO parent. Hence, we suggest the following processes to account for the observed NCO  $A \rightarrow X$  emission

$$\operatorname{CINCO} \frac{h\nu}{249} \operatorname{Cl} + \operatorname{N}(^2D) + \operatorname{CO}, \qquad (1)$$

$$N(^{2}D) + CINCO \rightarrow NCI + NCO (A^{2}\Sigma^{+}).$$
 (2)

#### Infrared emission from photolysis at 249 nm

Reaction (2) suggests that  $N(^{2}D)$  either abstracts the chlorine atom from CINCO or, more likely, attacks the NCO chain, forming a complex which eliminates NCl. It seems possible that, in such a process, the NCl might itself be generated in an excited state. As noted above, however, no NCl  $b^{1}\Sigma^{+} \rightarrow X^{3}\Sigma^{-}$  emission was found in the spectra measured. In order to search for emission from the lower lying  $a^{-1}\Delta$  state of this molecule, a germanium detector was used to probe the near IR region. The 0, 0 band of the strongly forbidden  $a^{-1}\Delta \rightarrow X^{-3}\Sigma^{-1}$ transition in NCl lies at 1.077  $\mu$ m,<sup>19</sup> in the region of high sensitivity of this detector. A portion of the spectrum measured is shown in Fig. 7. No indication of NCl  $a \rightarrow$ X emission is evident. A number of features were found,



FIG. 7. A portion of the near IR emission produced by 249 nm photolysis of a CINCO/N<sub>2</sub> mixture. The 0, 0 band of the NCI  $a^{-1}\Delta \rightarrow$  $X^{3}\Sigma^{-}$  system (1.077  $\mu$ m) is not present. The feature near 1.10  $\mu$ m is tentatively assigned as the 0, 0 band of the CN  $A^{2}\Pi \rightarrow X^{2}\Sigma^{+}$  system. The feature near 1.04  $\mu$ m may be the 0, 0 band of the N<sub>2</sub> first positive system.

however, the most prominent of these occurring at 1.10 and 1.04  $\mu$ m, as shown. The intense 1.10  $\mu$ m feature (and two other bands observed) can be tentatively assigned to the  $A^{2}\Pi \rightarrow X^{2}\Sigma^{+}$  transition in CN, the 1.10  $\mu$ m feature corresponding to the 0, 0 band of this system. The 1.04  $\mu$ m feature could be the 0, 0 band of the  $B^{3}\Pi_{g} \rightarrow A^{3}\Sigma_{u}^{+}$  (first positive) transition in N<sub>2</sub>. Although weaker features possibly attributable to other bands of this transition were found in the near IR, no bands of this system were observed in the visible region.

Electronically excited CN or  $N_2$  could be produced in the ClNCO system by second order processes as follows:

$$N(^{2}D) + NCO \rightarrow N_{2} + CO, \qquad (3)$$

$$N(^{2}D) + NCO \rightarrow CN + NO.$$
 (4)

Reactions (3) and (4) release energy easily sufficient for population of the N<sub>2</sub> ( $B^{3}\Pi_{g}$ ) or CN ( $A^{2}\Pi$ ) states, respectively. In order to further investigate this point, the variation of the intensity of the 1.10  $\mu$ m band with the incident laser fluence was measured in a manner similar to that described above. The data indicated that the intensity increased nonlinearly with the laser fluence, as would be the case if the emission were produced by a reaction such as Eq. (4) above, since one photon would be required to generate each of the reagents N(<sup>2</sup>D) and NCO.

#### DISCUSSION

From the data, it may be inferred that reactions (1) and (2) lead to the generation of excited NCO (A  ${}^{2}\Sigma^{+}$ ) in the CINCO system. Excited  $N(^{2}D)$  atoms can be generated directly by the photodissociation, or by predissociation of excited NCl or NCO generated as a direct fragment. For example, the initial fragments might be excited singlet NCl and ground state (singlet) CO, or ground state chlorine atoms and excited doublet NCO. Both pathways are spin allowed and have been observed to occur in other isocyanates and azides.<sup>12,15,25</sup> Predissociation of excited singlet NCl seems unlikely in the present case, however, in view of the fact that no  $b^{1}\Sigma^{+} \rightarrow X^{3}\Sigma^{-}$  or a  ${}^{1}\Delta \rightarrow X {}^{3}\Sigma^{-}$  emission from this molecule was observed. If excited singlet NCl were produced, some population of the lower lying  $b^{-1}\Sigma^+$  or  $a^{-1}\Delta$  states might well be expected, either directly or by cascade. On the other hand, recent work by Sullivan et al.9 has shown that excited NCO (B  $^{2}\Pi$ ) predissociates to N( $^{2}D$ ) and CO  $(X^{-1}\Sigma^{+})$  from its lower vibrational levels, by interaction with a repulsive curve  $({}^{2}\Sigma^{-})$  correlating to these products.<sup>20</sup> Hence  $N(^{2}D)$  might arise from production of NCO  $(B^{-2}\Pi)$  in these levels. As noted above, NCO  $B \to X$ emission generated by direct production of the  $B^2\Pi$  state would not have been observed in our system because of the constraints of the detection electronics. Direct production of  $N(^{2}D)$  could arise from photodissociation of CINCO to NCO  $(^{2}\Sigma^{-})$  or to NCO  $(X^{2}\Pi)$  above its dissociation limit.

Spin-allowed dissociation of an excited singlet state of CINCO at the N-C bond could produce excited singlet NCl and ground state CO  $(X^{1}\Sigma^{+})$ , or ground state NCl  $(X^{3}\Sigma^{-})$  and excited triplet CO. Since no emission from excited singlet states of NCl was found, and excited triplet states of CO are likely to be inaccessible, initial fragmentation at the C-N bond would not appear to be a major route. Hence, the branching fraction for spin-allowed paths producing doublet fragments, i.e., Cl + NCO or Cl + N(<sup>2</sup>D) + CO, may well be high. In view of the many ways that the available energy might be partitioned among accessible states of NCO, however, it seems unlikely that the yield of N(<sup>2</sup>D) is high.

Regardless of the actual photodissociation mechanism, Eq. (1) above sets a lower limit on the heat of formation of gaseous CINCO:

$$\Delta H_f(\text{CINCO}) \ge \Delta H_f(\text{CI}) + \Delta H_f[\text{N}(^2D)] + \Delta H_f(\text{CO}) - h\nu (249 \text{ nm}).$$

This treatment yields  $\Delta H_f$  (CINCO)  $\geq 52.9$  kcal mol<sup>-1</sup>. This value is to be compared with  $\Delta H_f$  (CIN<sub>3</sub>)<sup>26</sup> = 93.2 kcal mol<sup>-1</sup>,  $\Delta H_f$  (BrN<sub>3</sub>)<sup>3</sup>  $\geq 131$  kcal mole<sup>-1</sup>, and  $\Delta H_f$  (HNCO)<sup>9</sup>  $\geq -14.3$  kcal mol<sup>-1</sup>. Clearly, the present results indicate that replacement of the hydrogen atom in HNCO by chlorine destabilizes the molecule considerably. Further, the data are in accord with the observed greater chemical stability of the halogen isocyanates relative to the halogen azides.

Equation (2) above gives the collision process responsible for the generation of NCO ( $A^{2}\Sigma^{+}$ ). From the limit for  $\Delta H_{f}$  (CINCO), the energy released by process (2) is  $\geq 99.5$  kcal mol<sup>-1</sup>, easily sufficient for the generation of NCO ( $A^{2}\Sigma^{+}$ ), which lies 65.3 kcal mol<sup>-1</sup> above NCO ( $X^{2}\Pi$ ). The  $B^{2}\Pi$  state of NCO is also accessible, but such a process would require that nearly all the energy released be directed into electronic excitation of the NCO product. The rate constant measured for reaction (2) would appear to be reasonable for a process involving N(<sup>2</sup>D) atoms. The rate constant for the reaction of N(<sup>2</sup>D) with Cl<sub>2</sub> has been reported to be  $k = 3.6 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, about four orders of magnitude greater than the rate constant for reaction of N(<sup>4</sup>S) atoms with Cl<sub>2</sub>.<sup>27</sup>

From the value of  $\Delta H_f$  (ClNCO) inferred from the data, the energetics of the decomposition of CINCO to the ground states of NCl and CO can be considered. The enthalpy change for this process is calculated to be  $\leq$  -8.2 kcal mol<sup>-1</sup>. Hence, CINCO, like the halogen azides, is a metastable species with respect to dissociation processes forming the nitrene. The perturbation by the chlorine atom is clearly very strong relative to the perturbation in HNCO. The ground state of HNCO lies about 55 kcal mol<sup>-1</sup> below the ground states of NH and CO.<sup>9</sup> A similar treatment of the process  $CINCO \rightarrow Cl(^{2}P) + NCO$  $(X^{2}\Pi)$  yields a value  $\Delta H \leq +24$  kcal mol<sup>-1</sup>. This result is in reasonable accord with the fact that the N-Cl bond lengths in ClN<sub>3</sub> and ClNCO are nearly equal.<sup>7,8</sup> The N-Cl bond strength in  $ClN_3$  has been reported<sup>26</sup> to be near 32 kcal mol<sup>-1</sup>.

The data indicate that the photolysis of CINCO at 249 nm offers a unique pulsed source of N(<sup>2</sup>D) atoms. Since the NCO  $(A \rightarrow X)$  emission in the system tracks

the decay of the excited nitrogen atoms, it can be used as a convenient measure of their kinetic behavior. In principle, real time measurements of the kinetics of reactions or energy transfer processes involving  $N(^2D)$ can be made for species compatible with CINCO.

### ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHE-8210533.

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