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Low-Temperature Infrared Study of Intermediates in the Photolysis of HNCO and DNCO†

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HNCO and DNCO suspended in Ar and in N_2 matrices at 4° and at 20°K are shown to yield upon photolysis the corresponding tautomers, HOCN and DOCN, for which vibrational assignments are proposed. HOCN may be produced by recombination at the O atom of H+NCO produced in a primary photolytic rupture of the N–H bond, as well as by the attack of NH ($^3\Sigma^-$) on the carbon–oxygen bond of CO, giving an unstable cyclic intermediate.

INTRODUCTION

EARLIER speculation regarding the order of atoms in the species HNCO was ended by the studies of Herzberg and Reid[1] on the infrared spectrum of this substance in the vapor phase. Their work established that the species is indeed isocyanic acid (HNCO) rather than the tautomer, cyanic acid (HOCN). More recently, several studies of the microwave spectrum of HNCO have yielded structural parameters for this species. These investigations have very recently been supplemented by the millimeter wave spectral studies of Kewley, Sastry, and Winnewisser[2] who have derived very accurate structural constants for both HNCO and DNCO.

Woo and Liu[3] have shown that isocyanic acid vapor has diffuse ultraviolet absorption bands between 2570 and 2250 Å, with continuous absorption below 2240 Å. The mechanism of the photodecomposition of HNCO is not yet completely established, although it has been found that the predominant primary photolysis reaction produces NH+CO, in complete analogy to the photolytic rupture of the isoelectronic species CH_2CO to produce CH_2+CO and of the species HN_3, also isoelectronic, to produce $NH+N_2$. Under identical experimental conditions, Dixon has found the flash photolysis of HNCO to a suitable source of the free radicals NH[4] and NCO[5] for careful ultraviolet spectral analysis. Significant quantities of NH_2 were also found in these studies. Mui and Back[6] have recently reported kinetic studies on the photolysis of isocyanic acid vapor, supporting the supposition that the primary photolytic process is

$$\mathrm{HNCO}+h\nu\rightarrow\mathrm{NH}+\mathrm{CO}, \qquad (1)$$

with a secondary reaction,

$$\mathrm{NH}+\mathrm{HNCO}\rightarrow\mathrm{NH_2}+\mathrm{NCO}, \qquad (2)$$

responsible for the NH_2 and NCO radicals also observed by Dixon.

The matrix isolation technique appears to be very well suited to an experimental study of the primary photolytic process for HNCO, since in an inert matrix secondary reactions such as (2) should be minimized. It is anticipated that recombination of NH with CO within the "cage" in which they are produced should occur readily, just as has been found for the matrix recombination of CH_2 with CO to form ketene. However, if the primary photolytic reaction,

$$\mathrm{HNCO}+h\nu\rightarrow\mathrm{H}+\mathrm{NCO}, \qquad (3)$$

occurs to an appreciable extent, the relatively mobile H atom should have some chance of escaping the "cage," possibly leading to the stabilization of the free radical NCO in sufficient concentration for infrared study. Milligan and Jacox[7] have previously demonstrated that in the system $Ar:O_2:HI$ photolytically produced H atoms can escape the "cage" in which they are produced, reacting with O_2 in matrix sites sufficiently far removed from the remaining I atom to permit stabilization of the free radical HO_2. The results of the application of the matrix isolation technique to an infrared spectroscopic study of the products of the photolysis of HNCO and DNCO are communicated in the following discussion.

EXPERIMENTAL DETAILS

HNCO was prepared by strongly heating a sample of its cyclic trimer, cyanuric acid, in a quartz tube incorporated in an evacuated system. It has been found that the presence of water vapor encourages polymerization of the resulting sample. HNCO monomer appears to be quite stable either as a dry vapor or frozen for storage at the temperature of liquid nitrogen. Although HCN and NH_3 impurities have previously been reported as resulting in this procedure, NH_3 was not detected in the matrix isolation spectrum of the resulting HNCO, and only small amounts of HCN could be detected.

Two techniques were employed to produce DNCO

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[1] G. Herzberg and C. Reid, Discussions Faraday Soc. **9**, 92 (1950); C. Reid, J. Chem. Phys. **18**, 1544 (1950).

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[5] R. N. Dixon, Phil. Trans. Roy. Soc. (London) **A252**, 165 (1960).

[6] J. Y. P. Mui and R. A. Back, Can. J. Chem. **41**, 826 (1963).

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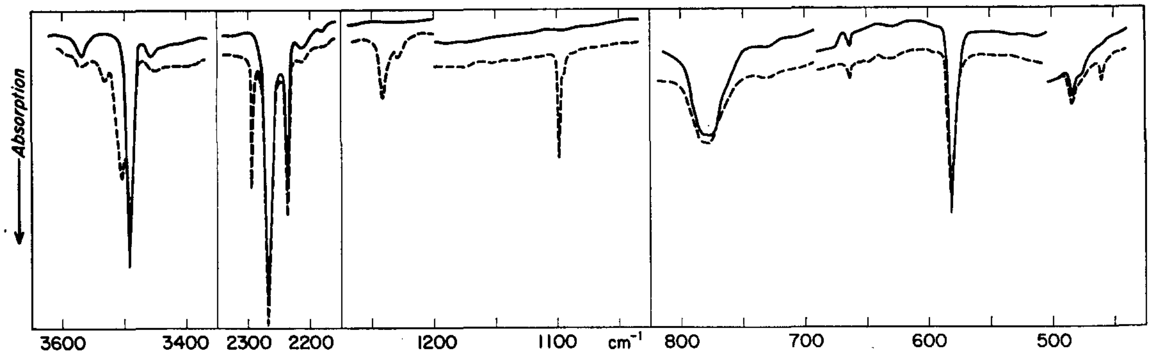

FIG. 1. N_2:HNCO=150. 4°K. ——, before photolysis; ----, after 2-h photolysis through Suprasil.

for the present experiments. HNCO very readily undergoes deuterium exchange with D_2O present in the system. Indeed, more than half of the HNCO in an Ar:HNCO mixture can be converted to DNCO by exchange with D_2O adsorbed on the glass walls of the sample preparation and deposition system. In some experiments DNCO was directly produced by thermal decomposition of a sample of cyanuric acid which had been recrystallized from a hot solution in D_2O.

The samples used for the matrix isolation experiments were prepared using standard manometric techniques. Typical mole ratios Ar (or N_2):HNCO (or DNCO) ranged between 100 and 300, with a deposit of about 50 micromoles of HNCO (or DNCO) on the cold window.

The cryostat used for these experiments is similar in principle to that described by Milligan.[8]

Observations were made at 4° and at 20°K, using liquid helium and liquid hydrogen, respectively, as coolants.

Photolysis was conducted by direct irradiation through a barium fluoride or sodium chloride window, permitting transmission of an appreciable fraction of the output in the effective spectral region beyond 2240 Å of a medium-pressure mercury lamp (General Electric AH-4) from which the outer glass casing had been removed. Since infrared spectral observations beyond the low frequency cutoffs of barium fluoride and sodium chloride were important, for some of the photolyses the cryostat base was rotated about its O-ring flange to bring an auxiliary sapphire or Suprasil window into position for direct irradiation of the sample. Following photolysis, the cryostat base was rotated back to its normal position for observation of the sample through potassium bromide windows. Photolysis periods of several hours were commonly employed.

Spectra in the range 400–4000 cm^{-1} were recorded on a double beam, prism-grating spectrometer (Beckman IR-9). Under the conditions of a typical experiment, the resolution and frequency accuracy are both approximately 1 cm^{-1} throughout the spectral range studied.

OBSERVATIONS

Regions of interest in the spectra of HNCO and DNCO suspended in N_2, scanned before and after photolysis, are shown in Figs. 1 and 2, respectively. Figure 3 shows a similar study on a mixture of HNCO and DNCO suspended in Ar. Details of the initial spectra, themselves of considerable interest, will be the subject of a separate communication. Of present concern are the several sharp absorptions which appear following photolysis. All of these absorptions continue to grow in intensity upon prolonged photolysis. They have been observed to disappear when the sample is permitted to warm to a temperature at which diffusion through the matrix is known to occur. Frequencies observed for these new absorptions, together with the assignment proposed in the following discussion, are summarized in Table I.

The region below 550 cm^{-1} was not observed in the Ar matrix experiments.

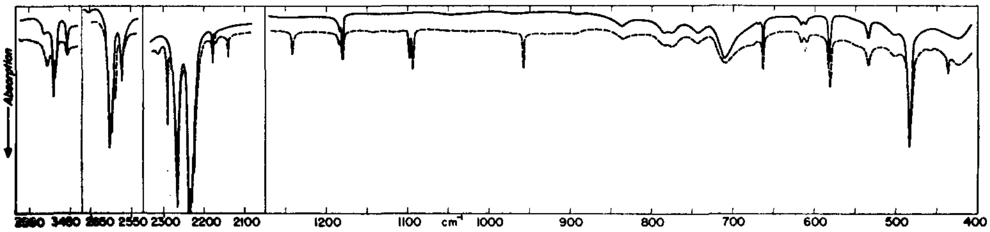

FIG. 2. N_2:DNCO=100. 20°K. ———, before photolysis; ----, after $6\frac{3}{4}$-h photolysis through small sapphire window.

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[8] D. E. Milligan, J. Chem. Phys. **35**, 1491 (1961).

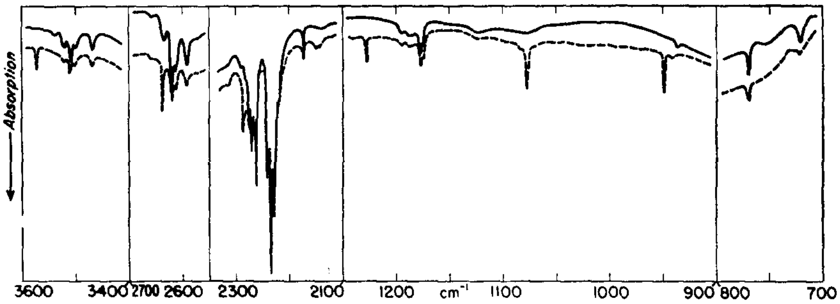

FIG. 3. Ar:(HNCO+DNCO)=100. 20°K. ——, before photolysis; – – – –, after 95-min photolysis through BaF_2.

In addition to the absorptions given in Table I, a weak absorption appears near 2140 cm^{-1}, contributed by small amounts of CO produced during photolysis.

Small frequency shifts are noted in comparing the results of argon and nitrogen matrix experiments. In general, the best photolytic yields have been obtained in the nitrogen matrix experiments conducted at 20°K. This observation may be attributed to greater mobility of the reactive fragments under these conditions. It is important to note that there are also marked variations in the relative intensities and bandwidths of several of the product absorptions depending on whether argon or nitrogen is the matrix material. For example, the 3572 and 2635 cm^{-1} absorptions appearing in the Ar:HNCO and Ar:DNCO experiments, readily recognized as contributed essentially by an X–H stretching vibration, are markedly lowered in frequency in the nitrogen matrix experiments. The 1228 and 949 cm^{-1} absorptions, apparently contributed by H and D bending modes, respectively, are appreciably broadened in the nitrogen matrix experiments, although their frequencies are relatively little affected. Such behavior has often been observed for modes contributed largely by H motions and is ascribed to hydrogen bonding with the nitrogen matrix.

A bluish-purple glow has been observed when the sample is warmed to a temperature at which diffusion through the matrix can occur. A similar phenomenon appears to be characteristic of systems in which the species NH is present. Although this observation suggests that a small concentration of NH may be stabilized in the matrix in the present experiments, the identification cannot be regarded as conclusive.

DISCUSSION

Evidence supports the assignment of all the absorptions given in Table I to a single relatively unstable species produced during photolysis. Although CO has also been identified as a product of the photolysis, it is not present in sufficient concentration to permit infrared spectral observation of NH, whose vibrational fundamental has recently been identified by Milligan and Jacox,[9] or of products of the reaction of NH with itself or with HNCO. Only limited diffusion of NH is to be anticipated under the conditions of these experiments. Since all of the new absorptions show at least a small spectral shift in the deuterated experiments, the possibility that some of them are contributed by NCO is excluded.

The 3572 cm^{-1} absorption appearing following photolysis of the Ar:HNCO system is much too high in frequency to be ascribed to a C–H stretching motion and is somewhat high for an N–H stretching motion, although Milligan and Jacox[10] have identified the N–H stretching mode of HNC at 3583 cm^{-1}. It appears most likely that this 3572 cm^{-1} absorption is contributed by an O–H stretching mode, for which it is in a suitable range. Its counterpart in the Ar:DNCO system at 2635 cm^{-1} shows a reasonable isotopic shift for such a mode. The 1228 and 949 cm^{-1} absorptions in the Ar:HNCO and Ar:DNCO systems, respectively, are suitably placed for the O–H and O–D bending modes. These two absorptions each have a weak lower frequency satellite in the argon matrix, and each is somewhat broadened in the nitrogen matrix. The absorption near 2290 cm^{-1} in each of the experiments, furthermore, is in the position anticipated for a C≡N stretching

TABLE I. Frequencies (cm^{-1}) observed following photolysis of HNCO and DNCO.

Ar:HNCO	N_2:HNCO	Ar:DNCO	N_2:DNCO	Assignment
	438?			
	460		437	OCN deformation
		949	957	OD bend
1080	1098	1078	1093	O–C stretch
1228	1241			OH bend
2288	2294	2285	2292	C≡N stretch
3572	3506*s*	2635	2590	O–H (O–D) stretch
	3530*w–m*			

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[9] D. E. Milligan and M. E. Jacox (to be published).

[10] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **39**, 712 (1963).

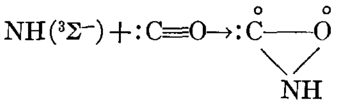
mode. These data strongly suggest that the new species is H–O–C≡N. On this supposition, the remaining assignments given in Table I appear reasonable. The 1080 cm^{-1} absorption is within the expected region for a C–O stretching mode. The assignment of one of the O–C≡N deformations at 460 and at 437 cm^{-1} for HOCN and DOCN, respectively, falls within the anticipated region for such a mode. The H–C≡N and D–C≡N bending frequencies are at 712 and 569 cm^{-1}, respectively. The doubly degenerate C–C≡N bending mode of CH_3–C≡N appears at 361 cm^{-1},[11] and the corresponding vibration of CD_3–C≡N falls at 335 cm^{-1}.[12]

An elementary consideration of the molecular orbitals involved in the bonding between an O–H group and a C≡N group suggests that the O–C≡N group of HOCN is linear and that the H atom is somewhat displaced from the molecular axis. Such a structure would require five normal vibrations in which the planar symmetry of the molecule is preserved and one, an OCN deformation, in which the atoms move perpendicular to the molecular plane. Apparently, one of the OCN deformation modes is sufficiently low in intensity to have escaped detection in the present experiments.

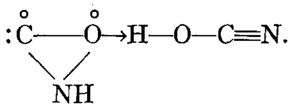
The mechanism by which HOCN is produced in the matrix is of considerable interest. It is easy to envision its production if reaction (3) occurs as a primary photolytic process. There would then be a finite probability that the H atom, instead of leaving the "cage" or recombining with the N atom following loss of energy by matrix collisions, would combine with the O atom, resulting in the species HOCN. Production of HOCN at least in part by this mechanism cannot be excluded. However, it is noteworthy that even on prolonged photolysis no absorptions assignable to the free radical NCO appear, although H atoms should in some instances succeed in leaving the "cage" in which they are produced.

The second possible mechanism involves the initial photolytic production of NH, as in Reaction (1). It is well established that this reaction occurs. Furthermore, an independent experiment involving the photolysis of an Ar:CO:HN_3 mixture has produced good yields of both HNCO and HOCN. Since during the relatively brief period of photolysis employed in this experiment very little HOCN could have been produced by secondary photolysis of the product HNCO, it is necessary to consider the mechanism by which NH may attack CO to produce HOCN.

The attack of NH on the "lone pair" of electrons which, according to the molecular orbital treatment of Moffitt,[13] is associated with the C atom of CO would, of course, yield HNCO. Attack of NH at the O atom would be expected to lead to the species HNOC. Since the species HOCN appears to account for all of the absorptions (other than those of HNCO) in this system, it must be concluded that, if HNOC is produced, it readily undergoes rearrangement in the matrix. The remaining possibility, involving attack of NH on the carbon–oxygen bond, appears to provide a more likely route for the formation of HOCN. Milligan and Jacox[9] have recently demonstrated that NH produced by the photolysis of HN_3 in an Ar or N_2 matrix is readily deactivated to its ground $^3\Sigma^-$ state. Triplet NH would be expected to attack a multiple bond to produce an unstable cyclic intermediate, as illustrated by the attack of NH on the isoelectronic species acetylene, studied by Jacox and Milligan.[14] Thus, Reactions (4) and (5) could lead to the observed HOCN:



(4)



(5)

The rearrangement in Reaction (5) is, of course, more complicated than the over-all reaction shown above, and a competing rearrangement to HNCO could contribute to the appreciable fraction of HNCO produced in the Ar:CO:HN_3 photolysis. However, the initial presence of a lone pair of electrons plus an unpaired electron on the C atom may facilitate the formation of a C≡N bond.

CONCLUSIONS

The photolysis of HNCO suspended in an inert matrix leads to the production of the unstable tautomer HOCN, for which a plausible vibrational assignment is suggested. Experiments on the deuterated system support the identification of HOCN and permit a corresponding vibrational assignment for DOCN. Two mechanisms may contribute to the production of the observed HOCN; this species may be produced by the recombination of H+NCO produced in a primary photolytic rupture of the N–H bond, or it may result from the attack of NH($^3\Sigma^-$) on the carbon–oxygen bond of CO, producing an unstable cyclic intermediate which may rearrange to give HOCN.

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