# Reaction between Hydrocyanic Acid and $O(^{1}D_{2})$ or $O(^{3}P)$ Oxygen Atoms in **Low-Temperature Matrices**

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The reactions of hydrocyanic acid with both excited and ground-state oxygen atoms have been examined in low-temperature matrices. The major products of HCN +  $O(^{1}D_{2})$  reaction were isocyanic acid (HNCO) and cyanic acid (HOCN), confirming predictions of the intermediacy of HNCO and oxazirine on the pathway to the final products seen in the gas-phase reaction. In contrast, no evidence was found for reaction between HCN and  $O(^{3}P)$  atoms in the matrix.

#### Introduction

The reaction between oxygen atoms and HCN is thought to be the most important oxidation process for HCN in both the atmosphere<sup>1</sup> and in combustion systems.<sup>2</sup> Several gas-phase studies have examined both the kinetics and final products of the HCN + O-atom reaction; these can be conveniently divided into reactions involving electronically excited oxygen atoms,  $O(^{1}D_{2})$ , and ground-state oxygen atoms,  $O(^{3}P)$ .

 $HCN + O(^{1}D_{2})$ . Several possible spin-conserving pathways for this reaction have been suggested by Carpenter et al.:<sup>3</sup>

$$HCN + O(^{1}D_{2}) + \dot{O}H(x^{2}\Pi) + \dot{C}O(x^{2}\Sigma^{+}) + \Delta H_{f}^{298}/kJmol^{-1} = -1953 (1)$$

$$HCN + O(^{1}D_{2}) + \dot{O}H(x^{2}\Pi) + \dot{O}N(x^{2}\Sigma^{+}) + \Delta H_{f}^{298}/kJmol^{-1} = -99.6 (3)$$

$$+ \dot{O}H(x^{2}\Pi) + \dot{O}N(x^{2}\Pi) + \Delta H_{f}^{298}/kJmol^{-1} = +10.9 (4)$$

$$+ H(^{2}S_{1/2}) + N\dot{O}O(x^{2}\Pi) + \Delta H_{f}^{298}/kJmol^{-1} = -197 (5)$$

Laser induced fluorescence techniques have been used to monitor products of the HCN and  $O(^{1}D_{2})$  reaction, where  $O(^{1}D_{2})$  was produced from 248-nm photolysis of  $O_3$ . The detected primary products were NH( $a^{1}\Delta$ ), OH( $X^{2}\Pi$ ), and CN( $X^{2}\Sigma^{+}$ ). NCO( $X^{2}\Pi$ ) and NH( $X^{3}\Sigma^{-}$ ) were also seen but apparently arise from secondary processes. In summary, only channels 1 and 3 are observed, of which reaction 1 is the more important, contributing about 90% of the products.

The mechanism by which products are reached was proposed to involve an HNCO intermediate. This is formed by rearrangement of oxazarine, the product of  $O(^{1}D_{2})$  addition to the  $\pi$  bond of HCN:

$$O(^{1}D_{2}) + HC \equiv N \longrightarrow H - C = N$$
 (6)

$$HNCO \rightarrow NH(a^{1}\Delta) + CO(X^{1}\Sigma^{+})$$
 (8)

Predictions of the intermediacy of HNCO in the HCN +  $O(^{1}D_{2})$ reaction are also based on observation of dissociation processes in HNCO photolysis. Suitable wavelength irradiation of HNCO is found to result exclusively in the production of  $NH(a^{1}\Delta)$  +  $CO(X^1\Sigma^+)$ ;<sup>4-7</sup> these products are also found in the reaction between HCN +  $O(^{1}D_{2})$ . In both cases NCO, which may arise through the exothermic channel (5), is not observed. This suggests strongly that the HCN +  $O(^{1}D_{2})$  reaction proceeds via the same electronically excited HNCO molecule that is formed upon photolysis. Dissociation of the intermediate occurs preferentially by the breaking of a weak C-N bond in the excited state, rather than a strong C=N double bond in the ground state.<sup>3</sup>

 $HCN + O({}^{3}P)$ . The possible products and calculated energies for the reaction between HCN and O(<sup>3</sup>P) are<sup>8</sup>

$$H + N\dot{C}O \Delta H_f^{298}/kJmol^{-1} = -25 \quad (9)$$

$$O(^{3}P) + HCN - CO + NH \Delta H_{t}^{298}/kJmol^{-1} = -146$$
 (10)

 $\rightarrow$  OH + CN  $\Delta H_{4}^{230}$ /kJmol<sup>-</sup> = +75 (11)

A series of gas-phase studies9-12 have shown that the products from this reaction arise mainly through channel 9, with channel 10 providing the balance except at higher temperatures where the endothermic channel 11 becomes more important. In this case reaction 11 occurs via an H-atom abstraction by O(<sup>3</sup>P) atoms. The two exothermic channels, on the other hand, are predicted to proceed via the intermediacy of a complex formed upon addition of  $O(^{3}P)$  to HCN. This predicted intermediate is NCHO, which is formed by insertion of O(<sup>3</sup>P) into the  $\pi$  bond of HCN. Insertion at the carbon end is energetically more favorable than at the nitrogen end and results in <sup>3</sup>NHCO formation.<sup>9</sup> This species may then dissociate directly to H + NCO or may rearrange by H-atom migration to form HNCO, which itself may dissociate to either NH + CO or H + NCO. The formation of H + NCO from <sup>3</sup>HNCO involves a smaller activation energy than is required for NH + CO. Thus kinetic arguments can explain why NCO + H is the dominant channel despite the fact that it is less exothermic than reaction 10.

In order to simplify product analysis and also to positively identify intermediate species, the reaction between HCN and O atoms [both  $O(^1D_2)$  and  $O(^3P)$ ] has been carried out in an inert matrix at 4.2 K. Under these conditions complications arising from secondary reactions can be minimized and intermediates may be stabilized sufficiently to enable direct infrared spectroscopic examination.

#### **Experimental Section**

The experimental procedure is described in detail elsewhere<sup>13</sup>

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Figure 1. FTIR spectra of HNCO formed in argon matrix after  $O(^{1}D_{2})$ + HCN reaction.

and is only briefly recounted here. Matrices were prepared by the pulsed deposition of 2-L gas mixtures containing HCN either diluted in a matrix gas (Ar or Ne) doped with NO<sub>2</sub> or N<sub>2</sub>O or mixed with pure oxygen. Between 100 and 150 pulses of the mixture were deposited over a period of approximately 1 h onto a CsI window held at 4.2 K by an Air Products Heliplex Model CS 308 closed-cycle cryogenic refrigeration system. Infrared spectra of the matrices were obtained on a Digilab FTS-20V FTIR spectrometer using an MCT detector at 77 K. The spectra shown in Figure 1 are the result of the coaddition of 1000 scans with boxcar apodization.

Accurate measurement of partial pressures of the gases was obtained on an MKS Instruments Inc. Baratron capacitance manometer (Model 310, 0-1 Torr) and a Wallace Tiernan precision dial manometer (Model FA 141, 0-1000 Torr), both attached to a mercury free vacuum line fitted with greaseless stopcocks.

Photolysis of the matrix was carried out at wavelengths of either 184.9, 253.7, or  $\lambda > 300$  nm. Photolysis at 184.9 and 253.7 nm was carried out with a Philips Model 93109 E low-pressure mercury lamp with quartz shroud. For 184.9-nm photolysis the lamp and immediate environment were flushed with nitrogen to prevent absorption of this line by atmospheric oxygen; the 253.7-nm line was not filtered out. Photolysis at  $\lambda > 300$  nm was carried out with light filtered by Pyrex glass from an Applied Photophysics 250-W medium-pressure mercury lamp. Argon and neon (Messer Griesheim GmbH, 99.999% stated purity) were passed through a glass spiral immersed in liquid nitrogen before use. Oxygen (Messer Griesheim GmbH) was passed through the same spiral immersed in a solid  $CO_2$ /acetone bath. HCN was prepared by the dropwise addition of concentrated sulfuric acid to potassium cyanide in an evacuated bulb. HCN evolved from the ensuing reaction was degassed at both 77 and 193 K before drying on a column of fresh  $P_2O_5$ . Infrared spectra of HCN revealed only small traces of CO<sub>2</sub> impurity.

### Results

 $HCN + O(^{1}D_{2})$ . In order to observe the products of this reaction, matrices containing HCN/N<sub>2</sub>O/Ar in the ratio 1/1/1000 were photolyzed for 9 h at 184.9 nm. (The 253.7-nm line is also present but not absorbed by HCN or N<sub>2</sub>O.) At this wavelength formation of both  $O({}^{3}P)$  and  $O({}^{1}D_{2})$  from N<sub>2</sub>O are energetically feasible. However, previous results have shown that O atoms thus produced are exclusively in the  $O(^{1}D_{2})$  electronic state.<sup>14</sup>

Table I shows the product absorptions arising from such an experiment. The strongest band in the spectrum is that at 2259.6 cm<sup>-1</sup> assigned by comparison to the directly deposited sample of Bondebey et al.<sup>15</sup> as the  $v_2$  vibration of HCNO. Bands at 771.2  $(v_4)$  and 573.5  $(v_5)$  are also assigned to HNCO. Those at 2286.4,

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TABLE I:	<b>Products from</b>	184.9-nm	Photolysis o	of Matrices
Containing	HCN/N <sub>2</sub> O/Ar	in the Ra	tio 1/1/1000	0

freq/cm <sup>-1</sup>	assignt	lit. value <sup>a</sup>	
2286.4	HOCN	2294	
2266.9	HNCO		
2260.6	HNCO		
2259.2	HNCO	2259.8	
2139.6	CO	2138.6	
1872.0	NO	1876.0	
1863.5	(NO) <sub>2</sub>	1863.6	
1775.6	$(NO)_2$	1775.9	
1623.7	H <sub>2</sub> O		
1242.8	HOCN		
1235.5	HOCN		
1228.1	HOCN		
1225.7	HOCN	1227	
1089.7	HOCN		
1084.9	HOCN		
1082.9	HOCN	1082	
771.2	HNCO	769.7	
578.6	HNCO		
573.5	HNCO	572.9	
564.1	HNCO		

<sup>a</sup>See text for references.



Figure 2. FTIR spectra of HOCN formed in argon matrix after  $O(^{1}D_{2})$ + HCN reaction.

1225.7, and 1082.9 cm<sup>-1</sup> are HOCN absorption bands. The band at 1242.8 cm<sup>-1</sup> is close to the frequency of the  $v_3$  vibration of HCNO, but the absence of strong bands at 2193.2 and 3317.9 cm<sup>-1</sup> for this molecule rules out this assignment. The only other products are NO,  $(NO)_2$ , and CO. NO and  $(NO)_2$  are both products of N<sub>2</sub>O photolysis in a matrix.<sup>13</sup> The presence of CO may be explained in two ways: it may arise as a product of HCN + O reaction or it may be the result of  $CO_2$  photolysis, where  $CO_2$ is present due to an atmospheric leak onto the surface of the matrix during the long photolysis period. The fact that no other fragments such as OH, NH, NCO, or CN are observed<sup>16,17</sup> tends to rule out the first possibility, whereas the presence of a strong broad band at ca. 2250  $\text{cm}^{-1}$ , due to nonisolated CO<sub>2</sub>, suggests that the second explanation is the more likely.

Those bands italicized in Table I are the strongest where more than one arises in the region of a fundamental. The others may be assigned either to (i) molecules in close proximity to either HCN or N<sub>2</sub>O in the matrix, or (ii) the result of HNCO rotation in the Ar matrix, a process that has been previously observed.<sup>18</sup> The fundamental absorptions of HNCO and HOCN are shown in Figures 1 and 2.

 $HCN + O({}^{3}P)$ . Matrices containing HCN/NO<sub>2</sub>/Ar in the ratios of 1/1/1000 were photolyzed at 253.7 nm for several hours. At this wavelength the primary process is the production of NO and O(<sup>3</sup>P) from NO<sub>2</sub>.<sup>14</sup> Alternatively, matrices containing HCN

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diluted in pure oxygen were photolyzed by the filtered light from a medium-pressure mercury lamp. The following processes are expected to occur in the matrix, under these conditions:

$$(O_2)_2 \xrightarrow{\mu\nu} O_3 + O(^3P)$$
$$O_3 \xrightarrow{\mu\nu} O_2 + O(^3P)$$

۱. ...

Although production of both  $O({}^{3}P)$  and  $O({}^{1}D_{2})$  are energetically possible processes following  $O_{3}$  photolysis at wavelengths less than 300 nm, the transmittance of the Pyrex filter at such wavelengths is low, and the large output in the visible region of the spectrum ensures that the major process is  $O({}^{3}P)$  production.

Analysis of the NO<sub>2</sub>/HCN/Ar matrix after several hours of 253.7-nm photolysis revealed a depletion in the concentration of NO<sub>2</sub> and the formation of NO, evidenced by a sharp band at 1876 cm<sup>-1</sup>. No other bands were observed. In order to increase the rate of NO<sub>2</sub> photolysis, the matrix was irradiated simultaneously at both 253.7 and 184.9 nm. The only additional band seen was a weak absorption at 2259.2 cm<sup>-1</sup>, assigned to HNCO and presumably the result of reaction between HCN and O(<sup>1</sup>D<sub>2</sub>), which is formed when NO<sub>2</sub> is photolyzed at wavelengths less than 244 nm.

The only reactions seen to occur in the  $HCN/O_2$  matrix experiments were  $O_3$  formation and HCN polymerization. The latter occurs as a result of localized matrix annealing originating with the exothermic reaction between  $O(^{3}P)$  and  $O_2$ .

#### Discussion

 $HCN + O({}^{1}D_{2})$ . The products of the matrix reaction between HCN and  $O({}^{1}D_{2})$  are HNCO and HOCN. Bondebey and English<sup>15</sup> have examined the photoisomerization processes of the known isomers of formula CHNO in low-temperature matrices, and found that the major process following HCNO (fulminic acid) photolysis at 121.6 nm is the formation of HNCO, with HOCN also being observed. In addition HNCO has been found to isomerize to HOCN:

 $HNCO \rightarrow HOCN$ 

The reverse process, formation of HCNO from HNCO, was found not to take place. In the matrix experiments of the present study HCNO was also not observed. An indication of the relative amounts of HNCO and HCNO in the matrix after 9 h of photolysis may be gained by comparison of the more intense lines in the spectrum. The observed ratio is approximately 10:1 in favor of HNCO.

A serial photolysis experiment was performed next in order to examine the possibility that HOCN formation arises from secondary photolysis of HNCO. Thus matrices containing HCN/N<sub>2</sub>O/Ar in the ratios 1/1/1000 were monitored for products after irradiation periods of 1, 3, 4, 7, and 9 h. If the HNCO to HOCN transformation is taking place, then the concentration of HNCO will fall off with time, whereas that of HOCN will increase linearity. The plot shown in Figure 3 is of peak height of the strongest bands in each spectrum versus photolysis time. The plot demonstrates clearly that both HNCO and HOCN show identical concentration/photolysis time behavior. This suggests that the compounds arise through the same reaction and that HOCN is not the photoisomerization product of HNCO. The shapes of the curves indicate some falling off in the rate of increase in intensity with time; the absence of other products that may arise from the photolysis of either HNCO or HOCN suggests that this is due to a depletion of cage-paired N<sub>2</sub>O/HCN molecules toward the end of the photolysis period rather than being due to their photolytic removal. The bands in the 1200-1250-cm<sup>-1</sup> region are also all found to grow at the same rate, confirming the as-



Figure 3. Absorbance vs photolysis time plot for production of HNCO and HOCN in argon matrix.

signment of that at 1242.8 cm<sup>-1</sup> to HOCN rather than HCNO.

In the case of the more fluid Ne matrix experiments, one further product observed was the cyano radical,  $\dot{C}N$ , which is presumably the result of HOCN photolysis followed by cage escape. The possibility that  $\dot{C}N$  arises from the direct photolysis of HCN is unlikely after consideration of the high absorption cross section of N<sub>2</sub>O at this wavelength where HCN absorbs only very weakly.<sup>14</sup>

Once it has been established that HCNO and HOCN are both primary products of the matrix reaction between HCN and O- $({}^{1}D_{2})$ , it remains to propose a reaction mechanism in which they are produced simultaneously.

Pople et al.,<sup>19</sup> in agreement with Carpenter,<sup>3</sup> suggest that the initial step in HCN +  $O(^1D_2)$  reaction is the formation of an oxazirine intermediate which may then undergo various rearrangements to form final products. By calculating the energetics of the various possible isomers, Pople et al. were able to predict pathways between the more stable species. Oxazirine was found not to be a metastable intermediate on the reaction pathway, and attempts to synthesize it were predicted to result in HNCO formation. These results appear to be in complete agreement with the results observed here for the HCN +  $O(^1D_2)$  reaction in a matrix. The formation of a loosely bound oxazarine complex on addition of  $O(^1D_2)$  across the C=N bond of HCN and the subsequent rearrangement to HCNO and HOCN account for the simultaneous formation of these products as shown:

The first pathway involves a 1,2 H-atom migration followed by the breaking of an N–O bond. The second pathway, to HOCN, must involve a 1,3 migration and the breaking of the same N–O bond. The 10:1 relative yields of the two routes (if the infrared absorption coefficients of the two bands are similar) may reflect the relative efficiencies of the two migration processes. Such a product distribution is seen to be in agreement with the work of Carpenter et al.,<sup>3</sup> who found a 10% contribution of  $\dot{O}H + \dot{C}N$ to the reaction, compared with 90% NH + CO. That is, HNCO breaks down to NH + CO in the gas phase and HOCN into  $\dot{O}H$  +  $\dot{C}N$ .

 $HCN + O({}^{3}P)$ . No products were observed for  $O({}^{3}P) + HCN$  reaction in these experiments. This may be interpreted in terms of  $O({}^{3}P)$  being insufficiently reactive to insert into the C=N bond in the matrix. The fact that no reaction occurs does, however, mean that the products in the N<sub>2</sub>O photolysis experiments can unambiguously be assigned as arising from  $O({}^{1}D_{2}) + HCN$  reaction rather than from the reaction between HCN and  $O({}^{3}P)$  atoms, which can be formed by matrix quenching of  $O({}^{1}D_{2})$ . This explains why HCN and N<sub>2</sub>O need to be in "reactive" sites in the matrix to ensure HNCO production. In this case a reactive site

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is one in which  $O(^{1}D_{2})$  can react with HCN before being quenched to  $(O^3P)$ .

#### Conclusions

The products of the matrix reaction between HCN and  $O(^{1}D_{2})$ are HNCO and HOCN. These findings support the predicted intermediacy of HNCO in the gas-phase reaction. The presence of HOCN also helps to confirm that this reaction passes through a nuclear configuration corresponding to oxazarine. The matrix environment apparently makes the HCN +  $O(^{3}P)$  reaction too inefficient to be observed.

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## Chain-Propagation Length of Linoleic Acid Peroxidation in Aqueous Monomeric and Micellar Systems

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The chain-propagation (CPL) length of radiation induced autoxidation of linoleic acid in aqueous solutions was determined by oxygen uptake measurements for various states of aggregation (monomeric, oligomeric, spherical, and rod-shaped micelles) of the acid at pH 9. The theoretically expected linear oxygen uptake vs (dose rate) $^{-1/2}$  relationship was found to follow the Russell mechanism and to hold only for monomeric and small oligomeric aggregates over a temperature range of 0-50 °C. Large increases in chain length with increasing structural features (e.g., 2 and 18 for oligomeric and rod-shaped micelles at 22 °C, and 0.01 Gy s<sup>-1</sup>) and temperature (e.g., 0 at 0 °C and 7 at 48 °C) were explained by entropic and thermokinetic factors.

#### Introduction

Autoxidation of fatty acids has been studied extensively in neat liquids and model nonpolar media (as esters) and the mechanisms are fairly well understood.<sup>1-3</sup> These mechanisms are of considerable interest because lipid peroxidation plays an important role in oxidative spoilage of food,<sup>4</sup> atherosclerosis,<sup>4,5</sup> and carcinogenesis.<sup>6</sup> In biological systems, of particular interest are fatty acid aggregates or aggregates of fatty acid derivatives in aqueous media, such as micelles, liposomes, and membranes, as well as complexes of lipids with proteins (lipoproteins). Autoxidation mechanisms of aggregates, however, are less understood than those for the neat systems. Linoleic acid has been used frequently as a model in the studies of autoxidation of fatty acids. In linoleic acid, the most sensitive site to oxidative attack is the bis(allylic) position between two double bonds at C11. Consequently, when a peroxy radical, ROO' reacts with linoleic acid (represented as LH<sub>2</sub> in which the two C11 hydrogens are emphasized), an H atom from C11 is abstracted

$$ROO' + LH, \rightarrow ROOH + LH$$
 (1)

The \*LH radical is believed to react rapidly with oxygen as do many other C-centered radicals.<sup>2</sup> Oxygen, however, does not add in the C11 position because of the resonant nature of the bis-(allylic) radicals.<sup>3</sup> Hence, reaction

$$^{\bullet}LH + O_2 \rightarrow ^{\bullet}OOLH \tag{2}$$

leads to addition of oxygen to mesomeric C9 and C13 radical sites. The C9 and C13 peroxy radicals react with another linoleic acid molecule to give C9 and C13 hydroperoxides<sup>7</sup>

$$\bullet OOLH + LH_2 \rightarrow HOOLH + \bullet LH$$
(3)

Linoleic acid concentration in aqueous media has been shown to have a large effect on the yield of hydroperoxides as measured by absorption of conjugated hydroperoxides at 235 nm.8-12 Dose-rate  $(D_r)$  effect on oxygen uptake (OU) was observed although large deviations were found from the expected  $D_r^{-1/2}$ relationship for chain reactions.<sup>13</sup> The yield of the conjugated hydroperoxide was also found to be dependent on the linoleic acid concentration, which was explained by the formation of micelles.8-12

In this work using radiolytic generation of initial free radicals, previous studies were extended to detailed investigation of the linoleic acid concentration, dose rate at which initial free radicals are generated, and temperature dependence of the oxygen uptake, as measured by a Clark electrode. It was demonstrated that two plateau regions exist for the oxygen uptake for the concentration relationship pertaining to spherical and rod-shaped micelles, while in the nonplateau regions, competition between monomeric, oligomeric, spherical, and rod-shaped micelles for initial radicals takes place. A new relationship for oxygen uptake and dose rate was developed and shown to be strictly a function of  $D_r^{-1/2}$  at concentrations only far below that of critical micellar concentration (cmc) of linoleic acid. It was also shown that structured aggregates

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