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Marilyn E. Jacox and Dolphus E. Milligan

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# Matrix-Isolation Study of the Reaction of Carbon Atoms with HCl. The Infrared Spectrum of the Free Radical HCCl

MARILYN E. JACOX AND DOLPHUS E. MILLIGAN

National Bureau of Standards, Washington, D. C.

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The infrared spectrum of samples of cyanogen azide plus hydrogen chloride isolated in an argon or a nitrogen matrix at 14°K and subjected to photolyzing radiation under conditions previously shown to lead to the production of carbon atoms includes features at 815 and 1201 cm<sup>-1</sup> which may be assigned to the free radical HCCl. 18C- and D-substitution experiments are consistent with this identification. A band system extending between about 7500 and 5600 Å corresponds to the band system previously reported for HCCl in the gas phase. These observations confirm the production of HCCl in the present experiments and indicate that the lower state of the transition observed for HCCl in the gas-phase studies is the ground state. The force constants and thermodynamic properties of HCCl have been estimated. Evidence is presented for the reaction of NCN, a photolytic intermediate in the production of carbon atoms from cyanogen azide, with HCl to produce an incompletely characterized species, probably either monochlorocyanamide or monochlorocarbodi-imide. HCCl reacts with HCl with little or no activation energy, leading to the stabilization of CH<sub>2</sub>Cl<sub>2</sub>.

# INTRODUCTION

Considerable attention has recently been given to the role played by monochloromethylene HCCl as a reaction intermediate.1 Heretofore, the only direct observation of this species has been that of Merer and Travis,<sup>2</sup> who have assigned a band system between 5500 and 8200 Å, seen in absorption within about 20  $\mu$ sec of a photolyzing flash through HCClBr<sub>2</sub>, to a  ${}^{1}A''-{}^{1}A'$  transition of HCCl. Rotational analysis has yielded the geometric parameters of the lower state, which is presumed to be the ground state. An appreciable increase in the valence angle occurs in the transition to the excited state, leading to an extended progression in the upper-state bending frequency.

Recent studies in this laboratory have shown that the photolysis of cyanogen azide isolated in a matrix at cryogenic temperatures leads to the production of carbon atoms.<sup>3</sup> Sufficient yields have been obtained to permit detection of the products of carbon-atom reaction with numerous simple molecules, including N2,4  $F_{2,5}$  and  $Cl_{2,6}$  In the light of these observations, it appeared quite possible that the reaction of carbon atoms with HCl in inert matrices might lead to the production and stabilization of HCCl in concentration sufficient for direct spectroscopic study. The results of these experiments, which have led to the identification of two of the vibrational fundamentals of this species, are detailed in the present manuscript.

#### **EXPERIMENTAL DETAILS**

The synthesis of cyanogen azide and of its isotopically substituted counterparts has been described in an earlier communication.<sup>3</sup> Hydrogen chloride (Matheson Company, Inc.)<sup>7</sup> and deuterium chloride (Volk Radiochemical Company)<sup>7</sup> were repeatedly condensed at 77°K, and the solid material was subjected to pumping to remove volatile impurities. The resulting sample was diluted with Ar or with N<sub>2</sub> to a typical matrix: HCl mole ratio between 25 and 200. Traces of water vapor were removed from the sample by placing a column packed with P<sub>2</sub>O<sub>5</sub> between the sample bulb and the vacuum line used for deposition The Ar (or  $N_2$ ):  $N_3$ CN sample, having a typical mole ratio of 100, was deposited simultaneously with a sample of HCl in the same matrix material, using separate deposition lines. Mixture of the two samples occurred at the entrance to the cryostat, only a few centimeters from the cold sample window. At the very low partial pressures (typically 5 or 10  $\mu$ ) of the potentially reactive species at this point in the deposition system, no evidence for their reaction could be detected in the infrared spectrum of the resulting solid sample.

The cryostats used for these observations are similar to that described by Milligan.<sup>8</sup> All samples were studied at 14°K, the triple point of hydrogen.

Photolysis sources were an Osram<sup>7</sup> cadmium lamp, with glass envelope removed, and a medium-pressure mercury arc. Radiation was focused on the sample by a quartz lens. Typically, photolysis was through a

<sup>&</sup>lt;sup>1</sup>G. L. Closs and J. J. Coyle, J. Am. Chem. Soc. 87, 4720 (1965).

<sup>&</sup>lt;sup>2</sup> A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 525 (1966). <sup>8</sup> D. E. Milligan, M. E. Jacox, and A. M. Bass, J. Chem. Phys.

**<sup>43</sup>**, 3149 (1965). <sup>4</sup> D. E. Milligan and M. E. Jacox, J. Chem. Phys. **44**, 2850

<sup>(1966).</sup> <sup>6</sup> D. E. Milligan and M. E. Jacox (unpublished data).
<sup>6</sup> D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 703

<sup>(1967).</sup> 

<sup>&</sup>lt;sup>7</sup> Certain commercial instruments and materials are identified in this paper in order adequately to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

<sup>&</sup>lt;sup>8</sup> D. E. Milligan, J. Chem. Phys. 35, 1491 (1961).



FIG. 1. Ar:HCl=50. 304  $\mu$ M HCl. Ar:N<sub>3</sub>CN=100. 145  $\mu$ M N<sub>3</sub>CN. 14°K.—, initial; —, 100-min Cd photolysis through LiF. ---, 125-min Hg photolysis through LiF.

lithium fluoride window, brought into position for direct irradiation of the sample by rotating the cryostat base.

Infrared spectra were recorded on a double-beam, prism-grating spectrometer (Beckman IR-9).<sup>7</sup> Between 400 and 2000 cm<sup>-1</sup> the resolution and frequency accuracy under typical scanning conditions are approximately 1 cm<sup>-1</sup>, and between 2000 and 4000 cm<sup>-1</sup>, approximately 2 cm<sup>-1</sup>.

The 4000- to 9000-Å spectral region was studied using an 0.8-m Ebert-Fastie scanning monochromator<sup>9</sup> equipped with a 1200-groove/mm grating blazed at 6000 Å, with  $100-\mu$  slits, and with a Hamamatsu R-196 photomultiplier detector.<sup>7</sup> For observations at wavelengths longer than 5500 Å, a Corning<sup>7</sup> 3384 filter was used to exclude short wavelength radiation from the monochromator. By placing a Hilger<sup>7</sup> medium glass spectrograph on top of the infrared spectrometer and by suitably raising and lowering the cryostat, it has also been possible to study both the infrared and the visible spectrum of the same sample at various stages in the experiment. For these observations visible spectra were photographed on Eastman Kodak<sup>7</sup> I–N plates. Tungsten background sources were used for all of the 4000–9000-Å studies,

<sup>&</sup>lt;sup>9</sup> W. G. Fastie, J. Opt. Soc. Am. **42**, 641 (1952); **42**, 647 (1952); **43**, 1174 (1953).

Ar: N <sub>3</sub> <sup>12</sup> C <sup>14</sup> N	Ar: N <sub>8</sub> <sup>13</sup> C <sup>14</sup> N (50.5%)	Ar: N3 <sup>12</sup> C <sup>15</sup> N (95%)	N <sub>2</sub> :N <sub>3</sub> <sup>12</sup> C <sup>14</sup> N
415	408 415	415	436
553	551	545 vw	
574 w	637	551 vw	584
640	640	637 w	631
690			676 w
836 vw			845
896 w-m	894 1339 2024 2028 sh	890 w 894 w	890
	2056	2062 sh 2066	
2072	2074	2070	
2080			
		3354	
3360	3360	3360 3369	3348
3375	3375	3376	3372

TABLE I. Absorptions  $(cm^{-1})$  appearing after cadmium photolysis of cyanogen azide in the presence of HCl.

## **OBSERVATIONS**

In a typical experiment, the cyanogen azide is first photolyzed to NCN+N<sub>2</sub>, using the intense 2288-Å cadmium-arc line.<sup>4,10</sup> Subsequent irradiation with a medium-pressure mercury arc leads to the disappearance of NCN and to the production of carbon atoms.<sup>4</sup> Such an experiment is shown in Fig. 1.

In addition to the initial features shown in Fig. 1, which are, with unimportant exceptions (e.g., a weak BrCN absorption at 708  $\rm cm^{-1}$  and HCN absorption at 722 cm<sup>-1</sup> and a relatively intense 660-cm<sup>-1</sup> peak contributed by both CO<sub>2</sub> and N<sub>3</sub>CN), contributed by cyanogen azide, numerous intense absorptions in the 2600-2900-cm<sup>-1</sup> region are contributed by various associated forms of HCl. With the exception of the intense 2684–2696-cm<sup>-1</sup> doublet in initial scans of argon matrix samples and of the intense 2660-cm<sup>-1</sup> feature in nitrogen matrix samples, none of these features changes during the course of photolysis. In contrast, the 2684–2696 (or 2660)  $\text{cm}^{-1}$  feature disappears as the initially present cyanogen azide is photolyzed. Conceivably, this feature is contributed by HCl molecules in sites adjacent to cyanogen azide molecules; the spectrum of matrix-isolated HCl is remarkably sensitive to perturbation by even traces of species such as nitrogen.11

Frequencies of features which appear following cadmium-arc irradiation of matrix-isolated cyanogen azide and of its isotopically substituted counterparts in the presence of HCl are summarized in Table I. It should be noted that the frequencies of features which are also observed in experiments in which HCl is not present have been omitted from this and the following tables. Thus, the intense 423- and 1475-cm<sup>-1</sup> NCN features, readily recognized in the spectrum of Fig. 1, are not included. In general, the intensities of the features of Table I are diminished in higher Ar:HCl mole-ratio experiments. The intensities of these features become virtually constant when photolysis of the cyanogen azide is complete; only a slight diminution in their intensities has been noted upon prolonged mercury-arc photolysis. The intensity of the strongest absorption, at 3360 cm<sup>-1</sup>, remains completely unchanged upon prolonged photolysis, but that of the companion feature at 3375 cm<sup>-1</sup> decreases slightly. With this exception, the growth pattern of the features listed in Table I is consistent with their assignment to a single species. Nevertheless, because of the breadth and weakness of most of these features, it cannot be definitely concluded that, with the possible exception of the 3360-cm<sup>-1</sup> feature, all of them are indeed contributed by a single species. It is conceivable that the different behavior of the 3360- and 3375-cm<sup>-1</sup> features on prolonged photolysis arises from the trapping of a single product species in two or more sites in the matrix, with certain sites affording protection from photolysis. Unfortunately, the breadth and weakness of most of the features also has prevented obtaining complete data on the isotopically substituted species. The relatively prominent 2072-2080-cm<sup>-1</sup> feature of argon matrix experiments is also broad, with poorly resolved structure on the low-frequency side of the absorption. This feature is additionally broadened in experiments employing <sup>13</sup>C and <sup>15</sup>N substitution, and only the frequencies of intensity maxima within this broad absorption pattern could be reported. The 2024-2028cm<sup>-1</sup> feature of the <sup>13</sup>C experiments correlates in neither intensity nor contour with features reported in other experiments.

When the sample is warmed above about 35°K, the 3360-3375-cm<sup>-1</sup> features disappear. Warmup data on the less prominent features are inconclusive.

When a sample previously photolyzed with the cadmium arc is subjected to photolysis with a mediumpressure mercury arc, the NCN absorptions readily disappear, and the features previously assigned<sup>4</sup> to CNN appear, together with the HCl-dependent features for which frequencies are summarized in Table II. None of the features included in Table II exhibits a significant shift or acquires a lower frequency counterpart in experiments employing  $N_3C$  <sup>16</sup>N. The 753-cm<sup>-1</sup> feature is relatively more intense in experiments employing a low Ar:HCl mole ratio. When the sample is warmed to approximately 35°K, permitting diffusion to

 <sup>&</sup>lt;sup>10</sup> D. E. Milligan and M. E. Jacox, J. Chem. Phys. 45, 1387 (1966).
<sup>11</sup> M. T. Bowers and W. H. Flygare, J. Chem. Phys. 44, 1389 (1966).

 Ar:N <sub>8</sub> <sup>12</sup> C <sup>14</sup> N	Ar:N <sub>3</sub> <sup>13</sup> C <sup>14</sup> N (50.5%)	Ar:N <sub>3</sub> <sup>12</sup> C <sup>16</sup> N (95%)	$N_2:N_3^{12}C^{14}N$	Assignment
753	730 752	752	750	<sup>13</sup> CH <sub>2</sub> Cl <sub>2</sub> <sup>12</sup> CH <sub>2</sub> Cl <sub>2</sub>
	783 786 sh 788 791		}	H13CCl
806.5 810.0 812.5 814.8	806 810 sh 812 815	806 810 sh 812 815	804 808 810 814	H <sup>12</sup> CCl
1201 1270 w	1197.5 1201	1201	1204	$H^{13}CCl$ $H^{12}CCl$ $^{12}CH_2Cl_2$

TABLE II. Absorptions (cm<sup>-1</sup>) appearing after mercury photolysis of cyanogen azide in the presence of HCl.

occur in the matrix, this feature is observed to grow in intensity. An equally intense companion feature appears at 730 cm<sup>-1</sup> when cyanogen azide enriched to 50.5% N<sub>3</sub> <sup>13</sup>CN is used. All of these data are consistent with the assignment of the 753-cm<sup>-1</sup> absorption to methylene chloride, for which the most intense gasphase infrared absorption appears at 756 cm<sup>-1</sup>.<sup>12</sup> In experiments in which essentially complete photolysis of cyanogen azide is achieved during cadmium irradia-



FIG. 2. Features appearing after mercury photolysis of matrixisolated cyanogen azide in the presence of HCl. (a) N<sub>2</sub>:HCl=75, 321  $\mu$ M HCl; N<sub>2</sub>:N<sub>3</sub>CN=75, 242  $\mu$ M N<sub>3</sub>CN; 14°K. Photolyzed overnight through Pyrex, 65 min through LiF. (b) Ar:HCl=50, 304  $\mu$ M HCl; Ar:N<sub>3</sub>CN=100, 145  $\mu$ M N<sub>3</sub>CN; 14°K. Photolyzed 125 min through LiF, after 100 min Cd photolysis. (c) Ar:HCl= 50, 347  $\mu$ M HCl; Ar:N<sub>3</sub><sup>13</sup>CN (50.5%) = 100, 166  $\mu$ M N<sub>3</sub>CN; 14°K. Photolyzed 180 min through Suprasil, after 150 min Cd photolysis.

tion, a very weak feature of growth behavior appropriate to methylene chloride also appears at 1270 cm<sup>-1</sup>, corresponding very well to the 1268-cm<sup>-1</sup> gas-phase absorption, the second most intense band in the spectrum of this species.

Figure 2 shows the relative intensities and absorption contours of the features near 800 and 1200 cm<sup>-1</sup> listed in Table II. These absorptions continue to grow during mercury photolysis until all of the NCN has been photolyzed, when their intensities become constant. Four absorption maxima appear between 805 and 815  $cm^{-1}$ , together with a moderately intense peak at 1201  $cm^{-1}$ . In an argon matrix, the two highest frequency peaks in the 805-815-cm<sup>-1</sup> quartet are the most prominent and are approximately equally intense, whereas in a nitrogen matrix the highest frequency peak is less prominent than is the feature at  $810 \text{ cm}^{-1}$ . The 1201-cm<sup>-1</sup> peak is shifted upward to 1204 cm<sup>-1</sup> in nitrogen matrix experiments. In experiments employing cyanogen azide enriched to 50.5% in <sup>13</sup>C, the pattern of absorptions between 805 and 815 cm<sup>-1</sup> is duplicated between 783 and 791 cm<sup>-1</sup>, and the 1201-cm<sup>-1</sup> feature is doubled, suggesting that the species giving rise to these features contains one carbon atom. When the sample is warmed to  $35^{\circ}$ K, the 1201- and 805-815-cm<sup>-1</sup> features and their <sup>13</sup>C counterparts disappear.

Experiments in which DCl is substituted for HCl are quite analogous to those just described. An intense absorption appearing before photolysis at 1950–1957 cm<sup>-1</sup> in argon matrix experiments and at 1923–1933 cm<sup>-1</sup> in nitrogen matrix experiments diminishes markedly in intensity during cadmium irradiation of the sample. This absorption, by analogy with the feature of similar behavior at 2684–2696 cm<sup>-1</sup> in HCl experiments, apparently is contributed by DCl perturbed by a nearby N<sub>3</sub>CN molecule. Only fragmentary data are available on features appearing during cadmium irradiation; in typical experiments, features appearing below 2000 cm<sup>-1</sup> are very weak, and the 1900–2100-cm<sup>-1</sup> spectral region is complicated by DCl absorptions.

<sup>&</sup>lt;sup>12</sup> T. Shimanouchi and I. Suzuki, J. Mol. Spectry. 8, 222 (1962).

TABLE III. Absorptions (cm<sup>-1</sup>) appearing after mercury photolysis of cyanogen azide in the presence of DCl.

Ar: N3 <sup>12</sup> C <sup>14</sup> N	Ar: N <sub>3</sub> <sup>13</sup> C <sup>14</sup> N (50.5%)	$N_2: N_3^{12}C^{14}N$	Assignment
725 735			$CD_2Cl_2$ CHDCl_2
	778 781 sh 784 787	}	D <sup>13</sup> CCl
796 800 sh 802.6 805	796 802.5 805.5	794 798 sh 800 803.5	D <sup>12</sup> CCl
889	948	060	$\begin{array}{c} CHDCl_2\\ {}^{13}CD_2Cl_2\\ {}^{12}CD_2Cl_2 \end{array}$
730	×30	900	CD <sub>2</sub> Cl <sub>2</sub>

Features appearing in Ar matrix experiments at 2070 and 2074 cm<sup>-1</sup> are analogous to features reported near this frequency in HCl experiments. A relatively prominent 2492–2512-cm<sup>-1</sup> doublet in Ar matrix experiments (2482 and 2510 cm<sup>-1</sup> in N<sub>2</sub> matrix experiments) appears to be the counterpart of the 3360–3375 cm<sup>-1</sup> absorptions of HCl experiments.

Table III summarizes the frequencies of the new features appearing after mercury-arc photolysis of matrix-isolated cyanogen azide in the presence of DCl, omitting features characteristic of the undeuterated experiments. The frequency correspondence between the 889- and 958-cm<sup>-1</sup> features and intense features of the gas-phase spectrum of  $CHDCl_2$  and  $CD_2Cl_2$ , respectively, is very close.<sup>12</sup> Furthermore, these features are relatively more prominent in experiments of low Ar: DCl mole ratio, and they are observed to grow in intensity when the sample is warmed to 35°K. Rather broad, weak features at 725 and 735 cm<sup>-1</sup> also correspond well to intense gas-phase absorptions of the deuterated methylene chlorides.<sup>12</sup> In the <sup>13</sup>C experiments, a 948-cm<sup>-1</sup> feature appears with intensity equal to that of the 958-cm<sup>-1</sup> CD<sub>2</sub>Cl<sub>2</sub> feature, and may be assigned to <sup>13</sup>CD<sub>2</sub>Cl<sub>2</sub>. Since in the <sup>13</sup>C study the extent of deuteration has been estimated to approach 90%, features assigned to CHDCl<sub>2</sub> were not observed. A group of four absorptions appearing between 795 and 805 cm<sup>-1</sup> possesses a relative intensity pattern similar to that of the 805-815-cm<sup>-1</sup> group of absorptions in the undeuterated experiments. This group acquires an equally intense counterpart with similar contour between 778 and 787 cm<sup>-1</sup> in experiments employing 50.5% <sup>13</sup>C enrichment. On warmup to 35°K, the 795-805-cm<sup>-1</sup> system disappears.

In experiments in which the concentration of the species responsible for the 805-815- and 1201-cm<sup>-1</sup> absorptions is relatively great, several broad, weak bands also appear between about 7500 and 5600 Å. Table IV compares the estimated frequencies for these bands with those of bands reported by Merer and

Travis<sup>2</sup> for the main progression of HCCl, with K'=0. The breadth and weakness of the bands observed in the present experiments are sufficient to introduce a relatively large error, estimated to be approximately 50 cm<sup>-1</sup>, in the frequencies given in Table IV. Nevertheless, allowing for a matrix shift to shorter wavelengths of approximately 250 cm<sup>-1</sup>, six of the observed features correspond reasonably well to features expected for HCCl, with band separations agreeing within experimental error. Although matrix shifts of this magnitude commonly occur in visible-ultraviolet spectral observations, more frequently the shift is to lower frequencies. Thus, it is uncertain whether the assignment given for the gas-phase bands is the correct one for the matrix bands or whether, for example, the 13 370-cm<sup>-1</sup> matrix absorption might more properly be assigned to the (020-000) transition. It should, however, be noted that the principal progression reported by Merer and Travis involves a transition between K''=1 and K'=0 states, with associated frequencies appreciably less than those observed when K''=0, presumably the lower state of nonrotating HCCl trapped in a matrix. At frequencies greater than 15 000 cm<sup>-1</sup>, an unassigned feature appears approximately equidistant between each feature tentatively assigned to HCCl. The origin of these features is not known. However, it is noteworthy that Merer and Travis have observed that at energies greater than about 15 000 cm<sup>-1</sup>, when more than three quanta of the bending vibration of the upper state of HCCl are excited, the barrier to linearity of this species is exceeded, and the rotational band structure becomes characteristic of a linear molecule. These workers also have noted numerous perturbations in the HCCl spectrum, especially in absorptions not belonging to the main progression. In summary, the occurrence of a band system in the region for which one has been observed for HCCl and the reasonable correspondence of six of the observed bands to those of HCCl suggest the presence of HCCl in the matrix experiments.

TABLE IV. Absorptions appearing in the 8000–5000-Å spectral range after mercury photolysis of  $Ar:HCl+Ar:N_3CN$  samples.

Matrix observations		H	HCCl (g), $K' = 0$		
(cm-1)	Separation (cm <sup>-1</sup> )	Assign- ment	$T_{v,0}$ (cm <sup>-1</sup> )	Separa- tion (cm <sup>-1</sup> )	
13 370		(010-000)	13 153		
	855	(,		856	
14 225	000	(020-000)	14 009	040	
15 105 )	880	(030-000)	14 857	848	
15 480 {	820	(000 000)		857	
15 925		(040-000)	15 714		
16355	835	(050,000)	16 505	871	
17 240	970	(000-000)	10 282	875 935	
17 730 \$	210	(060-000)	17 460 17 520	070, 200	

## DISCUSSION

Since the radiation of the cadmium arc and of the medium-pressure mercury arc produce little or no photodissociation of HCl in a matrix environment, it is necessary to postulate that all of the features observed after photolysis in the present experiments (excepting, of course, NCN and CNN) must be contributed by species produced by the reaction of fragments of the photodecomposition of cyanogen azide with one or more molecules of HCl. The isotopic substitution data of Table I indicate that the species produced on cadmium irradiation of the sample contains both carbon and nitrogen, as would be anticipated for species formed by the reaction of HCl with NCN, the principal product (together with  $N_2$ ) of the photolysis of matrix-isolated cyanogen azide with the intense 2288-Å cadmium-arc emission.<sup>4,10</sup> Possible products of the reaction of a single HCl molecule with NCN might include monochlorocyanamide,



and monochlorodiazomethane,



as well as less familiar type structures such as that of chlorocarbodiimide,

# HN=C=NCl.

The substituted diazomethane structure appears to be quite unlikely, both because this species, like the parent compound, would be expected to photolyze rather readily and because the 3360-3375-cm<sup>-1</sup> features must be assigned to an N-H stretching mode. The feature near 2070 cm<sup>-1</sup> is surprisingly insensitive to isotopic substitution. However, isotopic shifts of relatively complex molecules are likely to be less dramatic than for simple species. An absorption near 2070 cm<sup>-1</sup> would be expected for either of the two likely structures; for the cyanamide structure the C=N stretching mode would most likely possess a frequency near this value, and for the carbodiimide structure the -N=C=N- antisymmetric stretching frequency might be anticipated between about 1900 and 2300 cm<sup>-1</sup>. Cyclic structures such as monochlorodiazirine,



would be relatively unlikely to have a fundamental absorption in this spectral region. Monochlorodiazirine also would be expected to photolyze with relative ease. The nature of the prominent 2024-cm<sup>-1</sup> feature in the <sup>13</sup>C species remains obscure; perhaps it is contributed by a Fermi resonance between the 2070-cm<sup>-1</sup> mode and an overtone or combination mode. A weak, broad absorption observed in some experiments near 1340 cm<sup>-1</sup> may conceivably be contributed by the N-H deformation. A feature in the 700-900-cm<sup>-1</sup> spectral region would be expected for the N-Cl stretching mode of either likely structure. Unfortunately, it has not been possible to demonstrate a splitting in any feature due to the 25% <sup>37</sup>Cl present in the sample. It does not appear possible definitely to associate a specific feature with either a C-N stretching mode (for the cyanamide structure) or a symmetric -N=C=Nstretching mode (for the carbodiimide structure). The features appearing below about 700 cm<sup>-1</sup> are most likely contributed by various skeletal bending modes and cannot be used to differentiate between the two likely structures. Present data could, in summary, be used to support the presence of either or both the cyanamide and the carbodiimide structures.

Chemical evidence, on the other hand, suggests that the cyanamide structure may be somewhat favored. This structure is commonly found to be more stable than the carbodiimide structure. Furthermore, relatively extensive atomic rearrangement would be expected to be required to form a carbodiimide, making it somewhat less probable. Finally, difluorocyanamide<sup>13</sup> has been identified as the principal product of the reaction of NCN with  $F_2$  in a matrix environment.<sup>5</sup>

Contributions by species containing two HCl units, while relatively less likely, cannot be excluded. One might, however, expect the concentration of such species to undergo at least an initial increase during warmup. Such an increase has not been observed.

Since carbon atoms have been demonstrated<sup>4,10</sup> to be the principal reactive species produced by the photolysis of NCN with radiation near 2537 Å, the formation of HCCl when the samples of the present experiments are subjected to the radiation of a medium-pressure mercury arc is suggested. Furthermore, the appearance of a band system in the spectral range in which HCCl is known to possess an electronic transition and the approximate correspondence of at least six features in this band system to prominent bands of the spectrum of gaseous HCCl provide evidence for the presence of HCCl in Ar: HCl+Ar: N<sub>3</sub>CN samples which have been subjected to mercury-arc irradiation. The correspondence of the spectral features in the visible region also suggests that the lower state of this band system, assumed by Merer and Travis<sup>2</sup> to be the ground state of HCCl, is indeed the ground state of this species. The appearance of this band system can be correlated with

<sup>13</sup> M. D. Meyers and S. Frank, Inorg. Chem. 5, 1455 (1966).

TABLE V. "Best fit" force constants for HCCl.

$F_{C-C1}$	=3.80  mdyn/Å
$F_{\rm CC1,ben}$	$_{\rm d}$ = 0.523 mdyn/rad
$F_{bend}$	$=0.971 \text{ mdyn} \cdot \text{\AA}/\text{rad}^2$

relatively prominent 815- and  $1201\text{-cm}^{-1}$  spectral features. Warmup studies indicate that the species responsible for the infrared absorptions is reactive, and as it disappears the concentration of methylene chloride is observed to grow. Thus, a variety of evidence points to the association of the 815- and 1201-cm<sup>-1</sup> absorptions with HCCl.

Detailed infrared studies lend further support to this assignment. Isotopic substitution experiments indicate that the species which contributes these absorptions possesses one atom each of carbon and hydrogen and no nitrogen atoms. The relatively complicated pattern of absorptions observed between 805 and 815 cm<sup>-1</sup> suggests their assignment to a C-Cl stretching mode, for which the isotopic shift characteristic of <sup>37</sup>Cl should be readily observable. Although the intensity pattern of this group of features in the argon matrix experiments might suggest the presence of several Cl atoms in the absorbing species, in a nitrogen matrix this pattern is considerably altered, and the highest frequency feature becomes considerably less intense than the next highest frequency feature. Such a variation in the intensity pattern suggests that the species is stabilized in two or more distinct sites in the matrix. If the first and third features are associated with one site and the second and fourth with another, a <sup>35</sup>Cl-<sup>37</sup>Cl isotopic shift of 5 or 6 cm<sup>-1</sup> is readily inferred. Although overlap of the features prevents more quantitative estimates of the ratios of their intensities, the spectra of Figs. 2(a) and 2(b) suggest that 3:1 intensity ratios for the members of each pair might reasonably be obtained. Thus, the 805-815-cm<sup>-1</sup> absorption pattern is consistent with that anticipated for a species containing one chlorine atom, isolated in two different sites in the matrix. It is concluded that the 815- and 1201-cm<sup>-1</sup> absorptions may be identified with the free-radical HCCl.

TABLE VI. Comparison between frequencies observed for HCCl and frequencies calculated using "best fit" force constants.

Species	Observed		Calculated	
	$(\text{cm}^{-1})$	ν <sub>3</sub> (cm <sup>-1</sup> )	$(cm^{-1})^{\nu_2}$	ν3 (cm <sup>-1</sup> )
H12C35Cl	1201	815	•••	•••
H13C35Cl	1197	790	1197.7	791.8
D12C35Cl		805	891.1	806.0
D13C36Cl		786	883.8	786.3
H <sup>12</sup> C <sup>37</sup> Cl	1201	810	1200.4	809.2

<sup>5</sup> The geometric parameters found for ground state HCCl by Merer and Travis<sup>2</sup> and the frequencies observed for the various isotopic forms of HCCl may be used to estimate force constants for this species. Unfortunately, no absorption attributable to the C-H stretching fundamental of HCCl has been observed, either because the absorption is weak or because it is obscured by the intense HCl features between about 2600 and 2950 cm<sup>-1</sup>. For values of the unobserved C-H stretching fundamental near or above 2800 cm<sup>-1</sup>, a typical frequency region for such a mode, the approximate separation of this mode by the procedure outlined by Wilson, Decius, and Cross<sup>14</sup> is found to introduce very little error into the calculations. The ratio of the product of the two observed frequencies of H<sup>13</sup>C<sup>35</sup>Cl to the product of the two observed frequencies of H<sup>12</sup>C<sup>35</sup>Cl equals 0.966, compared to a value of 0.969 calculated using the appropriate G-matrix elements

TABLE VII. Thermodynamic properties (cal mole<sup>-1</sup>  $\cdot^{\circ}K^{-1}$ ) of HCCl (assuming  $\nu_1 = 2800 \text{ cm}^{-1}$ ).

<i>T</i> (°K)	C <sub>p</sub> °	$(H^{\circ}-H_{0}^{\circ})/T$	$-(F^{\circ}-F_{0}^{\circ})/T$	S°
273.16	8.61	8.09	47.24	55.32
298.16	8.78	8.14	47.95	56.09
300	8.79	8.14	48.00	56.14
400	9.48	8.39	50.37	58.76
500	10.07	8.67	52.27	60.95
600	10.56	8.95	53.88	62.83
700	10.96	9.21	55.28	64.48
800	11.31	9.45	56.52	65.97
900	11.62	9.67	57.65	67.32
1000	11.88	9.88	58.68	68.56
1100	12.10	10.07	59.63	69.70
1200	12.30	10.25	60.52	70.76
1300	12.47	10.41	61.34	71.76
1400	12.62	10.57	62.12	72.69
1500	12.74	10.71	62.85	73.56
1500*	12.66	10.66	62.83	73.49

<sup>a</sup> Assuming  $\nu_1 = 3000 \text{ cm}^{-1}$ .

corrected for the separation of the C-H stretching frequency. Agreement is seen to be quite satisfactory. Unfortunately, a similar comparison cannot be made for the deuterated species, since the absorption due to the bending vibration is too weak to be observed in these experiments. In order to obtain reasonable agreement between observed and calculated frequencies for the isotopically substituted species, it is necessary to add a C-Cl stretch-bending interaction term to the valence force potential. The procedure adopted for these calculations involves the use of the two equations

and

$$(G_{22}{}^{0}G_{33}{}^{0}-G_{23}{}^{02})(F_{\rm CC1}F_{\rm bend}-F_{\rm int}{}^{2})=\lambda_{2}\lambda_{3},$$

 $G_{33}{}^{0}F_{\rm CC1} + G_{22}{}^{0}F_{\rm bend} + 2G_{23}{}^{0}F_{\rm int} = \lambda_2 + \lambda_3$ 

<sup>14</sup> E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955), pp. 74-76.

in which the notation of Wilson, Decius, and Cross<sup>14</sup> has been employed for the G-matrix elements.  $\lambda$  is defined as  $(\nu/1302.9)^2$ . It is noteworthy that the frequency product ratio derived from the ratio of the second equation for two different isotopic species is independent of the presence of an interaction term in the potential. The observed frequencies for H<sup>12</sup>C<sup>35</sup>Cl are introduced into the two relationships given above, and  $F_{\text{bend}}$  and  $F_{\text{int}}$  are expressed in terms of  $F_{\text{CCl}}$ . For a sequence of assumed values of  $F_{CCI}$ , the values of  $F_{\text{bend}}$  and  $F_{\text{int}}$  and the frequencies appropriate for the observed isotopically substituted species are calculated. The force constants found to give the best fit to the observed frequencies are summarized in Table V, and the frequencies calculated using these force constants are compared with the observed frequencies in Table VI. Except for a 1.8-cm<sup>-1</sup> deviation for  $\nu_3$  of H<sup>13</sup>C<sup>35</sup>Cl, agreement is within experimental error.

Using the structural parameters deduced for HCCl in its ground  ${}^{1}A'$  state by Merer and Travis<sup>2</sup> and the vibrational frequencies obtained in the present studies, together with an assumed value of 2800 cm<sup>-1</sup> for  $\nu_1$ , the thermodynamic properties of HCCl given in Table VII are readily derived. As is indicated, the values obtained are relatively insensitive to the magnitude of  $\nu_1$ ; for a value of 3000 cm<sup>-1</sup> none of the thermodynamic properties is changed by more than 0.08 cal mole<sup>-1</sup> °K<sup>-1</sup> at 1500°K.

Little can be said regarding the mechanism of formation of HCCl in the present experiments. Although it has been suggested that the photolysis of NCN to  $C+N_2$  occurs by an allowed process,<sup>10</sup> producing  $C({}^{3}P)$ , the production of  $C({}^{1}D)$  from an unstable excited singlet state of NCN cannot be entirely excluded. Triplet carbon atoms would, of course, initially react with HCl to produce HCCl in an excited triplet state, subject to collisional deactivation by the matrix to the ground singlet state. On the other hand, the reaction of <sup>1</sup>D carbon atoms with HCl could lead directly to the formation of HCCl in its ground state. The stability of the product of NCN reaction with HCl on prolonged photolysis suggests that photodecomposition of this species is not an important source of HCCl. It is conceivable that the reaction of CNN with HCl leading to the photolytically unstable species monochlorodiazomethane may contribute to the HCCl yield. However, in a typical experiment the yield of CNN is comparable to that in experiments in which HCl is not present. Thus, it appears likely that the principal process leading to the formation of HCCl is the reaction of carbon atoms with HCl.

The observation of methylene chloride in these experiments and the growth in its absorptions during warmup indicate that the reaction of HCCl with HCl occurs with little or no activation energy. Since HCCl has been found to be stabilized in a ground singlet state, it appears likely that the methylene chloride is initially formed in its ground state.

# CONCLUSIONS

NCN is found to react with HCl in a matrix environment to produce an incompletely characterized species, most likely either monochlorocyanamide or monochlorocarbodiimide. When the unreacted NCN is photolyzed, producing carbon atoms, the species HCCl appears. Two of the vibrational fundamentals of this species, at 815 and 1201 cm<sup>-1</sup>, have been identified. Observation of the visible band system of HCCl confirms that this species possesses a ground singlet state. Reaction of HCCl with HCl to produce  $CH_2Cl_2$  occurs with little or no activation energy.