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Matrix-Isolation Study of the Reaction of F_2 and of F Atoms with NCN. The Infrared Spectra of the Species NF_2CN and FNCN

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NCN, produced by the photolysis of cyanogen azide isolated in an Ar matrix at 14°K, has been found to react readily with F_2 also present in the system, leading to the stabilization of NF_2CN. The absorption patterns observed for the most prominent infrared absorptions of $NF_2{}^{13}CN$ and of the two singly ^{15}N-substituted difluorocyanamides are consistent with the previous vibrational assignment. When both NCN and F atoms are present in appreciable concentration, absorptions appear at 873 and at 2068 cm^{-1} which may be tentatively assigned to the FNCN free radical. Upon prolonged photolysis, incompletely characterized products of more extensive fluorination reactions are observed.

INTRODUCTION

Recent studies have shown cyanogen azide to be a suitable photolytic source of the NCN free radical, which, in turn, may undergo photodecomposition to produce N_2 and atomic carbon.[1-3] The reactions of carbon atoms produced in a matrix environment with a number of simple molecules, including CO[4] and Cl_2,[5] have subsequently been studied, as has been the reaction of carbon atoms with F_2. Although in the studies of carbon-atom reaction with CO and with Cl_2 no evidence has been found for the production of nitrogen-containing species, in the $C+F_2$ experiments a rich spectrum is obtained, including numerous features which are shifted in ^{15}N-substitution experiments. Among the species identified is difluorocyanamide, NF_2CN, the synthesis[6] and spectrum[6,7] of which have recently been reported. Details of these experiments, in which isotopic substitution data have also been obtained on NF_2CN and on other products of the reaction of atomic and molecular fluorine with NCN, are given in the present manuscript.

EXPERIMENTAL DETAILS

$Ar:F_2$ mixtures of mole ratio 50 and 100 were prepared in an all-metal vacuum system using standard manometric procedures. Flexible stainless-steel bellows tubing connecting a variable leak to the cryostat sample injection system was cooled with liquid nitrogen to trap possible impurities in the $Ar:F_2$ mixture. Except for a weak feature at 899 cm^{-1}, contributed by a small concentration of NF_3, no infrared absorptions attributable to impurities could be detected in the resulting samples.

$Ar:N_3CN=100$ samples and their isotopically substituted counterparts were prepared using techniques previously described.[1] To avoid the complications of gas-phase reaction between F_2 and N_3CN, it was necessary to mix $Ar:F_2$ and $Ar:N_3CN$ samples maintained at suitable deposition pressures at the entrance to the cryostat, only a few centimeters from the cold window. The resulting solid films showed only infrared absorptions characteristic of N_3CN; no features attributable to products of reaction of F_2 with N_3CN could be detected.

The cryostat used for these experiments is similar in principle to that described by Milligan.[8] All observations were at 14°K, the triple point of hydrogen.

Samples were first photolyzed using the full light of a cadmium arc; the intense 2288 Å of this source has previously been shown[3] to provide almost quantitative conversion of N_3CN to N_2+NCN. Samples were sub-

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[1] D. E. Milligan, M. E. Jacox, and A. M. Bass, J. Chem. Phys. **43**, 3149 (1965).

[2] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **44**, 2850 (1966).

[3] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **45**, 1387 (1966).

[4] M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. **43**, 3734 (1965).

[5] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 703 (1967).

[6] D. M. Meyers and S. Frank, Inorg. Chem. **5**, 1455 (1966).

[7] N. B. Colthup, Spectrochim. Acta **23A**, 2167 (1967).

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

TABLE I. Behavior of features appearing in Ar:F_2+Ar:N_3CN samples after photolysis by Cd- and Hg-arc radiation.

	Relative intensity		Change on prolonged	
(cm^{-1})	Cd arc	Hg arc	Hg photolysis	Assignment
423	vs	···		NCN
455	···	m	+	NF_2CN, (?)
458	···	sh		
464	···	w		
497	···	vw	−	
512	···	vw	+	CF_3
580	···	w	+	NF_2CN, (?)
618	···	vw		NF_2CN
631	···	w–m	+	CF_4
703	···	w–m	+	CF_3
827	w	m	−	
840	w–m	m–s	−	NF_2CN
874	···	s	−	
888	s	vs	−	NF_2CN
909	···	m	−	
931	···	m	−	NF_2
934	···	m	−	
958	···	w	+	
1021	m	s	−	NF_2CN
1083	···	sh	+	
1087	···	w–m		CF_3
1102	m	vvs	none	CF_2
1222	w–m	vs	none	CF_2
1235	···	w	+	$^{13}CF_4$
1241	···	m	none	CNN
1250	w	vs	+	CF_3
1258	···	s	+	CF_4
1274	m	vvs	+	CF_4
1295	···	w–m	+	CF
1342	···	w	+	
1475	vvs	···		NCN
1733	···	m	+	
1770	···	w		
2058	···	w	−	$(CN)_x$
2068	···	s	−	
2848	···	m	none	CNN

sequently photolyzed using a medium-pressure mercury arc, leading to the photodecomposition of NCN and to the production of carbon atoms.[2] In some experiments 1 atm of chlorine gas contained in a 10-cm cell with quartz windows was used to filter radiation of wavelength between about 2800 and 4000 Å [9] from the sample. This filter has been found to suppress photodissociation of fluorine, shown by Steunenberg and Vogel[10] to have an absorption maximum near 2800 Å.

Infrared spectra were recorded on a double-beam, prism-grating spectrometer (Beckman IR-9).[11] Under the conditions of a typical experiment, the resolution and frequency accuracy are both approximately 1 cm^{-1} between 400 and 2000 cm^{-1} and 2 cm^{-1} between 2000 and 4000 cm^{-1}.

OBSERVATIONS

Table I summarizes the behavior of features which appear in Ar:F_2+Ar:N_3CN experiments following photolysis by the 2288-Å cadmium-arc line and subsequent photolysis by the full light of a medium-pressure mercury arc. Following cadmium-arc photolysis, intense absorptions due to NCN[1] appear at 423 and 1475 cm^{-1}, and moderately prominent features, absent in experiments in which F_2 is not present, appear at 827, 840, 888, 1021, 1102, 1222, and 1274 cm^{-1}. The 1102- and 1222-cm^{-1} features are contributed by CF_2, which exhibits extremely intense absorption at these two frequencies.[12] Moreover, the 1274-cm^{-1} absorption may be assigned to CF_4. The frequencies of the 840-, 888-, and 1021-cm^{-1} absorptions are found to correspond, with allowance for a small matrix shift, to the frequencies reported by Colthup[7] for the band centers of the three most intensely absorbing fundamentals of gaseous NF_2CN.

On subsequent mercury-arc irradiation, the intensities of all of these absorptions grow dramatically, and

TABLE II. Behavior of features appearing in Ar:F_2+Ar:$N_3C^{15}N$ (95%) samples after photolysis by Cd- and Hg-arc radiation.

	Relative intensity		
(cm^{-1})	Cd arc	Hg arc	Assignment
421	vs	···	^{15}NCN
464	w	m	
580	w	w–m	NF_2CN, (?)
615	···	w, broad	NF_2CN
630	···	m	CF_4
703	···	w–m	CF_3
817	w	m	
825	w	m	$^{15}NF_2CN$
837	w	m	$NF_2C^{15}N$
854	···	m–s	
869	m	vs	$^{15}NF_2CN$
873	···	sh	
888	m	vs	$NF_2C^{15}N$
912	···	m	$^{15}NF_2$
931	···	m	$^{14}NF_2$
998	m	s	$^{15}NF_2CN$
1018	m	s	$NF_2C^{15}N$
1074	···	w	$^{13}CF_2$
1087	···	m	CF_3
1102	m–s	vs	CF_2
1213	···	w	
1218	···	w, sh	$CN^{15}N$
1222	m	s	CF_2
1234	···	w	$^{13}CF_4$
1238	···	w	$C^{15}NN$
1251	···	vs	CF_3
1260	···	vs	CF_4
1274	s	vvs	CF_4
1295	···	w–m	CF
1469	vvs	···	^{15}NCN
1715	···	m–s	
2032	···	s	
2067	···	s	
2790	···	w	$C^{15}NN$
2838	···	w	$CN^{15}N$
2848	···	w	CNN

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[9] D. J. Seery and D. Britton, J. Phys. Chem. **68**, 2263 (1964).

[10] R. K. Steunenberg and R. C. Vogel, J. Am. Chem. Soc. **78**, 901 (1956).

[11] 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.

[12] D. E. Milligan, D. E. Mann, M. E. Jacox, and R. A. Mitsch, J. Chem. Phys. **41**, 1199 (1964).

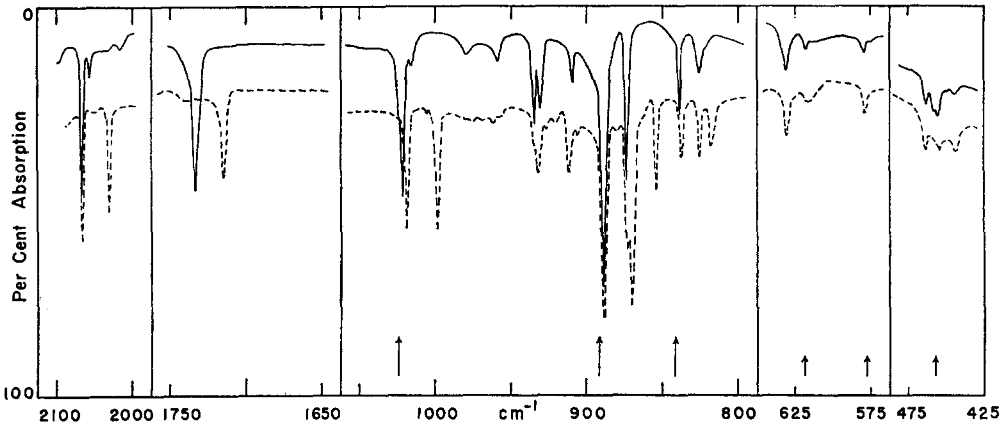

FIG. 1. ——, $Ar:F_2=50+Ar:N_3CN=100$. 14°K. 166 μM F_2; 111 μM N_3CN. 185-min Cd photolysis through LiF+55-min Hg photolysis through CsI, LiF. - - -, $Ar:F_2=50+Ar:N_3C^{15}N(95\%)=100$. 14°K. 248 μM F_2; 134 μM N_3CN. 120-min Cd photolysis through LiF+90-min Hg photolysis through CsI, LiF.

a number of new features appear. Among these are weak to moderately intense absorptions near 455, 580, and 618 cm^{-1}, which also correspond well in frequency and relative intensity with absorptions of gaseous NF_2CN. It should be noted that in typical experiments conversion of cyanogen azide to NCN is substantial but not complete at the end of the period of cadmium-arc irradiation. Thus, more NCN is produced during the mercury-arc photolysis, when photodecomposition of NCN to produce carbon atoms also occurs. Accordingly, growth in the features assigned to NF_2CN during the mercury-arc irradiation is not surprising. As might be expected, the growth in the CF_2 and CF_4 concentration is even more dramatic. New features at 703, 1087, and 1250 cm^{-1} are readily assigned to the CF_3 free radical, for which absorptions having similar relative intensities have previously been reported[13] very near these frequencies. The moderately intense absorption shown by gaseous NF_2CN at 2244 cm^{-1} has not been observed in these experiments; presumably it is obscured by the absorption of residual cyanogen azide. Moderately intense absorptions due to CNN are recognized at 1241 and 2848 cm^{-1},[2] and a weak feature tentatively ascribed to a CN polymer[14] appears at 2058 cm^{-1}. In the later stages of photolysis, a sharp, moderately intense absorption appears at 1295 cm^{-1}. This feature agrees reasonably well in frequency with the ground-state vibrational fundamental of CF.[15] Detailed arguments supporting this assignment have been presented in a separate article.[16] A pair of absorptions at 931–934 cm^{-1} may be assigned to NF_2.[17] Finally, prominent, unidentified absorptions appear at 827, 874, 909, 1733, and 2068 cm^{-1}.

On prolonged irradiation of the sample with light from the mercury arc, absorptions due to NF_2CN undergo a very slow decrease in intensity. The weak to moderately intense 455- and 580-cm^{-1} features, on the other hand, increase in intensity, presumably because of the formation of more highly fluorinated species having absorption frequencies closely similar to those of NF_2CN. New features appear between 950 and 1000, 1100 and 1200, 1300 and 1350, and 1650 and 1700 cm^{-1}. These absorptions are, in general, broad, and the species giving rise to them have not been characterized; they may be contributed by products of the fluorination of NF_2CN and of other species present in the sample at earlier stages in the photolysis. Evidence for the continuing importance of such fluorination processes is provided by the steady growth in absorptions due to CF_3 and CF_4 in the later stages of photolysis. The features at 827, 874, 909, and 2068 cm^{-1} decrease slowly in intensity when F atoms are produced but NCN is no longer present, while the 1049- and 1733-cm^{-1} features continue to grow.

Frequencies of features appearing following photolysis of $Ar:F_2+Ar:N_3C^{15}N$ (95%) samples are summarized in Table II, together with proposed assignments. Regions of particular interest in the infrared spectra of ordinary and ^{15}N-substituted samples after periods of photolysis sufficient for full development of characteristic product features are compared in Fig. 1. Assignment of the 931-cm^{-1} feature to NF_2 receives further support from the appearance of an equally intense feature at 912 cm^{-1}, in reasonable correspondence with the frequency recently reported for $^{15}NF_2$.[18] The three tall arrows in Fig. 1 designate the frequencies of band centers of the three most

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[13] D. E. Milligan, M. E. Jacox, and J. J. Comeford, J. Chem. Phys. **44**, 4058 (1966).

[14] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 278 (1967).

[15] E. B. Andrews and R. F. Barrow, Proc. Phys. Soc. (London) **A64**, 481 (1951).

[16] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **48**, 2265 (1968).

[17] M. D. Harmony and R. J. Myers, J. Chem. Phys. **37**, 636 (1952).

[18] M. E. Jacox and D. E. Milligan, J. Chem. Phys. **46**, 184 (1967).

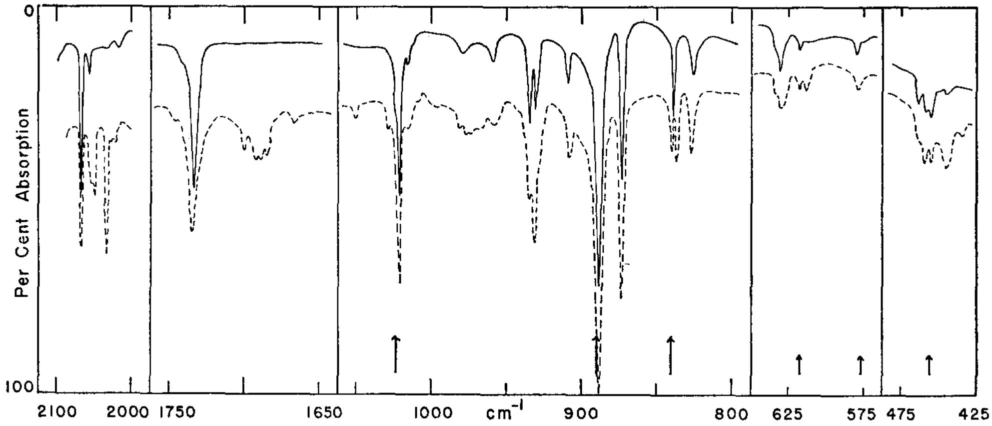

FIG. 2. ——, Ar:F_2=50+Ar:N_3CN=100. 14°K. 166 μM F_2; 111 μM N_3CN. 185-min Cd photolysis through LiF+55-min Hg photolysis through CsI, LiF. - - -, Ar:F_2=100+Ar:$N_3{}^{13}CN$(54%)=100. 14°K. 95 μM F_2; 142 μM N_3CN. 120-min Cd photolysis through LiF+60-min Hg photolysis through KBr.

intense stretching fundamentals of gaseous NF_2CN, and the three shorter arrows designate the frequencies of band centers of the three bending fundamentals of gaseous NF_2CN which appear within the presently accessible spectral range. Absorptions near 500, 700, and 1050–1300 cm^{-1}, which, as is seen in Table II, are characteristic of species for which spectral shifts do not occur on ^{15}N substitution, are omitted from this figure. The 425–475-cm^{-1} pattern of absorption in both spectra is somewhat complicated by features due to unphotolyzed cyanogen azide.

Table III and Fig. 2 present the corresponding data for samples in which ^{13}C substitution is employed. The 567- and 576-cm^{-1} features are assigned to $NF_2{}^{13}CN$ and to $NF_2{}^{12}CN$, respectively, since their intensities are approximately constant in the later stages of photolysis, while the intensities of the 560- and 580-cm^{-1} absorptions continue to grow. As in the other experiments, the last traces of cyanogen azide are photolyzed only with considerable difficulty, presumably because of the filtering effect of CF_2 and other product species. The absorptions near 500 and 700 cm^{-1} and between 1050 and 1300 cm^{-1}, for which a complicated pattern of spectral shifts is observed on ^{13}C substitution, are contributed by species which do not contain nitrogen. Their detailed assignment is the subject of a separate article.[16] The spectral trace shown in Fig. 2 for the products of a ^{13}C-substitution experiment was taken rather late in the course of photolysis, when products characteristic of secondary fluorination had begun to appear. The broad, poorly resolved features near 950 and 1700 cm^{-1}, which appear to be characteristic of more highly fluorinated products, are more prominent in this trace than in certain of the others. It should also be noted that the moderately intense doublet appearing in this trace near 2052 cm^{-1} also appears on photolysis of matrix-isolated Ar:$N_3{}^{13}CN$ samples in the absence of F_2.[3]

In several of the Ar:F_2+Ar:$N_3{}^{13}CN$ (54%) experiments, the development of NCN by cadmium-arc irradiation was followed by an extended period of mercury-arc photolysis through the chlorine gas filter, permitting C-atom production but suppressing the production of F atoms. During this period growth of the features assigned to NF_2CN, CF_2, and CF_4 and of the 827- and 1734-cm^{-1} features proceeded steadily, but features assigned to CF and to CF_3 were slow to appear, as were the absorptions at 873, 907, 931–934, 2034, and 2068 cm^{-1}. When the chlorine filter was removed, all of the features underwent accelerated growth, but the growth of these latter features was especially dramatic.

When selected regions of the spectrum were followed during warmup of the sample, the features assigned to NF_2CN were, in general, found to persist. On the other hand, the 827- and 874-cm^{-1} features disappeared, indicating that the species responsible for them are highly reactive.

DISCUSSION

Spectrum and Properties of NF_2CN

As has been indicated, both the frequencies and the relative intensities of features assigned to NF_2CN in the present experiments agree very well with those of infrared absorptions reported by Colthup[7] for gaseous NF_2CN, except that the 2244-cm^{-1} region is complicated by residual cyanogen azide absorption. Although the frequencies of the more prominent NF_2CN fundamentals are here reported for the ^{13}C– and both singly ^{15}N-substituted species, data do not suffice for a more detailed normal-coordinate analysis than that of Colthup. Qualitatively, it may be concluded that the frequency shifts observed on isotopic substitution are entirely consistent with those to be expected assuming a pyramidal structure for NF_2CN and the previous assignment. Thus, relatively great shifts have been observed on ^{13}C substitution for the 840-, 619-, and 576-cm^{-1} features, identified with modes in which appreciable C-atom motion occurs, while the frequencies of the 1021- and 888-cm^{-1} modes, which involve primarily N–F stretching motion, are unaffected. In the ^{15}N-substitution study, the 888-cm^{-1} feature has an equally intense counterpart at 869 cm^{-1}, and the 1021-cm^{-1} feature is replaced by a pair of features of equal intensity at 1018 and 998 cm^{-1}. Assignment of these features to the two singly ^{15}N-substituted difluorocyanamides is readily made. The contribution of motion of the CN nitrogen to the 891-cm^{-1} absorption was found by Colthup to be very small, while that to both the 841- and 1024-cm^{-1} absorptions is appreciable. Accordingly, there is a downward shift in both ^{15}N-substitution counterparts of the 841- and 1021-cm^{-1} features, but the intense 888-cm^{-1} absorption is unshifted. The intense absorption at 869 cm^{-1} must be identified with the corresponding fundamental of $^{15}NF_2CN$. Assignment of the 817-cm^{-1} feature, rather than of the 825-cm^{-1} feature, to $^{15}NF_2CN$ appears to be precluded by the relatively broad contour of the 817-cm^{-1} feature, probably the counterpart of the 827-cm^{-1} feature of experiments in which isotopic substitution is not employed. The 618-cm^{-1} feature, which appears only very weakly in the present experiments, is primarily an NCN deformation mode. Accordingly, some downward shift has been observed in the ^{15}N-substitution study, and the feature is broadened.

TABLE III. Behavior of features appearing in Ar:F_2+Ar:$N_3{}^{13}CN$ (54%) samples after photolysis by Cd- and Hg-arc radiation.

	Relative intensity		
(cm^{-1})	Cd arc	Hg arc	Assignment
412	vs	···	$N^{13}CN$
423	vs	···	$N^{12}CN$
455	···	w	
460	···	m	
464	···	w	
512	···	w	$^{13}CF_3$, $^{12}CF_3$
560	···	vw	
567	···	w	$NF_2{}^{13}CN$
576	···	vw	$NF_2{}^{12}CN$
580	···	w–m	
615	···	vw	$NF_2{}^{13}CN$
619	···	vw	$NF_2{}^{12}CN$
630	···	m–s	$^{12}CF_4$, $^{13}CF_4$
643	···	w	
695	···	w	$^{13}CF_3$
703	···	w	$^{12}CF_3$
827	m	m–s	
836	w–m	m–s	$NF_2{}^{13}CN$
840	w–m	m–s	$NF_2{}^{12}CN$
873	···	s	
888	s	vs	NF_2CN
907	···	m	
931	···	s	NF_2
934	···	s	
942	···	w–m	
959	···	w–m	
975	···	m, broad	
1021	m–s	s–vs	NF_2CN
1049	···	w–m	
1063	···	w–m	$^{13}CF_3$
1074	m	vs	$^{13}CF_2$
1080	···	sh	
1087	···	m, sh	$^{12}CF_3$
1102	m	vs	$^{12}CF_2$
1114	···	w	
1191	w	s	$^{13}CF_2$
1201	···	s	$^{13}CF_3$
1219	···	vs	$^{13}CF_3$
1222	w	s	$^{12}CF_2$
1234	m–s	vvs	$^{13}CF_4$
1251	w	vs	$^{12}CF_3$
1260	···	vs	$^{12}CF_4$, $^{13}CF_4$
1274	s	vvs	$^{12}CF_4$
1295	···	m	^{12}CF
1435	vvs	···	$N^{13}CN$
1475	vvs	···	$N^{12}CN$
1666	···	w–m	
1686–93	···	m, broad	
1700	···	m	
1734	m	vs	
2034	···	s	
2052	w	m	
2068	···	s	
2268	···	m	
2836	···	w–m	^{13}CNN
2848	···	w–m	^{12}CNN

Failure of the absorptions of NF_2CN to disappear during warmup of the sample is consistent with the stability of gaseous NF_2CN at room temperature.

A small concentration of CF_2 is detected in the early stages of photolysis using cadmium-arc radiation, suggesting that photoisomerization of NF_2CN to difluorodiazirine, CF_2N_2, followed by photolysis of CF_2N_2 to produce CF_2, may occur; Meyers and Frank[6] have found that in the presence of CsF, difluorocyanamide rearranges readily to difluorodiazirine. However, since very little CF_2 would need to be present to account for the observed intensities of the CF_2 absorptions, this species may be formed by the reaction with F_2 of a small concentration of C atoms produced on photolysis of NCN by relatively weak cadmium lines in the appropriate spectral region.

The slow disappearance of difluorocyanamide on prolonged mercury-arc irradiation can be explained either by photolysis of this species or by its reaction with F atoms. Meyers and Frank have observed unstructured absorption for NF_2CN at wavelengths shorter than approximately 2620 Å. Photolysis of NF_2CN would be expected to be inhibited by the strong absorption of CF_2 in the 2300–2600-Å region.

Evidence for FNCN

The 873- and 2068-cm^{-1} features behave similarly under all of the conditions imposed in the present experiments, suggesting that they are contributed by a single species. Their growth appears to be maximized when both F atoms and NCN are present, behavior paralleled by that of the absorptions of HNF, which achieve their maximum growth during the simultaneous photoproduction of NH and of F atoms.[18] This parallel suggests the possible formation of FNCN in the present experiments. Disappearance of these two features on warmup indicates that they are contributed by a reactive species. An absorption near 2068 cm^{-1} would be expected for a species containing a $-C{\equiv}N$ or $-N{\equiv}C$

group, and the isotopic shift observed on both ^{13}C and ^{15}N substitution corresponds well with that predicted for a stretching vibration localized in either of these two groups. The 873-cm^{-1} absorption, which is insensitive to ^{13}C substitution but possesses a counterpart at 854 cm^{-1} in the ^{15}N-substitution study, behaves appropriately for assignment to an N–F stretching mode. Unfortunately, the region near 873 cm^{-1} is partly obscured in the ^{15}N-substitution study by the very strong 869-cm^{-1} absorption assigned to $^{15}NF_2CN$. However, a partly resolved feature is observed in this study at 873 cm^{-1}, within limits of observation unshifted from the value obtained in experiments using ordinary cyanogen azide. Such behavior would be anticipated for FNCN.

Features near 460 and 910 cm^{-1} are also observed to grow dramatically when F atoms are present in the sample. Unfortunately, present data do not suffice for the assignment of these features to FNCN or to a possible second product of the F-atom reaction in this system.

Other Nitrogen-Containing Species

The 1734-cm^{-1} feature, which appears rather early in the course of photolysis, even when the chlorine filter is used to suppress F-atom production, may well be contributed by a relatively simple species. The observation of a single counterpart of this feature at 1715 cm^{-1} in the ^{15}N-substitution study suggests that the nitrogen atoms in this species may be symmetrically placed; if the species were to contain only one nitrogen atom, the unshifted feature should, of course, also appear, and if two nitrogens, its formation from $^{15}NC^{14}N$ would result in random positioning of the ^{15}N in an unsymmetrical structure. Possible symmetrical structures are those of the carbodi-imide, FN=C=NF, and of the difluoraminocarbene, $(F_2N)_2C$:. The carbodi-imide structure appears to be rather unlikely, since the observed frequency is about 300 cm^{-1} lower than a typical value[7] for the –N=C=N– antisymmetric stretching mode of a carbodi-imide and since the intensity of the 1734-cm^{-1} feature continues to grow when very little NCN remains in the system, suggesting that it is contributed by a more highly fluorinated species. The carbene structure would probably be relatively unstable; its rearrangement to F_2N–CF=NF would most likely occur. Since the carbon–nitrogen stretching mode of perfluoromethylenimine has been observed[19] at 5.77 μ (approximately 1733 cm^{-1}), the magnitude of the observed frequency, if not its behavior on isotopic substitution, is certainly consistent with its assignment to the C=N stretching mode of a derivative of perfluoromethylenimine.

Little can be said regarding the identity of the species responsible for the moderately intense 827-cm^{-1} absorption, which shifts to 817 cm^{-1} on ^{15}N substitution but is unaffected on ^{13}C substitution. Although the isotopic substitution behavior and the growth rate of this feature in chlorine filter experiments parallel those of the 1734-cm^{-1} feature, on prolonged photolysis the intensity of the 827-cm^{-1} feature, unlike that of the 1734-cm^{-1} feature, begins to diminish.

The mechanism by which the small concentration of NF_2 is formed cannot be determined with certainty. Conceivably, a small concentration of N atoms is produced in the photodecomposition of NCN—some CN is observed in this system—and these N atoms may react with F_2. Alternatively, the reaction of F atoms with NF_2CN to produce NF_2 and FCN may occur. It is uncertain whether a small concentration of FCN is formed in these experiments; the regions of the two more intensely absorbing fundamentals, which appear at 455 and at 1076–1081 cm^{-1} in an argon matrix, are partly obscured by absorptions of other species in the present experiments. Since the growth rate of NF_2 increases rather dramatically when F atoms are present, this latter mechanism may well play a significant role in the production of NF_2. On the other hand, the concentration of NF_2 does appear to level off and then to diminish slightly in the later stages of the experiment, when the reaction of F atoms with NF_2CN should still occur with reasonable probability.

CONCLUSIONS

When NCN is produced by the photolysis of matrix-isolated cyanogen azide in the presence of F_2, an appreciable concentration of difluorocyanamide is also formed. The earlier vibrational assignment of the fundamentals of this species is confirmed by observation of the most prominent infrared absorptions of $NF_2{}^{13}CN$ and of the two singly ^{15}N-substituted species in the present experiments. When light of wavelength appropriate for F-atom production is present in the photolyzing radiation, two absorptions attributable to FNCN also appear. Upon prolonged photolysis, incompletely characterized products of the further fluorination of NF_2CN are formed.

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[19] D. H. Dybvig, Inorg. Chem. 5, 1795 (1966).