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Matrix-Isolation Study of the Photolysis of Cyanogen Azide. II. The Symmetric Stretching Fundamental of the Free Radical NCN

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The photolysis of Ar:N₃CN samples at 14°K with the full light of a cadmium arc has been found to permit complete conversion of the cyanogen azide to the free radical NCN, plus molecular nitrogen. At the high concentration of NCN thus achieved, a weak absorption appears at 2672 cm⁻¹. The photolytic behavior of this feature and its shifts upon isotopic substitution support its assignment as the combination band $(\nu_1+\nu_3)$ of NCN, permitting deduction of a value of 1197 cm⁻¹ for ν_1 of this species. The thermodynamic properties of NCN have been revised in accord with this assignment. The carbon-nitrogen stretching force constant approaches a value characteristic of a doubly bonded species, and the stretching interaction constant is relatively large and positive. Cyanogen azide photolyzes in both its 2750- and its 2200-Å absorption regions to produce NCN+N2. However, NCN itself photolyzes when subjected to radiation near 2500 Å, producing carbon atoms in the ${}^{3}P$ state, which, in turn, may react with N₂ to form the free radical CNN.

I. INTRODUCTION

THE free radical NCN has been shown by Milligan, Jacox, and Bass¹ to be the principal spectroscopically observable product of the photolysis of matrixisolated cyanogen azide with the Pyrex-filtered radiation of a medium-pressure mercury arc. Sufficient concentrations of NCN are obtained in this manner for direct observation of both infrared-active fundamentals, at 423 and 1475 cm⁻¹, of the 3290-Å absorption, previously shown by Herzberg and Travis² to result from the $A({}^{3}\Pi_{u}) - X({}^{3}\Sigma_{g})$ transition of NCN, and of a previously unobserved band system of NCN between 3000 and 2400 Å. Further studies have shown that photolysis of matrix-isolated cyanogen azide with the full light of the medium-pressure mercury arc provides a convenient source of carbon atoms, which have been found to react with CO in a matrix environment to produce the free radical CCO3 and with N2, also a product of the photodecomposition of cyanogen azide, to produce the free radical CNN.⁴

Several unsolved problems remained following the earlier study. The carbon-nitrogen bond lengths of ground state NCN had been shown by Herzberg and Travis² to approximate those of an N=C=N structure. On the other hand, the stretching force constant derived from the 1475-cm⁻¹ antisymmetric stretching frequency of NCN corresponds much more closely to values characteristic of carbon-nitrogen single bonds. This apparent contradiction could be resolved if the stretching interaction force constant were relatively large and positive. However, because the symmetric stretching frequency of NCN could not be observed directly, the magnitude of this interaction constant could not be assessed. The second major unresolved problem of the earlier studies is that of the mechanism of photodecomposition of cyanogen azide. Even upon prolonged Pyrex-filtered photolysis with a mercury lamp, only a fraction of the cyanogen azide could be converted to NCN, so that processes occurring in this system upon short-wavelength photolysis of cyanogen azide and of NCN could not be separated and the electronic state of the resultant carbon atoms remained uncertain.

Recently, it has been found that complete photodecomposition of cyanogen azide to NCN can be achieved using a cadmium-arc lamp as the source of photolytic radiation. As is shown, the resultant yield of NCN in a typical experiment is several times greater than the highest concentration previously achieved, permitting the observation of a combination band from which the value of the symmetric stretching frequency may be deduced. Furthermore, the characteristics of the cadmium photolysis source and its separation of the photolysis of NCN from that of cyanogen azide have led to clarification of the mechanism of the photolytic processes.

II. EXPERIMENTAL DETAILS

The procedures used in sample preparation and the instrumentation are identical to those described in the earlier publication.1 However, samples were first photolyzed with the full light of an Osram⁵ cadmiumarc lamp from which the outer glass envelope had been removed. Supplementary ultraviolet observations were conducted on a Perkin-Elmer⁵ Model 112 spectrometer

¹ D. E. Milligan, M. E. Jacox, and A. M. Bass, J. Chem. Phys. **43**, 3149 (1965). ² G. Herzberg and D. N. Travis, Can. J. Phys. **42**, 1658 (1964). ³ M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. **43**, 3734 (1965).

⁴ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 44, 2850 (1966).

⁵ 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.



FIG. 1. Ar: N_{3}^{13} CN (50.5%) = 100, 14°K; 100 mm×2 liter. —, Before photolysis; — –, 105-min Cd photolysis; - – –, 30-min Hg photolysis.

used in double-pass operation with a quartz prism, a 1P28 photomultiplier detector, and hydrogen and tungsten background sources.

III. OBSERVATIONS

The great increase in the intensities of features previously assigned to NCN and the extent of separation of the photolysis of cyanogen azide and of NCN are illustrated by Figs. 1 and 2, which show typical studies of the photodecomposition of N₃¹³CN (50.5%) and of N₃C¹⁵N(95%), respectively, in an argon matrix. The intensities of features assigned to NCN are found to be at least five times as great as those achieved in typical experiments in which NCN is produced using a Pyrexfiltered medium-pressure mercury arc. Despite the great increase in the concentration of NCN coupled with the removal of cyanogen azide absorptions which obscured the 2100–2250-cm⁻¹ spectral region in the earlier studies, no new feature in the 1900–2400-cm⁻¹ region can be assigned to NCN. In contrast to the NCN features, the absorption appearing near 2100 cm⁻¹ remains on unfiltered mercury-arc photolysis of this system, and does not disappear readily on warmup. In an argon matrix, but not in a nitrogen matrix, the intense antisymmetric stretching absorption of NCN at 1475 cm⁻¹ is accompanied by prominent satellite features at 1463 and 1482 cm⁻¹, with features of similar spacing and intensity accompanying the corresponding absorption of isotopically substituted NCN. In addition, a weak feature of photolytic behavior similar to that of NCN appears at 2672 cm⁻¹. In Ar:N₃¹³CN (50.5%) experiments, a pair of equally intense features appears at 2630 and 2672 cm⁻¹; and in Ar:N₃C¹⁵N (95%) experiments a single weak feature appears at 2646 cm⁻¹.

Utilization of the full light of the cadmium arc is found to be required for efficient production of NCN. When the 2288-Å cadmium line is filtered from the sample with a cesium iodide window, relatively little photolysis results. Thus, the 2288-Å cadmium line,



rather than the cadmium radiation in the 2800–3000-Å spectral region, appears to be primarily responsible for the photoproduction of NCN.

The concentrations of the products of unfiltered mercury-arc photolysis of samples in which cyanogen azide has first been fully converted to NCN by cadmium-arc photolysis are comparable to the concentrations observed without prephotolysis by the cadmium arc.

IV. DISCUSSION

A. Properties of NCN

Both the photolytic behavior of the 2672-cm^{-1} feature and the pattern of the corresponding absorptions observed in the isotopically substituted systems are consistent with its assignment to NCN. It appears possible to attribute this feature either to the combination $(\nu_1 + \nu_3)$ or to a combination involving multiple excitation of ν_2 . Since the excitation of three or more quanta of

 ν_2 together with ν_1 or ν_3 would be required in such a combination, the assignment as $(\nu_1+\nu_3)$ appears to be more likely. Table I compares the values of ν_1 derived from the known value of ν_3 and the postulated assignment of the observed feature to $(\nu_1+\nu_3)$ with the calculated value of ν_1 , assuming a value of 1197 cm⁻¹ for $^{14}N^{12}C^{14}N$. The calculated value for $^{15}N^{12}C^{14}N$ is taken as the mean of the value for $^{14}N^{12}C^{14}N$ and that calculated for $^{15}N^{12}C^{15}N$. Agreement is seen to be within experimental error. Although at first glance the alternative assignment as $(\nu_3+3\nu_2)$, calculated to appear at

TABLE I. Comparison of calculated and observed values of ν_1 for isotopically substituted NCN.

Species	$\nu_1 + \nu_3$ (cm ⁻¹)	$(\nu_1 + \nu_3) - \nu_2$ (cm ⁻¹)	Calculated ν_1 (cm ⁻¹)
¹⁴ N ¹² C ¹⁴ N	2672	1197	•••
¹⁴ N ¹³ C ¹⁴ N	2630	1195	1197
¹⁵ N ¹² C ¹⁴ N	2646	1178	1177

TABLE II. Thermodynamic properties (calories per mole per degree Kelvin) of NCN.

<i>T</i> (°K)	C_p°	$(H^{\circ}-H_{0}^{\circ})/T$	$-(F^{\circ}-H_{0}^{\circ})/T$	S°
273.16	9.83	8.06	45.10	53.15
298.16	10.09	8.22	45.81	54.03
300	10.11	8.23	45.86	54.09
400	11.04	8.82	48.31	57.13
500	11.82	9.34	50.34	59.68
600	12.42	9.81	52.08	61.89
700	12.90	10.22	53.63	63.84
800	13.26	10.58	55.01	65.59
900	13.54	10.89	56.28	67.17
1000	13.76	11.16	57.44	68.61
1100	13.93	11.41	58.52	69.93
1200	14.06	11.63	59.52	71.15
1300	14.18	11.82	60.46	72.28
1400	14.27	11.99	61.34	73.33
1500	14.34	12.14	62.17	74.32
2000	14.58	12.72	65.74	78.47
3000	14.75	13.38	71.05	84.43

2744 cm⁻¹ for ¹⁴N¹²C¹⁴N, also seems to be reasonable, large discrepancies are found between the observed and calculated isotopic shifts.

Further evidence in support of the assignment of the 2672-cm⁻¹ feature as ($\nu_1 + \nu_3$) is provided by the ultraviolet observations. In the earlier study1 a weak unassigned feature was reported at 3221 Å in an argon matrix and at 3193 Å in a carbon monoxide matrix. More recent ultraviolet observations on samples in an argon matrix have shown the photolytic behavior of this feature to be identical to that of the other absorptions assigned to NCN. Since the linearity of NCN is preserved in the 3290-Å transition, the assignment of this weak feature, located 1136 cm⁻¹ to the violet of the main feature in an argon matrix (1142 cm⁻¹ in a carbon monoxide matrix), to the (100-000) band of the NCN $A({}^{3}\Pi_{u})-({}^{3}\Sigma_{g}^{-})$ system is suggested. Although Herzberg and Travis² were unable to obtain direct evidence for any of the stretching frequencies of NCN, they were able to deduce that $\nu_1' - \nu_1'' = -5$ cm⁻¹ for this transition. Thus, a value of 1141 cm⁻¹ may be deduced for the symmetric stretching frequency of ground state NCN, using the argon-matrix data. Although the discrepancy between this value and the 1197-cm⁻¹ value deduced from the infrared data appears at first glance to be rather large, it should be noted that an error of only 1 Å in an observation near 3300 Å corresponds to 10 cm⁻¹. In view of the breadth of the extremely intense (000-000) band in the matrix, a discrepancy as large as 50 cm⁻¹ appears to be not at all unreasonable. Indeed, in an argon-matrix experiment in which the (000-000) band was observed very early in the photolysis, while still relatively sharp, and the weak (000-000) band after the maximum concentration of NCN had been achieved, the observed wavelengths of peak absorption were found to be 3354 and 3226 Å, respectively, permitting the deduction of a value of 1188 cm⁻¹ for ν_1'' .

The assignment of the symmetric stretching mode of NCN at 1197 cm⁻¹, together with the previous assignment of v_3 at 1475 cm⁻¹, permits the deduction of a stretching force constant of 8.60 mdvn/Å and of an interaction constant of +3.22 mdyn/Å. Although the stretching force constant is still somewhat small for a doubly bonded species, the discrepancy between the bond orders predicted from the force constant and the bond-length data is certainly greatly reduced.

With the determination of the symmetric stretching frequency of NCN, the thermodynamic properties previously derived for this species (Table IX of Ref. 1) are superseded by the values given in Table II.

The discussion of the physical significance of interaction constants by Linnett and Hoare⁶ suggests that the relatively large, positive value of the interaction constant for NCN implies the presence of delocalized electrons in the ground state of this species and that, at infinite separation of one of the nitrogen atoms of NCN, the remaining CN fragment should be appreciably more strongly bonded than in NCN. Thus, one might expect ground state NCN to correlate with $N(^{4}S)$ and with CN in either its $X(^{2}\Sigma)$ or its $B(^{2}\Sigma)$ state, since only these two low-lying states of CN are found⁷ to have bond lengths appreciably less than those observed for ground state NCN. An extension of these arguments to NCN in its $A({}^{3}\Pi_{u})$ state, for which Herzberg and Travis² have found bond lengths and stretching frequencies closely similar to those of the ground state, would require that NCN $A({}^{3}\Pi_{u})$ correlate with CN $X(^{2}\Sigma) + N(^{2}D)$ or with CN $B(^{2}\Sigma) + N(^{2}D)$ rather than with CN $A(^{2}\Pi) + N(^{4}S)$.

B. Mechanism of Photodecomposition

Marsh and Hermes⁸ have found cyanogen azide to have a weak ultraviolet absorption near 2750 Å and a second absorption, 20 times as intense, near 2200 Å. The 2750-Å absorption apparently is responsible for the previously reported¹ photolysis of cyanogen azide to produce NCN when a Pyrex filter is employed. In the earlier experiments it was not possible to separate the photolysis of cyanogen azide from that of NCN when the sample was subjected to the full light of the mercury arc. Thus, it seemed reasonable to suggest the possibility that not only the photolysis of NCN but also the photoisomerization of N₃CN to N₃NC in the matrix environment, followed by decomposition of N₃NC to $2N_2+C$, might provide a route for the production of carbon atoms when more energetic photolyzing radiation is used.

Using a cadmium arc for photolysis, it has been found that relatively little NCN is produced by the cadmium radiation in the 2800–3000-Å region but that the 2288-Å cadmium line is extremely efficient for photolyzing cyanogen azide to produce NCN. Thus, it must be

⁶ J. W. Linnett and M. F. Hoare, Trans. Faraday Soc. 45, 844 (1949).

⁷ P. K. Carroll, Can. J. Phys. **34**, 83 (1956). ⁸ F. D. Marsh and M. E. Hermes, J. Am. Chem. Soc. **86**, 4506 (1964).

(1)

concluded that both of the absorption regions known for cyanogen azide lead to NCN+N₂ as the primary photolysis products. In view of the relatively low absorption intensity of the 2750-Å band of cyanogen azide, possibly this transition involves excitation to an unstable triplet state of cyanogen azide. On the other hand, the great intensity of the 2200-Å system requires that it be associated with an allowed transition of cyanogen azide to an unstable singlet state. Kroto⁹ has observed the initial production of NCN in a ${}^{1}\Delta_{g}$ state, which undergoes collisional deactivation to the ground triplet state, following the flash photolysis of cyanogen azide. In summary, the following processes are suggested:

N₃CN+
$$h\nu$$
(2750 Å)→(triplet N₃CN)
→NCN($^{3}\Sigma_{g}^{-}$)+N₂,

 $N_{3}CN + h\nu(2200 \text{ Å}) \rightarrow NCN(^{1}\Delta_{g}) + N_{2}, \qquad (2)$

$$NCN({}^{1}\Delta_{g}) + matrix \rightarrow NCN({}^{3}\Sigma_{g}^{-}).$$
(3)

When NCN is subjected to radiation from a mediumpressure mercury arc, it photolyzes completely within about $\frac{1}{2}$ h. Thus, its photodecomposition appears to occur by an allowed process. Assuming that N₂ is formed in its ground state, spin conservation would require that NCN photolyze to produce carbon atoms in the ground ³P state by the process

$$\operatorname{NCN}({}^{3}\Sigma_{g}^{-}) + h\nu \rightarrow \operatorname{C}({}^{3}P) + \operatorname{N}_{2} X({}^{1}\Sigma_{g}^{+}).$$
(4)

As has been shown,⁴ a significant fraction of the carbon atoms produced by this process undergo reaction with N_2 trapped in the cavity:

$$C(^{3}P) + N_{2} \rightarrow CNN.$$
 (5)

Since, irrespective of the extent of photolysis, there is no evidence for back reaction of C atoms produced upon photolysis of N₃C¹⁵N to yield ¹⁴NC¹⁴N in a proportion greater than that expected from the 5% N₃C¹⁴N present in the initial sample, the reaction of C(³P) with N₂ must form CNN only. On the other hand, when carbon atoms are produced in a nitrogen matrix by the vacuum-ultraviolet photolysis of carbon suboxide, both NCN and CNN are produced.^{4,10} However, Stief and DeCarlo¹¹ have shown that at wavelengths shorter than 1660 Å, photodecomposition of carbon suboxide into $2CO+C(^{1}D)$ is energetically possible, and that beyond 1394 Å the species $C(^{1}S)$ may also be produced. Thus, it appears reasonable to postulate that

$$C(^{1}D) + N_{2} \rightarrow NCN(^{1}\Delta_{g}), \qquad (6)$$

followed by Reaction (3).

The photolysis of NCN to produce carbon atoms appears to result from an absorption continuum underlying the shorter wavelength NCN absorption system. Presumably, the maximum of this continuum absorption lies relatively close to the intense 2537-Å mercury line, permitting stabilization of a high concentration of NCN in samples subjected to 2288-Å irradiation and of an easily detectable concentration of NCN in samples subjected to vacuum-ultraviolet photolysis with krypton and xenon discharge sources.

A previously unassigned absorption appearing at 3825 Å following unfiltered mercury-arc irradiation of cyanogen azide in an argon matrix has been found to coincide exactly with the (0, 0) band of the CN $B(^{2}\Sigma)-X(^{2}\Sigma)$ transition, observed following the vacuum-ultraviolet photolysis of an Ar:HCN sample. Thus, a small fraction of the NCN may also undergo photolysis to the products N+CN. However, even in a CO matrix insufficient concentrations of these species are produced for the appearance of infrared absorptions characteristic of their further reaction.³

V. CONCLUSIONS

The weak 2672-cm⁻¹ feature which appears when high photolytic yields of NCN are present may be assigned to the combination band $(\nu_1+\nu_3)$ of NCN, permitting deduction of a symmetric stretching frequency of 1197 cm⁻¹. Isotopic data support this assignment. The carbon-nitrogen stretching force constant approaches a magnitude typical of doubly bonded species, and the stretching interaction force constant is relatively large and positive. Cyanogen azide is observed to photolyze in both its 2750- and its 2200-Å absorption regions to produce NCN. At wavelengths near 2500 Å, NCN also photolyzes, producing $C({}^{3}P) +$ N_{2} . These species may react to form the free radical CNN, but not to re-form NCN.

¹¹ L. J. Stief and V. J. DeCarlo, J. Chem. Phys. 43, 2552 (1965).

⁹ H. W. Kroto, J. Chem. Phys. 44, 831 (1966).

¹⁰ N. G. Moll and W. E. Thompson, J. Chem. Phys. 44, 2684 (1966).