The Production of NCN, HNCN, and Other Free Radicals by Cyanogen Radical Reactions

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THE spectra of NCN ($^3\Sigma$),[1–4] NCN ($^1\Delta$),[5,6] and HNCN ($^2A''$)[7,8] have been observed in absorption together with NH ($^3\Sigma$) following the isothermal flash photolysis of mixtures of cyanogen with ammonia or water. Seven absorption bands involving at least two unknown transients were also seen.

A mixture of NH_3, C_2N_2, and N_2 (0·2 : 40 : 210 mm. Hg) produced the strongest spectrum of HNCN and of four of the absorption bands (spectrum A). The other three bands (spectrum B), together with rather stronger NCN spectra were also obtained from a mixture of cyanogen with oxygen, but for this mixture spectrum A was not observed. For the oxygen and water mixtures NCO[9,10] was produced and OH was present with the water mixture. The spectra were recorded on Ilford HP3 plate using a Hilger quartz spectrograph model 742. The absorption path was 50 cm., and the flash energy ~1000 J. The optimum delay time was 2 sec., and all spectra decayed rapidly.

Spectrum A consists of four sharp, regularly spaced bands near 3171, 3072, 2980, and 2896 Å with sub-bands visible in the first three of these (Table). The 3171 Å band is the strongest, and there is a progressive decrease in intensity, in sharpness, and in the regularity of the sub-band spacing towards lower wavelength. In each band, the strongest feature is the central apparently red-degraded component (R) with the sub-bands to the violet rather stronger than those to the red. The weakness of the spectrum with H_2O and D_2O compared to NH_3 allowed accurate measurement of only three sub-bands of the 3171 Å band for the deuteriated species, and these are also listed in the Table. The sub-band structure is particularly evident in the 3171 Å band with a regular spacing of ~24 cm.$^{-1}$. Like the 3440 Å band of HNCN which has a similar, though more widely spaced (~40 cm.$^{-1}$) sub-band structure, the spacing of the sub-bands is halved on deuteriation. The 3171 Å band is the same as the 3170 Å band mentioned by Herzberg and Travis[1] and the other three bands have been observed by Herzberg, Shoosmith, Travis, and Kroto.[11]

Spectrum B consists of three red-degraded bands at **4264**, **3924**, and **3639** Å of which the first two have been previously reported.[3,12]

TABLE

Wavelengths of spectrum A

A			Deuteriated A	
λ_{air}(Å)	ν_{vac}(cm.$^{-1}$)	ΔG_R(cm.$^{-1}$)	λ_{air}(Å)	ν_{vac}(cm.$^{-1}$)
3175·9	31478			
3173·6	31501		3172·5	31512
3170·8 R	31529		3171·2	31525
3170·3	31534			
3168·4	31553		3170·1	31536
3166·1	31576			
3165·6	31581			
		1014		
3078·7	32472			
3075·4	32507			
3072·7	32535			
3072·0 R	32543			
3070·8	32555			
3066·3	32603			
3062·0	32649			
		1001		
2981·5	33530			
2980·3 R	33544			
2974·7	33607			
		982		
2895·5 R	34526			

R, Band component degraded to red.

The mechanism suggested to account for the observed species may be summarized as follows. The CN radical, produced in the photolysis of C_2N_2, reacts rapidly and successively with NH_3 and NH_2 producing NH, and this radical is also produced in the photolysis of NH_3.[13] The essential reactions are then

$$\mathrm{CN}(X\,^2\Sigma) + \mathrm{NH}(X\,^3\Sigma) \rightarrow$$

$$\mathrm{H}(^2S) + \mathrm{NCN}\ (X\,^3\Sigma_g^-, {}^1\Delta_g) \xrightarrow{\mathrm{M}}$$

$$\mathrm{HNCN}(\tilde{X}\,^2A'')$$

With water, CN produces OH which in turn reacts with CN to produce NH[12] or NCO. The reaction of CN with oxygen[12] also produces NCO, and NCN is produced in the reactions of CN with NCO.[3] While the definite assignment of spectra A and B must await complete spectroscopic analysis, the following considerations are relevant to an interim identification. Spectrum B is believed to be three bands of one species on the grounds that the bands occur together with similar relative intensities and time dependance and because of the similarity in the two spacings (**2028** and **1996** cm.$^{-1}$). The species can only contain C and N and is not NCN ($^3\Sigma$) since, under some conditions, its decay is faster. Though its rate of decay is similar to that of NCN($^1\Delta$), there is a small difference in their relative intensities in different chemical systems. Since the known spectra of CNN,[14] CCN,[15] and CNC[16] were not observed, it is concluded that the species responsible for spectrum B is either another metastable state of NCN (? $^1\Sigma_g^+$) or a more complicated combination of the elements N and C.

The species responsible for the **3171** Å band of spectrum A evidently contained no elements other than C and N except for at least one H atom. The other three bands seem to belong to the same species for the reasons given in connection with spectrum B, but this is not proven. The species is produced by or following the reaction of CN with NH. If it is a primary product, it is either HNNC or a metastable state of HNCN. However, secondary reactions of the products could produce several other species and further speculation is not warranted.

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