Unstable Intermediates. Part CVI.[1] γ-Irradiation of Frozen Aqueous Solutions of Alkali-metal Cyanides

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Exposure of aqueous solutions of alkali-metal cyanides to ^{60}Co γ-rays at 77 K yields hydroxyl radicals, $(CN)_2^-$, H_2CN, and HCN^-. The magnetic parameters of these species are compared with existing data. Under these conditions the radical HCN^- is readily protonated to H_2CN even in strongly alkaline rigid solutions. Some evidence for the formation of the radical $HCNO^-$ was also obtained. If this is correct, then this radical, having $A_{iso}(^1H)$ = 78 G, is probably structurally similar to H_2CN. Possible mechanisms for the formation of these radicals are outlined.

WE have recently reported the results of e.s.r. studies of frozen aqueous solutions of alkali-metal halides, the chief paramagnetic products being H•, MH^+, •OH, $HalOH^-$, and Hal_2^-.[1] These studies are now extended to aqueous solutions of the alkali-metal cyanides. γ-Irradiation of pure alkali-metal cyanides is known to produce *F*-centres,[2] and the species $(CN)_2^-$, which has two magnetically equivalent nitrogen atoms, and is in some ways comparable with V_K-centres in alkali halides.[3] The radical HCN^- has also been detected in irradiated alkali-metal cyanides crystallized from water;[4] and H_2CN has been detected in rare-gas matrices[5] and in γ-irradiated hydrogen cyanide.[6]

EXPERIMENTAL

Reagent grade sodium cyanide (May & Baker) and potassium cyanide (Hopkin & Williams) were used as supplied. Solutions were prepared by dissolving the respective salts in water doubly distilled from alkaline permanganate. Samples were irradiated in the form of small beads at 77 K in a Vickrad ^{60}Co source (4 Mrad/h), to total doses of approximately 2 Mrad.

E.s.r. spectra were recorded on a Varian E-3 spectrometer at 77 K. Samples were annealed by allowing the beads to warm for fixed periods and recooling to 77 K.

RESULTS AND DISCUSSION

Aqueous solutions of sodium cyanide formed good glasses, and e.s.r. spectra were comparable in the presence or absence of sodium hydroxide. In contrast, aqueous potassium cyanide gave polycrystalline solids at 77 K which, gauged by our Mn^{2+} probe,[1] had undergone extensive phase separation. This was confirmed by our e.s.r. results: the spectra showed features characteristic of $C_2N_2^-$,[3] (Table) in addition to those for the radicals detected for the sodium salt. When enough potassium hydroxide was added to give a good glass, no $C_2N_2^-$ could be detected. Since $C_2N_2^-$ is formed in irradiated crystalline potassium cyanide[3] we conclude that $C_2N_2^-$ is not a normal product of the rigid aqueous solutions. This is a good illustration of the difficulties caused by phase separation.

E.s.r. parameters for H_2CN, D_2CN, HDCN, HCN^-, DCN^-, and $C_2N_2^-$

Radical	Nucleus	g_{av}	A	$A_\perp$	A_{iso}	$2B$
H_2CN [a]	^1H	2·0025 ± 0·0005			87·5	
H_2CN [b]	^1H				89·0	
H_2CN [a]	^{14}N		32	0 ± 2	11·0	21·0
H_2CN [b]	^{14}N				15·0 ± 2	
D_2CN [a]	^2D	2·002			13·3 ± 1·0	
	^{14}N		32	0 ± 2	11·0	21·0
HDCN [a]	^1H	2·002			87·5	
	^2D				13·8 ± 1·0	
	^{14}N		32	0 ± 2	11·0	21·0
HCN^- [a]	^1H	2·003			137	
HCN^- [c]	^1H	2·0021			136·5	
HCN^- [a]	^{14}N		16·5	0	5·5	11·0
HCN^- [c]	^{14}N		20·9	0	6·9	14·0
DCN^- [a]	^2D	2·002			21·2	
	^{14}N		16·5	0	5·5	11·0
$C_2N_2^-$ [a]	^{14}N	$g_x = 2·001$	15·6		3·6	12·0
	^{14}N	$g_y = 2·006$		2·5		
		$g_z = 1·985$		2·5		
$C_2N_2^-$ [d]	^{14}N	$g_x = 2·0013$	14·8		3·9	10·9
		$g_y = 2·0058$		2·5		
		$g_z = 1·9851$		2·5		

[a] This work. [b] Ref. 6. [c] Ref. 7. [d] Ref. 3.

Hydroxyl radicals formed in the glassy solids were

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[1] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, **143**.

[2] T. A. Claxton, D. J. Greenslade, K. D. J. Root, and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 2050.

[3] K. D. J. Root and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 21.

[4] K. D. J. Root, M. C. R. Symons, and B. C. Weatherley, *Mol. Phys.*, 1966, **11**, 161.

[5] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1962, **36**, 1938.

[6] K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2163.

[7] I. S. Ginns and M. C. R. Symons, *Chem. Comm.*, 1971, 893.

lost rapidly on annealing but no other radicals appeared to be formed. Both HCN^- and H_2CN were positively identified (Figures 1 and 2), their magnetic parameters (Table) being close to those previously reported for these radicals.[4-6] On annealing, even in the presence of 4M-hydroxide, HCN^- was converted into H_2CN.[7] The fact that the central features for the species described as H_2CN were generally obscured by intense lines from other radicals, made the presence of two equivalent protons unsure. However, an irradiated 1 : 1 mixture of H_2O and D_2O gave features clearly assignable to HDCN, in addition to those for H_2CN (Figure 3).

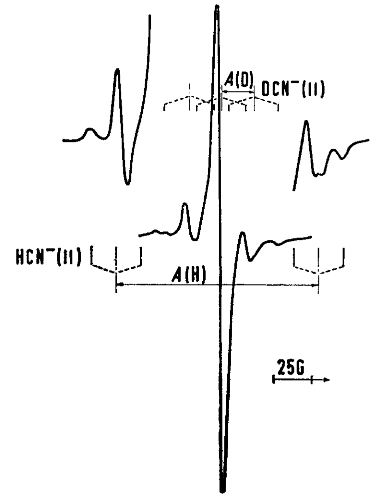

FIGURE 1 Spectrum of HCN^- formed in small quantities during irradiation of NaCN in 1M-NaOD. The main central features are assigned to DCN^-, and additional features to OD and D_2CN

The $M_I = \pm 1$ ^{14}N hyperfine features for both HCN^- and H_2CN were very broad, and are better interpreted as parallel features rather than as isotropic lines. In fact, in many spectra, only the $M_I = 0$ components were clearly detectable. We have previously shown that the hyperfine coupling to ^{14}N for H_2CN is markedly dependent upon environment,[6] and imagine that in the present case the prime cause of the broadening is environmental.

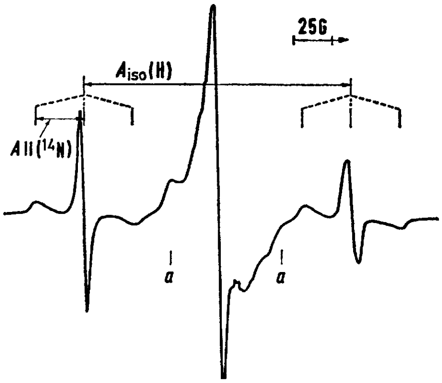

FIGURE 2 Spectrum of H_2CN from aqueous NaCN in 1M-NaOH. The parallel features are indicated. Features due to $HCNO^-$ are marked *a*

Protonation.—Although we had expected that CN^{2-} would be protonated readily if formed, we were surprised that HCN^- was also extensively protonated even at 77 K. It was thought possible that small quantities of HCN were initially present since this is known to form H_2CN on irradiation.[5,6] However, similar yields of H_2CN were obtained even in the presence of 4M-alkali, which would completely remove any HCN. It thus seems certain that reaction (1) is efficient, even in rigid

$$HCN^- + H_2O \rightleftharpoons H_2CN + OH^- \qquad (1)$$

glasses. That this is not suppressed by alkali demonstrates the highly local character of the process which probably involves proton transfer from a water molecule originally hydrogen bonded to the cyanide.[7]

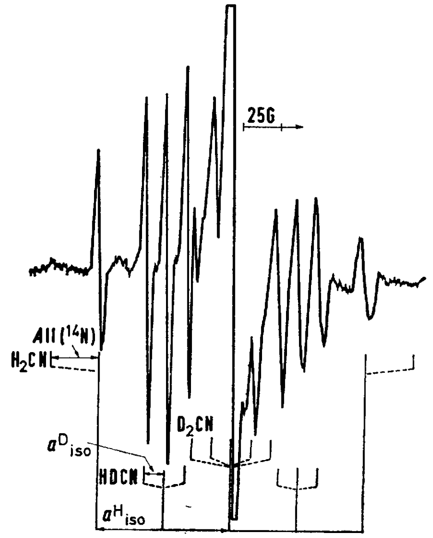

FIGURE 3 E.s.r. spectrum of HDCN formed during irradiation of NaCN in 1 : 1 mixture of H_2O and D_2O. Features due to H_2CN and D_2CN are also marked

It is somewhat surprising that reaction (1) occurs to such an extent in view of the fact that cyanide ions are only slightly protonated in neutral aqueous solution. Simple arguments based on 2*s*–2*p* orbital hybridization suggest that CN^- should be a stronger base than HCN^-, as does comparison with $HC{\equiv}C^-$ and $H_2C{=}CH^-$. Also protonation of HCN^- occurs at the orbital formally containing the unpaired electron and hence again, simple theory implies considerable electronic reorganisation on protonation. However, this is not necessarily particularly significant since there is considerable σ-delocalization onto the protons in H_2CN.[8]

The unknown radical $HCNO^-$ could not be firmly identified from the features detected in the present work (Figure 2) but our preliminary work on irradiated cyanates has given clear evidence for this species, and the proton hyperfine coupling of 78 G is well established. If this is correct, then this radical probably has the structure indicated in (I) which, by comparison with that for H_2CN (II) is expected to have an unusually

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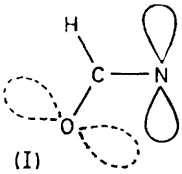
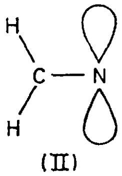
[8] J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc. (A)*, 1969, 1942.



(I)



(II)

large proton hyperfine coupling. The structure of this radical will be considered in more detail in our report on the cyanates.

Radiation Mechanisms.—The following are considered to be probable steps contributing to the reactions studied:

$$H_2O \longrightarrow H_2O^+ + e \qquad (2)$$

$$H_2O^+ \longrightarrow {\cdot}OH + (H^+) \qquad (3)$$

$$CN^- + e \longrightarrow CN^{2-} \qquad (4)$$

$$CN^{2-} + H_2O \longrightarrow HCN^- + OH^- \qquad (5)\ (+1)$$

$$(H^+) + e \longrightarrow H{\cdot} \qquad (6)$$

$$CN^- + H \longrightarrow HCN^- \qquad (7)\ (+1)$$

$$OH + CN^- \longrightarrow HCNO^- \qquad (8)$$

We had expected to be able to detect the cyanide radical, but no clear e.s.r. features assignable to this species were observed. The cyanide radical has been well characterised in a rare gas matrix,[5,9] and would probably give an isotropic spectrum at 77 K. The hyperfine tensor to ^{14}N is very small and the *g*-values are close to 2·00 so that the broad central components in our spectra could well include a contribution from this radical. Both CN and OCN^{2-} are expected to have large coupling constants for interaction with ^{13}C, but unfortunately the satellite features are expected to occur just in the region where H_2CN absorbs strongly. A careful study of solutions in D_2O in this region, however, revealed only residual H_2CN features, there being no indication of extra lines from ^{13}C satellites.

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[1/1327 *Received, July 30th,* 1971]

[9] W. C. Easley and W. Weltner, *J. Chem. Phys.*, 1970, **52**, 197.