Unstable Intermediates. Part CXXV.[1] $H(R)C\dot{N}$ Radicals in γ-Irradiated Cyanoacetic Acid and Acidic Solutions of Methyl Cyanide

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Exposure of cyanoacetic acid to ^{60}Co γ-rays at 77 K gave radicals whose e.s.r. spectra were characteristic of $H_2\dot{C}CN$ and $H(CH_2CO_2H)C\dot{N}$ radicals. The latter had $a(^1H)$ = 85 G, $a_{\parallel}(^{14}N)$ = 32 G, $a_{\perp}(^{14}N) = 0 \pm 2$ G, and $a(^1H)(CH_2)$ = 3 G. Similarly, aqueous sulphuric or acetic acid glasses containing methyl cyanide gave, amongst several radicals, $H(Me)C\dot{N}$, with similar magnetic parameters. These results were supported by studies of CD_3CN in D_2SO_4–D_2O. Possible mechanisms are discussed.

In a recent e.s.r. study of γ-irradiated methyl cyanide,[2] we identified the dimer anion $(MeCN)_2^-$ together with the previously detected[3] $H_2\dot{C}CN$ radical. A set of weak satellite lines were also detected which could possibly have been from radicals containing ^{13}C, but which, in our view,[2] were more likely to be caused by H(Me)CN radicals in relatively low abundance. More recently Williams and his co-workers, who have studied this system very extensively,[4,5] were able to show that $MeCN^-$ anions can be trapped as such under the correct conditions.[6] These workers have not detected the protonated radical in their studies.

The radicals $H(R)C\dot{N}$, which are characterised by a very large coupling to hydrogen (*ca.* 85 G) have recently been formed under isotropic conditions in adamantane, from various amines, by exposure to *X*- and u.v. radiation.[7,8] They have also been detected in the liquid phase by Netta and Fessenden.[9] Their data are included with ours in the Table.

In our studies of rigid aqueous glasses, we have found that radical anions are frequently protonated by solvent molecules even at 77 K,[10] and in particular that $H_2\dot{C}N$ radicals are formed together with $H\dot{C}N^-$ from aqueous alkali metal cyanides. These studies have now been extended to aqueous solutions of methyl cyanide, in the expectation that $Me\dot{C}N^-$ anions would

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[1] Part CXXIV, S. P. Mishra and M. C. R. Symons, preceding paper.

[2] R. Egland and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1326.

[3] P. B. Ayscough, R. G. Collins, and T. J. Kemp, *J. Phys. Chem.*, 1966, **70**, 2220.

[4] M. A. Bonin, K. Tsuji, and F. Williams, *Nature*, 1968, **218**, 946.

[5] M. A. Bonin, K. Takeda, and F. Williams, *J. Chem. Phys.*, 1969, **50**, 5423.

[6] E. D. Sprague, K. Takeda, and F. Williams, *Chem. Phys. Letters*, 1971, **10**, 299.

[7] D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 4115.

[8] T. Richerzhagen and D. H. Volman, *J. Amer. Chem. Soc.*, 1971, **93**, 2062.

[9] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1970, **74**, 3362.

[10] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 185; *J.C.S. Faraday II*, 1972, **68**, 631.

readily protonate. We have also studied cyanoacetic acid since this again was expected to form $H(CH_2CO_2H)C\dot{N}$ radicals by protonation of $[CH_2(CN)CO_2H]^-$ anions.

EXPERIMENTAL

Cyanoacetic acid (B.D.H.), methyl cyanide (Fisons), and CD_3CN (Koch-Light) were used without further purification. Acidic solutions of methyl cyanide, prepared by adding sulphuric acid to aqueous methyl cyanide at 0 °C, were frozen immediately after preparation in order to prevent significant hydrolysis. These solutions were frozen into small beads by dropping directly into liquid nitrogen prior to irradiation. Samples were exposed to ^{60}Co γ-rays in a Vickrad cell at a nominal dose rate of 4Mrad h^{-1} for *ca.* 1 h. E.s.r. spectra were run on a Varian E3 spectrometer, and were annealed by allowing samples to warm slowly from 77 K in an empty Dewar flask whilst the e.s.r. spectrum was continuously monitored, followed by recooling to 77 K when any marked change in the spectrum was noticed.

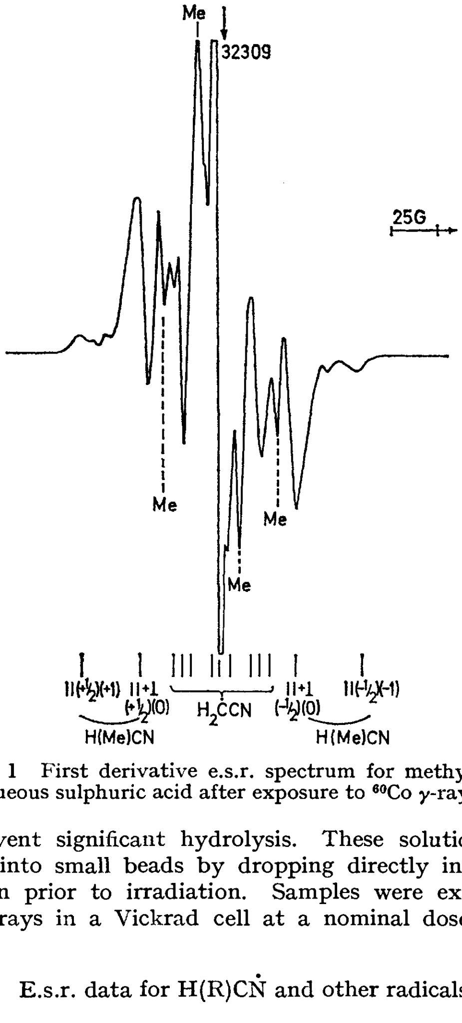

FIGURE 1 First derivative e.s.r. spectrum for methyl cyanide in aqueous sulphuric acid after exposure to ^{60}Co γ-rays at 77 K

RESULTS AND DISCUSSION

Directly after irradiation, acidified aqueous solutions of methyl cyanide had broad e.s.r. spectra which had definite wing lines suggesting the presence of $H(Me)C\dot{N}$ radicals. On annealing slightly, resolution was improved, and a typical spectrum is shown in Figure 1. The central lines are assigned to $H_2\dot{C}CN$ radicals without much ambiguity, although the coupling constants are a bit smaller than those reported previously. The data for these radicals, given in the Table, suggest that they are rotating relatively freely, even in the water matrix, which is somewhat surprising since the parent methyl cyanide molecules are almost certainly hydrogen bonded to water, albeit weakly.

The outer lines are assigned to $H(Me)C\dot{N}$ radicals. This assignment is strongly supported by results for CD_3CN in acidic aqueous solutions and in $D_2O-D_2SO_4$ (Table). Methyl radicals were also detected, so presumably in this strongly solvating medium loss of cyanide by $Me\dot{C}N^-$ competes with protonation.

The radical $H(Me)C\dot{N}$ was also clearly identified in e.s.r. spectra from acetic acid solutions of methyl cyanide. However, the spectra were complicated by intense signals from solvent radicals, and so they were not used for obtaining e.s.r. parameters.

Cyanoacetic acid, irradiated at 77 K, gave very good e.s.r. spectra after slight annealing (Figure 2). The outer features are clearly assignable to $H(CH_2CO_2H)C\dot{N}$ radicals, the small triplet splitting being assigned to the coupling to the methylene protons which appear to be magnetically equivalent under these conditions. Most of the central lines can be explained in terms of rotating $\dot{C}H_2CN$ radicals (Figure 2), though other broad features are also present.

E.s.r. data for $H(R)C\dot{N}$ and other radicals formed from irradiated methyl cyanide and cyanoacetic acid

Host	Radical	Hyperfine coupling constants (G)				g Values
			^{14}N			
		^1H	∥	⊥	*iso*	
$H_2C(CN)CO_2H$	$H(CH_2CN)C\dot{N}$	87(∥), 85(⊥) $(H_\beta)3 \pm 0{\cdot}5$	32 ± 1,	0 ± 2		$2{\cdot}002 \pm 0{\cdot}001$
$MeCN/H_2O$	$H(Me)C\dot{N}$	85 ± 2	33 ± 1,	0 ± 2		$2{\cdot}002 \pm 0{\cdot}001$
CD_3CN/H_2O	$H(CD_3)C\dot{N}$	85 ± 1	33 ± 1,	0 ± 2		$2{\cdot}002 \pm 0{\cdot}001$
CD_3CN/D_2O	$D(CD_3)C\dot{N}$	13 ± 1	33 ± 1,	0 ± 2		$2{\cdot}002 \pm 0{\cdot}001$
MeCN in adamantane [a]	$H(Me)C\dot{N}$	93	21			2·0017
$CH_3CH_2CH_2NH_2$ [b]	$H(Et)C\dot{N}$	78·5 $(H_\beta)2{\cdot}77$			9·5	2·0030
$RCN-H_2O$ [c]	$H(R)C\dot{N}$	*ca.* 82 (H_β) *ca.* 2·5			10·2	2·0028
$H_2C(CN)CO_2H$	$H_2\dot{C}CN$ [d]	18 ± 1	6 ± 1			$2{\cdot}003 \pm 0{\cdot}001$
$MeCN-H_2O$	$H_2\dot{C}CN$ [d]	18 ± 1	6 ± 1			$2{\cdot}003 \pm 0{\cdot}001$

[a] Ref. 2. [b] Ref. 7. [c] Ref. 9 (R = alkyl). [d] Rotating.

On further annealing, these signals were lost irreversibly, being replaced by a set of lines comprising, essentially, a doublet of triplets. These we assign to $\dot{C}H(CN)CO_2H$ radicals having a_H *ca.* 17 G and a_N *ca.* 5 G. Exposure to γ-rays at room temperature gave only these radicals, as judged by the e.s.r. spectra.

Electronic Structure.—We have previously discussed the structure of $H_2C\dot{N}$ radicals in terms of extensive hyperconjugative interaction which is strongly favoured by the planar geometry and short carbon–nitrogen bond.[11] There seems to be almost no modification to this interaction on replacing one hydrogen by an alkyl group. It would be interesting to obtain the hyperfine coupling tensor to ^{13}C for such alkyl groups, but unfortunately our signal-to-noise ratio was too unfavourable to enable us to detect any satellites from radicals containing ^{13}C in natural abundance.

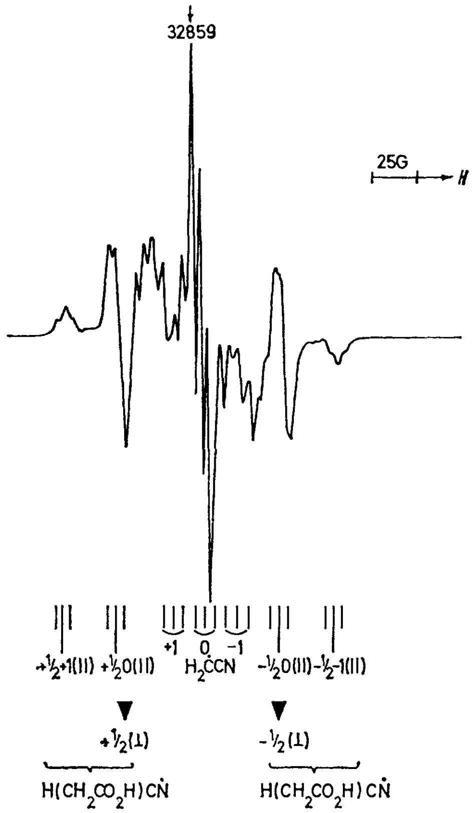

FIGURE 2 First derivative e.s.r. spectrum for cyanoacetic acid after exposure to ^{60}Co γ-rays at 77 K followed by slight annealing and recooling to 77 K

The spin density on nitrogen can be roughly estimated from the ^{14}N hyperfine tensor in the usual manner[12] to give a_s^2 *ca.* 1·8% and a_p^2 *ca.* 70%. The small 2*s* contribution undoubtedly stems from spin polarisation, the orbital being essentially pure 2*p* on nitrogen. These values are very similar to that found for H_2CN.[11]

The isotropic proton coupling of *ca.* 85 G is *ca.* 6 G greater than those measured from liquid-phase spectra. We have previously found a fairly large dependence of the isotropic ^{14}N hyperfine coupling for $H_2C\dot{N}$ radicals upon the medium, and suggested that hydrogen bonding to nitrogen was responsible.[13] We did not then observe any trend in the proton hyperfine coupling. Thus the present result is probably not a medium effect and we tentatively suggest a vibration involving changes in the C–C–H bond angle as the cause. The degree of hyperconjugation in radicals such as ethyl is known to be strongly dependent upon bond angle, but it is hard to see how this particular dependence could apply for $H(R)C\dot{N}$ radicals.

Mechanisms.—The formation of the radicals detected by e.s.r. spectroscopy can be explained most economically by the reactions (1)—(9). The subsequent formation of $\dot{C}H(CN)CO_2H$ radicals presumably occurs *via* attack by one of the primary radicals on the parent compound.

$$CH_3CN \xrightarrow{\gamma} CH_3CN^+ + e^- \quad (1)$$

$$CH_3CN + e^- \longrightarrow CH_3CN^- \quad (2)$$

$$CH_3CN^+ + H_2O \longrightarrow \dot{C}H_2CN + H_3O^+ \quad (3)$$

$$CH_3CN^- + H_3O^+ \longrightarrow H(CH_3)C\dot{N} + H_2O \quad (4)$$

$$CH_3CN^- + aq \longrightarrow \dot{C}H_3 + CN_{aq} \quad (5)$$

$$CH_2(CN)CO_2H \xrightarrow{\gamma} CH_2(CN)CO_2H^+ + e^- \quad (6)$$

$$CH_2(CN)CO_2H + e^- \longrightarrow CH_2(CN)CO_2H^- \quad (7)$$

$$CH_2(CN)CO_2H^+ \longrightarrow (H^+) + CO_2 + \dot{C}H_2CN \quad (8)$$

$$CH_2(CN)CO_2H^- + RCO_2H \longrightarrow H(CH_2CO_2H)C\dot{N} + RCO_2^- \quad (9)$$

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

[12] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[13] K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2162.