

## Electron Spin Resonance Evidence for Protonation of the Radical Anions $\text{NH}_2^-$ and $\text{HCN}^-$ in Frozen Aqueous Solutions

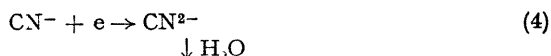
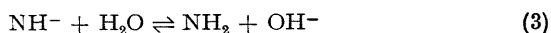
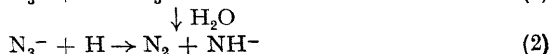
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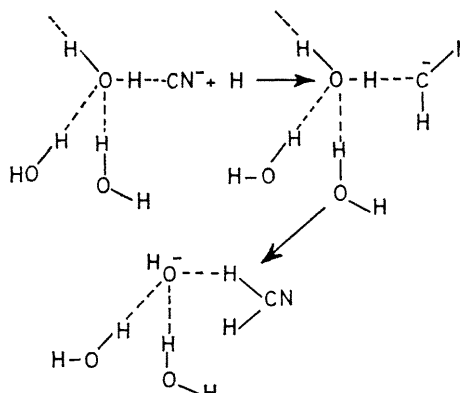
**Summary** Clear e.s.r. evidence is provided for the formation of  $\text{NH}_2$  and  $\text{H}_2\text{CN}$  radicals during the radiolysis of frozen aqueous solutions of alkali metal azides and cyanides respectively; these unexpected products may be formed by protonation of  $\text{NH}_2^-$  and  $\text{HCN}^-$ .

$\text{NH}_2$  formation in the liquid phase, since  $\text{NH}_2^-$  should have a basicity comparable with that of  $\text{NH}_2^-$ . Similarly, in fluid solution, equilibrium (6) would be expected to occur, although appreciable formation of  $\text{H}_2\text{CN}$  in neutral solution is not immediately predictable.

ALTHOUGH proton loss from radical cations is thought to play an important role in solid-state radiation chemistry,<sup>1</sup> proton gain by radical anions is uncommon, so far as we are aware. We have found, unequivocally, by e.s.r. spectroscopy that  $\text{NH}_2$  radicals are formed from aqueous azides on exposure to  $\gamma$ -rays at 77 K, and both  $\text{HCN}^-$  and  $\text{H}_2\text{CN}$  are formed from aqueous alkali metal cyanides. We assume that both  $\text{NH}_2$  and  $\text{H}_2\text{CN}$  are formed by protonation by water, following electron or hydrogen atom capture [reactions (1)–(6)].



Equilibrium (3) would certainly be expected to favour



SCHEME

Perhaps the most surprising aspect of these results is that such reactions occur readily in the solid state. In the particular case of water, however, this need not involve much reorganisation, as the scheme illustrates for the

*E.s.r. data for NH<sub>2</sub>, HCN<sup>-</sup>, and H<sub>2</sub>CN radicals in aqueous media*

Radical	Temp. (K)	$A_{180}(\text{G})^1\text{H}$	$A_{180}(\text{G})^{14}\text{N}$	Ref.
NH <sub>2</sub>	77	24 ± 1	$A_{\parallel} = 39 \pm 1$ $A_{\perp} = 3.0$	a
NH <sub>2</sub> in H <sub>2</sub> O	77	24 ± 1	$A_{\parallel} = 41.1$ $A_{\perp} = 0 \pm 3$	b
HCN <sup>-</sup>	77	137	$A_{\parallel} = 15.0$	a
HCN <sup>-</sup>	4	$A_{\parallel} = 136.5$	$A_{\parallel} = 20.9$	c
H <sub>2</sub> CN	77	87.5	15	a
H <sub>2</sub> CN	77	89.0 ± 0.2	15.0 ± 0.2	b

<sup>a</sup> This work.

<sup>b</sup> K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc. (A)*, in the press.

<sup>c</sup> F. J. Adrian, E. L. Cochran, V. A. Bowers, and B. C. Weatherley, *Phys. Rev.*, 1969, **177**, 129.

formation of H<sub>2</sub>CN. The resulting hydroxide ion is strongly solvated without the need for any major migration.

Data for the radicals detected are given in the Table. No evidence for the presence of NH<sup>-</sup> or N<sub>3</sub><sup>2-</sup> was obtained. The latter can be formed in irradiated barium azide,<sup>2</sup> but is evidently too strong a base to be stable in aqueous solutions even when rigid. The former might have escaped detection because of a broadening resulting from residual orbital magnetism. However, NH<sup>-</sup> is isoelectronic with OH, which is readily detected under these conditions.<sup>3</sup> Details of these and other radicals detected in these systems will be reported in full later.

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<sup>1</sup> M. C. R. Symons, *Radiation Res.*, 1966, 131.

<sup>2</sup> P. L. Marinkas, *J. Chem. Phys.*, 1970, **52**, 5144.

<sup>3</sup> J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 212.