Unstable Intermediates. Part CXXVI.[1] Electron Spin Resonance Studies of the Effect of High Energy Radiation on Amines and their Solutions in Water and Sulphuric Acid

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Exposure of a range of amines and their solutions in water or sulphuric acid to ^{60}Co γ-rays gave, either directly or after annealing, radicals whose e.s.r. spectra were characteristic of $R_2\dot{N}$, $R^1{}_2\dot{C}NR^2{}_2$, $R_3\dot{N}^+$, or $R_2\dot{C}{-}CH_2\overset{+}{N}R_3$ radicals. The sequence of reactions leading to the formation of these radicals is discussed, together with various structural aspects. In addition to $H_2\dot{C}NH_3{}^+$ radicals, a species was detected in irradiated solutions of methylamine in sulphuric acid that is tentatively identified as a methyl radical weakly bonded to an ammonia molecule ($H_3\dot{C}\cdots NH_3$).

WHEN this study was initiated several years ago, there was a remarkable dearth of e.s.r. data pertaining to amine radicals.[2] A few solid-state studies had given rather poor e.s.r. spectra, the derived data being somewhat questionable.[3,4] However, during the course of this work, a variety of liquid-phase or pseudo liquid-phase studies have been reported, the resulting isotropic e.s.r. spectra being, as usual, quite unambiguous, so that the isotropic parameters are now well authenticated [5-10] (see Tables).

These studies have included X-irradiation of amines in adamantane, which at room temperature gave α-radicals, $R^1{}_2\dot{C}NR^2{}_2$,[8] whilst at 77 K the cyclic amines pyrrolidine and pyrroline gave the corresponding amino-radicals $R_2\dot{N}$.[6] U.v. photolysis of tetra-alkyltetrazenes, $R_2N{-}N{=}N{-}NR_2$ in cyclopropane gave $R_2\dot{N}$ directly,[5] and Roberts and Ingold have shown that these dimerise reversibly to give R_2NNR_2 on cooling.[9] Danen and his co-workers have recently obtained $R_2\dot{N}H^+$ radicals by photolysis of N-chloro-amines in concentrated sulphuric acid.[10] These studies have been of considerable help in confirming the analyses of the solid-state spectra obtained in the present study. Despite the far greater difficulty involved in spectral interpretation, the present studies have the advantage that primary radicals are more likely to be detected, and also, the anisotropic parameters that result can shed further light on the electronic structures of the radicals concerned.

We have already reported our results for radicals of type $R_2\dot{C}{-}NR_2$ (α-radicals) in connection with our studies of radicals containing α-boron atoms ($R^1{}_2\dot{C}{-}BR^2{}_2$).[11] We now report results for $R_2\dot{N}$ (amino-radicals), $R_2\dot{C}{-}CH_2\overset{+}{N}R_3$ (β-ammonium radicals), $R_3\dot{N}^+$ (ammonium radicals), and $R_2\dot{C}{-}\overset{+}{N}R_3$ (α-ammonium radicals) and discuss them in the light of the liquid-phase work of others.

Other techniques used to study photochemical and radiochemical processes in these systems include pulse-radiolysis combined with u.v. spectroscopy,[12] and product analyses.[13]

EXPERIMENTAL

Amines were the best grades available commercially (Eastman Kodak, B.D.H., and Koch–Light) and were generally used without purification. Solutions in purified water or D_2O (99·7% D; Koch–Light) were between 1 and 5M (in the case of methylamine, a wide range of concentrations was studied, but no marked differences were observed) and solutions in 98% sulphuric acid or D_2SO_4 were *ca.* 1M. Solutions were degassed by a freeze–thaw procedure and immediately frozen to 77 K as small glassy beads.

These were exposed to ^{60}Co γ-rays for periods up to 1 h in a Vickrad source having a nominal dose rate of 4 Mrad h^{-1}.

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[1] Part CXXV, S. P. Mishra and M. C. R. Symons, *J.C.S. Perkin II*, 1973, 394.

[2] See, for example, W. V. Sherman, 'Advances in Free Radical Chemistry,' ed. G. H. Williams, Logos Press, New York, vol. 3, 1969.

[3] S. G. Hadley and D. H. Volman, *J. Amer. Chem. Soc.*, 1967, **89**, 1053.

[4] N. Y. Petrukhin and S. A. Kamenetshaya, *Khim. Vys. Energ.*, 1970, **4**, 425.

[5] W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, 1971, **93**, 5582.

[6] D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, 1971, **75**, 3486.

[7] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.

[8] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1971, **53**, 3932.

[9] J. R. Roberts and R. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 6686.

[10] W. C. Danen and R. C. Rickard, *J. Amer. Chem. Soc.*, 1972, **94**, 3254.

[11] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 502.

[12] M. Simic, P. Neta, and E. Hayon, *Internat. J. Radiat. Phys. Chem.*, 1971, **3**, 309.

[13] See, for example, P. G. Clay and M. Rashid, *Internat. J. Radiat. Phys. Chem.*, 1971, **3**, 367, and references therein.

E.s.r. spectra were obtained with a Varian E3 spectrometer, generally at 77 K. The solids were annealed either using a Varian variable temperature accessory or by allowing the liquid nitrogen to evaporate and monitoring the e.s.r. spectra continuously, recooling to 77 K when any well defined changes were detected. Effects of u.v. light were studied by *in situ* exposure to a high pressure mercury lamp (mainly 365 nm light), at 77 K.

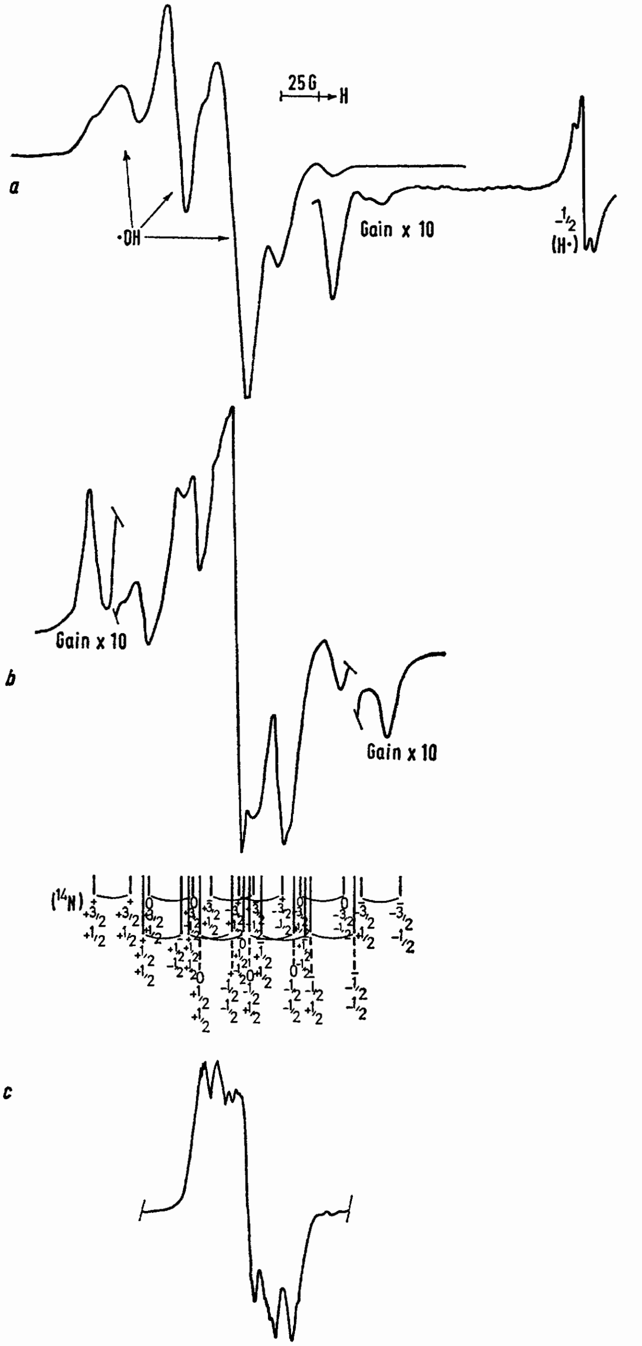

FIGURE 1 First derivative *X*-band e.s.r. spectra for aqueous methylamine after exposure to ^{60}Co γ-rays at 77 K: (*a*) directly after irradiation, showing features assigned to •OH radicals, the $M_I = -1/2$ component of the hydrogen atom doublet, and some features assigned to Me$\dot{N}$H radicals; (*b*) after partial annealing, showing more clearly the features assigned to Me$\dot{N}$H radicals (only the parallel features are indicated); (*c*) after further annealing, showing features assigned to H$_2\dot{C}$NH$_2$ radicals (*cf.* ref. 11)

RESULTS AND DISCUSSION

Typical e.s.r. spectra are given in the Figures. For methylamine and its aqueous solutions, the major radical at 77 K was CH$_3\dot{N}$H (Figure 1 and Table 1). The interpretation indicated in Figure 1 was confirmed by using CH$_3$ND$_2$. The anisotropic ^{14}N hyperfine coupling constants show that in an aqueous matrix there is little libration. This was also found for $\dot{N}$H$_2$ radicals formed from aqueous ammonia[14] and implies that the radicals are quite firmly held in place by hydrogen bonding. Unfortunately, the perpendicular coupling to ^{14}N was never resolved in the spectra obtained, so that we are not able to report an accurate isotropic coupling to ^{14}N. This is unfortunate since, in our studies of $\dot{N}$H$_2$ radicals,[11] we were able to demonstrate a clear increase in $A_{\text{iso}}(^{14}\text{N})$ as the strength of hydrogen bonding increased, and it would have been interesting to see if the same occurred for these amino-radicals.

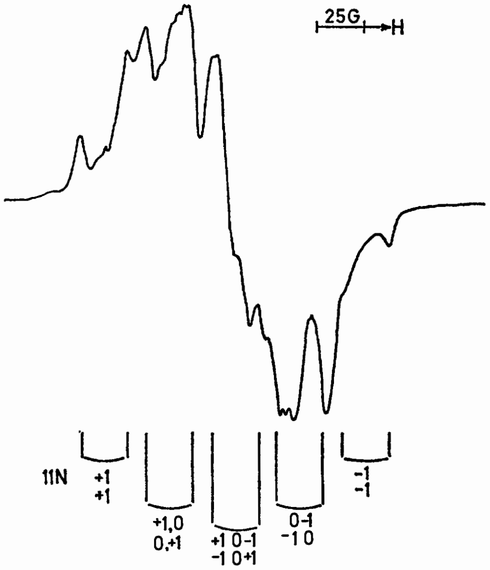

FIGURE 2 First derivative *X*-band e.s.r. spectrum for ethylamine after exposure to ^{60}Co γ-rays at 77 K showing features assigned to Et$\dot{N}$H radicals (only the parallel components are indicated)

Similar species were detected for ethylamine (Figure 2), dimethylamine (Figure 3), and diethylamine, both pure and as concentrated aqueous solutions, the spectral interpretations being fairly rigorous.

However, trimethylamine and triethylamine, as expected, give no evidence for the formation of amino-radicals. For the former, the central regions of the

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

spectra were dominated by features assigned to $H_2\dot{C}NMe_2$ radicals,[11] but well resolved wing lines readily assignable to freely rotating Me_3N^+ cations were clearly discernible. These were rapidly lost on annealing, leaving only the features assigned to $H_2\dot{C}NMe_2$ radicals. Similarly, broad outer lines coming in the regions predicted for Et_3N^+ were obtained from triethylamine. This is strongly suggestive that Et_3N^+ ions were formed, but poor resolution precludes firm identification. Again, the dominating radical was clearly the α-radical $Me\dot{C}HNEt_2$.

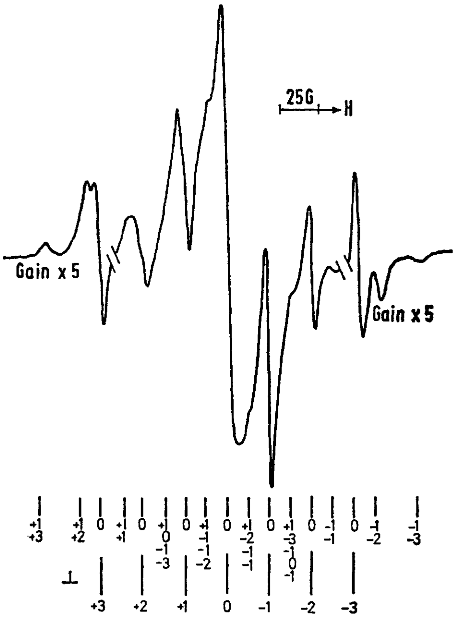

FIGURE 3 First derivative X-band e.s.r. spectrum for dimethylamine after exposure to ^{60}Co γ-rays at 77 K showing features assigned to $Me_2\dot{N}$ radicals

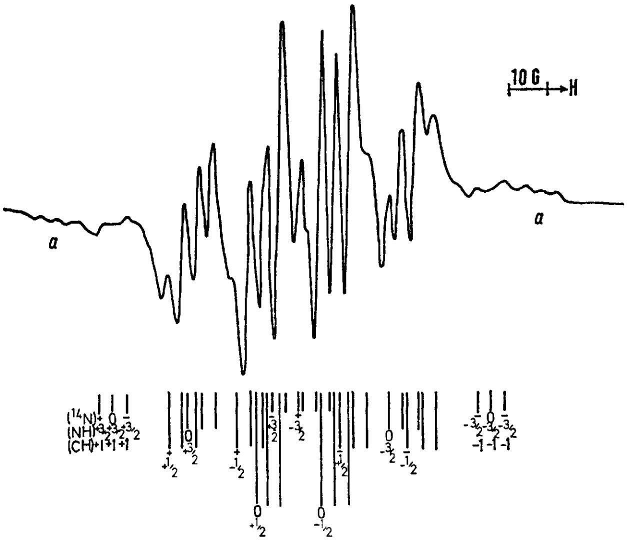

FIGURE 4 First derivative X-band e.s.r. spectrum for methylamine in sulphuric acid after exposure to ^{60}Co γ-rays at 77 K and slight annealing, showing features assigned to $H_2\dot{C}NH_3^+$ radicals, together with extra lines (a) tentatively assigned to $H_3\dot{C}\cdots NH_3$ radicals

On carefully annealing the solutions of primary and secondary amines containing trapped amino-radicals, the features assigned thereto were lost irreversibly, being replaced by features readily assigned to α-radicals. Thus methylamine gave $H_2\dot{C}NH_2$ radicals, typical spectra being given in Figure 1. Again, use of D_2O solutions helped to confirm these identifications.

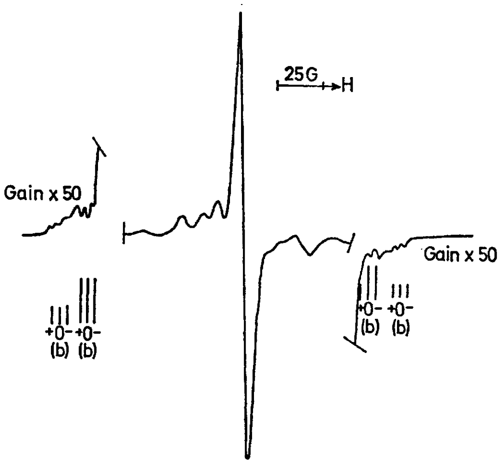

FIGURE 5 First derivative X-band e.s.r. spectrum for ethylamine in sulphuric acid after exposure to ^{60}Co γ-rays at 77 K and slight annealing, showing a central line assigned to SO_3^- radicals, broad features (a) assigned to $H_2\dot{C}CH_2NH_3^+$ and outer features (b) assigned to $Me\dot{C}HNH_3^+$

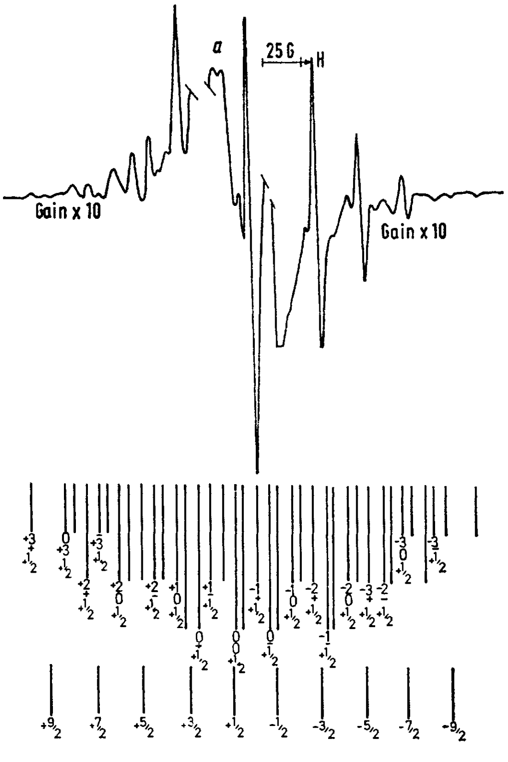

FIGURE 6 First derivative X-band e.s.r. spectrum for dimethylamine in sulphuric acid containing a trace of trimethylamine, showing (a) features assigned to HSO_4 radicals; (b) SO_3^- radicals (central line), $Me_2\dot{N}H^+$ radicals; and (c) $Me_3\dot{N}^+$ radicals

TABLE 1

E.s.r. data for various amino-radicals $R'_2\dot{N}$

Hyperfine components (G)

Radical	Material	^{14}N		$^1H(N)$	$^1H(C)$	g	
		∥	⊥			∥	⊥ [a]
$H_2\dot{N}$	$NH_3 + H_2O$ [b]	41·1	0 ± 3	24 ± 1			
$Me\dot{N}H$	$MeNH_2$–H_2O	40	0 ± 3	26 ± 1	33 (Me)	2·002	2·005
$Me_2\dot{N}$ [c]	Me_2N–N_2–NMe_2	$14{\cdot}7_8$ (iso)			27·36 (Me)		
$Me_2\dot{N}$	Me_2NH–H_2O	41	0 ± 3		27 (Me)	2·002	2·005
$Et\dot{N}H$	$EtNH_2$	35	0 ± 5	25	35 ± 2	2·002	2·005
$Et_2\dot{N}$ [c]	Et_2N–N_2–NEt_2	14·27			36·9		
$Et_2\dot{N}$	Et_2NH	38 ± 2	0 ± 3		38 ± 2	2·002	2·005
$Bu^t\dot{N}H$	Me_3CNH_3	37 ± 2	0 ± 3	25		2·002	2·005
$(Bu^t)_2\dot{N}$	$(Bu^t)_2NH$	14·2 (iso)				2·0045	
$\cdot\overline{N\cdot CH_2\cdot CH_2\cdot CH_2\cdot C}H_2$ [d]	Pyrrolidine in adamantane	14·4 (iso)			39·1 (4)	2·0046	
$\cdot\overline{N\cdot CH_2\cdot CH{:}CH\cdot C}H_2$ [d]	Pyrroline in adamantane	14·4 (iso)			44·7 (4)	2·0045	
$H\dot{N}CH_2CO_2H$ [e]	Glycine	31	≤7	33∥, ≤20	46 (2H)		

[a] Probably not axial; this cannot be judged satisfactorily from the powder e.s.r. spectra. [b] K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2163. [c] Ref. 5. [d] Ref. 6. [e] Ref. 25.

TABLE 2

E.s.r. data for various α-amine radicals $R_2\dot{C}NR_2$

Radicals	Medium	^{14}N	$^1H(N)$	$^1H(C)$	g
$H_2\dot{C}NH_3^+$	MASD [a]	4·1	19	25	
$H_2\dot{C}NH_3^+$	$MeNH_3^+$–H_2SO_4	3·7 ±0·2	18 ±1	23 ±1	2·00
$MeH\dot{C}NH_3^+$ [b]	$EtNH_3^+$–H_2SO_4	4	16	31(Me) *ca.* $30_{\parallel}$, $20_{\perp}$ (α-H)	2·00
$MeH\dot{C}NH_2Et$ [b]	$Et_2NH_2^+$–H_2SO_4	4	18	30(Me) *ca.* $30_{\parallel}$, $20_{\perp}$ (α-H)	2·00

[a] MASD = Methylammonium aluminium sulphate dodecahydrate. [b] Inner features hidden by those assigned to $H_2\dot{C}CH_2\overset{+}{N}R_3$.

When dilute aqueous glasses were used, the initial spectra were dominated by the characteristic doublet of hydroxyl radicals [15] (Figure 1*a*), a central line (and blue-violet colour) assignable to trapped electrons (e^-_t),[16] and a 505 G doublet from trapped hydrogen atoms. [The satellite lines found in the trapped hydrogen atom spectra increased strongly in intensity with increase in the microwave power, and extra lines (giving overall quintets) also appeared. These lines are, therefore, assigned to neighbouring proton 'spin-flips,' first observed and explained by Livingston and his co-workers.[17] They are remarkably well resolved in these glasses.] In addition, features for amino-radicals were clearly present. On careful annealing, these features became stronger, and the trapped electron line and colour were lost, together with the trapped hydrogen atom features. Further annealing destroyed the hydroxyl radicals, and at this stage, features from $H_2\dot{C}NH_2$ radicals appeared. Finally, all the $Me\dot{N}H$ features were lost, leaving $H_2\dot{C}NH_2$ features only. This was typical of the behaviour of the spectra from dilute aqueous solutions.

The sulphuric acid glasses gave rather different results, primarily because the amines are fully protonated in this medium, whereas in fairly concentrated aqueous solutions the conjugate acids are only minor constituents.

Initially, features from SO_4^- (HSO_4) radicals (com-

TABLE 3

E.s.r. data for various ammonium radicals $R_3\dot{N}^+$

Radicals	Medium	Temp. (K)	^{14}N			$^1H(N)$			$^1H(C)$	g [b]
			∥	⊥	iso	∥	⊥	iso		
$H_3\dot{N}^+$ [a]	NH_4ClO_4	77	37·0	10·5	19·3	28	24·7	25·8		
$Me_2\dot{N}H^+$ [c]	$H_2SO_4 + Me_2NCl$	*ca.* 300	19·28			22·73			37·19	2·0036
	$Me_2NH_2^+$–H_2SC_4	77	50		0 ± 4	25	*ca.* 20		37 (Me)	2·004
$Me_3\dot{N}^+$ [d]		77	49	2	18				27	
$Me_3\dot{N}^+$ [e]	Me_3NH^+–H_2SO_4	77			19				28	2·004
$Et_2\dot{N}H^+$ [c]	$H_2SO_4 + Et_2NCl$	*ca.* 300			18·65	22·24			37·19	2·0036
$Et_3\dot{N}^+$ [f]	Et_3NH^+–H_2SO_4	77			*ca.* 18				*ca.* 28	*ca.* 2·003

[a] K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2163. [b] g Values were isotropic within an error of *ca.* ±0·001. [c] Ref. 10. [d] J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.* (*A*), 1969, 1942. [e] $M_1 = \pm 1$ (^{14}N) lines severely broadened. [f] Poorly resolved septet.

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[15] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 2112.

[16] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1965, 1127.

[17] R. Livingston, H. Zeldes, and E. H. Taylor, *Discuss. Faraday Soc.*, 1955, **19**, 166.

prising a broad asymmetric line largely to low-field of the free-spin region) and from SO_3^- (HSO_3) radicals (comprising a narrow, symmetrical, central line, with ^{33}S satellites often discernible in the wings) generally dominated the spectra for dilute solutions. These could be destroyed either by careful annealing or by exposure to u.v. light, leaving the features for the organic species more clearly defined. Thus in Figure 4, the resultant spectrum for methylamine in sulphuric acid,* comprises sets of well resolved features assigned to $H_2\dot{C}NH_3^+$ radicals, which appear to be fairly isotropic. These radicals were first detected in γ-irradiated aluminium methylammonium sulphate dodecahydrate [18] (Table 2). It is unlikely that they are really rotating freely, but since the ^{14}N tensor components are likely to be nearly equal, and provided there is free rotation about the carbon–nitrogen bond, only a broadening of the $M_I = \pm 1$ lines of the methylene triplet is expected. This is certainly observed (Figure 4).

This analysis leaves the outermost lines (*a*) shown in Figure 4 unexplained. Because of their similarity to the lines assigned to $H_2\dot{C}NH_3^+$ radicals, we initially endeavoured to explain them in terms of this species, but to no avail. In fact, they are displaced slightly to high field of the central lines. Rather similar sets of outer lines were also obtained in the wings of the spectrum from ethylamine in sulphuric acid (Figure 5). The most obvious candidate for these radicals from methylamine is methylammoniumyl $Me\dot{N}H_2^+$. However, these radicals are expected to be almost stationary in sulphuric acid because of hydrogen bonding, in which case parallel features well outside those under discussion (*a* in Figure 4) should be present. Such features were not detected, even at maximum gain and high modulations. Another factor against this identification is that when solutions in D_2SO_4 were studied, the features separated by *ca.* 4 G were replaced by single features, thus suggesting that these lines can be assigned to ^1H coupling. (This is unfortunately not a compelling argument, since loss of a large triplet from two equivalent protons, as in $MeNH_2^+ \longrightarrow MeND_2^+$ could also destroy all resolution of the $M_I = 0$ components. This requires, however, that the $M_I = \pm 1$ lines are broadened beyond detection for the H_2SO_4 solutions, which does seem unlikely.) Thus $MeNH_2^+$ radicals do not seem to be responsible for these lines. In searching for an alternative species, it was noticed that the SO_3^- line, very prominent in some of this work directly after irradiation, could be largely suppressed by increasing the concentration of methylamine, although no such loss occurred when, for example, trimethylamine was used. [The latter did, however, strongly suppress the formation of SO_4^- (or HSO_4) features.] This implies that there is an electron trap present in solution. I recall that in our earlier studies of solutions of sulphuric acid solutions of protonated alcohols, efficient dissociative electron capture ensued [reaction (1)] [19] even at 77 K. I had, therefore,

$$ROH_2^+ + e^- \longrightarrow R\cdot + H_2O\ (\longrightarrow H_3O^+) \quad (1)$$

expected a similar process [reaction (2)] with primary

$$RNH_3^+ + e^- \longrightarrow R\cdot + NH_3\ (\longrightarrow NH_4^+) \quad (2)$$

amines but in no instance could I detect features assignable to alkyl radicals, although these were well resolved for the irradiated alcohols in sulphuric acid.[19]

It is most unlikely that the radical H_3CNH_3 would exist as a stable entity under these conditions, but it is certainly possible that a radical describable as a weak complex between a methyl radical and an ammonia molecule should result. Just such a species has recently been detected by Williams and his co-workers.[20] They found that irradiated solutions of methyl bromide in methyl cyanide (CD_3CN) solvent gave, at 77 K, a species $Me\cdots Br^-$, having essentially the e.s.r. spectrum of a methyl radical, but with a weak extra hyperfine coupling to ^{79}Br and ^{81}Br nuclei. We have recently extended these studies and fully agree with this assignment.[21] By analogy, we expect the species $H_3\dot{C}\cdots NH_3$ to have an essentially planar methyl radical, with only a slightly reduced ^1H hyperfine coupling, weakly bonded to a normal pyramidal ammonia molecule, which would contribute a small ^{14}N hyperfine coupling as a result of very weak bonding. This would, reflecting the strong hybridisation of the lone-pair of electrons involved, appear as an almost isotropic interaction (just as is found for the ^{14}N coupling in $H_2\dot{C}NH_3^+$ radicals, for example). We would expect to detect only a very small hyperfine coupling to the ammonia protons, since the unpaired electron is in a σ^* orbital which, in contrast with $H_2\dot{C}NH_3^+$ radicals, cannot delocalise onto these protons by a hyperconjugation mechanism.

When the outer lines (*a*, Figure 4) are fitted to these requirements, we find $a(^1H,Me)$ *ca.* 20 G, $a(^{14}N)$ *ca.* 32 G, and $a(^1H,NH_3)$ *ca.* 4 G, the last splitting being lost for '$H_3C\cdots ND_3$'. These results are certainly reasonable, and we favour this assignment in the absence of reasonable alternatives. The weakest aspect is that the small features (*a*) do not have the appearance of 1 : 3 : 3 : 1 quartets, their relative intensities being more nearly equal. However, the protons of the NH_3 group will probably remain hydrogen bonded to the polymeric sulphuric acid medium so that rotational averaging cannot occur. Under such circumstances, it is certainly possible to have a marked broadening of the $M_I \pm 1/2$ components, which could, fortuitously, give rise to the apparent equivalence observed. This is the preferred explanation for the features *a* in Figure 4, but all our

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* This was initially obtained by Dr. J. H. Sharp working in these laboratories.

[18] R. P. Kuhin and P. G. Nadeau, *J. Chem. Phys.*, 1966, **44**, 691.

[19] D. R. G. Brimage, J. D. P. Cassell, J. H. Sharp, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2619.

[20] E. D. Sprague and F. Williams, *J. Chem. Phys.*, 1971, **54**, 5425.

[21] S. P. Mishra and M. C. R. Symons, *J.C.S. Perkin II*, 1973, 391.

attempts to define this species more satisfactorily have failed.

The same explanation could be invoked to explain the outer lines for ethylamine in sulphuric acid (Figure 5), and again, there is no clear proof that this is correct. The outer lines are accommodated by a mean ^1H hyperfine coupling of *ca.* 22 G, and a fairly isotropic ^{14}N hyperfine coupling of *ca.* 32 G. A better fit is obtained for $a(\alpha\text{-H})$ 18 G and $a(\beta\text{-H})$ 25 G. These numbers are reasonable for the species $H_3C\dot{C}H_2 \cdots NH_3$, the ^{14}N and $^1N(NH_3)$ coupling constants being identical with those for the supposed methyl radical adduct. Again, the identification cannot be confirmed, and in this case, there is a very probable alternative species, namely the α-ammonium radical $CH_3\dot{C}HNH_3^+$.

The major species formed from $EtNH_3^+$ ions is almost certainly the β-radical $H_2\dot{C}CH_2NH_3^+$ (Figure 5). However, some α-attack should also occur, so that $CH_3\dot{C}HNH_3^+$ radicals in low concentration are highly probable. The resulting parameters (Tables) are all reasonable, except for the very large hyperfine coupling of *ca.* 31 G that has to be assigned to the methyl protons. This is not so high as to be impossible, however. This radical is isoelectronic with the isopropyl radical, $Me_2\dot{C}H$, which exhibits an isotropic hyperfine coupling of 24·7 G, to the methyl protons, by what can loosely be described as a hyperconjugative interaction. For the radical $H_3C\dot{C}HNH_3^+$, hyperconjugative delocalisation onto the NH_3^+ group is greatly inhibited, and would thus be encouraged to occur more strongly with the methyl group. We[22] and others[23] have previously shown that the effect of a positive charge at the radical centre is to increase hyperconjugative interaction, so that the presence of the positive charge on the NH_3 group could also be to enhance the hyperfine coupling to the methyl protons. This should not be as great an enhancement as is found for $Me\dot{N}R_2^+$ radicals (*cf.* Table 3), but could still just account for the high value of 31 G that is needed to explain the results. This conclusion is supported by the negative results for $CH_3CH_2NH_3^+$ in D_2SO_4. This gave $H_2\dot{C}CH_2ND_3^+$ radicals very clearly, but no outer features of the type found for H_2SO_4 could be detected. This is expected for $CH_3\dot{C}HND_3^+$ radicals whose features would all be covered by those from the former radical.

The results for dimethylamine and diethylamine in sulphuric acid were similar, although the spectra were less well resolved. The latter gave mainly the β-radical $H_2\dot{C}CH_2\overset{+}{N}H_2Et$ together with outer shoulders that could either be from the ethyl radical adduct or the α-ammonium radical. The former ($Me_2NH_2^+$) gave mainly $Me_2\dot{N}H^+$ radicals (Figure 6), there being no clear indication of $H_2\dot{C}NH\overset{+}{M}e$ radicals despite their preponderance with methylamine.

Trimethylamine in sulphuric acid gave mainly $Me_3\dot{N}^+$ radicals. These are characterised by ten sharp features corresponding to transitions for which $M_I(^{14}N) = 0$, together with very broad intermediate lines for $M_I(^{14}N) = \pm 1$.

In an experiment to test the concept that process (3)

$$R_3NH^+ \longrightarrow R_3\dot{N}^+ + (H) \qquad (3)$$

is facilitated strongly as R goes from H to alkyl, a trace of trimethylamine (*ca.* 1% of the dimethylamine) was added to a solution of dimethylamine in sulphuric acid and the mixture was exposed to ^{69}Co radiation. The result (Figure 6) shows qualitatively that this is indeed the case. (It is almost impossible to obtain even a semi-quantitative gauge of this preference because the spectrum for $Me_2\overset{+}{\dot{N}}H$ radicals is clearly anisotropic, whilst that for Me_3N^+ is isotropic at least for the $M_I = 0$ lines.)

The spectrum assigned to $Me_2\dot{N}H^+$ radicals is unusual in that the perpendicular ^{14}N hyperfine coupling is greater than the parallel coupling, and at *ca.* 23 G, is far greater than could be expected for stationary radicals. These features can readily be explained, however, in terms of a relatively free motion about the N–H bond, as indicated in Figure 7.

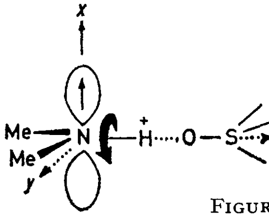

FIGURE 7

This seems reasonable since the amino-proton will be strongly bonded to the rigid polymeric solvent lattice. The effect of such rotation will be to average A_{xx} and A_{yy} so that $A_{\perp}' = 1/2(A_{xx} + A_{yy})$ and $A_{\parallel}' = A_{zz}$. Reasonable values for the tensor components of the stationary radical are $A_{xx} = 38$ G, $A_{yy} = A_{xx} = 8$ G. This then gives $A_{\perp}' = 23$ G, in accord with observation, and leads to a predicted value of $A_{\parallel}'$ of 8 G. Unfortunately, none of our spectra gave clear values for $A_{\parallel}'$, but certainly *ca.* 8 G is reasonable (see Figure 6). The fact that the low field perpendicular lines are stronger than the corresponding high field components shows that $g_{\parallel}' > g_{\perp}'$, which means that the real $g_{\perp} > g_{\parallel}$ for the stationary radical. This also accords well with expectation, and supports our analysis.

Structural Aspects.—The most interesting results concern the extent of π delocalisation and possible deviations from planarity for the α-amino-radicals, $R_2\dot{C}NR_2$. It has been maintained both on theoretical and experimental grounds that there is a marked deviation from local planarity both at carbon and nitrogen,[8] but our interpretation of the solid-state results[11] strongly

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suggests that the carbon centre is effectively planar, whilst the nitrogen centre does not deviate greatly from planarity.

Results for the amino-radicals confirm that a_{iso} is appreciably greater than that for the parent $\dot{N}H_2$ radical. This almost certainly stems from an increase in the R^1–N–R^2 bond angle (θ), which is only 103·4° for $\dot{N}H_2$ but is certainly considerably greater for, say, $Me_2\dot{N}$. That a_{iso} should increase with increase in θ follows from the increased (nitrogen) s character in the σ bonding orbitals and the observation that spin polarisation stems predominantly from polarisation of σ electrons.[24] This contention is supported by INDO calculations.[8]

Some Aspects of Mechanism.—It seems probable that, for the unprotonated primary and secondary amines, amino-radicals are one of the primary radiation products. These, I suggest, are formed by positive hole capture, or direct electron ejection to give $R_2\dot{N}H^+$ radicals, which promptly lose a proton to the medium to give $R_2\dot{N}$. In contrast, in sulphuric acid solutions, the medium is not able to accept this proton so that $R_2\dot{N}H^+$ radicals are trapped as such.

The formation of α-radicals is clearly a secondary process for the amines and their aqueous solutions and probably arises both from ·OH radical attack, as inferred by Neta and Fessenden [7] and by Simic *et al.* using pulse radiolysis methods,[12] and also by attack of amino-radicals themselves. In both cases, α-radicals are most readily formed because of the resulting π bond stabilisation.

In contrast, attack by $\dot{O}H$ or SO_4^- radicals goes primarily β rather than α for the substituted ammonium ions such as $EtNH_3^+$. This result accords with the well recognised electrophilic behaviour of such radicals, which tend to favour attack on hydrogen atoms remote from the positive centre. This conclusion accords with those of Hayon and his co-workers,[12] but Neta and Fessenden [7] inferred that α-attack predominated in acidic solution.

It is curious that $Me\dot{N}H_2^+$ radicals were not clearly detected for methylamine in sulphuric acid. This suggests that the medium itself is a better hole-trap than $MeNH_3^+$, but that the extra stability of $Me_2\dot{N}H^+$ and still more of $Me_3\dot{N}^+$ makes the secondary and tertiary ammonium cations more efficient hole-traps.

We had not expected to observe significant interaction between the unprotonated amines and electrons under these conditions. It is well known that electrons are, in fact, stable as solvated entities in many amines even at room temperature, and our results show that for the glassy aqueous amines, trapping is efficient at 77 K.

However, for the ammonium ions in sulphuric acid, by analogy with our results for protonated alcohols,[19] we had hoped to detect alkyl radicals for the dissociative electron capture process (2). As discussed above, this may indeed have occurred, especially with methylamine, the adduct $Me \cdots NH_3$ being a possible product.

Just such a reaction involving loss of ammonia has recently been shown to be a major pathway for the thermal loss of radical anions of glycine [reaction (4)].[25]

$$H_3\overset{+}{N}CH_2\dot{C}O_2H^- \longrightarrow \dot{C}H_2CO_2H + NH_3 \qquad (4)$$

In this case, however, the radical $\dot{C}H_2CO_2H$ shows no sign of any residual interaction with the ammonia molecule.

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