THE IMPORTANCE OF IMINO RADICALS (R₂C=N) AS REACTION INTERMEDIATES

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Abstract—ESR studies of γ-irradiated methylamine and formamide at 77 K show that the methylene-imino radical, H₂CṄ, is an important intermediate during the annealing process. Similarly, irradiated ethylamine gave MeHCṄ after annealing. Several other reactions leading to the formation of these unique radicals are reviewed, and possible reasons for their frequent appearance discussed.

The methylene imino radical, H₂CṄ, was first detected by ESR spectroscopy several years ago by Cochran *et al.*[1] These workers exposed matrix isolated hydrogen iodide and hydrogen cyanide in argon at 4·2 K to UV light and found that the resulting ESR spectrum was dominated by a triplet of triplets which they assigned to H₂CṄ radicals. The results were remarkable in that the hyperfine coupling of *ca* 87 G was very large for β-protons. This large splitting almost certainly stems from a hyperconjugative interaction made ,very favourable by the planar character of the radical (Insert I) and the
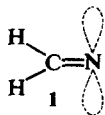
short C=N double bond which favours overlap between the C—H σ-orbitals and the formally nonbonding nitrogen 2*p* orbital of the unpaired electron.[2] Such strong hyperconjugation should contribute appreciably to the stability of these radicals, and the purpose of this paper is to present ESR evidence in favour of this suggestion.

Methylene imino radicals have also been detected in γ-irradiated hydrogen cyanide,[3] and in photolysed formaldazine at 77 K:[4]

$$H_2C=N-N=CH_2 \xrightarrow{h\nu(2537\,\text{Å})} 2H_2C=\dot{N} \qquad (1)$$
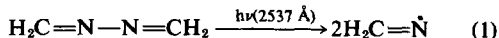
This photolysis, thought to proceed *via* an $n \rightarrow \pi^*$ transition of the parent formaldazine, is important since it demonstrates the tendency of the dimer to dissociate.

We have found that even cyanide ions are readily converted into H₂CN radicals in irradiated aqueous solutions, probably *via* double protonation:[5]

$$CN^- + e^- \rightarrow CN^{2-}, \qquad (2)$$

$$CN^{2-} + 2H_2O \rightarrow H_2C\dot{N} + 2OH^-. \qquad (3)$$

Exposure of solid methyl cyanide to γ-rays gave

mainly the conjugate base, MeCN⁻, which usually forms a dimer, (MeCN₂⁻.[6,7] However, ESR evidence for the formation of MeHCN was obtained,[6] and Fessenden and his coworkers have recently shown by liquid-phase ESR studies, that RCN⁻ radicals generated in aqueous solution have a marked tendency to protonate to give RHCN radicals.[8]

Similarly, we find that solutions of methyl cyanide in glassy aqueous sulphuric acid at 77 K gives, on exposure to γ-rays, HMeCṄ radicals in good yield, there being no evidence for MeCN⁻ anions.[9] Again, cyanoacetic acid gave well resolved spectra for H(CH₂CO₂H)CN radicals,[9] the conjugate base being absent. Presumably in both these cases, the conjugate base was readily protonated by neighbouring acid molecules even at 77 K.

None of these processes is surprising, but they serve to establish the relatively high stability of these imino radicals. This has recently been very clearly demonstrated by the studies of Hudson *et al.*,[10] who found that the radicals R₂C=N are formed thermally from oxime thionocarbamates (R₂C=N—OC(S)NMe₂), during their rearrangement to thioxime carbamates, and that these radicals are present in such high stationary concentrations that they were readily detected by ESR spectroscopy. Probably the steric effect of the substituents (R = phenyl or substituted phenyl groups) contributes considerably to the stability of these radicals, but their structures are such that they cannot contribute *via* a π-delocalisation mechanism.

We find that these ubiquitous radicals are often detected even in circumstances where their formation would not normally be expected.

RESULTS

Formamide. The central regions of the ESR spectra were dominated by features previously assigned to OĊNH₂ radicals.[11] Wing lines associated with HCO radicals and OĊNH₂ radicals containing ¹³C were also detected.[11,12] However, when

these samples were carefully warmed above 77 K, extra wing lines began to grow, and soon dominated the outer regions of the spectrum (Fig 1). These are unambiguously the outer ($M_I = \pm 1$) lines of H_2CN, the data derived therefrom and given in Table 1 being quite characteristic of these radicals. At 77 K, these radicals were not rotating and hence the anisotropic hyperfine coupling could be estimated. Aqueous solutions gave very similar results, except that the $H_2C\dot{N}$ radical spectra indicated that these radicals were rotating in this medium even at 77 K.

Exposure of methylamine and its aqueous solutions to ^{60}Co γ-rays gave, initially, ESR spectra which we have assigned to $H\dot{N}Me$ radicals, together with features due to trapped H atoms, and for aqueous solutions, trapped OH radicals. On careful annealing, wing lines characteristic of $H_2C\dot{N}$ radicals appeared, and at about the same temperature, the features for $H\dot{N}Me$ radicals OH radicals and H atoms were lost and replaced by spectra characteristic of $H_2\dot{C}NH_2$ radicals (Fig 2). When solutions of $MeND_2$ in D_2O were studied, well resolved lines from $H_2C\dot{N}$ were again obtained. Once again, the spectra of aqueous solutions were characteristic of rotating radicals and gave only the isotropic constants, whilst those from the pure amine were characteristic of stationary radicals.

Similar treatment of dimethylamine or trimethylamine and their aqueous solutions gave no evidence for the formation of H_2CN or related radicals. However, ethylamine, and its aqueous solutions which gave mainly $EtNH$ radicals initially at 77 K, gave wing lines on annealing which are almost cer-
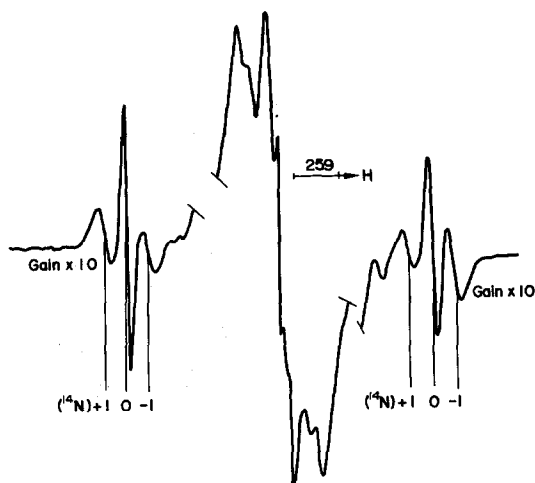

Fig 2. First derivative X-band ESR spectrum for aqueous methylamine after exposure to ^{60}Co γ-rays at 77 K and partial annealing, showing features assigned to H_2CN radicals undergoing restricted rotation in the lattice. (Central features assigned to H_2CNH_2 radicals.)

tainly due to $MeHC\dot{N}$ radicals (Fig 2). Identification is less clear since the total splitting is only half that for H_2CN, and so overlap with the central features is more serious. Nevertheless, the data given in Table 1 agree well with expectation and with those of others for these radicals.

Again, di- and triethylamine on irradiation gave no features characteristic of imino radicals, and we conclude that only primary amines are converted into imino radicals under our conditions. Also,
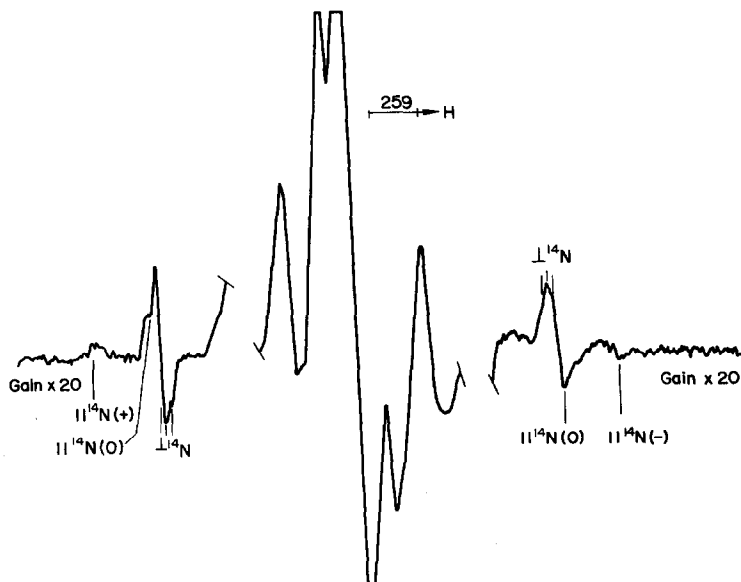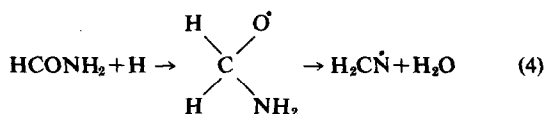

Fig 1. First derivative X-band ESR spectrum for formamide after exposure to ^{60}Co γ-rays at 77 K and partial annealing, showing features assigned to H_2CN radicals held rigidly in the lattice. (Central features assigned to $OCNH_2$ radicals.)
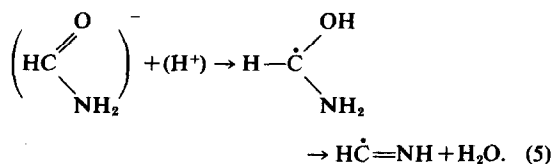
t-butylamine, after exposure to γ-rays at 77 K and annealing, had no ESR features that could be associated with imino radicals.
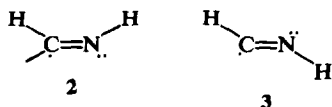
DISCUSSION

Formamide. Formation of H$_2$CṄ from HCONH$_2$ and its aqueous solutions is not an obvious chemical process. Dainton *et al.*[13] have shown that carbon monoxide and dimethylamine are important products in the radiolysis of dimethylformamide which suggests that the C—N bond is readily cleaved, and Jones and Gesser also conclude that N-alkyl amides give R$_2$Ṅ radicals on photolysis.[14] Such a breakdown, HCONR$_2$ → HĊO + ṄR$_2$, explains the formation of HCO radicals, but not H$_2$CN. Indeed, this intermediate has apparently not been considered in discussions of results from photolytic and pulse-radiolysis studies.[13-15] It is, of course, possible to write the reaction in terms of hydrogen atom addition and subsequent loss of water:

$$HCONH_2 + H \rightarrow \begin{array}{c} H \quad \dot{O} \\ \diagdown \diagup \\ C \\ \diagup \diagdown \\ H \quad NH_2 \end{array} \rightarrow H_2C\dot{N} + H_2O \qquad (4)$$

but this remains a chemically obscure process, which seems to be unlikely at *ca* 100 K. The aqueous solution results show that the reaction must be intra-molecular, and a more likely set of reactions begin with the radical anion:

$$\left(\begin{array}{c} O \\ \diagup\diagup \\ HC \\ \diagdown \\ NH_2 \end{array} \right)^- + (H^+) \rightarrow \begin{array}{c} OH \\ \diagup \\ H - \dot{C} \\ \diagdown \\ NH_2 \end{array}$$

$$\rightarrow H\dot{C} = NH + H_2O. \qquad (5)$$

It is then necessary to postulate that HC=NH radicals are inately unstable relative to H$_2$CN and that a low temperature tautomeric change occurs. The radical HC=NH is likely to be structurally similar to HC=CH$_2$ radicals, and there should be a *cis* and a *trans* form (2 and 3). Rearrangement of
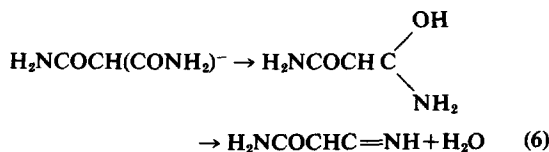
$$\begin{array}{cc} \begin{array}{c} H \\ \diagdown \\ \diagup C=N \diagdown \\ H \qquad \overset{..}{} H \end{array} & \begin{array}{c} H \\ \diagdown \\ \diagup C=\dot{N} \\ H \qquad \diagdown H \end{array} \\ \mathbf{2} & \mathbf{3} \end{array}$$

the *trans* isomer should involve a relatively low activation energy. If this is correct, it again underlines the stability and importance of H$_2$CN radicals.

Both Neta and Fessenden[7] and Symons[16] have

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*The bond angle for NH$_2$ os 103·4°, and that for MeNH is probably between this value and *ca* 117° postulated for R$_2$N radicals.[18]

independently suggested that a radical formed in γ-irradiated malonamide might be of the form RCH=Ṅ, rather than being the σ-radical originally postulated.[17] However, a reasonable alternative that seemed to fit the spectral features remarkably well was the radical NH$_3^+$, and this was somewhat favoured[16] since it seemed to be chemically more reasonable. In the present case, however, there is no such ambiguity, so that we can conclude with some confidence that amides *can* give rise to imino radicals when exposed to high energy radiation. By analogy, we write

$$H_2NCOCH(CONH_2)^- \rightarrow H_2NCOCH\,C\begin{array}{c} \diagup OH \\ \diagdown \\ NH_2 \end{array}$$

$$\rightarrow H_2NCOCHC=NH + H_2O \qquad (6)$$

followed by rearrangement to give H$_2$NCOCH—CH=N. In a very recent study[18] Lin *et al.* showed, by use of ^{15}N labelling, that cyanoacetamide gave imino radicals on irradiation but that only the cyano-group was involved. Thus, in this case, the amido group was not involved so that no light was shed on the problem of the conversion of an amido group into an imino-radical.

Amines. It seems most probable that H$_2$CṄ radicals were formed directly from MeṄH radicals during the annealing process, since once the reaction in which MeNH radicals are converted into H$_2$CNH$_2$ radicals was complete, no further growth of the H$_2$CN features occurred. It is then tempting to write the reaction as a thermal unimolecular 1:2-dehydrogenation:

$$H_3C—\dot{N}H \rightarrow H_2C=\dot{N} + H_2. \qquad (7)$$
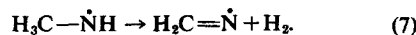
In previous studies of imino radicals formed from amines,[16,17] R$_2$ĊNH$_2$ radicals rather than amino radicals have clearly been precursors. These were photolysed by ultraviolet light to give loss of hydrogen:

$$R_2\dot{C}NH_2 \xrightarrow{h\nu} R_2C=\dot{N} + H_2. \qquad (8)$$
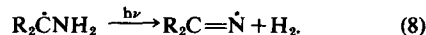
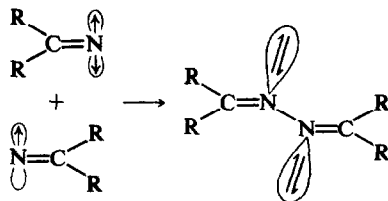That reaction (7) should not require the assistance of light energy but (8) should, can be at least partially rationalised by the following. The H$_3$C—ṄH radicals already have the unpaired electron confined to a 2p orbital on nitrogen, and the protons lost as molecular hydrogen are quite close together because the C—N—H bond angle expected for these radicals is relatively small.*

This requirement explains why Me$_2$Ṅ radicals obtained from dimethylamine show no tendency to form H$_2$C=N radicals, whereas EtNH from ethylamine give MeHC=N quite readily.

Possible reasons for the stability of imino radicals. I have already stressed that powerful hyper-

conjugative interaction, clearly established by the large ^{1}H hyperfine coupling constants, must be a contributing factor to the stability of these radicals. Another factor is that dimerisation to give the corresponding azine, $R_2C\!=\!N\!-\!N\!=\!CR_2$, requires considerable orbital readjustment, as can be seen in a qualitative sense from the equation:

$$\begin{array}{c}\text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{R} \end{array} + \begin{array}{c} \text{R} \\ \diagup \\ \text{N}=\text{C} \\ \diagdown \\ \text{R} \end{array} \longrightarrow \begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{R} \end{array} \begin{array}{c} \text{R} \\ \diagup \\ \text{N}=\text{C} \\ \diagdown \\ \text{R} \end{array}$$

A very similar change is required when $SO_2{}^-$ radicals dimerise to give dithionite ions,[19] and we have suggested that such readjustment of orbitals again contribute to the weakness of the sulphur–sulphur bond in dithionites.[19]
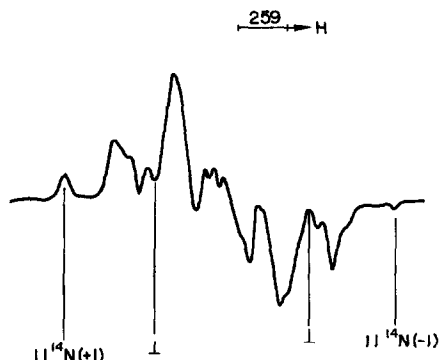

Fig 3. First derivative X-band ESR spectrum for ethyl-amine after exposure to ^{60}Co γ-rays at 77 K and partial annealing, showing features assigned to MeHC ^{W}N radicals held rigidly in the lattice. (Central lines are mainly due to EtNH radicals.)

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Table 1. A selection of hyperfine coupling constants for various imino radicals

Radical	Medium	^{14}N $\parallel$	^{14}N $\perp$	^{14}N iso	^{1}H $\parallel$	^{1}H $\perp$	^{1}H iso
H$_2$CN	HCONH$_2$	30±1	ca 2	ca 11	93	87	89
"	HCONH$_2$+H$_2$O		13±1				86±1
"	MeNH$_2$+H$_2$O		13±1				86±1
" a	Argon (4·2 K)	34·4			87·4		
" b	KCl		9·5				91·2
" b	HCN		15·0				89·0
MeHCN	EtNH$_2$	36			ca 85	80	ca 82
" c	MeCN+H$_2$SO$_4$	33±1	0±2	ca 11	85±2		
EtHCN	CH$_3$CH$_2$CH$_2$NH$_2$		9·5				78·5
"d	+Adamantane				(βH; 2·77)		

[a] Ref 1.
[b] Ref 3.
[c] Ref 9.
[d] Ref 17.

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