Unstable Intermediates. Part CXXXIV.[1] Electron Spin Resonance Studies of Positive Hole Centres in γ-Irradiated Glycine

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Single crystals and powders of α-glycine, *N*-deuterioglycine, and *C*-deuterioglycine have been exposed to ^{60}Co γ-rays at 77 K, and their e.s.r. spectra studied as a function of annealing temperature. Initial radical products comprised $H_3\overset{+}{N}CH_2\dot{C}O_2^{2-}$, $H_2{}^+\dot{N}CH_2CO_2^-$, and $H_3\overset{+}{N}-\dot{C}H_2$. On annealing, $H_3\overset{+}{N}CH_2\dot{C}O_2^{2-}$ gave $H_2\dot{C}CO_2^-$ radicals, $H_2{}^+\dot{N}CH_2CO_2^-$ probably gave $H_3\overset{+}{N}\dot{C}HCO_2^-$ radicals, whilst $H_3\overset{+}{N}-\dot{C}H_2$ gave $H_2N\dot{C}H_2$. On further annealing intermolecular attack gave mainly $H_3\overset{+}{N}\dot{C}HCO_2^-$ radicals.

MANY e.s.r. studies of irradiated glycine have appeared since the initial report by Gordy and his co-workers.[2] Thus the powder, irradiated at room temperature, gave a broad triplet, identified by one of us as $H_2\dot{C}CO_2^-$,[3] but by others as $\dot{C}H_2NH_3^+$ and NH_2. Ghosh and Whiffen,[4,5] in one of the first single crystal studies of trapped radicals, clearly identified $H_3\overset{+}{N}-\dot{C}HCO_2^-$ radicals and suggested that the second species was NH_2. Yet another species suggested to explain e.s.r. results was NH_4,[6] but, using ^{13}C enriched material, Morton showed that by far the most probable species were, in fact, $H_2\dot{C}CO_2^-$ and $H_3\overset{+}{N}-\dot{C}HCO_2^-$.[7] Subsequently, Collins and Whiffen[8] obtained a doublet after irradiation at 77 K which they assigned to 'molecular ions.' They reported the detection of other weak lines, but suggested that they were caused by $H_3\overset{+}{N}-\dot{C}HCO_2^-$ radicals. The doublet species was later identified as the parent radical anion.[9]

Recently,[10] Ayscough and Mach have made a thorough study of glycine and *N*-deuterioglycine after exposure to γ-rays at 77 K and during the annealing process. A variety of radicals were detected, all apparently stemming from the parent radical-anions. Indeed, it was stated that these anions are the only species trapped at 77 K and that no paramagnetic intermediates attributable to the radical cations were formed.

The purpose of the present study was to endeavour to detect paramagnetic products associated with the parent cations, or, failing that, to discover their fate, since the detection of the parent radical-anions surely establishes that the cations must have been formed.

EXPERIMENTAL

α-Glycine was recrystallised from purified water, and *N*-deuterioglycine ([$^2H_3$]glycine) was prepared by repeated recrystallisation from 99·8% D_2O. *C*-Deuteriated glycine [$^2H_2$] (Prochem) was recrystallised from water or from D_2O to obtain [$^2H_5$]glycine. Single crystals were grown by slow cooling of the appropriate solutions.

Samples were irradiated at 77 K in a ^{60}Co Vickrad γ-ray source for up to 2 h at a nominal dose rate of 4 Mrad h^{-1}. E.s.r. spectra were obtained at 77 K or room temperature using a Varian E3 spectrometer. After annealing at selected temperatures samples were recooled to 77 K prior to measurement. To obtain e.s.r. spectra at intermediate temperatures a Varian variable temperature accessory was used.

RESULTS AND DISCUSSION

(1) *Central Features.*—Our results were, in general, similar to those previously reported.[9,10] Even the powder spectra for the radical-anions showed a small second splitting of *ca.* 5 G (Figure 1) previously attributed to a carboxy-proton.[9] However, on slight annealing, this doublet splitting was lost irreversibly, and the major doublet splitting fell from 26·3 to 22·5 G (Table). Similar results were obtained with [$^2H_3$]glycine, but the spectrum after annealing showed signs of further weak coupling [Figure 1(b)]. [$^2H_3$]Glycine gave only a singlet as did [$^2H_5$]glycine. Thus an alternative to the concept of carboxy-protonation would be a conformation such that one of the CH_2 protons coupled strongly and the other weakly [see (I)]. On annealing, this conformation could change to one more stable such as (II). This would account for the change in *a*(1-H) and the apparent loss of coupling from 2-H. The extra structure appearing on the main features is probably from ^{14}N, which is in a more favourable position for interaction in (II).

On annealing to *ca.* 135 K a poorly resolved triplet was obtained, which became better resolved on further annealing to give the well defined anisotropic features shown in Figure 2. This can be compared with the extremely well defined features recently obtained by Kasai *et al.* for $H_2\dot{C}CO_2H$ radicals randomly oriented in a rare-gas matrix at 4·2 K. The near axial symmetry displayed in the present case suggests a more symmetrical radical and we suggest that the present radical is $H_2\dot{C}CO_2^-$ rather than $H_2\dot{C}CO_2H$. The resulting data are given in the Table.

On further annealing to *ca.* room temperature, clear features for the secondary product $H_3\overset{+}{N}\dot{C}HCO_2^-$ were

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[1] Part CXXXIII, S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1973, 1425.

[2] W. Gordy, W. B. Ard and H. Shields, *Proc. Nat. Acad. Sci. U.S.A.*, 1955, **41**, 983.

[3] M. C. R. Symons, *J. Chem. Soc.*, 1959, 277.

[4] D. K. Ghosh and D. H. Whiffen, *Mol. Phys.*, 1959, **2**, 285.

[5] D. K. Ghosh and D. H. Whiffen, *J. Chem. Soc.*, 1960, 1869.

[6] R. F. Weiner and W. S. Koski, *J. Amer. Chem. Soc.*, 1963, **85**, 873.

[7] J. R. Morton, *J. Amer. Chem. Soc.*, 1964, **86**, 2325.

[8] M. A. Collins and D. H. Whiffen, *Mol. Phys.*, 1966, **9**, 317.

[9] P. B. Ayscough and A. K. Roy, *Trans. Faraday Soc.*, 1968 **64**, 582.

[10] P. B. Ayscough and K. Mach, *J.C.S. Faraday II*, 1972, 1139.

obtained [Figure 3(b)], as previously described for single crystals.[10]

(2) *Outer Features.*—Since we anticipated that the radicals $H_2^+\dot{N}CH_2CO_2^-$ or $H_3\overset{+}{N}\dot{C}H_2$ would be the main electron-loss species at 77 K, and since the overall spread of the hyperfine features for these radicals is expected[11] to be in the region of 200 G, the outer regions of the spectra were recorded at higher gain. This revealed the expected features (Figure 4) and although these were poorly defined for $[^1H_5]$glycine [Figure 4(a)] it was possible to assign features both to $H_2^+\dot{N}CH_2CO_2^-$ and $H_3\overset{+}{N}\dot{C}H_2$ radicals (Table). Single crystals of $[^1H_5]$-glycine showed similar broad features in the wings of the main doublet, and it was observed that the outermost lines [assigned to $H_2^+\dot{N}CH_2CO_2^-$ in Figure 4(a)] were strongly anisotropic, whereas the narrower lines assigned to $H_3\overset{+}{N}\dot{C}H_2$ were almost isotropic. This accords well with expectation and observation for similar radicals.[12]

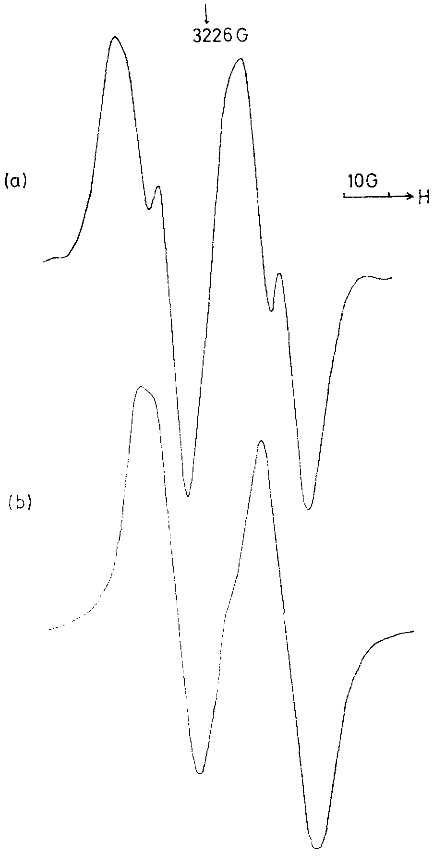


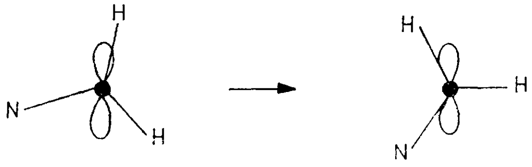
FIGURE 1 First derivative X-band e.s.r. spectra for powdered $[^1H_5]$glycine after exposure to ^{60}Co γ-rays at 77 K: (a) at 77 K and (b) after annealing to *ca.* 100 K and recooling to 77 K, showing features assigned to $H^3N^+-CH_2-\dot{C}O_2^{2-}$ radical anions

Powders and crystals of $[^2H_2]$glycine gave relatively well defined features for both $H_2^+\dot{N}-CD_2CO_2^-$ and $H_3\overset{+}{N}-\dot{C}D_2$ [Figure 4(b)] thus strongly supporting our assignments. These were the best resolved spectra, and the single crystal data were in good agreement with our analysis of the powder spectra. Again, $[^2H_3]$glycine showed the expected features for both radicals, and $[^2H_5]$glycine gave broad outer shoulders for the $^{14}N \pm 1$ parallel components of $D_2^+\dot{N}CD_2CO_2^-$.

Hyperfine coupling data for selected radicals in γ-irradiated glycine

	Hyperfine coupling (G)[a,b]		
Anionic	$^1H(N)$	$^1H(C)$	^{14}N
$H_3\overset{+}{N}-CH_2-CO_2^{2-}$ (i)		36·3 ± 5·0	
(ii)		22·5, 0 ± 2	*ca.* 3
$H_2\dot{C}CO_2^-$ (Narrow species)		∥28 ⊥17·5	
Cationic			
$H_2^+\dot{N}-CH_2-CO_2^-$	∥22 ± 1, ⊥15 ± 1	*ca.* 10 and 37[c]	∥41 ± 1, 10 ± 3[d]
$H_3\overset{+}{N}-\dot{C}H_2$	20 ± 1	33 ± 1	5 ± 0·5
$H_2N-\dot{C}H_2$	*ca.* 5	13 ± 1	5 (iso)

[a] 1 G = 10^{-4}T. [b] Data for various deuteriated species all agree with these values within the experimental error. [c] Results only clear for *C*-deuteriated radicals. [d] Based upon single crystal results for *C*-deuteriated material.



(I) (II)

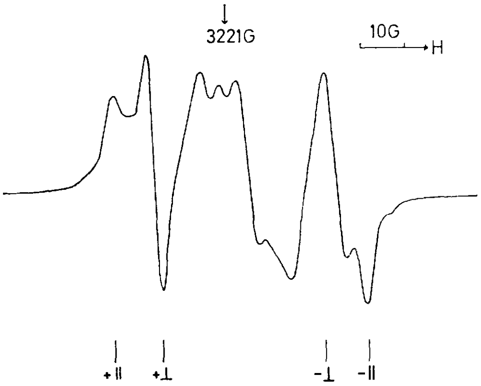


FIGURE 2 First derivative X-band e.s.r. spectrum for powdered $[^1H_5]$glycine after exposure to ^{60}Co γ-rays at 77 K and annealing to 135 K for 300 s, showing features assigned to $H_2\dot{C}CO_2^-$ radicals

We conclude that the radicals $H_2^+\dot{N}CH_2CO_2^-$ and $H_3\overset{+}{N}\dot{C}H_2$ are both formed from the primary hole-centre in glycine, the reason for their apparent absence in other studies being that the lines are weak, broad, and spread

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[11] M. C. R. Symons, *J.C.S. Perkin II*, 1973, 797.

[12] P. H. Kasai and D. McLeod, *J. Amer. Chem. Soc.*, 1972, **94**, 7975.

over a wide field range. Thus the relatively narrow central components tend to dominate.

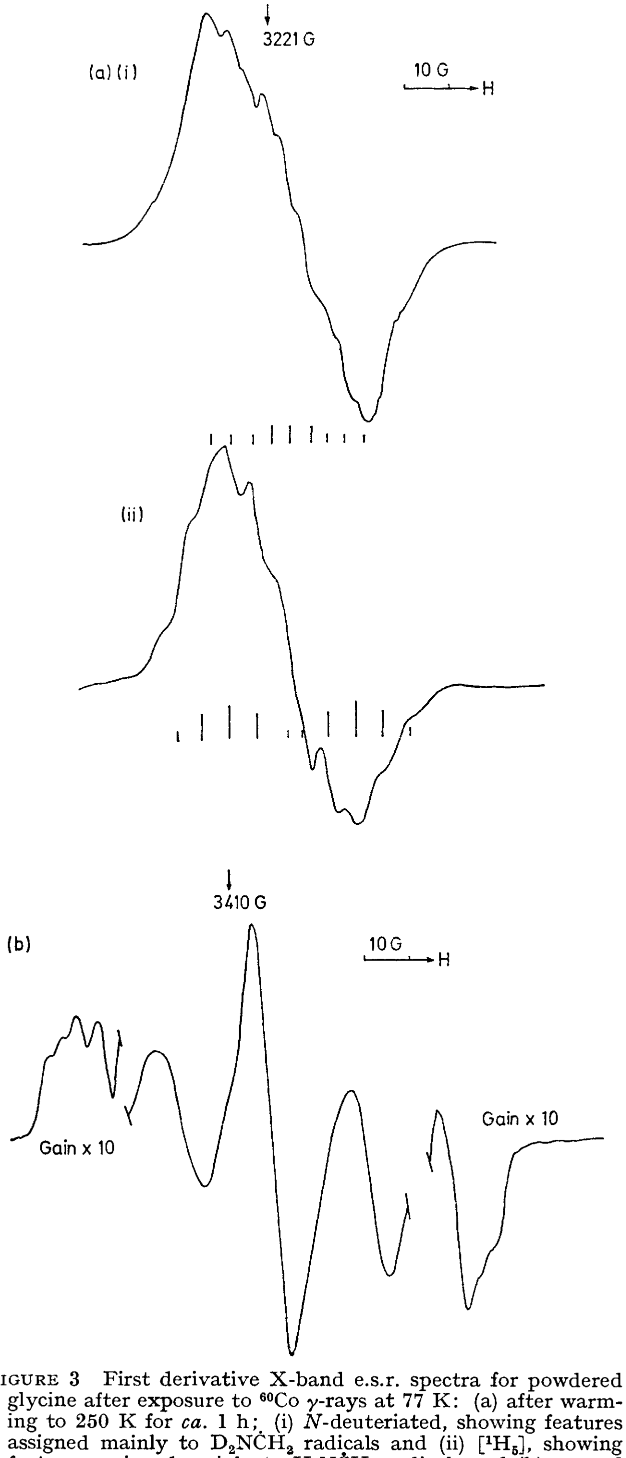

FIGURE 3 First derivative X-band e.s.r. spectra for powdered glycine after exposure to ^{60}Co γ-rays at 77 K: (a) after warming to 250 K for *ca.* 1 h; (i) *N*-deuteriated, showing features assigned mainly to $D_2N\dot{C}H_2$ radicals and (ii) [$^1H_5$], showing features assigned mainly to $H_2N\dot{C}H_2$ radicals and (b) normal glycine at room temperature, showing features assigned to $H_3\overset{+}{N}\dot{C}HCO_2^-$ radicals

On annealing to 150 K, both sets of outer lines were irreversibly lost, giving way to the outer lines for $H_3\overset{+}{N}\dot{C}HCO_2^-$ radicals [the outermost pair of lines shown in Figure 3(b) being well defined]. Thus the original suggestion that the primary outer features were due to $H_3\overset{+}{N}CHCO_2^-$ radicals[8] is incorrect.

We suggest that the intramolecular reaction (1)

$$H_2{}^+\dot{N}CH_2CO_2^- \longrightarrow H_3\overset{+}{N}\dot{C}HCO_2^- \qquad (1)$$

may be one route for the formation of $H_3\overset{+}{N}\dot{C}HCO_2^-$ radicals. The fate of $H_3\overset{+}{N}\dot{C}H_2$ radicals is less clear.

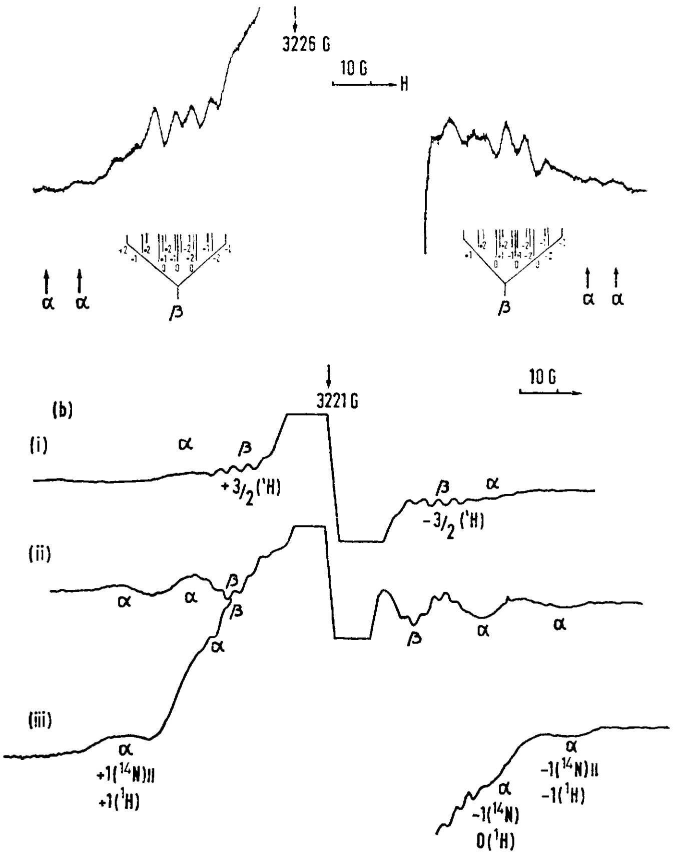

FIGURE 4 First derivative X-band e.s.r. spectra for glycine after exposure to ^{60}Co γ-rays at 77 K: (a) powdered [$^1H_5$] and (b) (i) and (ii) single crystal (*C*-deuteriated) at orientations close to ⊥ and ‖ for $\overset{+}{H}_2\dot{N}CH_2CO_2^-$ radicals and (iii) for the powdered material, all showing outer features for (α) $\overset{+}{H}_2NCH_2$-CO_2^- radicals and (β) $H_3\overset{+}{N}-\dot{C}H_2$ radicals

These are expected to behave as strong acids,[11] so a search was made for $H_2N-\dot{C}H_2$ radicals, whose parameters are well established.[13,14] Unfortunately, the spread of features is smaller, and would normally be concealed by those for $H_2\dot{C}CO_2^-$ and $H_3\overset{+}{N}\dot{C}H_2CO_2^-$ radicals or their deuteriated analogues.

However, by controlled annealing we were able to find a temperature (*ca.* 100 K) at which the lines from

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

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

$H_2\dot{C}CO_2^-$ radicals became relatively broad, and before those from $H_3\overset{+}{N}\dot{C}H_2CO_2^-$ radicals had become too intense. Under these circumstances features which may well be due to $H_2N\dot{C}H_2$ and $D_2N\dot{C}H_2$ radicals apparently undergoing relatively free rotation were obtained [Figure 3(a)]. Admittedly, these spectra are poorly resolved, but the reconstructions given are based upon the known e.s.r. data for these π*-radicals.[14] On further annealing, spectra similar to that in Figure 3(b) were obtained, the $H_2N\dot{C}H_2$ features being irreversibly lost.

Whilst there were definite differences between the various glycine species with respect to the relative yields of these radicals and the rates at which they were formed, these did not seem to be sufficiently marked to warrant careful monitoring. We agree with Ayscough and Mach[10] that, despite frequent reports, there is no evidence for H–D exchange in these radicals at low temperature. However in the particular case of the [$^2H_2$]-compound, clear evidence for such exchange was obtained for the radical $H_3\overset{+}{N}\text{-}\dot{C}DCO_2^-$ in the 50 °C temperature region. Thus on warming from 77 K there was no trace of the spectrum for $H_3\overset{+}{N}\text{-}\dot{C}HCO_2^-$, but on standing at 50 °C outer features for this species slowly appeared, and on exposure to γ-rays at *ca.* 40 °C these features were prominent. We suggest that reaction (1) is weakly reversible, and that intermolecular exchange of $H^+(D^+)$ from the NH_3^+ group is also possible. Further studies of the kinetic course of this exchange are in progress.

Mechanisms.—Electron loss leads to the radical-cation $(H_3N^+\text{-}CH_2\text{-}CO_2^-)^+$, which can act either as a carboxylate ion, losing carbon dioxide to give $H_3\overset{+}{N}\text{-}\dot{C}H_2$, or as an ammonium ion,[11] giving $H_2{}^+\dot{N}\text{-}CH_2CO_2^-$. It seems, somewhat surprisingly, that both processes are favoured by glycine at 77 K. The fate of these initial species has been discussed above. The radicals $H_2\dot{C}CO^{2-}$ are clearly formed by loss of ammonia from the parent radical-anion, so the overall process can be represented as (2)—(5).

$$G \xrightarrow{\gamma\text{-rays}} G^+ + e^-;\ G + e^- \longrightarrow G^- \qquad (2)$$

$$G^+ \longrightarrow CO_2 + H_3\overset{+}{N}\text{-}\dot{C}H_2 \qquad (3)$$

$$\llcorner\!\!\longrightarrow (H^+) + H_2\overset{+}{\dot{N}}\text{-}CH_2CO_2^- \qquad (4)$$

$$G \longrightarrow NH_3 + H_2\dot{C}CO_2^- \qquad (5)$$

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