An Electron Spin Resonance Study of Dissociative Electron-capture Processes in γ-Irradiated Amino-acids

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DISSOCIATIVE electron-capture processes such as (1) are thought to be important in the low-

$$RX + e^- \rightarrow (RX^-) \rightarrow R\cdot + X^- \qquad (1)$$

temperature radiolysis of alkyl halides,[1] nitriles,[2] halogeno-carboxylic acids[3,4] *etc.* where the reaction is favoured by the high electron affinity of X (halogen, CN, *etc.*). The resulting neutral alkyl radicals are readily detected by their e.s.r. spectra in the irradiated solid or when the electrons are generated photolytically in glassy matrices.[4] The intermediate species RX^- have not however been positively identified.

An early suggestion[5] concerning the radiolysis of amino-acids includes a similar reaction (2)

$$RCH(NH_3^+)CO_2^- + e^- \rightarrow$$
$$RCH(NH_3^+)CO_2^{2-} \rightarrow R\dot{C}H{\cdot}CO_2^- + NH_3 \qquad (2)$$

since NH_3 is a major product and radicals of the structure $R\dot{C}HCO_2^-$ are commonly observed following γ-irradiation at room temperature.[6] Recent reports of transient e.s.r. spectra observed at 77°K in γ-irradiated carboxylic and amino-acids and attributed to radical–ions such as $CH_2(CO_2H)_2^-$ and $NH_3^+CH_2{\cdot}CO_2^{2-}$ support this view.[7]

We have now examined the e.s.r. spectra of a group of amino-acids $RCH(NH_3^+)CO_2^-$ where R = H, Me, Et, $CH_2{\cdot}CO_2H$, and $CH_2{\cdot}SO_3H$. These have been γ-irradiated at 77°K and examined in single- or poly-crystalline form between 77° and 450°K and in frozen alkaline glasses between 77° and 160°K. We find evidence for transient radical–anions with $g = 2{\cdot}0035 \pm 0{\cdot}005$ in all the pure compounds but only for cysteic acid in the aqueous glasses. Salient features of the spectra are summarised in the Table.

Further details of the single-crystal spectra are described elsewhere[3,8] and only the most important general conclusions are mentioned here. In each case the spectra can be attributed to a species with two interacting protons (possibly three for the glycine and β-alanine radical–anions). One of these is replaced by ^2H in the $^2H_3$-compound and is presumably attached to the carboxyl group. The hyperfine anisotropy ($< \pm 3$ gauss) is typical of β-protons as is the dependence of the isotropic coupling on the orientation of the $\cdot C{-}C{-}H$ and $\cdot C{-}O{-}H$ groups. At temperatures above 130°K the spectra change to those corresponding to the structure $R\dot{C}H{\cdot}CO_2H$ [see reaction (2)] though the configuration is generally not precisely that observed at room temperature.

We therefore conclude that in all these compounds the species trapped initially at 77°K (*a*) are formed by electron capture and have the unpaired spin localised in the carboxyl group, (*b*) are probably stabilised by protonation, and (*c*) decay by loss of NH_3 to give radicals $R\dot{C}H{\cdot}CO_2H$ which may subsequently abstract H from the parent molecule.

The second conclusion is supported by studies of γ-irradiated aqueous alkaline glasses containing up to 10^{-2}M-amino-acid. In these systems protonation is unlikely. Only e^- and O^- are observed at 77°K in the absence of light, but when trapped electrons are remobilised by illumination with visible light or by warming to about 140°K, radicals of the type $R\dot{C}H{\cdot}CO_2^-$ are formed directly. Only when cysteic acid, $HSO_3CH_2{\cdot}CH(NH_3^+)CO_2^-$,

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TABLE

E.s.r. spectra observed in γ-irradiated amino-acids $RCH(NH_3^+)CO_2^-$ *at* 77°K

	Hyperfine spectrum						Average hyperfine splittings (gauss)		
R	$RCH(NH_3^+)\dot{C}O_2H^-$			$RCH(ND_3^+)\dot{C}O_2D^-$					
	Number of lines	Line separations	Line width	Number of lines	Line separations	Line width	$a^H_{\beta_1}$	$a^H_{\beta_2}$	a^H_{OH}
H[b]	2	27	13	2[a]	25	8	27	~7	small
Me	3	16	8	2[a]	18	8	17·9	—	14·8
Et	1	—	21	1[a]	—	10	<10	—	~15
$CH_2{\cdot}CO_2H$[c]	1	—	20	1[a]	—	5	<10	—	~15
	2	27		2	27	8	27		
$CH_2{\cdot}SO_3H$	3	16	<5	2[a]	17	<5	16·5	—	14·6

[a] Subsidiary splittings also seen.

[b] The spectrum of β-alanine, $NH_3^+CH_2CH_2CO_2^-$ is identical with that of glycine at 77°K.

[c] Two species seen, decaying at different rates.

is the solute is a spectrum characteristic of a radical–anion seen, and there is evidence to suggest that this may be formed by addition of e^- to SO_3^- rather than to CO_2^-.[8]

The summation of evidence presented above appears to rule out the possibility that the initially trapped species are the parent molecular cations, a possibility which had not been excluded in earlier studies.

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