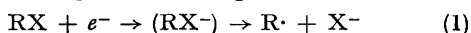


An Electron Spin Resonance Study of Dissociative Electron-capture Processes in γ -Irradiated Amino-acids

By P. B. AYS COUGH,* K. MACH,† J. P. OVERSBY, and A. K. ROY

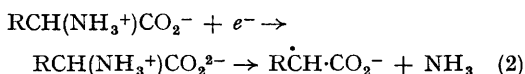
(Department of Physical Chemistry, University of Leeds, Leeds 2)

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



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 suggestion⁵ concerning the radiolysis of amino-acids includes a similar reaction (2)



since NH_3 is a major product and radicals of the structure $\dot{\text{R}}\text{CHCO}_2^-$ 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 $\text{CH}_2(\text{CO}_2\text{H})_2^-$ and $\text{NH}_3^+\text{CH}_2\cdot\text{CO}_2^{2-}$ support this view.⁷

We have now examined the e.s.r. spectra of a group of amino-acids $\text{RCH}(\text{NH}_3^+)\text{CO}_2^-$ where R = H, Me, Et, $\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{CH}_2\cdot\text{SO}_3\text{H}$. 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 $g = 2.0035 \pm 0.005$ 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^{8,9} 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 $^2\text{H}_3$ -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 $\cdot\text{C}-\text{C}-\text{H}$ and $\cdot\text{C}-\text{O}-\text{H}$ groups. At temperatures above 130°K the spectra change to those corresponding to the structure $\dot{\text{R}}\text{CH}\cdot\text{CO}_2\text{H}$ [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 $\dot{\text{R}}\text{CH}\cdot\text{CO}_2\text{H}$ 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 $\dot{\text{R}}\text{CH}\cdot\text{CO}_2^-$ are formed directly. Only when cysteic acid, $\text{HSO}_3\text{CH}_2\cdot\text{CH}(\text{NH}_3^+)\text{CO}_2^-$,

† On leave from the University of Prague, Czechoslovakia.

TABLE

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

R	Hyperfine spectrum						Average hyperfine splittings (gauss)		
	$RCH(NH_3^+)\dot{C}O_2H^-$			$RCH(ND_3^+)\dot{C}O_2D^-$			$a_{\beta_1}^H$	$a_{\beta_2}^H$	a_{OH}^H
	Number of lines	Line separations	Line width	Number of lines	Line separations	Line width			
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 ·CO ₂ H ^c ..	1	—	20	1 ^a	—	5	<10	—	~15
	2	27		2	27	8	27		
CH ₂ ·SO ₃ H	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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