Radiolysis of Solid L-α-Alanine

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The radiolysis of L-α-alanine was studied in comparison with that of glycine, the reaction mechanism of which had already been reported.[1,2] As is shown in Table 1, the similarity between L-α-alanine and glycine in the yield-relationship of the products suggested a glycine-like reaction mechanism in the radiolysis of L-α-alanine.

TABLE I. G-VALUES OF PRODUCTS

α-Alanine		
H_2	0.06	
NH_3	3.4	3.6
$CH_3CH_2NH_2$	~0.2	
CH_3CH_2COOH	(1.9)	3.6
$CH_3COCOOH$	1.5	
CO_2	~0.2	
CH_3CHO	trace	
CH_4	trace	

Glycine		
H_2	0.2	
NH_3	4.8	5.0
CH_3NH_2	0.2	
CH_3COOH	2.5	5.0
$HCOCOOH$	2.3	
CO_2	0.2	
$HCHO$	0.03	

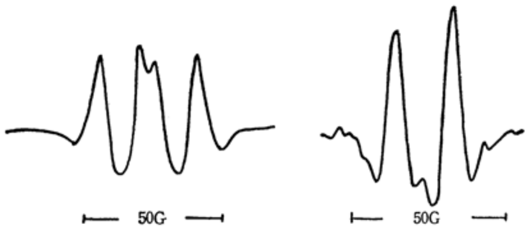
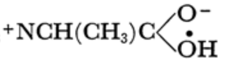


Fig. 1. Second derivative ESR spectra of powder of normal and deuterated L-α-alanine irradiated and measured at 77°K.
a) Normal L-α-alanine
b) Deuterated L-α-alanine

TABLE 2. THE PRINCIPAL VALUES OF HYPERFINE SPLITTING (A) AND g-VALUES FOR IRRADIATED L-α-ALANINE AT 77°K

	$A_{\alpha\text{-proton}}$	$A_{\beta\text{-proton}}$	g-Value
Principal value	23.0G	21.3G	2.0037
	12.1G	17.5G	2.0032
	9.9G	16.4G	2.0017
	(av. 15.0G)	(av. 18.3G)	

However, the fact that $CH_3\text{-}\dot{C}H\text{-}CO_2^-$ was the only radical which had so far been identified at room temperature in the radiolysis of L-α-alanine[3,4] made it very difficult to explain our experimental results by the glycine-like mechanism, in which several radicals are included in the initial processes.[2]

Therefore, an ESR study of solid L-α-alanine was made, using $H_3{}^+NCH(CH_3)CO_2^-$ and $D_3{}^+NCH(CH_3)CO_2^-$, both irradiated and measured at 77°K, in order to find out such a radical, other than $CH_3\dot{C}HCO_2^-$, which might be unstable at room temperature but stable at 77°K. From the X-band ESR data obtained[5] (shown in Fig. 1 and Table 2), it is clear that a radical containing one α-proton and one β-proton, a precursor of $CH_3\dot{C}HCO_2^-$, is formed at 77°K; this radical is identified as  $H_3{}^+NCH(CH_3)C\langle^{O^-}_{\dot{O}H}$ An unpaired electron of the radical is considered to be localized in a carboxyl group, as has been shown by Box *et al.*[6] in the case of irradiated succinic acid.

Considering the existence of this radical, the initial processes of the reaction, especially the formation of $CH_3\dot{C}HCO_2^-$, $CH_3CH_2CO_2^-$, NH_3, CH_3COCO_2H, and CH_3CHO, can be reasonably explained as follows:

$$(H_3{}^+NCHCH_3CO_2^-) \rightsquigarrow (H_3{}^+NCHCH_3CO_2^-)^+ + e$$

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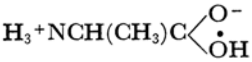
[1] G. Meshitsuka, K. Shindo, A. Minegishi, H. Suguro and Y. Shinozaki, This Bulletin, **37**, 928 (1964).
[2] K. Shindo, Y. Shinozaki and G. Meshitsuka, *Ann. Report, Tokyo Metropolitan Isotope Research Center*, **3**, 79 (1964).
[3] I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **32**, 255 (1960).
[4] A. Horsfield, J. R. Morton and D. H. Whiffen, *Mol. Phys.*, **5**, 115 (1965).
[5] Presented at the 9th Symposium on Radiation Chemistry, November, 1966, Osaka, Japan.
[6] H. C. Box, H. G. Freund and K. T. Lilga, *J. Chem. Phys.*, **44**, 2345 (1966).

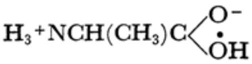
$$(H_3{}^+NCHCH_3CO_2{}^-) + e + (H_3{}^+NCHCH_3CO_2{}^-) \rightarrow$$



$$H_3{}^+NCH(CH_3)C\left\langle\begin{array}{l}O^-\\ \dot{O}H\end{array}\right.$$

$$+ H_2NCH(CH_3)CO_2{}^-$$

at room temperature,



$$H_3{}^+NCH(CH_3)C\left\langle\begin{array}{l}O^-\\ \dot{O}H\end{array}\right.$$

$$\rightarrow NH_3 + CH_3\dot{C}HCO_2H$$

dissolved in water,

$$CH_3\dot{C}HCO_2H + (H_3{}^+NCHCH_3CO_2{}^-) \rightarrow CH_3CH_2CO_2H + H_3{}^+N\dot{C}(CH_3)CO_2{}^-$$

$$2\ H_3{}^+N\dot{C}(CH_3)CO_2{}^- \rightarrow H_3{}^+NCH(CH_3)CO_2{}^- + H_2{}^+NC(CH_3)CO_2{}^-$$

$$H_2{}^+NC(CH_3)CO_2{}^- + H_2O \rightarrow NH_3 + CH_3COCO_2H \rightarrow NH_3 + CH_3CHO + CO_2$$

However, a remaining difficulty is the behavior of the cation radical $(H_3{}^+NCHCH_3CO_2{}^-)^+$, which can not be identified by ESR even at 77°K; this problem is left for further investigations.