Study of Radicals derived from Glycine and Alanine in Solution

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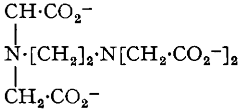
THE e.s.r. spectra of irradiated crystals of amino-acids have been studied extensively. The radicals are often produced through the abstraction of a hydrogen atom bonded to carbon. We have been studying amino-acid radicals in solution, produced in a flow system by the $TiCl_3$–H_2O_2 reagent, and find that different radicals are produced under acid and basic conditions. We have used the $TiCl_3$–H_2O_2 reagent at high pH values (*ca.* 11) by adding EDTA as a complexing agent. EDTA itself gives a free radical in this system,[1] but when glycine or alanine are added, this radical is not formed in detectable quantities, and the observed e.s.r. spectra can be ascribed to the amino-acid radicals.

We found that the seven-line spectrum of glycine in acid media (pH $\simeq$ 3), recently reported by Armstrong and Humphreys,[2] is in fact further split into a total of about 24 lines. Their origin has not yet been assigned.

TABLE

E.s.r. spectra of glycine, alanine, and EDTA radicals in basic solutions (pH 10—11)

Compound	Relative intensities and splittings (G)		Radical
Glycine	(1:1)	13·6	$NH_2{\cdot}CH{\cdot}CO_2^-$
	(1:1:1)	6·0	
	(1:1)	3·2	
	(1:1)	2·8	
α-Alanine	(1:3:3:1)	13·2	$NHX{\cdot}CMe{\cdot}CO_2^-$ X = OH (?)
	(1:1:1)	4·8	
	(1:1)	1·8	
EDTA	(1:1)	11·1	 $\begin{array}{l}CH{\cdot}CO_2^-\\ \vert\\ N{\cdot}[CH_2]_2{\cdot}N[CH_2{\cdot}CO_2^-]_2\\ \vert\\ CH_2{\cdot}CO_2^-\end{array}$
	(1:1:1)	7·1	
	(1:4:6:1)	4·1	

Two interesting conclusions may be derived from the results: (a) there is a considerable spin density at the nitrogen nucleus, (b) the two hydrogen atoms in the $-NH_2$ group of glycine radical are not equivalent. This implies that the rotation of the NH_2 group about the C–N bond is hindered, with rate slower than 7×10^6 sec.$^{-1}$. A similar situation occurs with the $CH_2{\cdot}CO{\cdot}NH_2$ radical.[3]

A close-shell SCF calculation, using the Paiser–Parr–Pople method, was carried out for the glycine radical. Bond integrals (β) and lengths (r) were allowed to vary with the calculated bond order at each stage of the iteration procedure.[4] The results are: $r_{CO} = 1{\cdot}29$ Å; $r_{CN} = 1{\cdot}38$ Å; $r_{CC} = 1{\cdot}45$ Å; $\rho_O = 0{\cdot}07$; $\rho_{C(1)} = 0{\cdot}002$; $\rho_{C(2)} = 0{\cdot}63$; $\rho_N = 0{\cdot}225$. With $Q^{H}_{CH} = 23$ G and the observed $A^{H}_{C_2}$ we find that the spin density, ρ, on C(2) is 0·59 which is in fair agreement with the calculated value.

In the alanine radical the results seem to be consistent with the suggested radical if we surmise that one of the hydrogens of the NH_2 group is replaced by a hydroxyl. This, however, is a tentative suggestion.

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