

The Structure and E.S.R. Spectra of α - and β -bromo- and iodo- carboxylate Radicals

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(Received in UK 16 June 1975; accepted for publication 10 July 1975)

Our original e.s.r. identification of α -bromo alkyl radicals¹ in irradiated organic bromides has recently been challenged, and a species with a very different e.s.r. spectrum has been assigned the α -bromo structure.² We label these Type A and Type B respectively. Particular data are summarised in Table 1.

Some magnetic data for typical Type A and Type B bromo-radicals

Type		Hyperfine Coupling Constants (G) ^a				
		A _x	A _y	A _z	A _{iso} (⁸¹ Br)	A _{iso} (¹ H)
A	CH ₃ Br+CD ₃ OD	85				21(2H _α)
	BrCH ₂ CO ₂ H	107	-48	-75	-5.3	20(1H _α)
	BrCHMeCO ₂ H	95				22(3H _α)
B	BrCH(CCNH ₂) ₂ ^b	289	83.79	83.79	152.2	14(1H _α)
	BrCH ₂ CO ₂ H	277	90	90	152.3	18(2H _α)

^a G = 10⁻⁴T.

^b Ref. 2.

Our aim is to establish which type is best assigned the α -bromo (R₂C[•]-Br) structure, and to propose an alternative structure for the other type. We include results for Type B radicals that we have studied during the past four years. Type A radicals have been prepared from simple alkyl bromides including methyl bromide, but also from substituted bromides including carboxylic acids, esters and amides (carboxylates). Type B radicals have only been prepared from carboxylate derivatives containing α -bromine. Type A radicals have parameters which closely resemble those of α -chloro radicals.³ In particular, A_{iso} is close to zero and the quadrupole axis lies along the C-Br direction, (z) for which the hyperfine coupling A_z is small but Δg_z is large, exactly as expected for an α -bromo species.¹ Type B radicals, in contrast, exhibit a large isotropic coupling to bromine, and the quadrupole axis lies along

the direction for $A_{\max}(A_x)$ apparently perpendicular to the C-Br direction. Type A radicals do not exhibit axial symmetry in agreement with the results for α -chloro-radicals and with expectation for α -bromo radicals. Type B radicals are nearly axially symmetrical with respect to their magnetic properties. Type A radicals in several instances exhibit proton hyperfine coupling in good agreement with expectation for α -bromo radicals. (see Table) Type B radicals agree less well. The results assigned to $\text{BrCH}(\text{CONH}_2)$ certainly give one α -proton, as expected, but our results for β obtained from bromoacetic acid show the presence of two α -protons, (Fig. 1a).

Neither Types A nor B radicals are formed at 77 K in methanol but, for the bromo-carboxylates, $\text{R}_2\dot{\text{C}}\text{CO}_2^-$ radicals are formed by dissociative electron capture. On annealing, CH_2OH radicals are lost, and Type A radicals are formed. When Type A and B radicals are present together at 77 K, Type B are invariably lost on annealing above 77 K, but Type A are thermally quite stable and are only lost when the medium softens. $\text{R}_2\dot{\text{C}}\text{COX}$ type radicals appear to be formed when Type B radicals decompose. These results suggest that Type B radicals are electron excess centres and that Type A radicals are formed by loss of a hydrogen atom.

Thus Type A radicals satisfy all criteria for α -bromo radicals and, hence, we need an alternative formulation for Type B. Our results suggest an electron-excess species: the carboxy-group is essential and is known to add an excess electron readily. If the resulting anions adopt a conformation giving maximum hyperconjugative overlap (1) then a β -bromo radical is obtained. The results for bromine are in good agreement with this structure but this is not Type B because the two protons should exhibit very small hyperfine coupling;^{4,5} however, migration of bromine to give II could give a species having all the required properties. In particular, the bromine hyperfine coupling and g -tensor could be axial (though this rules out significant p - p homoconjugation), the isotropic coupling to bromine should be large as for other β -bromo radicals^{4,5} because the negative spin-polarisation term is absent. Also, the quadrupole coupling axis now lies along the C-Br bond as required by theory.

These conclusions force us to reconsider our preliminary results for a species in irradiated α -Iodoacetamide⁶ thought to be $\dot{\text{I}}\text{CH}(\text{CONH}_2)$. For some orientations of the crystal we detected a well-defined doublet splitting, apparently in accord with this formulation, and Picone and Rogers have also been induced to make the same assignment for this reason.⁷ However, their more detailed crystal data show, once again, that the radical exhibits axial symmetry and that the quadrupole axis is apparently along (x) and perpendicular to the C-I bond

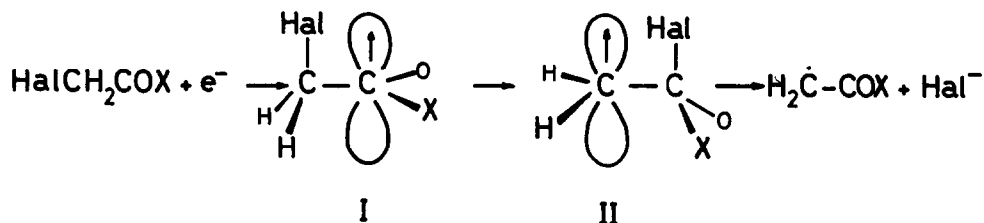
direction. Indeed, the data resemble closely those for Type B radicals.

Our recent studies have shown that alkyl iodides from Type A radicals having all the expected properties for α -Iodo radicals and our attention has been called to a very well-defined Type A radical in iodo-uracil⁸ which exhibits hyperfine coupling (38G) to two equivalent protons, making the α -Iodo assignment uncontroversial. (III)

We have, therefore, examined the single crystal spectra for irradiated iodo-acetamide and find, as expected for certain orientations, triplets or quartets rather than doublets. (Fig. 1b) Indeed, within the restricted limits of resolution, the results rule out coupling to a single α -proton but can be understood in terms of two α -protons. Hence structure (II) is once again favoured.

These results are significant in that they yield by far the most accurate set of data for β -bromo and β -iodo radicals yet obtained. They confirm many of our previous conclusions based on very poorly resolved powder spectra,⁵ but seem to rule out the p - p homoconjugation that would be expected if there was weak residual bonding indicative of a cyclic structure. However, they strongly support our hyperconjugative mechanism for electron delocalisation.^{4,5}

The results reveal in some detail the pathway for loss of halide ions:



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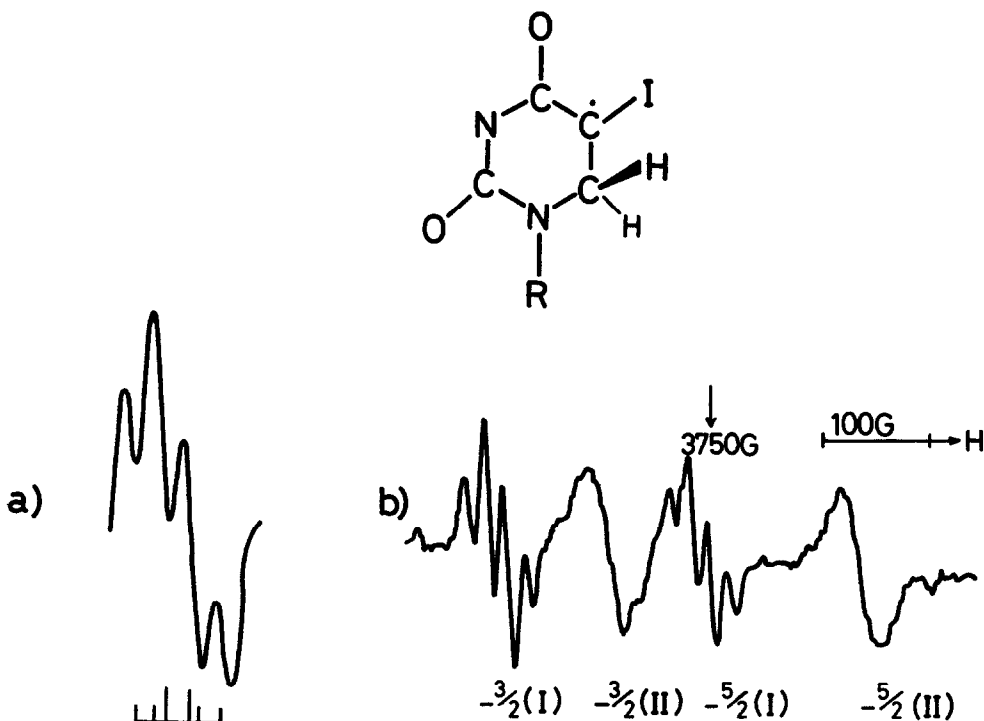


FIG. 1

First derivative e.s.r. spectra for single crystals after exposure to ^{60}Co γ -rays at 77K: a for bromoacetic acid, showing two sets of features assigned to type B radicals (α and β), the β features exhibiting the maximum coupling to ^{81}Br and ^{79}Br . The $M_I = -\frac{1}{2}$ feature shows hyperfine coupling to two equivalent protons in addition to the predicted $^{81}\text{Br} - ^{79}\text{Br}$ splitting. Some of the intense central and low-field features are for type A radicals also present. b for iodoacetamide, showing the $M_I = -\frac{3}{2}$ and $-\frac{5}{2}$ lines for two sites, I and II, for an orientation 30° from b in the a b plane. The quartet splitting is assigned to two inequivalent α -protons, but we are not able to explain the intensity distribution of the four lines, which varies with orientation.