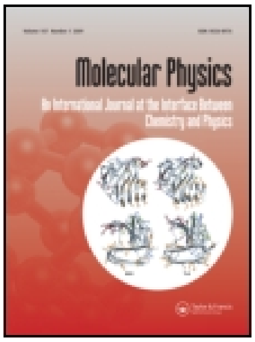

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Electron spin resonance detection of acrylic acid radical anions and related species in low temperature glasses

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Exposure of pure acrylic acid and related acrylic monomers to high energy radiation at 77 K generally results in the formation of a radical apparently formed by hydrogen atom addition to the β-carbon, giving, for example, $CH_3\dot{C}HCO_2H$ for acrylic acid. On annealing, these radicals add to neighbouring monomers to give $RCH_2\dot{C}HCO_2H$ or related radicals.

Recently a 14 G triplet has been obtained from various polymer and acrylic acid systems after irradiation at 77 K, which was very tentatively assigned to the acrylic acid radical cation [1]†. One clear-cut aspect of these results was the fact that for various acrylic monomers $R_2C=CR\ CO_2R$, hyperfine coupling was only obtained from the R_2C-moiety. Thus $H_2C=$ species gave a 12–14 G triplet, $MeCH=$ species gave a 12 G quintet, and $Me_2C=$ species gave a 12 G septet [1]. The purpose of this note is to suggest that the species responsible for these spectra are the radical anions rather than the cations. Our case hinges on the following points :

(i) A qualitative consideration of the π-electron orbitals suggests that the orbital of the unpaired electron should have a node at, or close to, the α-carbon atom for the anion, but not for the cation. Thus absence of coupling to α-substituents can only be understood for the anions.

(ii) Exposure of dilute solutions of acrylic acid in methyl tetrahydrofuran to γ-rays at 77 K gave a clear 14 G triplet in addition to the broad lines from the solvent radicals. The characteristic blue colour associated with trapped electrons (e_t^-) was suppressed and the singlet E.S.R. absorption for e_t^- was absent. Thus acrylic acid acts as an efficient electron scavenger, but not as a hole-scavenger.

(iii) A similar triplet was obtained from solutions in CD_3OD, but as the glass was annealed clear features for $DCH_2\dot{C}HCO_2^-$ radicals were obtained at the expense of the triplet (figure (*a*)). Thus, protonation of the anion is efficient under these conditions

$$CH_2=CHCO_2^- + e^- \rightarrow (CH_2=CHCO_2^-)^-$$

$$(CH_2=CHCO_2^-)^- + CD_3OD \rightarrow DCH_2\dot{C}HCO_2^- + CD_3O^-.$$

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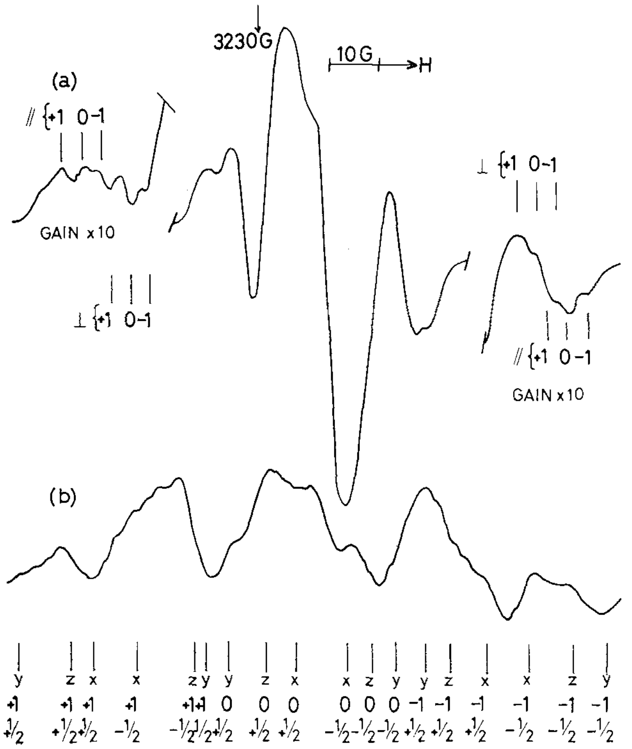
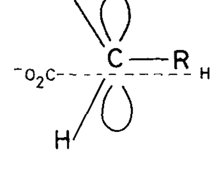
† $G=10^{-4}$ T.



First derivative X-band e.s.r. spectra for a solution of acrylic acid in CD_3OD after exposure to ^{60}Co γ-rays at 77 K; *a* showing features assigned to ($CH_2{=}CHCO_2^-$) radical anions (a) and $DCH_2\dot{C}HCO_2^-$ radicals (b). *b* After further annealing, showing features assigned to $RCH_2\dot{C}HCO_2^-$ radicals.

This strongly suggests that formation of $CH_3\dot{C}HCO_2H$ from the pure monomer arises via protonation of the radical anion by a neighbouring carboxylic acid rather than by hydrogen atom addition. Again in CD_3OD, the violet-black colour of e_t^- was almost completely suppressed, but formation of $\dot{C}D_2OD$ was not suppressed.



When the solutions in CD_3OD were further annealed, the $DCH_2\dot{C}HCO_2^-$ radicals were lost, and a new spectrum appeared (figure (*b*)) which we assign to dimer or polymer radicals, $RCH_2\dot{C}HCO_2^-$, having a preferred conformation as indicated in the insert. The asymmetry of this spectrum can be accounted for in terms of an axial *g*-tensor, the derived results being given in the Table, together with those for the parent anion and the $DCH_2\dot{C}HCO_2^-$ radicals.

Radical	Hyperfine coupling constants (G)	g-values
$(CH_2{=}CHCO_2^-)$	$^1H(CH_2)$ 14	2·003
$DCH_2\dot{C}HCO_2^-$	$(^2H_\beta)$ 3·5 $(^1H_\beta)$ 23 $(^1H_\beta)$‡ 21, 32	2·002, 2·004, 2·004
$RCH_2\dot{C}HCO_2^-$†	$(^1H_\alpha)$ 9, 20, 30 $(^1H_\alpha)$ 33 ± 2	2·002, 2·004, 2·004

† $R = CH_3CHCO_2^-$ or a polymeric group.
‡ Features hidden by those from the radical anion.

E.s.r. data for various radicals derived from acrylic acid.

Since this work was completed, we have learned that Gillbro and his co-workers have arrived at the same conclusions regarding the nature of the triplet species [2].

References

[1] Campbell, D., and Charlesby, A., 1972, *Chem. zvesti*, **26**, 250. Charlesby, A., and Campbell, D., 1973, *Nobel Symposium*, No. 22, edited by Per-Olof Kinell, Bengt Ranby and Vera Runnstrom-Reio (New York : John Wiley & Sons), p. 147.

[2] Gillbro, T. (personal communication to A.C.).