Electron Spin Resonance Studies of the Effect of γ-Radiation and of Hydrogen Atoms upon Various Olefinic Carboxylic Acids and Their Amides

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Olefinic carboxylic acids and amides have been studied at 77 K and room temperature after exposure to H atoms and γ-rays. At 77 K certain radicals (*e.g.*, $\mathrm{Me_2\dot{C}{\cdot}CO_2H}$, from α-methylacrylic acid and $\mathrm{Me_2\dot{C}{\cdot}CH_2{\cdot}CO_2H}$ from ββ-dimethylacrylic acid) were observed, some of which were converted into polymer radicals on annealing to room temperature [*e.g.*, $\mathrm{RCH_2{\cdot}\dot{C}Me(CO_2H)}$ from α-methylacrylic acid]. Several differences between H atom and γ-ray bombardment were noticed, especially the tendency of H atoms to add to olefinic bonds in cases where γ-rays gave allylic radicals. Results are discussed in terms of reaction mechanisms.

IRRADIATED acrylic acid has been studied at 77 K by e.s.r. spectroscopy, the predominating radical detected being $\mathrm{Me\dot{C}H{\cdot}CO_2H}$.[1,2] On warming, this radical reacted with neighbouring monomer molecules, the polymer radical $\mathrm{RCH_2{\cdot}\dot{C}H{\cdot}CO_2H}$ being detected by e.s.r. spectroscopy.

Arnold and Eastmond[3] have recently studied the n.m.r. spectra of acrylic and methacrylic acids, and have discussed their results in terms of various librations. In particular, the significance of lattice defects was stressed with respect to the solid-state polymerisations of these monomers. Their results support previous suggestions that these reactions can only occur at suitable dislocations when there is sufficient local molecular mobility.[4]

The main aim of the present work was to compare the effects of high-energy radiation with that of hydrogen-atom bombardment, especially with respect to the tendency of monomer radicals to initiate polymerisation. Another aim was to extend these studies to other methyl-substituted acrylic acids, and to the corresponding amides.

EXPERIMENTAL

Acrylamide (B.D.H.), methacrylamide (Ralph Emanuel), 3,3-dimethylacrylic acid, and crotonic acid (Koch–Light) were the highest grade available and were not further purified.

Samples were irradiated in a Vickrad ^{60}Co γ-ray source at a nominal dose rate of 4 Mrad h^{-1} for up to 2 h. Liquid samples were irradiated at 77 K as small glass beads. Solids were irradiated both at 77 K and at ambient temperatures.

Finely powdered solids were exposed to hydrogen or deuterium atoms obtained from a microwave discharge at room temperature *in situ* so that spectra could be observed during the process of irradiation. Liquid samples were adsorbed on fine silica beads. This had the advantage of providing a high surface area, and a matrix capable of trapping reactive radicals. For this work a Varian V.4502 spectrometer was used fitted with a V.4535 large access cavity. The microwave discharge assembly was similar to that described previously,[5] care being taken to ensure that the path betweem the discharge itself and the sample was such as to prevent any direct interaction between the sample and the discharge, or any photochemical damage. Hydrogen-atom irradiations at 77 K were carried out separately, irradiated samples being transferred to a special Dewar vessel before measurement with a Varian E3 spectrometer. Care was taken to prevent diffusion of oxygen into these systems, but occasionally features from peroxyl radicals $\mathrm{RO_2\cdot}$ were obtained. For example, the asymmetry of the spectrum in Figure 4 is caused by broad peroxyl features on the low-field side.

RESULTS AND DISCUSSION

Typical e.s.r. spectra are illustrated in the Figures, and the resulting data for identified radicals are listed in the Table. Although in most instances interpretation was reasonably unambiguous, certain factors should be mentioned. In general, interpretation was facilitated by the fact that radicals (such as $\mathrm{Me_2\dot{C}{\cdot}CH_2{\cdot}CO_2H}$) which only contain β-protons, gave narrow e.s.r. features.

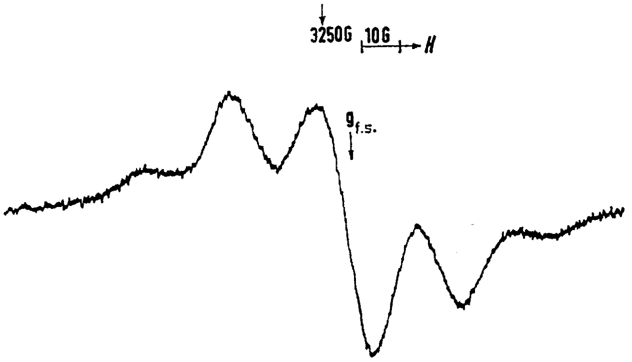

FIGURE 1 *X*-Band e.s.r. spectrum of acrylamide powder after hydrogen bombardment at 77 K

The e.s.r. spectrum for acrylamide γ-irradiated at 77 K was very similar to that for acrylic acid, there being no apparent damage to the $\mathrm{-CONH_2}$ group. Exposure to hydrogen atoms at 77 K also resulted in such spectra, both for the acid and the amide (Figure 1).

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[1] Y. Shioji, S. Ohnishi, and I. Nitta, *J. Polymer Sci.* (*A*), 1963, **1**, 3373.

[2] C. H. Bamford, G. C. Eastmond, and Y. Sakai, *Nature*, 1963, **200**, 1284.

[3] B. Arnold and G. C. Eastmond, *Trans. Faraday Soc.*, 1971, **67**, 772.

[4] C. H. Bamford, A. Bibby, and G. C. Eastmond, *J. Polymer Sci.* (*C*), 1967, **16**, 2417; *Polymer*, 1968, **9**, 629, 645.

[5] D. Campbell, M. C. R. Symons, and G. S. P. Verma, *J. Chem. Soc.* (*A*), 1969, 794.

Results for methacrylic acid and its amide were again very similar, the spectra at 77 K being characteristic of the monomer radicals $\mathrm{Me_2\dot{C}{\cdot}CO_2H}$ and $\mathrm{Me_2\dot{C}{\cdot}CONH_2}$ and at room temperature of the 'polymer' radicals $\mathrm{RCH_2{\cdot}\dot{C}Me{\cdot}CO_2H}$ and $\mathrm{RCH_2{\cdot}\dot{C}Me{\cdot}CONH_2}$ (Figure 2*a* and 2*b*).

We were unable to interpret the very poorly resolved spectra from crotonic acid γ-irradiated at 77 K, but fortunately a very well resolved spectrum was detected after annealing to room temperature which we assign to the allylic radical $\mathrm{H_2\dot{C}\overline{{-}CH{-}}\dot{C}H{\cdot}CO_2H}$ (Figure 3). The outermost shoulders which appear clearly on the $\pm\frac{3}{2}$ lines are probably caused by the anisotropy of the α-proton hyperfine tensors. They are unusually clearly defined and may imply partial averaging at room temperature. The $\pm\frac{1}{2}$ lines are less well resolved which suggests that the α-protons are not all equivalent. In fact, by comparison with the liquid-phase results for the parent allyl radical $\mathrm{\dot{C}H_2\overline{{-}CH{-}}\dot{C}H_2}$,[6] given in the Table, it is probable that these protons all differ slightly from one another. The central proton coupling is assigned a positive sign since the π-electron spin-density on the central carbon atom is expected to be negative.

A reversible change was found for the narrow features in the spectra of γ-irradiated $\beta\beta'$-dimethylacrylic acid on warming to room temperature which is interpreted in terms of the radical $\mathrm{Me_2\dot{C}{\cdot}CH_2{\cdot}CO_2H}$. The 77 K spectrum (Figure 4) appears as two sets of seven lines separated by 70 G. Since a coupling of 70 G is too large for a proton in a radical having any reasonable structure, we suggest that two nearly equivalent protons are responsible, with either a dynamic or static broadening of the central lines. Just this situation can be invoked to explain the spectrum of the polymeric radicals formed from acrylic and methacrylic acids, and the problem has been discussed in some depth elsewhere.[7,8] An average coupling of 35 G is correct

^{1}H Hyperfine tensor components/G

Material	Irradiation	T/K	Radicals	α-Protons a_{iso}	β-Protons β_1	β_2	β_3	g-Values $\pm0{\cdot}0005$
$\mathrm{H_2C{=}C(H){\cdot}CO_2H}$	γ [a]	77	$\mathrm{Me\dot{C}H{\cdot}CO_2H}$ and $\mathrm{Me\dot{C}H{\cdot}CONH_2}$	−21·5 [b]	23			2·0023
and	H [c]	77	$\mathrm{Me\dot{C}H{\cdot}CO_2H}$ and $\mathrm{Me\dot{C}H{\cdot}CONH_2}$	−23	23			
$\mathrm{H_2C{=}C(H){\cdot}CONH_2}$	H [c]	300	$\mathrm{Me\dot{C}H{\cdot}CO_2H}$ and $\mathrm{Me\dot{C}H{\cdot}CONH_2}$	−23	23			
			$\mathrm{R{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2H}$ and $\mathrm{R{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CONH_2}$	−24	24			
$\mathrm{H_2C{=}CMe{\cdot}CO_2H}$	γ [d]	77	$\mathrm{Me_2\dot{C}{\cdot}CO_2H}$ and $\mathrm{Me_2\dot{C}{\cdot}CONH_2}$		23			2·0023
and	H [c]	77	$\mathrm{Me_2\dot{C}{\cdot}CO_2H}$ and $\mathrm{Me_2\dot{C}{\cdot}CONH_2}$		23			
$\mathrm{H_2C{=}CMe{\cdot}CONH_2}$	H [c]	300	$\mathrm{Me_2\dot{C}{\cdot}CO_2H}$ and		23			
			$\mathrm{R{\cdot}CH_2{\cdot}\dot{C}Me{\cdot}CO_2H}$		8 [d]	15 [d]	23 [e]	
$\mathrm{Me_2C{=}C(H){\cdot}CO_2H}$	γ [c]	77	$\mathrm{Me_2\dot{C}{\cdot}CH_2{\cdot}CO_2H}$ and		35	23 [d]		
	H [c]	300	$\mathrm{H_2\dot{C}\overline{{\cdot}CMe{\cdot}}\dot{C}H{\cdot}CO_2H}$					
$\mathrm{Me(H)C{=}C(H){\cdot}CO_2H}$	γ [c]	77	$\mathrm{H_2\dot{C}\overline{{-}C(H)}\dot{C}(H){\cdot}CO_2H}$	12·5	3·5 [f]			
	H [c]	77	$\mathrm{MeCH_2\dot{C}(H){\cdot}CO_2H}$	22	35			

[a] Ref. 1. [b] A_x −24·2, A_y −31·8, A_z −8·5. [c] This work. [d] Ref. 2. [e] Methyl proton couplings. Central allylic proton.

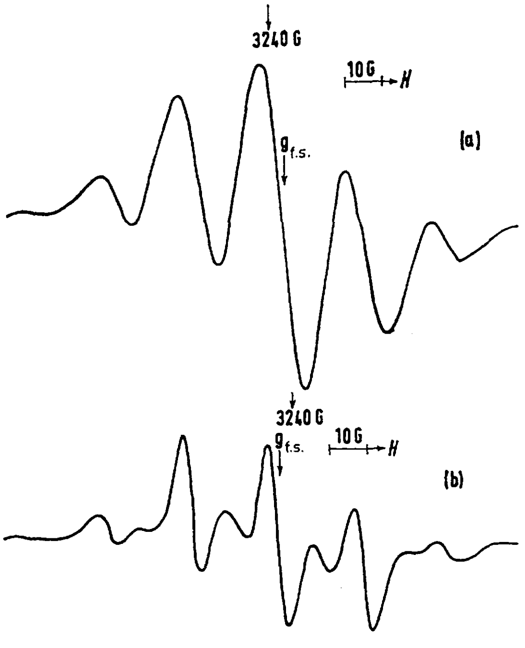

FIGURE 2 X-Band e.s.r. spectra of methacrylamide powder after γ-irradiation at 77 K (a) and 300 K (b)

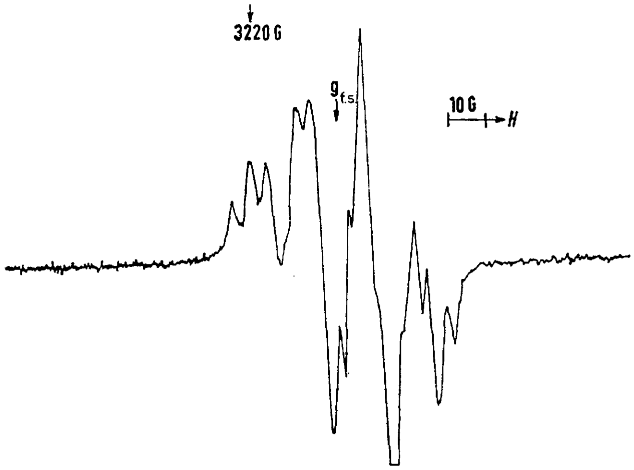

FIGURE 3 X-Band e.s.r. spectrum of room temperature annealed crotonic acid powder after γ-irradiation at 77 K

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[6] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[7] M. C. R. Symons, *J. Chem. Soc.*, 1963, 1186.

[8] M. C. R. Symons, 'Advances in Physical Organic Chemistry,' ed. V. Gold, vol. I, Academic Press, New York, 1963.

for configuration (I) which is the position which gives rise to maximum C–H hyperconjugation.[8] At room temperature, rotation about the C–C bond is rapid on the e.s.r. time-scale, and the coupling to H(1) and H(2) became close to that expected for the protons of the freely rotating methyl groups.

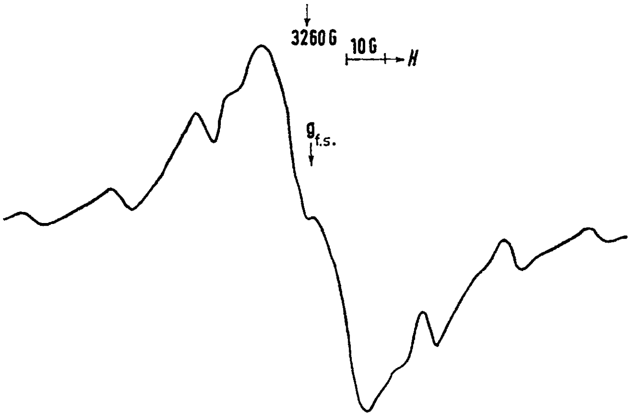
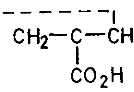
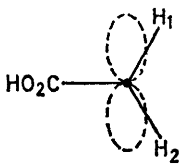


FIGURE 4 *X*-Band e.s.r. spectrum of ββ′-dimethylacrylic acid after γ-irradiation at 77 K



(I)



(II)

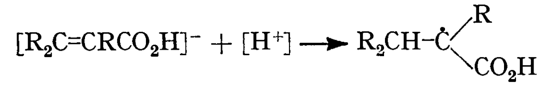
Hydrogen-atom Reactions.—In all cases, both at 77 K and room temperature, addition predominated over hydrogen atom abstraction. For all except ββ′-dimethylacrylic acid, addition occurred at the β-carbon atom to give α-radicals, $R_2\dot{C}{\cdot}CO_2H$. However, for the ββ′-dimethyl compound, addition occurred mainly at the α-carbon atom to give $Me_2\dot{C}{\cdot}CH_2{\cdot}CO_2H$ radicals. Thus it seems that the stability of the radical strongly affects the site of addition, and that the hyperconjugative stabilisation of two methyl groups outweighs the conjugative stabilisation of the CO_2H or $CONH_2$ groups. This is somewhat surprising but does correlate with the fact that carboxylic acid groups do not cause much loss of spin-density from the α-carbon atom in $R_2\dot{C}{\cdot}CO_2H$ groups. Thus, for example, *a*H(Me) for $Me_2\dot{C}{\cdot}CO_2H$ groups is *ca.* 23 G, whilst that in $Me_2\dot{C}H$ radicals is 24·7 G. This gives a delocalisation of only *ca.* 6·9% into the π-orbitals of the carboxy group.

γ-Irradiation.—At first sight we might conclude that the reactions undergone are very similar to those for hydrogen-atom bombardment. Thus, for example, acrylic acid at 77 K gave mainly $Me\dot{C}H{\cdot}CO_2H$ radicals by use of either technique. The normal explanation for this would be to invoke γ-ray-induced homolytic C–H bond fission, followed by H atom addition to the double bonds. However, all our previous experience suggests that electron ejection (1) and capture (2) ought to be observed with these acids. Protonation (3) of

$$R_2C{=}CR{\cdot}CO_2H \longrightarrow [R_2C{=}CR{\cdot}CO_2H]^+ + e^- \quad (1)$$

$$e^- + R_2C{=}CR{\cdot}CO_2H \longrightarrow [R_2C{=}CR{\cdot}CO_2H]^- \quad (2)$$

the radical anion could then lead to the radical detected



$$[R_2C{=}CRCO_2H]^- + [H^+] \longrightarrow R_2CH{-}\dot{C}\begin{smallmatrix}\diagup R\\ \diagdown CO_2H\end{smallmatrix} \quad (3)$$

by e.s.r. spectroscopy, but since only one type of radical was clearly detected for acrylic acid at 77 K, the fate of the radical cation is obscure. A reasonable reaction would be (4), but the radical $H_2C{=}CH$, which would be

$$[R_2C{=}CR{\cdot}CO_2H]^+ \longrightarrow R_2C{=}\dot{C}R + CO_2 + [H^+] \quad (4)$$

formed from acrylic acid and whose e.s.r. spectrum is well known, was not detected. Such a pathway is not available for the amides, however. It is possible that radicals of this type, formed from the primary radical cations, add to neighbouring monomers to give $R_2C{=}CR{-}CR_2{-}\dot{C}R{\cdot}CO_2H$ radicals. These would have e.s.r. spectra similar to those for the polymer radicals, and may indeed contribute to the signals assigned to ‘ polymer ’ radicals at room temperature (Table).

Formation of an allylic radical is not possible for acrylic acid, but for the remaining acids and amides these could well be formed by proton loss from the radical cations. Thus for crotonic acid, we suggest that reaction (5) could well occur. The advantages

$$[MeCH{=}CHCO_2H]^+ \longrightarrow H_2\dot{C}{\overset{..}{-}}CH{\overset{..}{-}}\dot{C}HCO_2H + [H^+] \quad (5)$$

of this ionic mechanism are not only that an ionic rather than a homolytic mechanism is expected, but also it explains why allylic radicals were only detected after γ-radiolysis and not after hydrogen-atom bombardment.

It is interesting that when allylic radicals were formed, ‘ polymer ’ radicals were not detected, and *vice versa.* This possibly lends some support to the idea that these ‘ polymer ’ radicals are, at least in part, radical (II). However, in favour of the ‘ polymer ’ concept is the fact that the acids $CH_2{=}CH{\cdot}CO_2H$ and $CH_2{=}C(Me)CO_2H$ polymerise far more readily than do the remainder.

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