Radicals formed from Acetylenes by High Energy Radiation and Hydrogen Atom Bombardment: an Electron Spin Resonance Study

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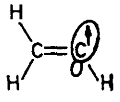
A variety of acetylenic compounds, including acetylenedicarboxylic acid, its salts, and its dimethyl ester, propiolic acid and its salt, mono- and di-phenylacetylene, phenylpropiolic acid, propargyl chloride and bromide, and 1,4-dichlorobut-2-yne have been exposed to ^{60}Co γ-rays at 77 K, and the radical products at 77 K and during annealing have been studied by e.s.r. spectroscopy. Several of these compounds were also exposed to beams of hydrogen or deuterium atoms and again examined by e.s.r. spectroscopy at 77 K. Radicals thus identified include hydrogen atom addition products, $R^1\dot{C}H{=}CR^2$, several of which are thought to be linear at the radical centre, rather than being bent as in the parent vinyl radical. Curiously, dipotassium acetylenedicarboxylate gave, on exposure to γ-rays at 77 K, $H_2C{=}\dot{C}CO_2^-$ radicals. On annealing, new radicals were detected which in several instances were probably dimers formed by addition of the parent radicals to neighbouring acetylene monomers. Other radicals identified include $HC{\equiv}C\dot{C}H_2$, $H_2C{=}\dot{C}Ph$, $HC{\equiv}C\dot{C}HCl$, and $HC{\equiv}C\dot{C}HBr$.

THE vinyl radical, $H_2C{=}\dot{C}H$, prepared by hydrogen atom addition to acetylene, was first detected by e.s.r. by Cochran *et al.*,[1] who obtained an eight line spectrum from which they deduced that $a(H_1) = 15{\cdot}7$, $a(H_2) = 34{\cdot}2$, and $a(H_3) = 68{\cdot}5$ G. In the liquid phase, this radical, which has the structure (I), was undergoing *cis–trans* isomerisation at a rate which broadened certain components leaving a doublet of doublets with apparent proton coupling constants of 102·4 and 13·4 G.[2]



(I)

More recently, several substituted vinyl radicals have been prepared, all of which are thought to have structures based upon that of the parent vinyl radical (I). Thus, for example, Iwasaki and his co-workers,[3,4] in an extensive study of radiation damage in unsaturated carboxylic acids have detected a radical in irradiated maleic acid having $a(H_1) = 58$ and $a(H_2) = 13{\cdot}5$ G, to which they assign the formula $H\dot{C}{=}CH(CO_2H)$ (*trans*). Since the present study was complete, their study of γ-irradiated acetylenedicarboxylic acid dihydrate appeared,[4] the major species detected being described as $CH(CO_2H){=}\dot{C}CO_2H$ (*trans*) with $a(H) = 51$—54 G.

The α-styryl radical $Ph\dot{C}{=}CH_2$ was formed by Bennett and Howard,[5] who proposed that this radical is π rather than σ, with extensive delocalisation into the benzene ring. The two β-protons were equivalent, with $a = 41{\cdot}5$ G.

Neta and Fessenden,[6] using their continuous electron irradiation technique with aqueous solutions, have detected the radical $^-O_2CCH{=}\dot{C}CO_2^-$ [$a(H) = 49{\cdot}79$ G] formed from acetylenedicarboxylic acid which they also consider to have the *trans*-configuration. Attack by hydroxyl radicals was thought to give $^-O_2CCOH{=}\dot{C}CO_2^-$ initially although the radical detected by e.s.r. spectroscopy was the rearranged species $^-O_2CCO\dot{C}HCO_2^-$.[6]

Radicals of general type $R^1C{\equiv}C\dot{C}R^2_2$ have been studied by several workers. Thus, for example, Kochi and Krusic[7] obtained $HC{\equiv}C\dot{C}H_2$ [$a(H_1) = 12{\cdot}68$, $a(H_2) = 18{\cdot}92$ G] and various alkyl substituted radicals.[7] The radical $PhC{\equiv}C\dot{C}H_2$ exhibited a coupling of 2·55 G to the *ortho*- and *para*-hydrogen atoms, thus establishing a considerable delocalisation into the benzene ring.

Our aim has been to use low temperatures to help probe the primary damage processes, to use hydrogen atom irradiation to discover the mode of addition to acetylenes, and to investigate the effect of varying substituents and environment upon these processes.

EXPERIMENTAL

Acetylenedicarboxylic acid, its mono- and di-potassium salts, potassium propiolate and phenylpropiolic acid (all supplied by Koch–Light) were recrystallised from water, and diphenylacetylene (Koch–Light) from ethanol. Polycrystalline samples were γ-irradiated at 77 and 300 K, in a Vickrad ^{60}Co source for up to 2 h at a nominal dose rate of 4 Mrad h^{-1}. Propiolic acid, dimethyl acetylenedicarboxylate, and phenylacetylene (all from Koch–Light), propargyl bromide, propargyl chloride, and 1,4-dichlorobut-2-yne (all from Ralph Emanuel) were γ-irradiated at 77 K in the form of small beads. E.s.r. spectra were recorded at 77 K directly, and after partial annealing. Powdered samples of all materials were subjected to H· and D· atom bombardment at 77 K and their e.s.r. spectra recorded at that temperature.

RESULTS AND DISCUSSION

Propiolic Acid.—The spectrum obtained for the pure acid following γ-irradiation at 77 K was initially dominated by outer lines separated by 104 G (Figure 1*a*). Quite the most probable species is $H_2C{=}\dot{C}CO_2H$, 104 G being the sum of the coupling constants to the two β-protons. Because of the complexity of the central

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[1] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1963, **40**, 213.

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

[3] M. Iwasaki, B. Eda, and K. Toriyana, *J. Amer. Chem. Soc.*, 1970, **92**, 3211; M. Iwasaki and B. Eda, *J. Chem. Phys.*, 1970, **52**, 3837; K. Toriyana and M. Iwasaki, *ibid.*, 1971, **55**, 2181; M. Iwasaki, K. Minakata, and K. Toriyana, *J. Amer. Chem. Soc.*, 1971, **93**, 3533.

[4] H. Muto, K. Toriyana, and M. Iwasaki, *J. Chem. Phys.*, 1972, **57**, 3016.

[5] J. E. Bennett and J. A. Howard, *Chem. Phys., Letters*, 1971, **9**, 460.

[6] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1972, **76**, 1957.

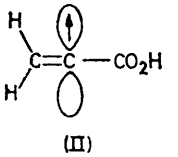
[7] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1970, **92**, 4110.

region of the spectrum, it is not possible to identify the other lines for this species. Recrystallisation of the acid from D_2O followed by irradiation resulted in loss of this doublet and the appearance of a doublet of triplets, the doublet separation being *ca.* 52 G and the triplet separation *ca.* 8 G (Figure 1*b*). This is surely the species $HDC=\dot{C}CO_2D$, since a coupling of 8 G for a deuteron corresponds to a coupling of *ca.* 53 G for a proton. This means that the added atom comes from the carboxy-group, since this is the only proton that exchanges with D_2O. It also means that the two β-protons have equal coupling constants, and hence that the radical is effectively 'linear' at the radical centre (II) the unpaired electron being in an orbital that has nearly pure 2*p* character on carbon rather than being an *sp* hybrid as is the case for $H_2C=\dot{C}H$ radicals. One reasonable explanation for this change in geometry is that better π-overlap with the π-orbitals of the carboxy-group can thereby be accomplished. Just the same situation was observed by Bennett *et al.*,[5] and by ourselves, for the $Ph\dot{C}=CH_2$ radical (see below). However, since the sum of the β-proton coupling constants for $H_2C=\dot{C}H$ radicals is *ca.* 103 G, which is very close to the sum for the $H_2C=\dot{C}CO_2H$ radical, it seems likely that delocalisation in this case is very small.

Selected e.s.r. data for various radicals formed from acetylenes (for other results, see text)

Radical	Source/host	Isotropic proton coupling (G) [a]
$H_2C=\dot{C}H$	$HC\equiv CH$ [b]	$\alpha = 15{\cdot}7$, $\beta_1 = 34{\cdot}2$, $\beta_2 = 68{\cdot}5$
$H_2C=\dot{C}CO_2H$	$HC\equiv CCO_2H$	$\beta_1 = \beta_2 = 52$
$HO_2CCH=\dot{C}H$ (*trans*)	$HO_2CCH=CHCO_2H$ [c] (*cis*)	$\alpha = 13{\cdot}5$, $\beta = 58$
$O_2^-CCH=\dot{C}H$ (*cis*)	$HC\equiv CCO_2K$	$\alpha = 14$, $\beta = 44$
$HO_2C\underset{H}{C}=\dot{C}CO_2H$	$HO_2CC\equiv CCO_2H$	$\beta = 52$
$MeO_2C\underset{H}{C}=\dot{C}CO_2Me$	$MeO_2CC\equiv CCO_2Me$	$\beta = 53$
$H_2C=\dot{C}Ph$	$HC\equiv CPh$	$\beta_1 = \beta_2 = 42$ [aH(ring) ≈ 6]
$PhCH=\dot{C}Ph$	$PhC\equiv CPh$	$\beta \doteqdot 45$
$HC\equiv C-\dot{C}H_2$	$HC\equiv CCH_2Cl$	$\alpha_1 = \alpha_2 = 19$, $\alpha_3 = 13$

[a] 1 G = 10^{-4} T. [b] Ref. 1. [c] Ref. 3.



(II)

The same species was obtained from concentrated aqueous solutions of propiolic acid, but in addition, a broad doublet with a 38 G separation was observed. On annealing irradiated aqueous solutions above 77 K, the outer lines were initially lost, followed by the 38 G doublet, which was replaced by a poorly defined pair of lines separated by *ca.* 18 G and shifted to low-field of the other sets of lines (*g ca.* 2·005). This species is probably the radical $HCO\dot{C}HCO_2^-$ in which case the 38 G precursor could well be the radical $HCOH=\dot{C}CO_2H$. This is presumably formed by ·OH radical addition, the sequence of events being the same as that proposed by Neta and Fessenden for the dicarboxylate.[6]

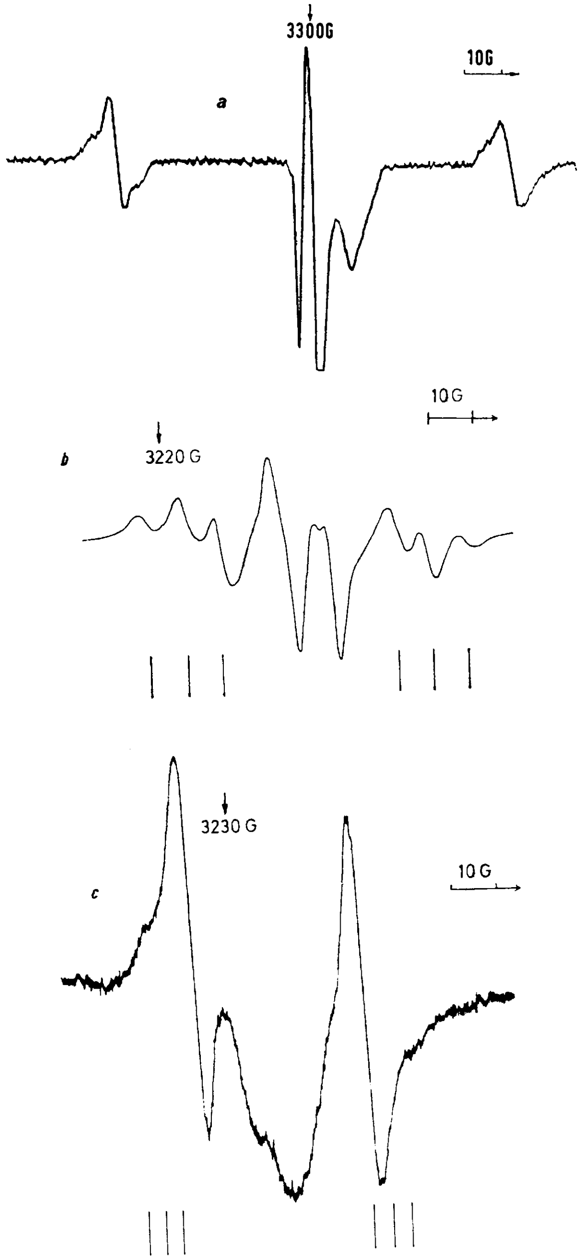


FIGURE 1 First derivative X-band e.s.r. spectra for propiolic acid: *a* after exposure at 77 K to ^{60}Co γ-rays and after partial annealing, showing the outer 104 G doublet assigned to $H_2C=\dot{C}CO_2H$; *b* after recrystallisation from D_2O and exposure to ^{60}Co γ-rays, showing the doublet of triplets assigned to $HDC=\dot{C}CO_2H$; and *c* after exposure to deuterium atoms at 77 K, showing the 38 G doublet mentioned in the text

When the irradiated pure acid was annealed above 77 K the outer (104 G) lines were again lost, but gave way to a clear 52 G doublet. Similarly, for the deuteriated acid ($HC{\equiv}CCO_2D$) the doublet of triplets gave way again to a 52 G doublet. This 52 G doublet is assigned to a radical of type $RCH{=}\dot{C}CO_2H$, when R· is probably $H_2C{=}\dot{C}CO_2H$. This accords with the fact that the radical formed from $HDC{=}\dot{C}CO_2H$ has an identical e.s.r. spectrum and with the fact that this species is not formed in aqueous glasses. Any further solid-state polymerisation would presumably give the same spectrum and hence we cannot judge the extent of the addition process from these results.

Results for the potassium salt of this acid are remarkably different. Thus irradiation at 77 K gave initially what appeared to be a 58 G doublet, there being no indication of the expected 104 G doublet. Presumably the radical $H_2C{=}\dot{C}CO_2^-$ was not present. We originally supposed that addition of this radical to give $RCH{=}\dot{C}CO_2^-$ radicals was occurring, but 58 G is then unexpectedly large for the β-proton coupling. Careful study of the spectra obtained during the annealing process showed that another pair of lines decayed at exactly the same rate as the 58 G doublet (Figure 2*a*). We therefore suggest that the spectrum is really a (1 : 1 : 1 : 1) quartet with $a(H_1) = 44$ and $a(H_2) = 14$ G. This would correspond reasonably to expectation for the $HCCO_2^-{=}\dot{C}H$ radical, H_2 being the α-proton and H_1 the β-proton in the *cis*-configuration (III). (By convention, *cis* and *trans* relate to the unpaired electron's orbital: we suggest that coupling constants between *ca.* 34 and 52 G indicate a *cis*-configuration, whilst those between *ca.* 52 and 69 G indicate a *trans*-configuration.)

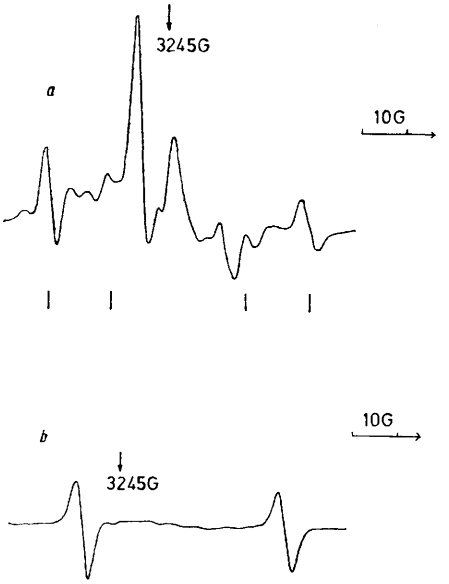
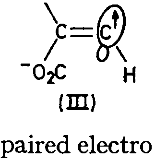


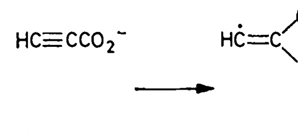
FIGURE 2 First derivative X-band e.s.r. spectra for potassium propiolate after exposure at 77 K to ^{60}Co γ-rays: *a* showing features assigned to the radical $HO_2CCH{=}\dot{C}H$ radicals; and *b* after annealing to room temperature, showing a 46 G doublet assigned to $RCH{=}\dot{C}CO_2H$ radicals



(III)

The potassium salt also differs from the acid in the changes observed on annealing above 77 K. Thus instead of obtaining a 52 G doublet on loss of the primary radical, a 43 G doublet initially developed, to be followed, on annealing further, by a 46 G doublet (Figure 2*b*).

We believe that the curious change from hydrogen addition to give $H_2C{=}\dot{C}CO_2H$ for the acid and $HCCO_2^-{=}\dot{C}H$ for the potassium salt arises for intermolecular steric reasons. This mode of addition is not characteristic of the anion, since in aqueous solution the $H_2C{=}CCO_2^-$ radical is formed preferentially. We suggest that addition proceeds *via* electron capture to give the radical anion, which, in the case of the potassium salt, must be protonated by a neighbouring $HC{\equiv}CCO_2^-$ ion [reaction (1)]. If the crystal structure is such that the acidic proton is able to add only as indicated in (1), then the change in the type of addition can be understood. It is interesting that the *cis*-conformation of this species is retained on annealing and re-cooling to 77 K, there being no tendency to change to the *trans*-species detected in irradiated maleic acid.[3] However, the four lines do reversibly broaden on heating, which strongly suggests an 'inversion' of the type observed by Fessenden and Schuler for $H_2C{=}\dot{C}H$ radicals.[2]



(1)

It is still difficult to understand the exact nature of the 43 and 46 G doublet species. The latter is quite stable at room temperature, being the major product on irradiating at that temperature. We suspect that the first species is dimeric and the second polymeric, both being of the type $RCH{=}\dot{C}CO_2^-$. We can only suppose that the magnitude of the proton coupling, which is a marked function of the geometry of the radical, is controlled by the crystal constants resulting from these solid-state processes.

Bombardment of the acid with hydrogen atoms at 77 K would thus be expected to give the radical $H_2C{=}\dot{C}CO_2H$. Indeed, a low intensity 104 G doublet was detected and, using deuterium atoms, this gave way to a broad 53 G doublet. However, in both experiments a strong 38 G doublet was also obtained (Figure 1*c*). At present, our only explanation for this doublet is that hydroxyl radicals were formed in the discharge (despite our normal drying precautions) and that the radical $HCOH{=}\dot{C}CO_2H$ was formed. Certainly on annealing, there were indications for the same broad 16 G doublet in the centre as was found for the irradiated aqueous solutions. However, this was superimposed upon a broad central line and was too poorly resolved to be very reliable.

Acetylenedicarboxylic Acid.—The most clearly defined features on irradiating at 77 K comprised a 52 G doublet which is surely due to the radical $HCCO_2H{=}\dot{C}CO_2H$

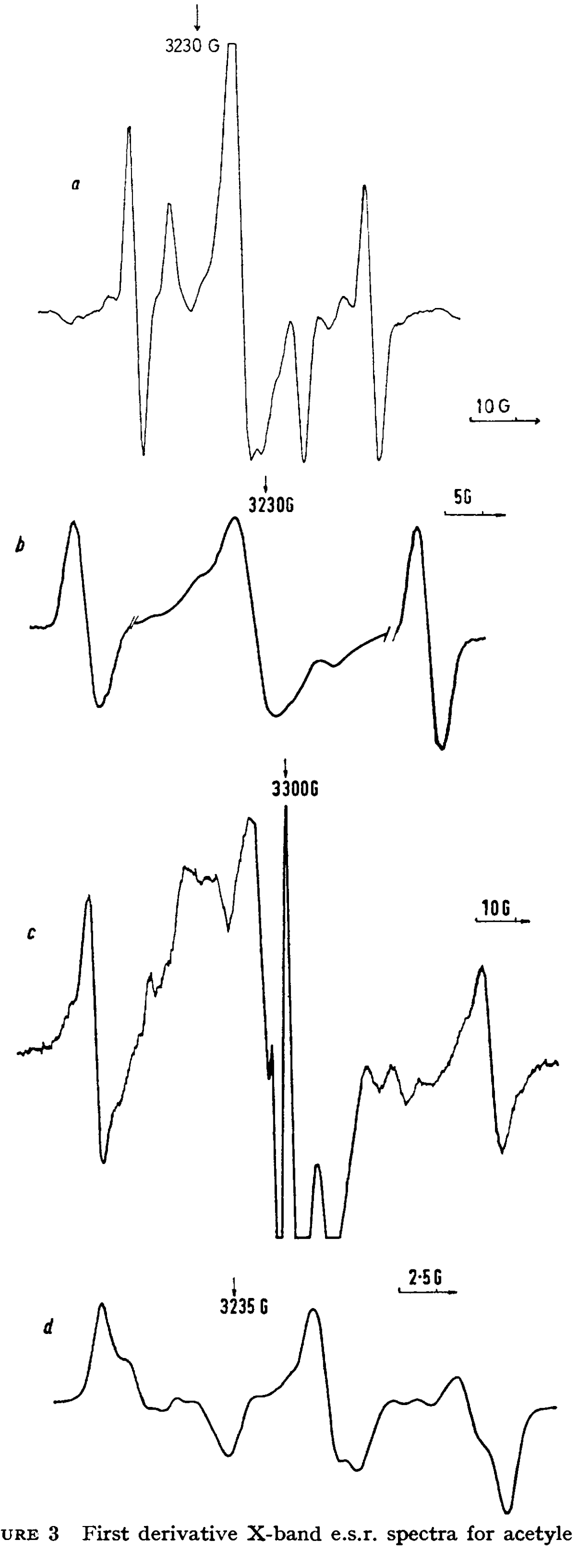
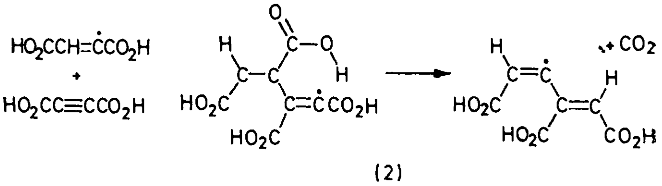


FIGURE 3 First derivative X-band e.s.r. spectra for acetylenedicarboxylic acid after exposure to: *a* ^{60}Co γ-rays at 77 K, showing the 52 G doublet assigned to $HO_2CCH{=}\dot{C}CO_2H$ radicals; *b* ^{60}Co γ-rays at room temperature, showing the 46 G doublet assigned to a dimeric radical; *c* ^{60}Co γ-rays at 77 K for the dipotassium salt, showing the 104 G doublet tentatively assigned to $H_2C{=}\dot{C}CO_2^-$ radicals; and *d* γ-rays at room temperature for the dipotassium salt, showing features assigned to $^-O_2CCO\dot{C}HCO_2^-$ radicals

(Figure 3*a*). The same doublet was observed by Iwasaki *et al.*[4] and by Neta and Fessenden[6] and similarly assigned. However, we contend that the radical is not *trans* as previously supposed, but linear [as in (II)], since 52 G is almost exactly the mean of the *cis*- and *trans*-values for $H_2C{=}\dot{C}H$ radicals and is almost equal to the value for linear $H_2C{=}\dot{C}CO_2H$ radicals.

Our single crystal results for the dihydrate show that this doublet is very nearly isotropic, as found by Iwasaki *et al.*[4] These authors have considered in some detail the nature of the other species responsible for several central lines in these spectra.[4] We feel less confident about identifying these central, poorly defined features, but their arguments certainly seem to be quite acceptable.[4] We also found that the intensity of the 52 G doublet increased initially on annealing, which does suggest that the radical anion is being protonated as suggested by Iwasaki *et al.*[4]

On annealing to room temperature, and on irradiating at room temperature, a 46 G doublet was obtained, together with a poorly defined doublet of *ca.* 16 G separation (Figure 3*b*). The splitting remained 46 G when measured at 77 K, so this is not simply a temperature effect. We cannot see why a polymeric radical $RCCO_2H{=}\dot{C}CO_2H$ should exhibit a large proton coupling, and it is tempting to suggest that this long-lived species is simply the original radical $HCCO_2H{=}\dot{C}CO_2H$ which has moved to a new environment in the crystal and been constrained (or relaxed) into a slightly modified geometry. However, since this radical exhibited a 52 G proton coupling even in aqueous solution at room temperature, we find this suggestion improbable. It is far more likely that a new radical, $R^1CH{=}\dot{C}R^2$ has been formed, and we tentatively suggest process (2) as a likely explanation. This solid-state intramolecular rearrangement is reasonable in terms of the crystal structure of the dihydrate.[8]



(2)

Exposure to hydrogen atoms gave a clear 52 G doublet together with a broad central line. Thus in this case, hydrogen atom addition follows the expected course. Deuterium atoms gave no 52 G doublet, the central line being too broad to reveal the expected 8 G triplet. (It is possible that OH radicals were again present in these experiments, since OH addition could be responsible for the broad singlet obtained in both experiments.)

Results for the mono- and di-potassium salts are in marked contrast, since in both cases, well resolved 104 G ' doublets ' were obtained (Figure 3*c*). When the salts were recrytallised from HOD [H_2O–D_2O (1 : 1)] a major doublet (53 G) of triplets (*ca.* 8 G) was obtained whilst after recrystallising from D_2O only a broad central

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[8] J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, 1947, 148.

feature resulted. These results suggest that the proton source is water of crystallisation. Presumably initial addition gives $HCCO_2{}^-{=}\dot{C}CO_2{}^-$ (not clearly detected), and this suffers loss of CO_2 and further protonation to give $H_2C{=}\dot{C}CO_2{}^-$ (or $HDC{=}\dot{C}CO_2{}^-$ or $D_2C{=}\dot{C}CO_2{}^-$).

We consider this to be one of the most interesting results of our study, but are at a loss to understand why the hydrated potassium salt is so efficiently decarboxylated but not the parent acid, or its aqueous solutions. Certainly radical cations, RCO_2H^+, or neutral radicals, RCO_2, readily lose carbon dioxide, but it seems most unlikely that the parent radical anions should do so. Thus process (3) is presumably responsible, but why should this proceed so rapidly at 77 K?

$$O_2^-CCH{=}\dot{C}O_2{}^- \longrightarrow :\dot{C}H{=}\dot{C}CO_2{}^- + CO_2 \quad (3)$$

Bombardment with hydrogen atoms failed to give an appreciable yield of radicals. This is often found with ionic compounds and probably reflects their relative impenetrability.

Other compounds have been studied in less depth than these acids.

Dimethyl acetylenedicarboxylate gave methyl radicals and $H_2\dot{C}OCOR$ radicals together with a 53 G doublet assigned to $MeOCOCH{=}\dot{C}CO_2Me$ radicals (Figure 4).

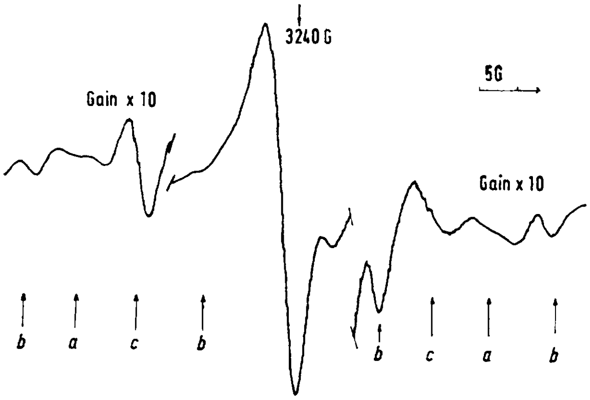

FIGURE 4 First derivative X-band spectrum for dimethyl acetylenedicarboxylate after exposure at 77 K to ^{60}Co γ-rays showing: *a* the 53 G doublet assigned to $MeO_2CCH{=}\dot{C}CO_2Me$ radicals; *b* a quartet assigned to methyl radicals; and *c* the outer two lines of a triplet assigned to $H_2\dot{C}OCOR$ radicals

Bombardment with hydrogen atoms also gave this 53 G doublet, whereas deuterium atoms gave only a broad central line.

Results for $PhC{\equiv}CCO_2H$ were disappointing in that γ-irradiation gave only a very broad central line, whilst hydrogen atoms at 77 K gave mainly cyclohexadienyl radicals from ring addition probably at the *para*-positions (2H ⟶ 48 G, 2H ⟶ *ca.* 10 G).

Phenylacetylene gave mainly the styryl radical, $Ph\dot{C}{=}CH_2$, previously reported by Bennett and Howard.[5] Our results confirm that the radical is 'linear' with $a(\beta\text{-H}) = 42$ G and $a(\text{ring-H}) \doteqdot 6$ G (Table). The fall from 52 to 42 G is presumably a measure of the extent of delocalisation into the ring (*ca.* 20%).

Diphenylacetylene gave a poorly defined 45 G doublet which we tentatively assign to $PhCH{=}\dot{C}Ph$. Two broad shoulders separated by *ca.* 100 G suggested some ring addition also.

Propargyl chloride and bromide both gave on exposure to γ-rays well resolved features assigned to $HC{\equiv}\dot{C}CH_2$ radicals, the data being similar to those previously reported[2,7] (see Table and Figure 5*a*). Features assignable to $HC{\equiv}C\dot{C}HCl$ and $HC{\equiv}C\dot{C}HBr$ radicals were also obtained (Figure 5*b*). The spectral analysis for these α-halogen radicals is difficult, but the characteristic set of features, especially for the bromide, can be used as a 'finger-print' for such radicals ($A_x \doteqdot 17$ G, $g_x = 2{\cdot}002$ for the chloride, and $A_x \doteqdot 100$ G, $g_x = 2{\cdot}002$ for the bromide). Results for several α-chloro- and -bromo-radicals have been briefly reported[9] and the spectral analyses will be considered in depth elsewhere.

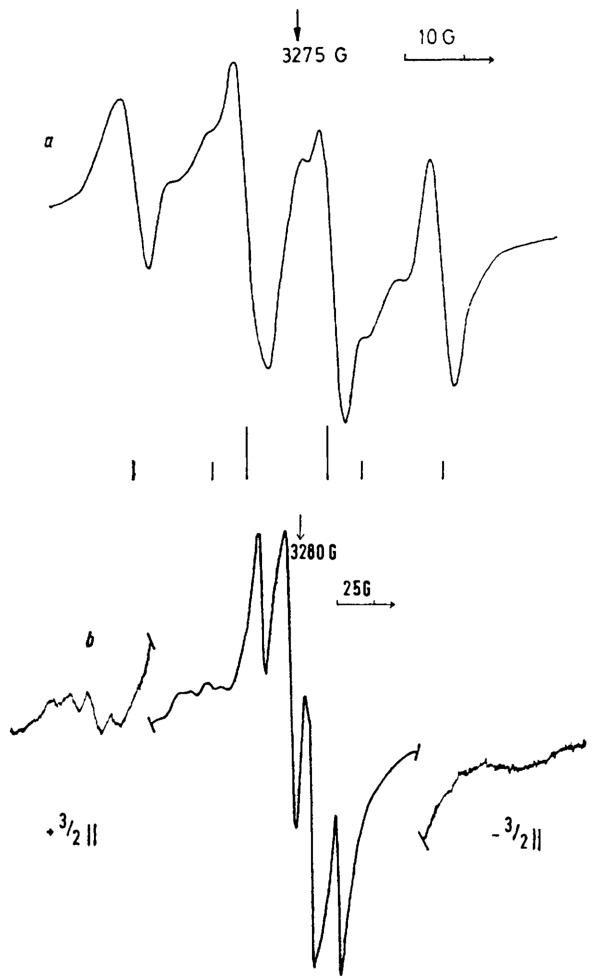

FIGURE 5 First derivative X-band spectra for propargyl bromide after exposure at 77 K to ^{60}Co γ-rays: *a* showing features assigned to $HC{\equiv}C\dot{C}H_2$ radicals; and *b* outer features assigned to $HC{\equiv}C{-}\dot{C}HBr$ radicals

Exposure to hydrogen atoms gave a doublet (68 G) of doublets (14 G) in accord with expectation for $HCCH_2X{=}\dot{C}H$ radicals with a *trans*-configuration. One important

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[9] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1973, **95**, 605.

aspect of these results is that apparently *trans*-addition is preferred in this case (or possibly the *trans*-configuration is the more stable and rapidly formed from the *cis*-radical). From their studies of aromatic annelation reactions, Cadogan and his co-workers[10] have concluded that radical addition to dimethyl acetylenedicarboxylate occurs equally *cis* and *trans*.

The major radical species formed from $ClCH_2C{\equiv}CCH_2Cl$ was undoubtedly $ClCH_2C{\equiv}C\dot{C}H_2$, the results for which are included in the Table. The spectrum comprised a major 19 G triplet flanked by poorly defined shoulders 15 G on either side. No clear indication of chlorine hyperfine coupling was detected despite the fact that coupling to β-chlorine atoms can be relatively large.[11]

Aspects of Mechanism.—On exposure to ^{60}Co γ-rays an initial ionisation and electron capture process is

$$R^1C{\equiv}CR^2 \longrightarrow (R^1C{\equiv}CR^2)^{+} + e^- \qquad (4)$$

$$R^1C{\equiv}CR^2 + e^- \longrightarrow (R^1C{\equiv}CR^2)^- \qquad (5)$$

expected [reactions (4) and (5)] Neither of these primary ions gives rise to a well defined e.s.r. spectrum although the broad central lines always detected surely comprise features for both these radicals.[4] Loss of a proton by the cations can give $R^1C{\equiv}C\cdot$ radicals either directly or *via* loss of CO_2 from the carboxylic acids, and in cases where R^1=H, some evidence for $HC{\equiv}C\cdot$ radicals has been adduced above. The anion radicals are expected to gain protons from neighbouring molecules, the net result being hydrogen addition. There does not seem to be any clear preference for *cis*- or *trans*-addition and we suspect that the course of addition is considerably dictated by the local geomety of the crystal lattice.

Subsequently these radicals can add to neighbouring acetylene molecules to give dimers (or possibly, polymers). We have concluded that for radicals $R^1CH{=}\dot{C}CO_2H$ there is a near-linear configuration at the radical centre, and that the β-proton coupling should then be *ca.* 52 G. It is then difficult to understand the rather wide range of β-proton coupling constants obtained on annealing which, in some cases, range from *ca.* 40 to 52 G. Possibly the process of dimerisation or even polymerisation is partially sterically controlled, the resulting radicals not having their preferred geometry immediately after exposure.

Equally obscure, unless the trivial explanation of water impurity is correct (see above), is the formation of a 38 G doublet species from propiolic acid exposed to H· or D· atoms. Why do we not obtain $H_2C{=}\dot{C}CO_2H$ or $HDC{=}\dot{C}CO_2H$ under these conditions?

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