Electron Spin Resonance Spectra of Carboxylic Acid Radical Anions at 77°K

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Sodium atoms have been deposited on a series of monocarboxylic acids, R—COOH, at 77°K in the rotating cryostat and the deposits examined by electron spin resonance (e.s.r.) spectroscopy. The spectra show that the primary paramagnetic species in each case is the corresponding radical O^-

anion, $R-\dot{C}$. The spectra are similar to those observed for the primary radicals formed by OH

X-, β - or γ -irradiation of mono- or di-carboxylic acids at 77°K and thus confirm that these radicals are the radical anions, and not cations, of the corresponding acids. The carbon-13 hyperfine coupling

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constants have been determined for the radical anion, CD_3C , of f

, of fully deuterated acetic acid.

The results show that the free valence centre has a pyramidal configuration, in contrast to the planar structure found in many alkyl radicals.

The radical anions are able to abstract hydrogen from adjacent neutral molecules at 77°K to give secondary radicals. The extent of reaction depends on the strength of the CH bonds in the acid. Negligible reaction occurs with acetic acid which possesses only primary hydrogens, whereas the radical anion reacts completely with the tertiary hydrogen in isobutyric acid to give the radical $(CH_3)_2$ CCOOH.

The free radicals that are formed when mono- or di-carboxylic acids are exposed to high energy radiation (electrons or X- or γ -rays) have been studied extensively by electron spin resonance (e.s.r.) spectroscopy. Most of the work has been concerned with the free radicals that are stable at room temperature, and has yielded valuable information about the anisotropic hyperfine interactions with α - and β protons. Recently, interest has turned to the primary species which are formed by irradiation at 77°K but which are unstable at higher temperatures. In particular, an intense doublet has been observed in the e.s.r. spectra of several carboxylic acids irradiated at 77°K. The doublet, which is basically similar in all of the acids, has a hyperfine splitting of 25-30 oe, and is unstable at temperatures much above 110°K.

In the recent studies some earlier results obtained by Gordy, Ard and Shields,¹ and by Miyagawa and Gordy,² on X-irradiated acetic acid appear to have been partially overlooked. They observed a doublet (hyperfine splitting about 30 oe) at 77°K from polycrystalline samples of CH₃COOH and CH₃COOD immediately after irradiation. When the samples were warmed slightly the doublet changed

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to a quartet (splitting about 15 oe) typical of that observed from a freely rotating methyl group. Miyagawa and Gordy assigned these spectra to the species.



where R = H or D. They concluded that at 77°K the methyl group was held in a fixed orientation with one proton lying in a plane perpendicular to the C—CO₂ plane, but that at higher temperatures the methyl group was able to rotate freely. Alger, Anderson and Webb³ also observed a doublet (splitting about 29 oe) in X-irradiated formic and acetic acids and several esters of these acids, but did not assign the spectra to definite paramagnetic centres.

Similar spectra with a doublet splitting of about 25 oe to 30 oe have been observed from single crystals of deuterated succinic acid,⁴ glycine,⁵ substituted malonic acids,⁶ 1-alanine⁷ and polycrystalline glycollic acid ⁸ after irradiation at 77°K. In each case the spectrum has been attributed to the carboxylic negative radical ion, but the possibility that the spectrum arose from the corresponding positive radical ion could not be excluded. Additionally, in several of these investigations other paramagnetic species were formed during irradiation at 77°K and their spectra were superimposed on those assigned to the radical ions.

We have found that specific radical anions can be generated by depositing alkali metal atoms on a suitable matrix at 77°K in a rotating cryostat. For example, deposition of sodium or potassium atoms on solid carbon dioxide yields the CO₂⁻ radical anion.⁹ In a similar manner, the radical anions of hydrogen sulphide¹⁰ and carbon disulphide¹¹ have been formed. Also, deposition of alkali metal atoms on aliphatic ketones yields the corresponding aliphatic ketyl radical anions.¹² It therefore seemed likely that deposition of an alkali metal atom on a carboxylic acid at 77°K would result in transfer of the valence electron from the alkali metal atom to the carboxyl moiety to yield a carboxylic acid radical anion. A particular advantage of this technique is that the probability of forming secondary paramagnetic species is much less than in the radiation studies. The unambiguous formation of these radical anions would aid in unravelling the identity of the unstable paramagnetic centres detected in the X- and γ -irradiated carboxylic acids. In addition, there would be intrinsic chemical interest in the preparation of new radical anions.

The present paper describes the preparation of several monocarboxylic acid radical anions in the rotating cryostat. Carboxylic acid radical anions were prepared from formic acid, acetic acid, deuterated acetic acids (d_1 and d_4), propionic acid, butyric acid, trimethylacetic acid and benzoic acid. isoButyric acid failed to give a carboxylic acid radical anion but instead gave the 2-carboxyl-2-propyl radical ((CH₃)₂CCOOH). The corresponding carboxylate radical anions were also prepared from methyl formate, methyl acetate and deuterated methyl acetate.

EXPERIMENTAL

ROTATING CRYOSTAT

The rotating cryostat has been described elsewhere.¹³ The technique was to deposit alternate layers of the carboxylic acid and the alkali metal on the outer surface of a drum which was cooled to 77°K and rotated rapidly (*ca.* 2,400 rev/min) in a high vacuum (10^{-6} torr). The gaseous reactants were directed on to the drum from jets located close to the surface. The flow rates were adjusted so that several monolayers of the carboxylic acid

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were laid down in each revolution, while considerably less than a monolayer of the alkali metal was deposited. In this manner, carboxylic acid radical anions were formed at isolated reaction sites in a matrix of the parent carboxylic acid. In a typical experiment 1.1 ± 0.25 g of the carboxylic acid and about 0.5 mg of sodium were deposited in 30 min. Samples of the deposit were removed from the surface of the drum and transferred to a tube suitable for e.s.r. measurements. The complete transfer operation was carried out at 77°K under high vacuum.

E.S.R. SPECTROSCOPY

The e.s.r. spectra were recorded with a Varian V4502-05 spectrometer fitted with Fieldial control of the magnetic field. Standard accessories were used for maintaining the sample at the required temperature. A proton resonance magnetometer was used to calibrate the magnetic field and the *g*-factors of the carboxylic acid radical anions were calculated by comparison with that of α, α' -diphenyl- β -picrylhydrazyl (g = 2.0036).

MATERIALS

The carboxylic acids were obtained from commercial sources and their purities as determined by gas-liquid chromatography (GLC) were : formic acid, BDH A.R. (90 % formic acid in water), acetic acid, BDH A.R. (99.9 %); propionic acid, Eastman Organic Chemicals (99.9 %); butyric acid, BDH laboratory reagent (98.8 %); isobutyric acid, BDH laboratory reagent (94.5 %; major impurity was propionic acid); trimethylacetic acid, BDH laboratory reagent (99.7 %); and benzoic acid, BDH laboratory reagent (99.5 %). Acetic acid-d₄ was obtained from Merck, Sharpe and Dohme, and had a minimum isotopic purity of 99.5 % D. Acetic acid-d₁ (hydroxyl deuterated) was obtained from Koch-Light Laboratory reagent (97.5 %). Deuterated methyl acetate CD₃(CO)OCH₃ was prepared from acetic acid-d₄. Methyl formate was a BDH laboratory reagent.

RESULTS

The first derivative e.s.r. spectra of the deposits from the reaction of sodium or potassium atoms with the carboxylic acids or esters are shown in fig. 1-4. The pertinent results are summarized in table 1.

ACETIC ACID, ACETIC ACID- d_1 AND ACETIC ACID- d_4

The e.s.r. spectrum of the deposit from reaction of sodium with acetic acid at 77° K (fig. 1) consisted of two equally intense lines with a hyperfine splitting constant of $32\cdot1$ oe and a width of $12\cdot3$ oe. When the deposit was warmed the spectrum did not alter until 140° K when the doublet began to decay sharply. At 150° K the doublet had decayed completely leaving a weak multi-line spectrum which eventually disappeared at about 220° K. Four lines in this spectrum were particularly prominent. They were equally spaced ($13\cdot7$ oe) and their relative intensities were in the ratio 1:3:3:1. When the sample was cooled again to 100° K these four lines (particularly the central pair) broadened considerably. This effect of temperature was completely reversible.

The e.s.r. spectrum of the deposit from the reaction of sodium with acetic acid- d_1 (hydroxyl group deuterated) at 77°K was also a doublet, nearly identical with that observed with nondeuterated acetic acid. When the deposit from the deuterated acetic acid was warmed, the e.s.r. spectrum decreased rapidly in intensity at about 140°K as was observed with the deposit from the nondeuterated acetic acid and, again, four lines were prominent in the spectrum observed above 140°K. The relative intensities of the lines, their hyperfine splitting (13.3 oe) and their temperature-dependence were similar to those observed for the nondeuterated acid.

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The e.s.r. spectrum of the deposit from the reaction of sodium with acetic acid- d_4 (fig. 2) consisted of a partially resolved triplet. A graphical analysis ¹⁴ of this spectrum showed that it consisted of three equally spaced and equally intense hyperfine lines with a splitting of 5.3 oe and a line width of 4.4 oe. When the deposit



FIG. 1.—First derivative spectrum of sodium and acetic acid at 77°K.



FIG. 2.—First derivative spectrum of sodium and acetic acid- d_4 at 77°K. Wings of spectrum (gain \times 120) showing carbon-13 satellite lines.

was warmed to 130° K the intensity of the spectrum decreased by about 75 % (this decrease was not nearly as marked as for the other acids) and then remained relatively unchanged until about 200°K when a fairly rapid decay set in. Above 150°K at least five poorly resolved hyperfine lines were visible with a splitting of 2.4 oe.

Carbon-13 satellite lines were observed when the spectrum of acetic acid- d_4 at 77°K was recorded at higher sensitivity (fig. 2). The integrated intensities of the

two satellite lines were approximately equal and about 0.5 % that of the main line. The shape of the lines showed that the carbon-13 coupling was axially symmetric, the principal values being $A_x = A_y = 88.5 \pm 3$ oe and $A_z = 164 \pm 5$ oe. Carbon-13



FIG. 4.—First derivative spectrum of sodium and isobutyric acid at $77^{\circ}K(a)$ in isobutyric acid matrix and (b) in hexamethylethane matrix.

satellites were just visible in the spectrum of acetic $acid-d_1$, and the hyperfine splittings appeared to be close to those for the fully deuterated acid.

*γ***-IRRADIATED ACETIC ACID**

This experiment, which was an extension of the work of Miyagawa and Gordy,² was carried out to ascertain whether the effect of temperature on the spectrum from the irradiated acid was reversible and, if so, to establish the range of temperature over which the effect occurred.

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TABLE 1.—E.S.R. DATA FOR CARBOXYLATE RADICAL ANIONS

compound	radical anion	g-factor	no. of lines	relative intensities	hyperfine splitting constants (oe) ±1.0 oe	line widths (oe)±0.50e
acetic acid	O- CH ₃ C· OH	2.0032	2	1:1	32.1	12.3
acetic acid-d1	O- CH ₃ C: OD	2.0027	2	1:1	32.9	11.6
acetic acid-d4	O- CD ₃ C· OD	2.0029	3	1:1:1	5.3	4.4
trimethylacetic acid	CH ₃ O- CH ₃ CC·	2.0028	1			19•8
propionic acid	O- CH ₃ CH ₂ C. OH	2.0027	2	1:1	30-2	11.7
butyric acid	O− CH₃CH₂CH₂C∙ OH	2.0029	2	1:1	30.0	13.8
isobutyric acid	CH ₃ O- CH ₃ CHC. OH	_	2	1:1	27	1 -1-1-1
benzoic acid	О- С. ОН	_	4	1:3:3:1	5-8	6•7
methyl acetate	O- CH ₃ C· OCH ₃	2.0026	2	1:1	25-4	9.9
formic acid	О- Н—-С. ОН	2•0028	2	1:1	17•7	14.7
methyl formate	O- HC· OCH3	2.0031	2	1:1	24-0	7.6

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At 77°K the spectrum observed from the γ -irradiated acid was similar to that of the deposit obtained from the cryostat, but with signs of additional structure on the two main lines. The spectrum changed markedly when the temperature was raised to 110°K. Two broad central lines appeared and one of the components in each of the original lines narrowed appreciably. As the temperature was raised further the two central lines decreased in width and increased in amplitude until at 150°K the spectrum consisted mainly of a quartet of lines with relative intensities of 1:3:3:1 and a hyperfine splitting of 13.5 oe. Over the temperature range up to 140° K the spectral changes were completely reversible. Above 140° K the quartet decayed slowly and a second more complex spectrum became evident.

The hyperfine splitting constants were identical with those observed from the deposits prepared by the reaction of sodium atoms with acetic acid in the cryostat. The values differ slightly from those obtained by Miyagawa and Gordy which were 30 oe for the doublet splitting, and 15 oe for the quartet splitting.

TRIMETHYLACETIC ACID

The e.s.r. spectrum of the deposit from sodium and trimethylacetic acid consisted of a single broad line with a width of 19.8 oe. When the deposit was warmed the signal decayed rapidly at $160-170^{\circ}$ K and a weak multi-line spectrum appeared.

PROPIONIC ACID

The e.s.r. spectrum of the deposit from reaction of sodium with propionic acid at 77° K (fig. 3) was more complex than that observed with acetic acid and consisted of two dominant lines together with several less intense lines. When the deposit was warmed to 140°K, the two main lines disappeared leaving basically a five-line spectrum. Thus the spectrum at 77° K can be interpreted as consisting of a two-line spectrum with a hyperfine splitting constant of 30.2 oe (similar to that observed from acetic acid) superimposed upon a five-line spectrum with a hyperfine splitting of about 25 oe. The five-line spectrum decayed slowly over the temperature range 140-250°K.

BUTYRIC ACID

The e.s.r. spectrum of the deposit from reaction of sodium with butyric acid at 77°K consisted of a dominant doublet with a hyperfine splitting constant of 30.0 oe superimposed on several less intense lines. At 140°K both sets of lines decayed rapidly leaving a complex spectrum which finally decayed at about 220°K.

ISOBUTYRIC ACID

The e.s.r. spectrum of the deposit from the reaction of sodium and iosbutyric acid was markedly different from those obtained from the other acids. The spectrum (fig. 4(a)) consisted of seven equally spaced lines with relative intensities of approximately 1:6:15:20:15:6:1, a hyperfine splitting constant of 21.7 oe and a line width of 4.2 oe. When the deposit was warmed the spectrum decayed slowly without any change until at 160° K it dropped sharply in intensity.

The reaction of sodium with isobutyric acid was also investigated in an inert matrix, hexamethylethane (Considerably less than a monolayer of isobutyric acid was deposited during each revolution of the drum while about ten molecular layers of hexamethylethane were laid down, so that at least some of the acid molecules were isolated from each other). The e.s.r. spectrum of this deposit at 77°K consisted of the seven lines previously observed using neat isobutyric acid together with a

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doublet with a hyperfine splitting constant of 27 oe (fig. 4(b)). The doublet disappeared when the deposit was warmed to 110° K while the seven-line spectrum decayed slowly over the temperature range 170° to 210° K.

BENZOIC ACID

At 77°K the spectrum from the sample produced by depositing sodium atoms on benzoic acid was basically a single line (width 17 oe) with indications that some unresolved hyperfine structure was present. At 90°K four poorly resolved lines were just visible with a splitting of 5.8 ± 0.5 oe. The spectrum decayed slowly without any further increase in resolution as the temperature was raised to 160°K after which a rapid decay occurred.

METHYL ACETATE

The e.s.r. spectrum from the deposit resulting from reaction of potassium with methyl acetate consisted of a doublet with a hyperfine splitting constant of 25.4 oe and a line width of 9.9 oe. When the deposit was warmed to 113°K the intensity of the spectrum decreased markedly and a broader five-line spectrum was observed with a hyperfine splitting constant of 18 oe. A single line spectrum was obtained from the deposit formed from the reaction of sodium with tri-deutero-methyl acetate, $CD_3(CO)OCH_3$, and at high sensitivity the naturally abundant carbon-13 hyperfine lines were visible. The carbon-13 coupling constants were $A_x = A_y = 73$ oe and $A_z = 144$ oe.

FORMIC ACID

The e.s.r. spectrum of the deposit from the reaction of sodium with formic acid consisted of a partially resolved doublet. A graphical analysis ¹⁴ of this spectrum showed that it consisted of two equally intense hyperfine lines with a splitting of 17.7 oe and a line width of 14.7 oe. When the deposit was warmed the spectrum did not alter until 160°K when the doublet decayed rapidly.

METHYL FORMATE

The e.s.r. spectrum of the deposit from the reaction of sodium with methyl formate consisted of a well-resolved doublet with a hyperfine splitting constant of 24.0 oe and a line width of 7.6 oe. When the deposit was warmed the spectrum remained unchanged until 140° K when the doublet began to decay appreciably, disappearing completely at 190° K.

DISCUSSION

The e.s.r. spectrum of the primary species formed when sodium or potassium is deposited on a monocarboxylic acid at 77°K is either a singlet or a doublet. The doublet is observed for all of the acids which have at least one β -hydrogen,* and also for formic acid. A singlet is observed from trimethylacetic acid, which suggests that the hyperfine splitting is caused by interaction with a hydrogen bonded to the β -carbon atom rather than with the hydroxyl hydrogen. The results for the deuterated acetic acids, CH₃COOD and CD₃COOD, confirm this conclusion.

* The carbon atoms are labelled according to the standard method used in e.s.r. studies; that possessing the free valence electron is termed the α -carbon.

OH

E.S.R. OF RCOOH-

The individual results, which are discussed later, are consistent with the primary Ω^{-}

paramagnetic species being the carboxylic acid radical anion R-Ċ which is formed

by transfer of the valence electron from the alkali metal atom to the acid molecule. This behaviour is similar to that observed when alkali metal atoms are deposited on ketones ¹² or carbon dioxide ⁹ at 77°K to give the corresponding radical anions, R_1

$$\dot{C}$$
—O⁻ or CO₂⁻.

The result obtained with formic acid shows that loss of the hydroxyl group to give the radical, $R-\dot{C} = 0$, does not occur, as in this case the formyl radical HCO would be formed. The spectrum of the formyl radical is well characterized and is very different from that observed from formic acid.

The spectra observed from the carboxylic acid radical anions are similar to those observed from the primary species formed by γ - or X- irradiation of carboxylic acids at 77°K. Our method of preparation excludes the possibility that the spectra are due to radical cations and thus confirms the identification of the primary species in irradiated acids as the radical anions. The secondary spectra which appear when the samples are warmed presumably correspond to those observed in the irradiated acids which have been analyzed in detail.

ACETIC AND TRIMETHYLACETIC ACIDS

The spectra from the three acids, CH₃COOH, CH₃COOD and CD₃COOD

show that the radical anion, RC

, is the sole paramagnetic species formed

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O-

at 77°K. The doublet spectra observed from both CH_3COOH and CH_3COOD show that the hyperfine splitting is not caused by interaction with the hydroxyl proton but arises from coupling to one of the methyl protons. This assignment is confirmed by the replacement of the doublet by a closely spaced triplet in CD_3COOD . The ratio of the hyperfine splittings from the proton and deuteron in CH_3COOD and CD_3COOD respectively is 6.2 which is reasonably close to the theoretical ratio of 6.5. The single line observed from trimethylacetic acid, which has no β -protons, is also in accord with this assignment.

CARBON-13 HYPERFINE STRUCTURE

Within experimental error the principal values of the carbon-13 hyperfine coupling constant in the fully deuterated acetic acid are the same as those observed in a γ -irradiated single crystal of succinic acid.⁴ This equivalence is additional confirmation that the paramagnetic species have the same basic structure in both acids.

The carbon-13 splitting can be divided into two parts; an isotropic component A which arises from the participation of the carbon 2s-orbital in the orbital of the unpaired electron and an anisotropic component B arising from the 2p-orbital. The principal values of the hyperfine coupling constant can be expressed as

 $A_x = A_y = A - B$ and $A_z = A + 2B$.

Substitution of the observed values into these equations yields A = 114 oe and B = 25 oe. Comparison of these values with the theoretical values ¹⁵ for complete occupancy of the 2s-orbital ($A_0 = 1111$ oe) or 2p-orbital ($B_0 = 32.4$ oe) gives the corresponding spin densities in these orbitals as $\rho_s = 0.10$ and $\rho_p = 0.78$.

From these results it is evident that the unpaired electron is not in a pure carbon 2p-orbital but that there is a significant contribution from the carbon 2s-orbital. The total spin density on the carbon atom is less than unity showing that there is some delocalization of the electron on to the adjacent oxygen atoms (ca. 0.12 total). The participation of the carbon 2s-orbital implies that the free valence centre does not possess the planar sp^2 configuration found for most alkyl radicals, but that it is pyramidal. If it is assumed that the bonding orbitals of the free valence carbon atom are equivalent and orthogonal to the unpaired electron orbital, then the angular configuration of the



group can be calculated. The angle α between the free valence orbital and any one of the bonding orbitals is given by

$$(180 - \alpha) = \sin^{-1} \left\{ \frac{\eta + 1}{1 \cdot 5\eta + 1} \right\}^{\frac{1}{2}}$$

where $\eta = \rho_s / \rho_p$.

The experimental values of ρ_s and ρ_p give $\alpha = 104^\circ$ whereas, for a planar radical, $\alpha = 90^{\circ}$. Because of the assumptions made this value is approximate only but shows that the free valence carbon has a pyramidal configuration. This result confirms a suggestion made by Symons ¹⁶ that, by comparison with the structure of RNO₂ radical ions, the radical centre in the carboxylic acid anions should be pyramidal rather than planar. Further support for this conclusion can be obtained from the low value of the hyperfine splitting constant of the methyl protons in acetic acid. If the free valence centre is planar as in the ethyl radical then the methyl proton coupling constants should be proportional to the corresponding spin densities on the α -carbon atoms. The coupling constant for the freely rotating methyl protons in the ethyl radical is 26.9 oe and spin density in the 2*p*-orbital is approximately unity. For the radical anion of acetic acid the spin density will be close to that from the fully deuterated acid ($\rho_p = 0.78$) and thus the coupling constant for the freely rotating methyl group is predicted to be about 21 oe. This value is considerably larger than that observed experimentally (13.5 oe) for the freely rotating methyl group. However, if the free valence carbon is pyramidal then the unpaired electron will be in an orbital which is inclined further away from the methyl group than a pure 2*p*-orbital ($\alpha = 90^{\circ}$). In consequence, hyperconjugation between the unpaired electron and the methyl group will be less, which in turn will result in a lower hyperfine coupling than expected for a planar configuration, as found experimentally.

METHYL HYPERFINE INTERACTION

The interaction with a single proton (or deuteron) shows that the methyl group is not rotating freely at 77°K. For a stationary methyl group * in a planar radical the proton hyperfine splittings $(B_1, B_2 \text{ and } B_3)$ are given by $B_i = B_0 \cos^2 \theta_i$, where

^{*} The terms stationary or fixed are taken to imply that the rate of interconversion of the methyl group between its equilibrium positions is less than about 10^7 times per sec (i.e., less than the hyperfine splitting expressed in frequency units).

 B_0 is a constant, and θ_i is the angle between the projections of the CH_i bond and the axis of the orbital of the unpaired electron on a plane perpendicular to the C_{α} — C_{β} bond.

For a pyramidal structure, the angular dependence of the β -proton splittings will not follow this relationship rigorously. However, the deviations are probably not large for the small amount of 2s-character (0.1) involved in the valence orbital. Consequently the configuration of the radical anion will be discussed on the assumption that the methyl hyperfine splittings can be expressed by the cos² θ relationship.

Consideration of the hyperfine splittings which are predicted by the $\cos^2\theta$ dependence shows that unless one of the protons lies close to (within 5-10°) the symmetry plane of the radical (i.e., the plane defined by the C_{α} — C_{β} bond and the axis of the orbital containing the unpaired electron) then additional hyperfine structure from a second proton would be visible. Thus $\theta_1 = 0^\circ$, $B_0 = 32$ oe and the other two C—H bonds are equally inclined to the symmetry plane giving $B_2 = B_3 = 8$ oe. The same configuration has been postulated by Miyagawa and Gordy² for the radical anion formed in X-irradiated acetic acid at 77°K.

The results from the γ -irradiated acetic acid show that when the sample is warmed the rate of rotation of the methyl group increases steadily and at 150°K the spectrum is that of a freely rotating group. At intermediate temperatures the central hyperfine lines are broad showing that the rate of rotation is comparable to the hyperfine splitting, i.e., 50 Mc/sec.

In contrast, the spectra of samples prepared in the cryostat by vacuum deposition of acetic acid (CH₃COOH or CH₃COOD) show that the methyl group remains stationary up to 140°K. The rapid decay of the primary spectrum at this temperature suggests that a molecular rearrangement occurs in the deposit. The spectrum from those radical ions which survive above 140°K shows that the methyl group is freely rotating. When the deposit is cooled again the spectrum shows the same temperature dependence as that from the γ -irradiated sample.

Thus, the structure of the deposits formed in the cryostat is different from that produced by freezing the liquid acetic acid. The immediate environment of the radical anion is such that the methyl group is unable to rotate even at temperatures appreciably above 77°K. However, at 140°K a molecular rearrangement occurs and the structure of the deposit becomes similar to that of the frozen liquid.

The hyperfine splitting for the freely rotating methyl group is expected to be about 16 oe $(B_0 \langle \cos^2\theta \rangle_{av} = B_0/2)$. The observed value (13.5 oe) is in fact smaller than this predicted value and this deviation is probably caused by the non-planarity of the free valence centre.

The spectrum of the radical anion of CD_3COOD does not decay as markedly at 140°K as those from the other two acetic acids. Thus, the molecular rearrangement is either much less, or takes place more gradually, in the fully deuterated acid. Above this temperature at least five of the seven lines expected for a freely rotating deuteromethyl group are observed. The hyperfine splitting (2.4 oe) is again just under half that (5.3 oe) for the fixed CD_3 group at 77°K.

PROPIONIC, BUTYRIC AND ISOBUTYRIC ACIDS

The doublets observed from reaction of sodium with propionic and butyric acids are similar to that from acetic acid and are assigned to the corresponding radical anions. The configuration is again that in which one proton of the β -CH₂ group lies approximately in the symmetry plane of the radical. In contrast to acetic acid, a second radical is also formed from both propionic and butyric acids at 77°K. The additional five-line spectrum from propionic acid can be assigned to

 $CH_3\dot{C}HCOOH$ rather than to $\dot{C}H_2CH_2COOH$ which would be expected to give a six-line spectrum similar to that of the propyl radical at 77°K. The secondary spectrum from butyric acid is more complex and may arise from more than one free radical.

The absence of the characteristic doublet in the spectrum observed from isobutyric acid suggests either that the negative ion is not formed or that it reacts immediately after formation at 77°K to give a secondary radical. The seven-line spectrum is almost identical with that observed for the radical $(CH_3)_2$ CCOOH trapped in γ -irradiated α -aminoisobutyric acid,¹⁷ and thus identifies the secondary radical as that formed by loss of the tertiary hydrogen from an acid molecule. The appearance of the doublet when sodium reacts with isobutyric acid in a matrix of hexamethylethane suggests that the negative ion is formed initially but that in the isobutyric acid matrix it immediately abstracts the tertiary hydrogen from a neighbouring molecule. When the radical anion is formed in a matrix of hexamethylethane which possesses only primary hydrogens, then it cannot react and is trapped at 77°K.

As the C—H bond strength decreases in the order primary>secondary>tertiary, the degree of hydrogen abstraction at 77° K should increase in the series: acetic acid = trimethylacetic acid < propionic acid = butyric acid < isobutyric acid. The observed yields of secondary radical species are consistent with this progression.

Where both the carboxylic acid radical anion and the secondary radical were observed immediately after preparation in a matrix of the parent acid, as with propionic and butyric acids, no further reaction occurred at 77° K. This result suggests that the energy for the abstraction reaction at 77° K arises from the energy liberated in the initial reaction between the alkali metal and the acid. Also when these samples were warmed no further reaction was observed up to 140° K. Above this temperature all radical species decayed rapidly preventing the observation of any possible abstraction from the parent carboxylic acid.

A unimolecular reaction has been proposed for the formation of secondary radicals from the radical anions prepared by X- or γ -irradiation of single crystals of 1-alanine ⁷ or ammonium trifluoroacetate ¹⁸ at 77°K. The generalized reaction is



where $X = NH_3^+$, or F⁻. This reaction occurs quantitatively at 140-150°K in 1-alanine and in a similar temperature range with ammonium trifluoroacetate. However, it appears unlikely that a unimolecular reaction occurs in the present study because of the effect of the matrix observed with isobutyric acid.

BENZOIC ACID

The radical anion expected for benzoic acid will have the structure



which is effectively that of a substituted benzyl radical. Thus, the unpaired electron will not be located solely on the carboxyl group but will be delocalized around the ring. The four poorly resolved lines can be assigned to an approximately equal

hyperfine interaction with the ortho- and para-protons. The hyperfine splitting (5.8 oe) is similar to that found for the ortho- and para-protons of the benzyl and α -hydroxylbenzyl radicals.¹⁹ This similarity suggests that the conjugation between the free valence *p*-orbital of the substituent group and the π -electron system of the ring is comparable for all three radicals. Consequently, the radical centre in benzoic acid is unlikely to deviate very far from a planar configuration.

METHYL ACETATE

The doublet spectrum shows that the radical anion is also formed in methyl acetate at 77° K. However, the hyperfine splitting (25.4 oe) is less than that observed from acetic acid (32.1 oe). This decrease in the hyperfine splitting cannot be caused solely by a change in the orientation of the methyl group as the rotation necessary would simultaneously increase that of another proton to about 22 oe. Thus the decrease must be attributed mainly to either a reduction in the spin density on the carboxyl carbon atom caused by the ester group or to a change in the angular configuration of the radical anion.

The spin density and angular configuration can be determined from the carbon-13 hyperfine splittings in the deuterated anion, $CD_3 \stackrel{\circ}{\underset{i}{\subset}} O CH_3$, by making the same

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assumptions as those used for the radical anion from deuterated acetic acid. The spin densities in the 2s- and 2p-orbitals of the carboxylic carbon atom are found to be $\rho_p = 0.09$ and $\rho_p = 0.74$ respectively, giving a total spin density of 0.83 which is not significantly different from that for acetic acid (0.88). The angle α between the free valence orbital and any one of the bonding orbitals is calculated to be 103°, and is again not significantly different from that of the acid (104°). Hence, neither variation appears to be sufficiently large to account for the observed decrease in the hyperfine splitting from 32.1 oe for the acid to 25.4 oe for the ester.

Two considerations suggest that the difference in the splitting constants is due mainly to an angular change rather than a change in the spin density. First, for the corresponding radical anions from formic acid and methyl formate the opposite effect occurs, namely, the α -proton splitting constant is smaller in the acid (17.7 oe) than in the ester (24.0 oe). A simple reduction in the spin density caused by the ester group would be expected to reduce the hyperfine coupling of both α - and β protons. Secondly, the β -proton hyperfine splittings in the radicals CH₃CHOH (22.0 oe)²⁰ and CH₃CHOCH₂CH₃ (21.9 oe)²¹ are virtually identical and show that substitution of an ester group has negligible effect on the spin density distribution.

FORMIC ACID AND METHYL FORMATE

The doublet spectra from both formic acid (splitting 17.7 oe) and methyl formate (splitting 24.0 oe) are again consistent with the formation of the corresponding radical anions. Neither spectrum is similar to that of the HCO radical (doublet splitting *ca.* 135 oe) ²² and thus the possibility that loss of the hydroxyl or ester group occurs on reaction with the alkali metal is eliminated. This observation supports our conclusion that the primary paramagnetic species formed from the other carboxylic acids are the radical anions, R—C—OH, and not the free radicals RCO formed by

loss of the hydroxyl group.

The hyperfine splitting (17.7 oe) of the radical anion from formic acid is typical of that expected from a substituted methyl radical and could indicate that this anion

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is planar. However, it is more probable that the radical anion is pyramidal with an angular configuration similar to that for acetic acid. In this case, comparison with the calculated angular dependence 23 of the α -proton hyperfine splitting of the vinyl and formyl radicals shows that the absolute value of the splitting constant is likely to be positive and not negative as for a planar radical.

The increase of the α -proton hyperfine splitting caused by the ester group in the radical anion from methyl formate contrasts markedly with the effect of the ester group on the α -proton splittings in the pairs of radicals CH₃ĊHOH (15.0 oe)²⁰ and $CH_3\dot{C}HO\dot{C}H_2CH_3$ (13.8 oe),²¹ and $HO\dot{C}HCOO^-$ (18.2 oe) ²⁴ and $CH_3O\dot{C}HCOO^-$ (17.8 oe),²⁵ in which a slight decrease occurs. The increase is most readily explained by a slight change in the angular configuration of the radical anion caused by the presence of the ester group, as postulated for methyl acetate.

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