Electron Spin Resonance Studies. Part 69.[1] Oxidation of Some Aliphatic Carboxylic Acids, Carboxylate Anions, and Related Compounds by the Sulphate Radical Anion ($SO_4^{-\bullet}$)

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The results of e.s.r experiments involving *in situ* photochemical generation of the sulphate radical anion in the presence of some aliphatic carboxylic acids and their anions are interpreted in terms of attack at the carboxy group (to give alkyl radicals *via* decarboxylation) and hydrogen-atom abstraction from carbon atoms in the chain. The general order of reactivity of different sites is $CO_2^- > \beta$-H, γ-H, *etc.* > $CO_2H > \alpha$-H. For example, reaction with $EtCO_2H$ gives $^\bullet CH_2CH_2CO_2H$ (k 2×10^6 dm^3 mol^{-1} s^{-1}) and $Et^\bullet$ (k 7×10^4 dm^3 mol^{-1} s^{-1}). Radicals formed by abstraction of α-H (*e.g.* $^\bullet CH_2CO_2H$ from ethanoic acid) are shown to result usually from further reactions of first-formed alkyl radicals. The reactions of $SO_4^{-\bullet}$ with some amides, nitriles, and esters have also been investigated.

The sulphate radical anion ($SO_4^{-\bullet}$) is thought to be the key intermediate in photochemical, thermal, and some transition-metal-catalysed decompositions of peroxydisulphate (see *e.g.* ref. 2). It is known that $SO_4^{-\bullet}$ is a very electrophilic radical which behaves as an effective one-electron oxidant with, for example, aromatic compounds,[3] electron-rich alkenes,[1,4] and some sulphides and sulphoxides.[5] There is evidence from the similarities in the distribution of products from the oxidation of carboxylates anodically and with $SO_4^{-\bullet}$ that reaction of this species also involves one-electron oxidation[6] (see also the report[7] of an e.s.r. study of the oxidation of some carboxylates with the Ti^{III}–$S_2O_8^{2-}$ couple). On the other hand the relatively selective oxidation of alkanoic acids to δ- and γ-lactones by $Na_2S_2O_8$–$CuCl_2$ implies that hydrogen-atom abstraction can be effected[8] (*cf.* the report[9] of hydrogen abstraction from alkanols by $SO_4^{-\bullet}$), though it has been claimed[8] that this reaction proceeds *via* intramolecular hydrogen transfer in a first-formed acyloxyl radical ($RCO_2^\bullet$) or its protonated counterpart ($RCO_2H^{+\bullet}$). We here report the results of an e.s.r. study of the photolytic decomposition of peroxydisulphate in the presence of carboxylic acids and related compounds, an investigation designed to distinguish the primary processes of electron and hydrogen-atom abstraction and the effect upon these of variations of pH and substrate structure.

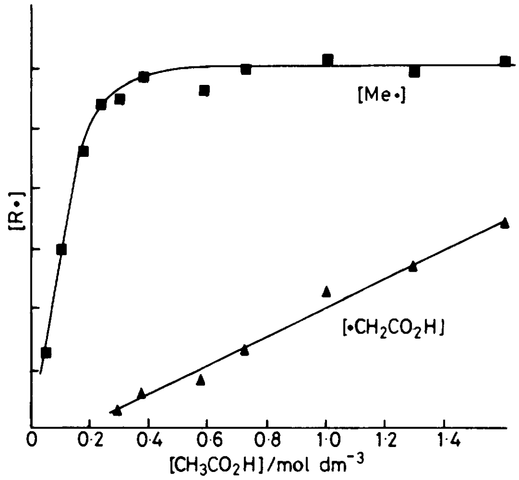

Figure 1. Variation of $[Me^\bullet]$ and $[^\bullet CH_2CO_2H]$ (in arbitrary units) with $[MeCO_2H]$ in the *in situ* photolysis of aqueous solutions of ethanoic acid containing $S_2O_8^{2-}$ (0.5 mol dm^{-3}) at room temperature

Results and Discussion

Two methods have been shown to be suitable for the rapid generation of $SO_4^{-\bullet}$ within the cavity of an e.s.r. spectrometer, namely the use of a flow system employing Ti^{III} and $S_2O_8^{2-}$ (see *e.g.* refs. 4 and 5) and photolytic generation[5,10] from $S_2O_8^{2-}$ (employing, typically, a mercury–xenon lamp and slowly flowing solutions). Both approaches were investigated, but we found that the latter system gave more intense spectra, especially when peroxydisulphate concentrations of *ca.* 0.5 mol dm^{-3} were employed (with a flow rate of *ca.* 2 cm^3 min^{-1}). All the results described here were obtained at room temperature using this approach, except for certain substrates (noted later) for which addition of propanone (*ca.* 0.5 mol dm^{-3}) and reduction of $[S_2O_8^{2-}]$ (to *ca.* 0.05 mol dm^{-3}) proved advantageous (the use of propanone as a co-solvent and sensitizer has been described previously[5,10]).

(a) *Reactions of Carboxylic Acids with* $SO_4^{-\bullet}$.—(i) *Ethanoic acid.* Photolysis of an aqueous 10% solution of ethanoic acid containing 0.5 mol dm^{-3} sodium peroxydisulphate led to the detection of e.s.r. signals from both $Me^\bullet$ and $^\bullet CH_2CO_2H$ (for parameters, see Table 1). Reduction in $[S_2O_8^{2-}]$ led to a corresponding reduction in the signal intensities of both radicals, until at a peroxydisulphate concentration of *ca.* 0.02 mol dm^{-3} the two signals could no longer be discerned; there was no significant change in the relative intensities of the signals throughout the concentration range examined. However, when $[S_2O_8^{2-}]$ was kept constant and $[MeCO_2H]$ reduced, the signal intensities varied as shown in Figure 1.

The observation that $Me^\bullet$ is the only species detected at relatively low substrate concentrations suggests that the primary reaction is oxidation at the carboxy group (*cf.* ref. 11). This presumably proceeds *via* formation of the acetoxyl radical (either by hydrogen abstraction or by electron abstraction followed by proton loss), with subsequent extremely rapid decarboxylation[11] [reactions (1) and (2)]. At substrate concentrations of 0.3 mol dm^{-3} or greater, $^\bullet CH_2CO_2H$ was also detected; the steady increase in $[^\bullet CH_2CO_2H]$ suggests that this radical arises largely *via* hydrogen-atom abstraction by $Me^\bullet$ [reaction (3)] rather than by direct attack of $SO_4^{-\bullet}$ on

Table 1. E.s.r. parameters of radicals detected during the oxidation of aliphatic carboxylic acids by $SO_4^{-\bullet}$

Substrate	Radical	Hyperfine splittings (mT)[a]		g[b]	Ref.
		a(α-H)	a(β-H)		
$MeCO_2H$	$Me^{\bullet}$	2.29(3)		2.0025	*d*
	$^{\bullet}CH_2CO_2H$	2.16(2)		2.0033	*d*
$EtCO_2H$	$^{\bullet}CH_2CH_2CO_2H$	2.24(2)	2.65(2)	2.0026	*e*
	$^{\bullet}CHMeCO_2H$	2.02(1)	2.49(3)	2.0033	*f*
	$Et^{\bullet}$	2.22(2)	2.71(3)	2.0025	*d*
$PrCO_2H$	$^{\bullet}CHMeCH_2CO_2H$	2.22(1)	2.22(2) 2.61(3)	2.0026	*e*
$BuCO_2H$	$^{\bullet}CHEtCH_2CO_2H$	2.125(1)	2.50(2) 2.125(2)	2.0026	
	$^{\bullet}CHMe[CH_2]_2CO_2H$	2.20(1)	2.45(2) 2.60(3)	2.0026	
Me_2CHCO_2H	$^{\bullet}CMe_2CO_2H$		2.16(6)	2.0032	*g*
Me_3CCO_2H	$^{\bullet}CH_2CMe_2CO_2H$	2.18(2)	0.07(6)[c]	2.0026	*e*
$CH_2(CO_2H)_2$	$^{\bullet}CH_2CO_2H$				
	$^{\bullet}CH(CO_2H)_2$	2.04(1)		2.0037	*h*
$(CH_2CO_2H)_2$	$^{\bullet}CH_2CH_2CO_2H$				
	$^{\bullet}CH(CO_2H)CH_2CO_2H$	2.07(1)	2.19(2)	2.0033	*d*
$CH_2(CH_2CO_2H)_2$	$^{\bullet}CH(CH_2CO_2H)_2$	2.25(1)	2.25(4)	2.0026	
	$^{\bullet}CH(CO_2H)[CH_2]_2CO_2H$	2.02(1)	2.39(2)	2.0033	
$(CH_2CH_2CO_2H)_2$	$^{\bullet}CH(CH_2CO_2H)[CH_2]_2CO_2H$	2.19(1)	2.54(4)	2.0026	*h*
	$^{\bullet}CH(CO_2H)[CH_2]_3CO_2H$	2.03(1)	2.35(2)	2.0033	*h*

[a] ±0.01 mT. [b] ±0.0001. [c] a(γ-H). [d] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 1969, 400. [e] H. Hasegawa and T. Maruyama, *J. Phys. Chem.*, 1968, **72**, 1926. [f] W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625. [g] Ref. 18. [h] D. Behar, A. Samuni, and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 2055.

ethanoic acid. It has been suggested previously[12] that when $Me^{\bullet}$ is generated from reaction of $^{\bullet}OH$ with Me_2SO in a flow system, the detection of $^{\bullet}CH_2CO_2H$ in the presence of added ethanoic acid is similarly explained. The kinetic implications are discussed later.

$$MeCO_2H + SO_4^{-\bullet} \longrightarrow MeCO_2^{\bullet} + HSO_4^{-} \quad (1)$$

$$MeCO_2^{\bullet} \longrightarrow Me^{\bullet} + CO_2 \quad (2)$$

$$Me^{\bullet} + MeCO_2H \longrightarrow MeH + {}^{\bullet}CH_2CO_2H \quad (3)$$

(ii) *Propanoic acid.* Photolysis of an aqueous 10% solution of propanoic acid containing 0.5 mol dm^{-3} sodium peroxydisulphate led to the detection of the three radicals $^{\bullet}CH_2CH_2CO_2H$, $^{\bullet}CHMeCO_2H$, and $Et^{\bullet}$ (see Table 1). Reduction in $[S_2O_8^{2-}]$ again resulted in a corresponding decrease in the overall signal intensity, with no noticeable changes in the relative concentrations of the radicals. However, reduction in $[EtCO_2H]$ led to the changes in radical concentrations depicted in Figure 2.

The fact that $^{\bullet}CH_2CH_2CO_2H$ is the only species detected at substrate concentrations less than 0.05 mol dm^{-3} suggests that the primary reaction is abstraction of a β-hydrogen atom [reaction (4)], rather than attack at the carboxy group or the α-position.* The detection of $Et^{\bullet}$ (in low concentrations) for $[EtCO_2H] \geqslant 0.1$ mol dm^{-3}, and its concentration profile as a function of substrate concentration, suggests that a minor reaction pathway involves direct decarboxylation *via* reactions (5) and (6). The marked increase in $[^{\bullet}CHMeCO_2H]$ with substrate concentration, coupled with the decrease in $[^{\bullet}CH_2CH_2CO_2H]$, may be explained if the primary alkyl radical $^{\bullet}CH_2CH_2CO_2H$ reacts with the parent compound *via* abstraction of an α-hydrogen atom [reaction (7)]; the decrease (though less marked) in $[Et^{\bullet}]$ implies that this radical can react similarly [reaction (8)]. This interpretation, and the analogous occurrence of reaction (3), would also be consistent with the previous finding[12] that methyl (and, presumably, other simple alkyl radicals) react selectively with aliphatic carboxylic acids by hydrogen abstraction at the α-position [reaction (9)]. This no doubt reflects the nucleophilic nature of alkyl radicals, and hence the creation of polar character [as represented by structure (1)] in the transition state for the reaction.

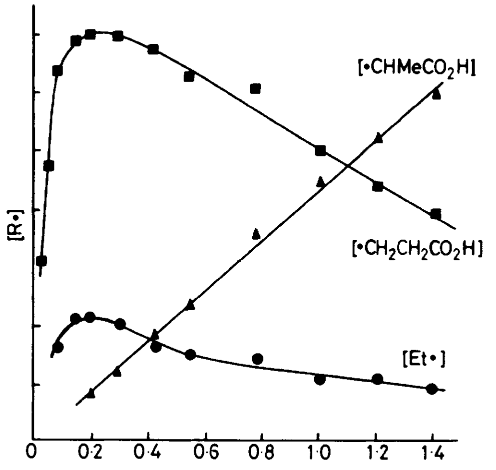

Figure 2. Variation of $[^{\bullet}CH_2CH_2CO_2H]$, $[Et^{\bullet}]$, and $[^{\bullet}CHMeCO_2H]$ (in arbitrary units) with $[EtCO_2H]$ in the *in situ* photolysis of aqueous solutions of propanoic acid containing $S_2O_8^{2-}$ (0.5 mol dm^{-3}) at room temperature

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* The detection of $^{\bullet}CH_2CH_2CO_2H$ from propanoic acid and (see later) $^{\bullet}CHMeCH_2CO_2H$ from butanoic acid is interpreted in terms of *direct* hydrogen-atom abstraction rather than *intramolecular* attack following formation of $RCO_2^{\bullet}$ or $RCO_2H^{+\bullet}$ (*cf.* ref. 8) since a relatively unfavourable 1,4-shift would be involved in the latter process.

$$EtCO_2H + SO_4^{-\bullet} \longrightarrow {}^{\bullet}CH_2CH_2CO_2H + HSO_4^- \quad (4)$$

$$EtCO_2H + SO_4^{-\bullet} \longrightarrow EtCO_2^{\bullet} + HSO_4^- \quad (5)$$

$$EtCO_2^{\bullet} \longrightarrow Et^{\bullet} + CO_2 \quad (6)$$

$$EtCO_2H + {}^{\bullet}CH_2CH_2CO_2H \longrightarrow {}^{\bullet}CHMeCO_2H + EtCO_2H \quad (7)$$

$$EtCO_2H + Et^{\bullet} \longrightarrow {}^{\bullet}CHMeCO_2H + EtH \quad (8)$$

$$R^{\bullet} + R'CH_2CO_2H \longrightarrow \underset{(1)}{\overset{+}{R}\cdots\overset{\bullet}{H}\cdots R'\overset{-}{C}HCO_2H} \longrightarrow RH + R'\dot{C}HCO_2H \quad (9)$$

In contrast, the sulphate radical anion is highly electrophilic, so the presence of the electron-withdrawing carboxy group destabilizes the transition state for attack of this radical at the α-position; direct attack at the carboxylate group itself (for $MeCO_2H$) and at more remote C–H bonds ($EtCO_2H$) is evidently favoured.

(iii) *Other monocarboxylic acids.* Low solubility prevented a full study of the effect of substrate concentrations for the higher acids, though signals were detected from saturated solutions of acids containing *ca.* 0.5 mol dm^{-3} sodium peroxydisulphate and also with propanone as co-solvent.

For butanoic acid, for example, the detection solely of $^{\bullet}CHMeCO_2H$ corresponds, as with propanoic acid, to selective hydrogen abstraction from the β-position [reaction (10)]: attack here rather than at γ-hydrogen is presumably encouraged by the greater stability of the secondary radical. Failure to detect $Pr^{\bullet}$ may well reflect the small extent of attack at the carboxy group (expected to be even lower than for $EtCO_2H$; Figure 2), and the lack of signals from $^{\bullet}CHEtCO_2H$ results from the low substrate concentration employed and the expected lower reactivity towards (α) hydrogen abstraction of $^{\bullet}CHMeCH_2CO_2H$ [contrast reactions (7) and (8)]. Pentanoic acid gave a weak and complex spectrum, with signals assigned to radicals from β- and γ-hydrogen abstraction (see Table 1), and dimethylpropanoic acid gave only $^{\bullet}CH_2CMe_2CO_2H$. The apparently anomalous detection of $^{\bullet}CMe_2CO_2H$ from methylpropanoic acid can be understood if the first-formed primary radical $^{\bullet}CH_2CHMeCO_2H$ reacts rapidly with the parent substrate by α-H abstraction to give a stabilized tertiary radical [reactions (11) and (12)]. 3-Methylbutanoic acid gave only complex (unanalysed) spectra.

$$PrCO_2H + SO_4^{-\bullet} \longrightarrow {}^{\bullet}CHMeCH_2CO_2H + HSO_4^- \quad (10)$$

$$Me_2CHCO_2H + SO_4^{-\bullet} \longrightarrow {}^{\bullet}CH_2CHMeCO_2H + HSO_4^- \quad (11)$$

$$^{\bullet}CH_2CHMeCO_2H + Me_2CHCO_2H \longrightarrow Me_2CHCO_2H + {}^{\bullet}CMe_2CO_2H \quad (12)$$

(iv) *Dicarboxylic acids.* The results from several dicarboxylic acids (*ca.* 0.2 mol dm^{-3} or as a saturated solution, whichever concentration was the lower) are also in Table 1: the signals from radicals resulting from α-hydrogen abstraction were always of lowest intensity. The overall signal intensity was again proportional to $[S_2O_8^{2-}]$, variation of this having little effect on the relative concentrations of the radicals.

These results can be interpreted as for monocarboxylic acids. Thus acids whose only methylene groups are next to a carboxy function [*i.e.* $CH_2(CO_2H)_2$ and $(CH_2CO_2H)_2$] undergo decarboxylation: evidently the resultant alkyl radicals then react with the substrate *via* hydrogen abstraction from the α-position [reactions (13) and (14)]. In contrast, higher homologues have methylene units that are not deactivated towards hydrogen abstraction, resulting in the formation of secondary alkyl radicals [*e.g.* $^{\bullet}CH(CH_2CO_2H)_2$ from pentanedioic acid]: these can also react with the parent substrate to give α-abstraction radicals.

$$(CH_2CO_2H)_2 + SO_4^{-\bullet} \longrightarrow HSO_4^- + {}^{\bullet}O_2CCH_2CH_2CO_2H \longrightarrow CO_2 + {}^{\bullet}CH_2CH_2CO_2H \quad (13)$$

$$^{\bullet}CH_2CH_2CO_2H + (CH_2CO_2H)_2 \longrightarrow EtCO_2H + {}^{\bullet}CH(CO_2H)CH_2CO_2H \quad (14)$$

(b) *Reaction of Carboxylate Anions with* $SO_4^{-\bullet}$.—Oxidation of sodium carboxylates at *ca.* pH 9 was also investigated, the concentration of the salt being, except where stated, the same as that of the parent acid in the corresponding experiments at low pH.

(i) *Ethanoate ion.* Oxidation of $MeCO_2^-$ with $SO_4^{-\bullet}$ paralleled the behaviour of the acid in that $^{\bullet}CH_2CO_2^-$ (see Table 2) and $Me^{\bullet}$ were detected: reduction of $[S_2O_8^{2-}]$ resulted in reduced signal intensity without change in the concentration ratio. Reduction of $[MeCO_2^-]$ changed the ratio in a similar manner to that depicted in Figure 1. However, for a given $[MeCO_2^-]$ the total signal intensity was much greater, and the ratio $[Me^{\bullet}]:[{}^{\bullet}CH_2CO_2^-]$ was also higher (than that for $[Me^{\bullet}]:[{}^{\bullet}CH_2CO_2H]$). We conclude from this that ethanoate is more reactive than ethanoic acid towards $SO_4^{-\bullet}$ [reaction (15)], the higher concentration of $^{\bullet}CH_2CO_2^-$ than of $^{\bullet}CH_2CO_2H$ reflecting in part the decrease in the rate constant for bimolecular termination which accompanies ionization[13] [$2k_t(^{\bullet}CH_2CO_2H)$ 1.8×10^9 dm^3 mol^{-1} s^{-1}; $2k_t(^{\bullet}CH_2CO_2^-)$ 1.0×10^9 dm^3 mol^{-1} s^{-1}] as well as an increase in the rate of abstraction by $CH_3^{\bullet}$ [reaction (16)].

$$\begin{tikzcd} MeCO_2^- + SO_4^{-\bullet} \arrow[r] & MeCO_2^{\bullet} \arrow[d, "-CO_2"] & + SO_4^{2-} \quad (15) \\ & Me^{\bullet} & \end{tikzcd}$$

$$Me^{\bullet} + MeCO_2^- \longrightarrow MeH + {}^{\bullet}CH_2CO_2^- \quad (16)$$

(ii) *Propanoate ion.* The overall signal intensity was again found to be proportional to $[S_2O_8^{2-}]$; the predominant species detected was $Et^{\bullet}$, but $^{\bullet}CHMeCO_2^-$ was also observed at higher substrate concentrations. In comparison with $EtCO_2H$, where signals from $Et^{\bullet}$ accompany those from $^{\bullet}CH_2CH_2CO_2H$, direct attack on the carboxylate ion (to give $Et^{\bullet}$) is now favoured and subsequent α-abstraction by $Et^{\bullet}$ is also rapid [*cf.* reactions (15) and (16)].

(iii) *Other monocarboxylate ions.* The detection of $Pr^{\bullet}$ and $^{\bullet}CHEtCO_2^-$ from butanoate parallels the behaviour of propanoate. However, $^{\bullet}CHMeCH_2CO_2^-$ was also just discernible, suggesting that direct β-abstraction from butanoate is faster than from the same site in propanoate, consistent with the stabilizing effect of a methyl group at a radical centre. Attack at β- and γ-hydrogen atoms also occurred with pentanoate, for which signals from $^{\bullet}CHEtCH_2CO_2^-$ and $^{\bullet}CHMeCH_2CH_2CO_2^-$ were accompanied by those assigned to $Bu^{\bullet}$ (rather than $^{\bullet}CH_2CH_2CH_2CH_2CO_2^-$) by comparison with behaviour of other anions. 3-Methylbutanoate gave rise to signals from $^{\bullet}CMe_2CH_2CO_2^-$ and $^{\bullet}CH(CHMe_2)CO_2^-$ as well as those assigned to $^{\bullet}CH_2CHMe_2$.

In contrast to the results at low pH for Me_3CCO_2H the

Table 2. E.s.r. parameters of radicals detected during the oxidation of aliphatic carboxylate anions by $SO_4^{-\bullet}$

Substrate	Radical	Hyperfine splittings (mT)[a] a(α-H)	a(β-H)	g[b]	Ref.
$MeCO_2^-$	$Me^{\bullet}$	2.29(3)		2.0025	*c*
	$^{\bullet}CH_2CO_2^-$	2.16(2)		2.0033	*c*
$EtCO_2^-$	$Et^{\bullet}$	2.22(2)	2.71(3)	2.0025	*c*
	$^{\bullet}CHMeCO_2^-$	2.04(1)	2.49(3)	2.0033	*c*
$PrCO_2^-$	$Pr^{\bullet}$	2.16(2)	2.86(2)	2.0025	*d*
	$^{\bullet}CHEtCO_2^-$	2.02(1)	2.38(2)	2.0033	*c*
	$^{\bullet}CHMeCH_2CO_2^-$	2.15(1)	2.15(2) 2.48(3)	2.0026	*e*
$BuCO_2^-$	$Bu^{\bullet}$	2.19(2)	2.725(2)	2.0027	*f*
	$^{\bullet}CHMe[CH_2]_2CO_2^-$	2.10(1)	2.425(2) 2.50(3)	2.0026	
	$^{\bullet}CHEtCH_2CO_2^-$	2.115(1)	2.10(2) 2.56(2)	2.0026	
$Me_2CHCO_2^-$	$^{\bullet}CMe_2CO_2^-$		2.20(6)	2.0033	*c*
$Me_2CHCH_2CO_2^-$	$^{\bullet}CH_2CHMe_2$	2.15(2)	2.75(1)	2.0026	*f*
	$^{\bullet}CMe_2CH_2CO_2^-$		1.70(2) 2.30(6)	2.0026	
	$^{\bullet}CH(CO_2^-)CHMe_2$	2.075(1)	1.21(1) 0.08(6 γ-H)	2.0033	*g*
$CH_2(CO_2^-)_2$	$^{\bullet}CH_2CO_2^-$	2.16(2)		2.0033	*c*
	$^{\bullet}CH(CO_2^-)_2$	1.99(1)		2.0034	*h*
$(CH_2CO_2^-)_2$	$^{\bullet}CH_2CH_2CO_2^-$	2.22(2)	2.58(2)	2.0026	*c*
	$^{\bullet}CH(CO_2^-)CH_2CO_2^-$	2.03(1)	2.32(2)	2.0033	*c*
$CH_2(CH_2CO_2^-)_2$	$^{\bullet}CH_2[CH_2]_2CO_2^-$	2.18(2)	2.76(2)	2.0026	*e*
	$^{\bullet}CH(CO_2^-)[CH_2]_2CO_2^-$	2.02(1)	2.39(2)	2.0033	
$(CH_2CH_2CO_2^-)_2$	$^{\bullet}CH_2[CH_2]_3CO_2^-$	2.18(2)	2.84(2)	2.0026	
	$^{\bullet}CH(CO_2^-)[CH_2]_3CO_2^-$	2.04(1)	2.40(2)	2.0033	

[a] ±0.01 mT. [b] ±0.0001. [c] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 1969, 400. [d] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147. [e] F. R. Hewgill and G. M. Proudfoot, *Aust. J. Chem.*, 1976, **29**, 639. [f] J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, 1969, **91**, 3940. [g] M. D. Sevilla, *J. Phys. Chem.*, 1970, **74**, 2096. [h] G. P. Laroff and R. W. Fessenden, *J. Chem. Phys.*, 1971, **55**, 5000.

corresponding anion failed to give detectable signals. The absence of $^{\bullet}CH_2CMe_2CO_2^-$ is consistent with the behaviour of propanoate, which also showed no abstraction from its terminal site. The absence of $Bu^{t\bullet}$, the product of decarboxylation, is at first sight surprising: however it is probably a result of its rapid oxidation by $S_2O_8^{2-}$ to a relatively stable carbocation (*cf.* values[5] for oxidation of primary alkyl radicals by peroxydisulphate ion of *ca.* 10^4 dm^3 mol^{-1} s^{-1}). The detection of $^{\bullet}CMe_2CO_2^-$ from 2-methylpropanoate presumably reflects the relative ease of abstraction of the tertiary hydrogen in the parent substrate: since $Pr^{i\bullet}$ (from decarboxylation) is not detected (like $Bu^{t\bullet}$, it may well undergo rapid oxidation[5]) it is suggested that direct attack by $SO_4^{-\bullet}$ on the α-H is responsible for its generation.

These results appear to confirm those obtained with the Ti^{III}–$S_2O_8^{2-}$ couple and suggest that the principal mode of reaction under these conditions is decarboxylation, but that competitive loss of a secondary (and presumably tertiary) β- and/or γ-hydrogen is a significant pathway.

(vi) *Dicarboxylate ions.* The results from the oxidation of some dicarboxylate anions are also included in Table 2. In each case the predominant radical was that resulting from decarboxylation, the relative concentration of the other radicals present increasing with substrate concentration (evidently as a result of the attack of non-conjugated alkyl radicals at the α-position in the parent compounds).

(c) *Reactions of* $SO_4^{-\bullet}$ *with Related Substrates.*—The reactions of a series of amides were studied *via* photolysis of aqueous solutions containing $[S_2O_8^{2-}]$ (0.5 mol dm^{-3}), substrate (typically 0.025 mol dm^{-3}), and propanone (*ca.* 0.5 mol dm^{-3}) at pH *ca.* 4. Reactions of methanamide and ethanamide led to the detection of signals[14] from $^{\bullet}CONH_2$ [a(N) 2.125, a(1H) 3.00, 0.125 mT, g 2.0017] and[15] $^{\bullet}CH_2CONH_2$ [a(2H) 2.15, a(1H) 0.261, 0.22, a(N) 0.18 mT, 2.0030], respectively, both of which presumably arise *via* direct hydrogen-atom abstraction. With higher amides a clear pattern of reactivity at the β- and γ-hydrogen atoms is established: thus propanamide gave a clearly detectable signal from $^{\bullet}CH_2CH_2CONH_2$ [a(2H) 2.24, a(2H) 2.56 mT, g 2.0026; *cf.* ref. 15], together with some weak unanalysable lines, and butanamide gave $^{\bullet}CHMeCH_2CONH_2$ [a(1H) 2.12, a(3H) 2.51, a(2H) 2.18 mT, g 2.0026] and $^{\bullet}CH_2[CH_2]_2CONH_2$ [with a(2H) 2.16, a(2H) 2.725 mT, g 2.0026]. Although, as with $EtCONH_2$, other weak lines were present (these may be due in each case to the corresponding radicals formed by α-hydrogen-atom abstraction $^{\bullet}CHRCONH_2$, whose signals would be expected to be complex; *cf.* $^{\bullet}CH_2CONH_2$) it appears that the pattern of attack largely resembles that observed for the alkyl chains of the carboxylic acids already described.

Photolysis of an aqueous solution of ethanenitrile (1.0 mol dm^{-3}) containing $S_2O_8^{2-}$ (0.5 mol dm^{-3}) failed to yield a detectable concentration of radicals at low pH. Only when a pH of *ca.* 12 was employed were signals detected, from $^{\bullet}CH_2CN$ [a(2H) 2.09, a(N) 0.35 mT, g 2.0030].[16] Oxidation of propanenitrile gave $^{\bullet}CH_2CH_2CN$ [a(2H) 2.28, a(2H) 2.68 mT,[12] g 2.0026] in the pH range 1—10, and a mixture of this radical and $^{\bullet}CHMeCN$ [a(1H) 2.03, a(3H) 2.30, a(N) 0.35 mT, g 2.0029][16] at pH 12. 2-Methylpropanenitrile gave both $^{\bullet}CH_2CHMeCN$ [a(2H) 2.24, a(1H) 2.44 mT,[12] g 2.0026] and $^{\bullet}CMe_2CN$ [a(6H) 2.07, a(1N) 0.34 mT, g 2.0030] under both sets of conditions, with a greater proportion of the latter radical above pH *ca.* 10.

The failure to detect $^{\bullet}CH_2CN$ from ethanenitrile under acidic and mildly basic conditions is consistent with the behaviour of ethanoic acid in that an electron-withdrawing cyano group evidently inhibits attack by $SO_4^{-\bullet}$ at the adjacent C–H bonds; further, under similar conditions propanenitrile behaves like propanoic acid giving $^{\bullet}CH_2CH_2CN$ by direct β-H abstraction [reaction 17)]. The formation, from these two substrates, of α-substituted radicals at pH 12 is attributed to the production of the hydroxyl radical [reaction (18): *cf.* ref. 17] and its subsequent abstraction of both α- and β-hydrogen atoms [reaction (19)].

$$EtCN + SO_4^{-\bullet} \longrightarrow {}^{\bullet}CH_2CH_2CN + HSO_4^- \quad (17)$$

$$SO_4^{-\bullet} + OH^- \longrightarrow SO_4^{2-} + {}^{\bullet}OH \quad (18)$$

$${}^{\bullet}OH + EtCN \xrightarrow{-H_2O} {}^{\bullet}CHMeCN + {}^{\bullet}CH_2CH_2CN \quad (19)$$

These results confirm that $SO_4^{-\bullet}$ is more selective (*i.e.* more electrophilic) than $^{\bullet}OH$. The formation of $^{\bullet}CMe_2CN$, as well as $^{\bullet}CH_2CHMeCN$ from reaction of Me_2CHCN with $SO_4^{-\bullet}$ (as well as $^{\bullet}OH$) presumably reflects the extra stability associated with the more highly alkylated radical centre in the former.

Oxidation of a saturated solution of ethyl ethanoate containing sodium peroxydisulphate (0.5 mol dm^{-3}) resulted in the detection only of $^{\bullet}CH_2CH_2OCOCH_3$ [a(2H) 2.20, a(2H) 2.59 mT, g 2.0026].[18] Formation of $^{\bullet}CHMeOCOMe$ would also be anticipated, since the $+M$ effect of the alkoxy oxygen atom would be expected to encourage attack of $SO_4^{-\bullet}$ at the adjacent hydrogen: our failure to detect this species is attributed to the ease of oxidation of this oxygen-conjugated radical. A similar explanation is thought to underlie our failure to detect significant concentrations of radicals derived from the alkanols MeOH, EtOH, and Pr^{i}OH, and for which initial attack at the α-position would be expected (*cf.* the trapping of the appropriate radicals, ref. 9). On the other hand, strong signals were observed from $^{\bullet}CH_2CMe_2OH$ [a(2H) 2.13, a(6H) 0.14 mT, g 2.0026],[19] together with a weaker signal (*ca.* 20%) from methyl in the oxidation of 2-methylpropan-2-ol. We attribute the formation of the former to direct C–H hydrogen abstraction by $SO_4^{-\bullet}$ (*cf.* ref. 9); formation of the latter (which has not been previously reported) evidently involves rapid fragmentation of Bu^{t}O$^{\bullet}$ formed either by direct O–H hydrogen abstraction or electron abstraction and proton loss [reactions (20a) and (20b)].

$$Me_3COH + SO_4^{-\bullet} \longrightarrow \begin{cases} {}^{\bullet}CH_2CMeOH + HSO_4^- & (20a) \\ Me^{\bullet} + Me_2C{=}O + HSO_4^- & (20b) \end{cases}$$

(d) *Kinetic investigations.* The rate at which the sulphate radical anion reacts with an organic compound to give a specific radical is given by equation (21) and, providing the only significant mode of destruction of the radical so formed is bimolecular termination, its rate of decay is given by equation (22). If steady-state conditions apply, equation (23) should be obeyed.

$$\text{Rate of formation of } R^{\bullet} = k[RH][SO_4^{-\bullet}] \quad (21)$$

$$\text{Rate of termination of } R^{\bullet} = 2k_t[R^{\bullet}]^2 \quad (22)$$

$$d[R^{\bullet}]/dt = 0 = k[RH][SO_4^{-\bullet}] - 2k_t[R^{\bullet}]^2 \quad (23)$$

When there are two competing substrates (R^1H and R^2H) the rate of destruction of each radical contains a contribution from the cross-termination reaction; the appropriate steady-state equations for this system are (24)—(27).

Thus the relative rates of formation of radicals $R^{1\bullet}$ and $R^{2\bullet}$ should be given by equation (28). As the rate constants for bimolecular termination reactions of small, uncharged radicals are very similar[20] [*i.e.* $k_t = 2k_t(1) = 2k_t(2)$], equation (28) may be reduced to equation (29).*

$$d[R^{1\bullet}]/dt = 0 = k_1[R^1H][SO_4^{-\bullet}] - 2k_t(1)[R^{1\bullet}]^2 - k_t[R^{1\bullet}][R^{2\bullet}] \quad (24)$$

$$d[R^{2\bullet}]/dt = 0 = k_2[R^2H][SO_4^{-\bullet}] - 2k_t(2)[R^{2\bullet}]^2 - k_t[R^{1\bullet}][R^{2\bullet}] \quad (25)$$

$$k_1[R^1H][SO_4^{-\bullet}] = 2k_t(1)[R^{1\bullet}]^2 + k_t[R^{1\bullet}][R^{2\bullet}] \quad (26)$$

$$k_2[R^2H][SO_4^{-\bullet}] = 2k_t(2)[R^{2\bullet}]^2 + k_t[R^{1\bullet}][R^{2\bullet}] \quad (27)$$

$$\frac{k_1[R^1H]}{k_2[R^2H]} = \frac{2k_t(1)[R^{1\bullet}]^2 + k_t[R^{1\bullet}][R^{2\bullet}]}{2k_t(2)[R^{2\bullet}]^2 + k_t[R^{1\bullet}][R^{2\bullet}]} \quad (28)$$

$$\frac{k_1[R^1H]}{k_2[R^2H]} = \frac{[R^{1\bullet}]}{[R^{2\bullet}]} \quad (29)$$

Thus from a knowledge of one of the rate constants for radical formation, the concentrations of the competing substrates, and a measure of the relative radical concentrations, it should be possible to calculate the second rate constant.

The rate constant for the (overall) oxidation of 2-methylpropan-2-ol by the sulphate radical anion [*i.e.* both reactions (20a) and (20b)] has been estimated[10] to be 4×10^5 dm^3 mol^{-1} s^{-1}; therefore, a measurement of the relative radical concentrations in the competitive oxidation of this alcohol and a suitable substrate should enable the rate constant for reaction of the substrate with $SO_4^{-\bullet}$ to be estimated.

Photolysis of solutions of 2-methylpropan-2-ol (*ca.* 0.1 mol dm^{-3}) and ethanoic acid (0.1—0.5 mol dm^{-3}) containing 0.5 mol dm^{-3} sodium peroxydisulphate (conditions under which there is effectively no secondary radical formation) gave signals from $^{\bullet}CH_2CMe_2OH$ and $^{\bullet}Me$, the concentration of the latter increasing with increase in [CH_3CO_2H], as expected if steady-state conditions are indeed established. When allowance is made for the low concentration of Me$^{\bullet}$ derived *via* equation (20b), kinetic analysis yields a value for the rate constant for the abstraction of the carboxylic hydrogen atom from ethanoic acid of 2×10^4 dm^3 mol^{-1} s^{-1},† in reasonable agreement with a value previously obtained[17] from pulse radiolysis data. A similar treatment for the competitive oxidation of 2-methylpropan-2-ol and propanoic acid by the sulphate radical anion yielded values of 2×10^5 and 7×10^4 dm^3 mol^{-1} s^{-1} for the rate constants of reactions (4) and (5) respectively.†

When an equimolar mixture of 2-methylpropan-2-ol and sodium ethanoate was oxidized as already described, only Me$^{\bullet}$ was detected. On the other hand, with a relative concentration of 25:1 in favour of 2-methylpropan-2-ol over ethanoate, both $^{\bullet}CH_2CMe_2OH$ and Me$^{\bullet}$ were observed (with relative concentrations 0.67:1). Application of equation (29) yields a value of 1.2×10^7 dm^3 mol^{-1} s^{-1} for the rate of reaction (15) (*cf.* a value of 5×10^6 dm^3 mol^{-1} s^{-1} from ref. 11), indicating that the ethanoate ion is considerably more reactive than ethanoic acid towards $SO_4^{-\bullet}$. A similar increase for the generation of Et$^{\bullet}$ from propanoate as compared with propanoic acid was also found (1.2×10^7 dm^3 mol^{-1} s^{-1}).

The kinetic results obtained provide a more quantitative measure of the qualitative conclusions presented earlier, namely that the order of reactivity of different sites in acids and anions is as follows:

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* This analysis is only valid in the absence of competing reactions such as oxidation of the intermediate radicals.

† The rate constants obtained for these competitive experiments are believed to be accurate to within ±20%.

$$\mathrm{CO_2^-} > \beta\text{-H (and } \gamma\text{-H } etc.) > \mathrm{CO_2H} > \alpha\text{-H}$$

Our results appear to refute the suggestion made previously[8] that the formation of γ- and δ-lactones in the oxidation of straight-chain acids with $\mathrm{Na_2S_2O_8}$–$\mathrm{CuCl_2}$ results from *intramolecular* hydrogen-abstraction by $\mathrm{RCO_2}^{\bullet}$ or $\mathrm{RCO_2H}^{+\bullet}$. We confirm that there is *some* attack by $\mathrm{SO_4}^{-\bullet}$ at the carboxy group but decarboxylation thereby results; the radicals formed from positions along the chain are evidently derived *via* direct attack by $\mathrm{SO_4}^{-\bullet}$. Whilst a reasonable yield of product from γ-H and δ-H abstraction (and subsequent lactone formation) might be expected (certainly α-H attack is significantly retarded by the polar effect of $\mathrm{CO_2H}$ and primary C–H bonds are less susceptible to attack than methylene units), the selectivity reported may reflect the operation of other factors including, for example, the production of $\mathrm{Cl_2}^{-\bullet}$ (from Cl^- and $\mathrm{SO_4}^{-\bullet}$, *cf.* ref. 11) or the intervention of carbocations (*via* oxidation of radicals by *e.g.* $\mathrm{Cu^{II}}$) with the subsequent possibility of rapid rearrangements, or both.

Finally, we have suggested that in the oxidation of $\mathrm{MeCO_2H}$ the radical $^{\bullet}\mathrm{CH_2CO_2H}$ arises *via* hydrogen abstraction by $\mathrm{Me}^{\bullet}$, formed in the initial oxidative decarboxylation [reaction (3)]. Now under conditions where $[^{\bullet}\mathrm{CH_2CO_2H}] < [\mathrm{Me}^{\bullet}]$, the bimolecular termination of the former will occur essentially by reaction with the latter [reaction (30)]. Application of the

$$\mathrm{Me}^{\bullet} + {}^{\bullet}\mathrm{CH_2CO_2H} \longrightarrow \text{molecular product} \qquad (30)$$

steady-state principle to the concentration of $[^{\bullet}\mathrm{CH_2CO_2H}]$ leads to the expression (31). From this it follows that a

$$k_3 = k_{30}[^{\bullet}\mathrm{CH_2CO_2H}]/[\mathrm{MeCO_2H}] \qquad (31)$$

measurement of the absolute concentration of $^{\bullet}\mathrm{CH_2CO_2H}$ during the oxidation of ethanoic acid by the sulphate radical anion should enable the value of k_3 to be calculated. Photolysis of a solution (0.3 mol $\mathrm{dm^{-3}}$) of ethanoic acid containing sodium peroxydisulphate (0.5 mol $\mathrm{dm^{-3}}$) led to the detection of $^{\bullet}\mathrm{CH_2CO_2H}$ at a concentration of 1×10^{-7} mol $\mathrm{dm^{-3}}$. By assuming the rate constant for bimolecular termination to be 1.8×10^9 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$,[13] a value of k_3 of $6(\pm 3) \times 10^2$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ is obtained, which is in reasonable agreement with the value derived from related experiments with ethanoic acid in which the methyl radical was generated from the reaction of the hydroxyl radical (from the $\mathrm{Ti^{III}}$–$\mathrm{H_2O_2}$ couple) with dimethyl sulphoxide.[12]

Experimental

E.s.r. spectra were recorded with a Varian E-104 spectrometer equipped with 100 kHz modulation and an X-band klystron. Splitting constants were measured to within ±0.01 mT and *g* factors to within ±0.0001 by comparison with an aqueous solution of Fremy's salt [*a*(N) 1.3091 mT (ref. 21), *g* 2.0055 (ref. 22)]. Relative radical concentrations were determined by measurement of peak heights (where the appropriate linewidths were the same) or by spectrum simulation (using a program kindly supplied by Dr. M. F. Chiu). Absolute radical concentrations were obtained by comparison (using a Datalab DL4000 microcomputer) of the doubly integrated first-derivative signals with those obtained under identical conditions from a standard solution of $\mathrm{VOSO_4}$.

The flow-photolysis experiments were carried out using a flattened aqueous solution sample cell with a built-in two-way mixer, through which the solutions were forced either by gravity feed or by using a Watson-Marlow MHRE flow inducer (flow rate 1.5—2.5 $\mathrm{cm^3\ min^{-1}}$). The cell was irradiated in the cavity of the spectrometer using the unfiltered output of an Hanovia 977B-1 1 kW mercury–xenon compact arc. The two streams typically contained $\mathrm{Na_2S_2O_8}$ (either 0.2—0.5 mol $\mathrm{dm^{-3}}$ or 0.05 mol $\mathrm{dm^{-3}}$ with *ca.* 0.5 mol $\mathrm{dm^{-3}}$ propanone) and the substrate (typically up to *ca.* 10% solution). pH Adjustment was made using either ammonia solution (*d* 0.880) or concentrated sulphuric acid, and the pH measurements were made using a Pye-Unicam PW9410 pH meter with the electrode inserted into the effluent stream. All solutions were degassed prior to and during use by purging with oxygen-free nitrogen. The chemicals employed were commercial samples and used as supplied.

Acknowledgements

We thank the S.E.R.C. for studentships (for M. J. D. and J. Y.).

References

1 Part 68, M. J. Davies and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1809.
2 F. Minisci and A. Citterio, *Acc. Chem. Res.*, 1983, **16**, 27.
3 M. E. Snook and G. A. Hamilton, *J. Am. Chem. Soc.*, 1974, **96**, 860; C. Walling and D. M. Camaioni, *ibid.*, 1975, **97**, 1603.
4 R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc. B*, 1970, 1087.
5 M. J. Davies, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1984, 503.
6 L. Eberson, S. Gränse, and B. Olofsson, *Acta Chem. Scand.*, 1968, **22**, 2462.
7 W. C. Vasudeva, *J. Chem. Soc., Perkin Trans. 2*, 1975, 697.
8 G. I. Nikishin, I. V. Svitanko, and E. I. Troyansky, *J. Chem. Soc., Perkin Trans. 2*, 1983, 595.
9 H. Eibenberger, S. Steenken, P. O'Neill, and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1978, **82**, 749.
10 G. Behrens, E. Bothe, G. Koltzenburg, and D. Schulte-Frohlinde, *J. Chem. Soc., Perkin Trans. 2*, 1980, 883.
11 O. P. Chawla and R. W. Fessenden, *J. Phys. Chem.*, 1975, **79**, 2693.
12 B. C. Gilbert, R. O. C. Norman, G. Placucci, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 885.
13 P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 4207.
14 T. Yonezawa, I. Noda, and T. Kawamura, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 766.
15 T. Yonezawa, I. Noda, and T. Kawamura, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 650.
16 R. Livingston and H. Zeldes, *J. Magn. Reson.*, 1969, **1**, 169.
17 L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1967, **71**, 2511.
18 P. Smith, J. T. Pearson, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, 1965, **43**, 1535.
19 W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.
20 P. Neta, *Adv. Phys. Org. Chem.*, 1976, **12**, 223.
21 R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.
22 J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **46**, 654.

Received 15*th October* 1984; *Paper* 4/1759