An Electron Spin Resonance Study of Reactions of Carboxylic Acids with the Sulphate Radical-anion

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Radicals which mediate in the reactions of aliphatic carboxylate ions with the sulphate radical-anion, generated from the Ti^{III}–$K_2S_2O_8$ couple, have been observed by e.s.r. spectroscopy. Both oxidative decarboxylation ($RCO_2^- \longrightarrow R\cdot$) and hydrogen-atom abstraction from C–H occur. The behaviour of $SO_4^{-\cdot}$ is compared with that of ·OH.

THE sulphate radical-anion, $SO_4^{-\cdot}$, and the hydroxyl radical show some distinct differences in their reactions with organic compounds in aqueous solution. Thus, unlike the latter, $SO_4^{-\cdot}$ abstracts a hydrogen atom from the O–H bond of methanol[1] (the resulting MeO· radical can yield $\cdot CH_2OH$ in a subsequent reaction), and shows a greater propensity for effectively removing one electron from some aromatic compounds.[2] Certain similarities in the distribution of products from carboxylates with the sulphate radical-anion and upon anodic oxidation have led to the suggestion that the former occurs as in reaction (1).[3] This would again contrast with the reactions of carboxylates with the hydroxyl radical, where abstraction of hydrogen from C–H is observed, and in order to gain further information we have studied the reactions of some carboxylates with $SO_4^{-\cdot}$ by e.s.r. spectroscopy.

$$RCO_2^- + SO_4^{-\cdot} \longrightarrow R\cdot + CO_2 + SO_4^{2-} \quad (1)$$

The reactions were carried out by mixing aqueous solutions of titanium(III) chloride, potassium persulphate, and the carboxylic acid shortly before passage of the combined solution through the cavity of the e.s.r. spectrometer; the titanium(III) solution contained EDTA as a sequestering agent and enough ammonia to give pH *ca.* 9 after mixing. Under these conditions, the sulphate radical-anion is generated according to reaction (2).[2] The radicals detected, and their hyperfine splitting constants and *g*-factors, are shown in the

$$Ti^{III} + S_2O_8^{2-} \longrightarrow Ti^{IV} + SO_4^{-\cdot} + SO_4^{2-} \quad (2)$$

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[2] R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc.* (*B*), 1970, 1087.

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Table; for those radicals for which measurements have been reported previously for aqueous solution at room temperature, we obtained the same e.s.r. parameters within experimental error. No radicals could be detected from ethylene glycol, glycerol, or sorbitol. Likewise, no radicals or only weak signals were obtained from the carboxylates at pH 6—8, although the acids are essentially fully ionised in this region; possibly the rate at which $\mathrm{SO_4^{-\cdot}}$ is removed by reduction by $\mathrm{Ti^{III}}$–EDTA complexes decreases at higher pH owing to acquisition of increased negative charge on the complexes and thus of charge repulsion between these reactants.

When the oxidation of acetic acid was carried out with hydrogen peroxide in place of potassium persulphate, so as to generate the hydroxyl radical, the only radical which could be detected was $\cdot\mathrm{CH_2CO_2^-}$. This result, in contrast to the detection of solely the methyl radical with the persulphate system, demonstrates two points. First, although the sulphate radical-anion is converted in water into the hydroxyl radical at a rate which increases rapidly as the pH is increased above *ca.* 8 [reaction (3)],[4] this process can be

$$\mathrm{SO_4^{-\cdot} + OH^- \longrightarrow SO_4^{2-} + \cdot OH} \qquad (3)$$

of little importance under our conditions compared with the rate at which the sulphate radical-anion reacts with acetate ion. Secondly, $\mathrm{SO_4^{-\cdot}}$, unlike $\cdot\mathrm{OH}$, reacts preferentially at the carboxylate group; we infer the occurrence of electron transfer, as in reaction (1; R = Me), possibly with mediation of $\mathrm{MeCO_2\cdot}$ in the formation of $\mathrm{Me\cdot}$.

Radicals detected during the oxidation of carboxylic acids with the $\mathrm{Ti^{III}}$–$\mathrm{S_2O_8^{2-}}$ couple at pH *ca.* 9

		Hyperfine splitting constants (mT) [a]			
Reactant	Radical	α-H	β-H	*g*	Ref.
$\mathrm{HCO_2^-}$	$\cdot\mathrm{CO_2^-}$			2·0005	*c*
$\mathrm{CH_3CO_2^-}$	$\cdot\mathrm{CH_3}$	2·30		2·0025	*d*
$\mathrm{CH_3CH_2CO_2^-}$	$\cdot\mathrm{CH_2CH_3}$	2·23	2·73	2·0026	*d*
	$\cdot\mathrm{CHMeCO_2^-}$	2·04	2·50	2·0034	*d*
	$\cdot\mathrm{CH_2CH_2CO_2^-}$	2·22	2·58	2·0026	*d*
$\mathrm{Me_2CHCO_2^-}$	$\cdot\mathrm{CHMe_2}$	2·18	2·51	2·0026	
	$\cdot\mathrm{CMe_2CO_2^-}$		2·21	2·0032	*d*
	$\cdot\mathrm{CH_2CHMeCO_2}$	2·23	2·54	2·0027	
$\mathrm{Me_3CCO_2^-}$	$\cdot\mathrm{CMe_3}$		2·27	2·0025	*e*
	$\cdot\mathrm{CH_2CMe_2CO_2^-}$	2·18	0·06 [b]	2·0025	
$\mathrm{CH_2(CO_2^-)_2}$	$\cdot\mathrm{CH_2CO_2^-}$	2·13		2·0033	*d*
$\mathrm{^-O_2C(CH_2)_2CO_2^-}$	$\cdot\mathrm{CH_2CH_2CO_2^-}$	2·23	2·59	2·0026	*d*
	$\cdot\mathrm{CH(CO_2^-)CH_2CO_2^-}$	2·06	2·34	2·0033	*d*
$\mathrm{HOCH_2CO_2^-}$	$\cdot\mathrm{CH(OH)CO_2^-}$	1·43		2·0043	
$\mathrm{^-O_2CCH(OH)CH_2CO_2^-}$	$\cdot\mathrm{CH_2CH(OH)CO_2^-}$	2·21	2·77	2·0026	
$\mathrm{^-O_2CCH_2C(OH)(CO_2^-)CH_2CO_2^-}$	$\cdot\mathrm{CH_2C(OH)(CO_2^-)CH_2CO_2^-}$	2·23		2·0026	
	$\cdot\mathrm{CH(CO_2^-)C(OH)(CO_2^-)CH_2CO_2^-}$	2·02		2·0033	*f*
$\mathrm{OCHCO_2^-}$	$\cdot\mathrm{CH(OH)CO_2^-}$	1·43		2·0043	

[a] α- and β-H refer respectively to protons attached to the tervalent carbon atom and to an adjacent carbon atom. [b] Splitting from the six protons in the methyl groups (γ-H). [c] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389. [d] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 400. [e] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 308. [f] H. Zeldes and R. Livingston, *J. Amer. Chem. Soc.*, 1971, **93**, 1082.

The propensity for attack by $\mathrm{SO_4^{-\cdot}}$ at carboxylate groups is also revealed by all the other reactants in the Table except formate, glycolate, and glyoxylate; these three are discussed later. The ratios of the observed concentrations of radicals from propionate were $[\mathrm{Et\cdot}]:[\cdot\mathrm{CHMeCO_2^-}]:[\cdot\mathrm{CH_2CH_2CO_2^-}] =$ *ca.* 3 : 4 : 1, and, for those from isobutyrate, $[\cdot\mathrm{CHMe_2}]:[\cdot\mathrm{CMe_2CO_2^-}]:[\cdot\mathrm{CH_2CHMeCO_2^-}] =$ *ca.* 1 : 2 : 1; thus, along the series acetate, propionate, isobutyrate, abstraction of hydrogen from the carbon adjacent to carboxylate increases in importance relative to reaction (1), probably because increased alkylation is electronically favourable to reaction of the electrophilic [2] sulphate radical-anion at the adjacent C–H bond.

The failure of glycolate to yield a detectable concentration of the radical, $\cdot\mathrm{CH_2OH}$, which would result from oxidative decarboxylation probably results from the rapid rate of oxidation of this radical by persulphate,[2] rather than from an unusually slow rate of formation. The absence of radicals from the oxidation of ethylene glycol, glycerol, and sorbitol is likely to stem also from rapid oxidation of hydroxy-conjugated radicals, for, as judged by the rate constants for reaction of some simple alcohols by $\mathrm{SO_4^{-\cdot}}$ which are in the range [4] 10^7—10^8 l $\mathrm{mol^{-1}\ s^{-1}}$, the formation rates for the radicals from the diol and the two polyols should be fast. It is notable that the radical $\cdot\mathrm{CH(OH)CO_2^-}$ can be detected from glycolate; possibly the carboxylate ion reduces the rate of oxidation of this radical by persulphate ion, compared with that of $\cdot\mathrm{CH_2OH}$, through charge repulsion.

The formation of the same radical, $\cdot\mathrm{CH(OH)CO_2^-}$, from glyoxylate ion as from glycolate suggests that the former ion is oxidised as its hydrate (oxidation should be facilitated by the two hydroxy-groups) to give radical (1) which, again on account of the two hydroxy-substituents,[5] should be an effective one-electron reducing agent for a further molecule of glyoxylate as in reaction (5).

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Finally, the formation of $\cdot CO_2^-$ from formate ion may occur by electron transfer to $SO_4^{-\cdot}$ to give $HCO_2\cdot$,

$$(HO)_2CH\cdot CO_2^- \xrightarrow{SO_4^{-\cdot}} \underset{(1)}{(HO)_2\dot{C}\cdot CO_2^-} \qquad (4)$$

$$(HO)_2\dot{C}\cdot CO_2^- + O{:}CH\cdot CO_2^- \longrightarrow H^+ + HO_2C\cdot CO_2^- + {}^-O\cdot\dot{C}H\cdot CO_2^- \qquad (5)$$

followed by proton loss, in preference to direct hydrogen-atom abstraction. It is interesting that $\cdot CO_2^-$ is less rapidly oxidised by persulphate ion (k[6] $5{\cdot}3 \times 10^4$ l mol^{-1} s^{-1}) than by hydrogen peroxide (k[7] 7×10^5 l mol^{-1} s^{-1}), although evidently the reverse holds for (uncharged) hydroxy-conjugated radicals; this may represent a further example of the importance of charge repulsion.

EXPERIMENTAL

A Varian E-3 spectrometer with 100 kHz modulation and an X-band klystron was employed in conjunction with an aqueous flat cell and a mixing chamber which enabled three reagent streams to be mixed simultaneously *ca.* 0·02 s before the combined solution entered the spectrometer cavity. One reagent stream contained 0·04M-potassium persulphate; the second contained 0·008M-titanium(III) chloride, disodium ethylenediaminetetra-acetate (6 g l^{-1}), and enough ammonia (*d* 0·88) (*ca.* 4M) to give a pH after mixing of *ca.* 9; and the third stream contained the carboxylic acid. The following concentrations were found to give radical concentrations in the cavity suitable for e.s.r. measurements: formic and acetic acids, 3M; propionic acid, 0·5M; isobutyric acid, 0·3M; pivalic, malonic, succinic, and malic acid, 0·2M; glycolic and citric acid, 0·1M; glyoxylic acid, 0·07M.

Splitting constants were measured to within ±0·01 mT and *g* factors to within ±0·0001 by comparison with Fremy's salt [*a*(N) 1·3091 mT,[8] *g*[9] 2·0055].

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