Electron Spin Resonance Studies. Part 56.[1] An Investigation of the Role of Aromatic Radical-zwitterions and Acyloxyl Radicals in the One-electron Oxidation of Aromatic Carboxylates and Reduction of Aromatic Peroxy-acids

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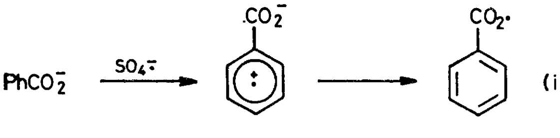
The results are described of an e.s.r. investigation into the reactions of some aromatic radical-zwitterions $^{+\cdot}ArCO_2^-$ (derived by one-electron oxidation of benzoate and related ions with $SO_4^{-\cdot}$) and some aroyloxyl radicals $ArCO_2\cdot$ (derived by reduction of some peroxybenzoic acids with Ti^{III}). The radicals have been generated in an aqueous flow system at high pH: the nitromethane anion $CH_2{:}NO_2^-$ has been employed as a spin trap in order to elucidate the reaction mechanisms. Evidence is presented which accords with the suggestion that the species $^{+\cdot}ArCO_2^-$ and $ArCO_2\cdot$ are distinct chemical entities, rather than canonical forms of a single intermediate. A variety of differently substituted aroyloxyl radicals ($ArCO_2\cdot$) rapidly lose CO_2 to give aryl radicals ($Ar\cdot$); an exceptional case is the rapid intramolecular hydrogen atom abstraction reaction of 2-methylbenzoyloxyl. There is evidence that the radical-zwitterions $^{+\cdot}ArCO_2^-$ undergo a variety of reactions depending on their structure: most undergo conversion into aroyloxyl radicals; in addition, 2- and 4-methyl-substituted derivatives also rapidly deprotonate (to yield the appropriate benzyl species), whereas methoxy-substituted species undergo ready one-electron reduction by Ti^{III}. Rate constants are reported for the one-electron reduction of persulphate ion by titanium(III) at pH 2.5 and 9.

E.S.R. investigations of the reactions of a variety of benzenoid compounds with the sulphate radical-anion, $SO_4^{-\cdot}$, have provided evidence that the first step is the removal of an electron from the aromatic ring to give a radical-cation.[2-4] With a variety of methoxy-substituted benzoate anions, the resulting species can be detected directly by e.s.r.,[4] but in other cases the evidence is circumstantial.

We now consider the oxidation of the benzoate ion itself and some derivatives. It is already known that benzoate yields the benzoyloxyl radical and thence the phenyl radical; both have been identified by e.s.r. through the adducts which they form with $CH_2{:}NO_2^-$,[5,6] and some substituted phenyl radicals have been themselves detected.[5] We are concerned particularly with the question of whether the first formed[3] radical-zwitterion (1) is converted into the benzoyloxyl radical (2), as represented in reaction (i), or whether (1) and (2) are simply representations of a single species; if the former were the case, we wished to ascertain the conditions under which the conversion occurs and the alternative fates of the radical-zwitterions.



(i)

(1) (2)

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[1] Part 55, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, (*S*) 173; (*M*) 1974.

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

[3] P. Neta, V. Madhavan, H. Zemel, and R. W. Fessenden, *J. Amer. Chem. Soc.*, 1977, **99**, 163.

[4] S. Steenken, P. O'Neill, and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1977, **81**, 26.

[5] H. Zemel and R. W. Fessenden, *J. Phys. Chem.*, 1975, **79**, 1419.

[6] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

RESULTS AND DISCUSSION

Our strategy was to study the reactions of the sulphate radical-anion, generated by reaction (ii), and benzoate and related ions, and to compare them with those of titanium(III) ion and the corresponding aromatic peroxyacids, since the latter reactions are already known to give aroyloxyl radicals such as (2) by reaction (iii) and thence aryl radicals.[7] Since aroyloxyl radicals cannot be detected directly by e.s.r. in fluid solution,[8] we made extensive use of the anion $CH_2{:}NO_2^-$ as a spin-trap [6] for e.s.r. characterisation [reactions (iv) and (v)].

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

$$Ti^{III} + ArCO_2OH \longrightarrow Ti^{IV} + ArCO_2\cdot + OH^- \quad \text{(iii)}$$

$$ArCO_2\cdot + CH_2{:}NO_2^- \longrightarrow ArCO_2CH_2NO_2^{-\cdot} \quad \text{(iv)}$$

$$Ar\cdot + CH_2{:}NO_2^- \longrightarrow ArCH_2NO_2^{-\cdot} \quad \text{(v)}$$

The method involved the simultaneous mixing of three reagent streams immediately before passage through the e.s.r. spectrometer cavity. One contained titanium(III) ion complexed with EDTA, the second contained nitromethane, and the third either potassium persulphate or the peroxy-acid; in the former case, the aromatic acid was contained in the titanium(III) solution. The pH after mixing was *ca.* 9.

Hyperfine splittings of radical-anions $RCH_2NO_2^{-\cdot}$ formed (A) by the reduction of $ArCO_2OH$ with Ti^{III}, and (B) by the oxidation of $ArCO_2^-$ with $SO_4^{-\cdot}$

			Hyperfine splittings (mT)		
Ar	R	Method	*a* (1 N)	*a* (2 H)	*a* (other)
Ph	Ph	A, B	2.58	0.95	
	$PhCO_2$	A, B	2.40	0.74	
m-ClC_6H_4	*m*-ClC_6H_4	A, B	2.60	0.88	
	m-$ClC_6H_4CO_2$	A, B	2.375	0.725	
o-$^-O_2CC_6H_4$	*o*-$^-O_2CC_6H_4$	A, B	2.57	1.00	
	o-$^-O_2CC_6H_4CO_2$	A, B	2.38	0.73	
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	A [a]	2.565	0.95	
	p-$CH_3C_6H_4CO_2$	A, B	2.39	0.74	
	p-$^-O_2CC_6H_4CH_2$	A, B	2.55	0.945	0.076 (2 H)
o-$CH_3C_6H_4$	*o*-$CH_3C_6H_4CO_2$	A, B	2.39	0.725	
	o-$^-O_2CC_6H_4CH_2$	A, B	2.55	0.945	0.076 (2 H)
p-$MeOC_6H_4$	*p*-$MeOC_6H_4$	A [a]	2.575	0.95	
	p-$MeOC_6H_4CO_2$	A	2.34	0.70	
o-$MeOC_6H_4$	*o*-$MeOC_6H_4CO_2$	A	2.335	0.71	

[a] Generated also from the diazonium salt with Ti^{III} in the presence of $CH_2{:}NO_2^-$.

Most of the results are collected in the Table; others are described later. For those radicals which have not been characterised by their e.s.r. spectra before, the assignments follow from the hyperfine splittings as discussed previously for similarly constituted radicals.[5-7] In addition, some or all of the following other radicals were usually identified when the titanium(III)–persulphate system was employed: $CH_3NO_2^{-\cdot}$,[9] $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$,[10] $^-O_3SO{\cdot}CH_2NO_2^{-\cdot}$,[5] and $HOCH_2NO_2^{-\cdot}$.[11] The first three are usually detected when this system is used, and the last could be the result either of hydrolysis of $^-O_3SO{\cdot}CH_2NO_2^{-\cdot}$ or of formation of hydroxyl radicals from $SO_4^{-\cdot}$ in the basic conditions.[12] With the titanium(III)–peroxyacid system, the radicals $CH_3NO_2^{-\cdot}$ and $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$ were usually detected [7] in addition to those from the aromatic compound.

The results obtained on oxidation by the sulphate radical-anion of benzoate, *m*-chlorobenzoate, and phthalate ion were essentially the same as those from the corresponding peroxyacids with titanium(III) ion, namely, the trapping of both aroyloxyl and aryl radicals. Moreover, for each method of generation, an increase in the concentration of the trap caused an increase in the ratio of the observed concentrations of the radical-anions $ArCO_2CH_2NO_2^{-\cdot}$ and $ArCH_2NO_2^{-\cdot}$. This is as expected if $Ar\cdot$ is formed by way of $ArCO_2\cdot$.

The reactivity of benzoate ion towards $SO_4^{-\cdot}$ was compared with that of acetate ion by oxidising an equimolar mixture of the two carboxylates with the titanium(III)–persulphate couple. The adducts formed by $CH_2{:}NO_2^-$ with both the phenyl and the benzoyloxyl radical were observed, but not that of the methyl radical (although this is known to be formed [13] when acetate ion alone is oxidised by $SO_4^{-\cdot}$); the same result was obtained even with a ten-fold excess of acetate over benzoate. This result would not be expected if benzoate were to be oxidised, like acetate, at the carboxylate group; indeed, because phenyl is electron attracting relative to methyl, the opposite would have been expected. However, it is in keeping with the view that benzoate is oxidised by attack at the aromatic nucleus, to form the radical-zwitterion; evidently this is kinetically preferred to simple one-electron transfer through the carboxylate ion.

When phthalate ion was oxidised by $SO_4^{-\cdot}$ in the absence of the trap, a radical with *a*(1H) 4.19, *a*(1H) 0.854, *a*(1H) 0.264, and *a*(1H) 0.769 mT was detected, consistent [5] with structure (3). It is notable that, when $SO_4^{-\cdot}$ is generated by photolysis, in the presence

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[7] B. C. Gilbert, R. G. G. Holmes, P. D. R. Marshall, and R. O. C. Norman, *J. Chem. Research*, 1977, (*S*) 172; (*M*) 1949.

[8] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

[9] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590.

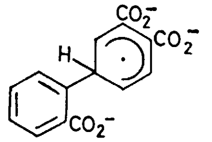
[10] D. J. Edge, R. O. C. Norman, and P. M. Storey, *J. Chem. Soc.* (*B*), 1970, 1096.

[11] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

[12] L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1967, **71**, 2511; E. Hayon, A. Treinin, and J. Wilf, *J. Amer. Chem. Soc.*, 1972, **94**, 47.

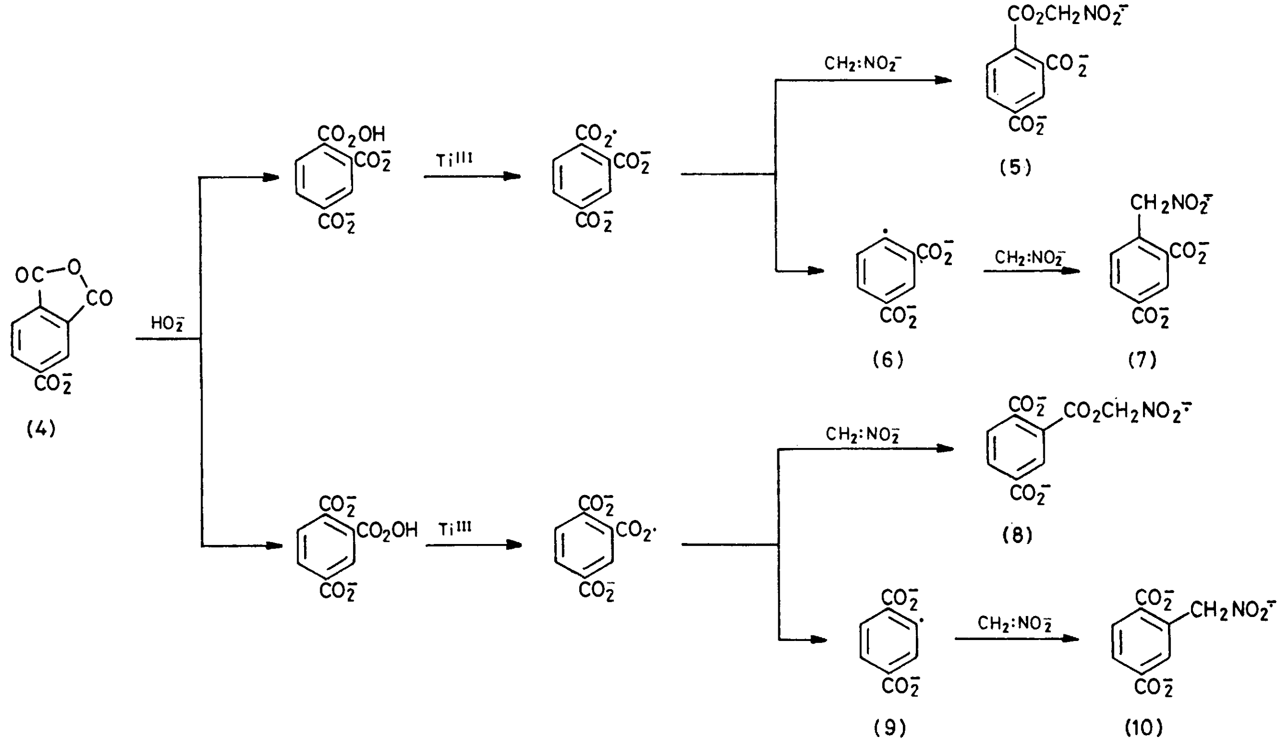
[13] W. C. Vasudeva, *J.C.S. Perkin II*, 1975, 697.

of a much lower concentration of phthalate ion than was necessary in our experiments, the aryl radical is itself detected.[5]



(3)

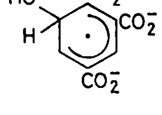
When the anhydride (4) was perhydrolysed[7] before reaction with titanium(III) ion, no radicals were detected in the absence of $CH_2{:}NO_2^-$, but in its presence two strong spectra [a(N) 2.55, a(2H) 0.975 mT; and a(N) 2.57, a(2H) 1.04 mT] and two weak spectra [a(N) 2.40, a(2H) 0.85 mT; and a(N) 2.37, a(2H) 0.74 mT] were recorded, together with those of $CH_3NO_2^{-\cdot}$ and a trace of $HOCH_2NO_2^{-\cdot}$. The parameters of the former pair are consistent with their being the adducts formed from the aryl radicals (6) and (9) [*i.e.* (7) and (10), although the individual assignments cannot be made] and those of the latter pair with their being the adducts formed from the corresponding aroyloxyl radicals. These results are entirely as expected.[7]



SCHEME

When the oxidation of benzene-1,2,4-tricarboxylate ion by $SO_4^{-\cdot}$ was carried out in the presence of the trap, the spectrum was complex, but lines from the adducts (7) and (10) were clearly discerned.

In this case, oxidation in the absence of the trap also gave detectable radicals providing that the pH was as high as *ca.* 10. They were identified by their hyperfine splittings[14] as the hydroxy-adducts (11)—(13); their relative concentrations (2 : 1 : 1) remained unchanged when [$S_2O_8^{2-}$] was reduced three-fold. These radicals are also formed by addition of the hydroxyl radical to benzene-1,2,4-tricarboxylate ion,[14] and it is probable that under our conditions they are formed in this way also, for two reasons. First, the rate of hydrolysis of $SO_4^{-\cdot}$, to give •OH, increases with pH, and at pH 10 can be expected[12] to be rapid. Secondly, when we generated hydroxyl radicals from the titanium(III)–hydrogen peroxide couple in the presence of benzene-1,2,4-tricarboxylate ion, the observed concentrations of the adducts (11)—(13) were again as 2 : 1 : 1, provided that a relatively low concentration of hydrogen peroxide was used.*



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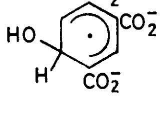

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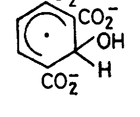

(13)

In the following two cases, oxidation of $ArCO_2^-$ by $SO_4^{-\cdot}$ and reduction of the corresponding peroxyacid by

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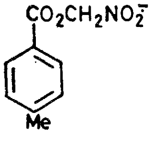
* Interestingly, the ratio changed to 1 : 1 : 0.75 when [H_2O_2] was increased three-fold, implying that the oxidations of the radicals (11)—(13) by H_2O_2 have different rate constants (*cf.* ref. 15). The constancy of the ratio with variation in [$S_2O_8^{2-}$] suggests that oxidation is in this case slow, perhaps because of charge repulsion.

[14] G. Filby and K. Gunther, *J. Phys. Chem.*, 1974, **78**, 1521.

[15] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1974, 824.

titanium(III) ion led to contrasting e.s.r. observations in the presence of the trap. First, *p*-peroxytoluic acid and titanium(III) ion gave not only the adducts (14) and (15) of the expected acyloxyl and aryl radicals, but also species (16), characterised by the two sets of methylene proton splittings, with the ratio [(16)] : [(14)] $\ll 1$. The *p*-toluate–$SO_4^{-\cdot}$ system also yielded both (14) and (16), with no detectable spectrum of (15), but in this case the ratio [(16)] : [(14)] was $\gg 1$. Of especial significance was the observation that, whereas with the former system the ratios [(16)] : [(14)] and [(15)] : [(14)] both decreased with increase of $[CH_2{:}NO_2^-]$, in keeping with the expected formation of both the *p*-tolyl and the benzylic radical (17) from the *p*-toluoyloxyl radical, with the latter system the ratio [(16)] : [(14)] remained constant when $[CH_2{:}NO_2^-]$ was increased. Further, in the absence of the trap, the titanium(III)–peroxyacid system and the *p*-toluate–$SO_4^{-\cdot}$ system gave, respectively, weak and strong signals assigned, from their hyperfine splittings [16] [*a*(2H) 1.613, *a*(2H) 0.506, *a*(2H) 0.176 mT], to the benzylic radical (17).



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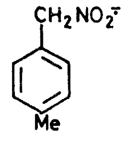

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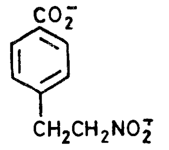

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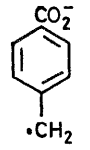
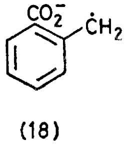


(17)

Exactly corresponding observations were made with *o*-toluate and the corresponding peroxyacid except that, first, the concentration of the radical (18) detected from the peroxyacid in the absence of the trap [*a*(2H) 1.625, *a*(1H) 0.615, *a*(1H) 0.512, *a*(2H) 0.176 mT] was far stronger than that of (17) from *p*-peroxytoluic acid; and secondly, in the trapping experiment, the detected concentration of the radical (19) was far higher than that of the trapped acyloxyl radical.



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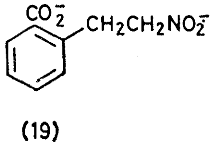


(19)

The e.s.r. observations of the *p*-methoxyperoxybenzoic acid–titanium(III) and the *p*-methoxybenzoate–$SO_4^{-\cdot}$ systems also differed markedly. In the presence of the trap, the former system yielded the expected acyloxyl and aryl adducts, as well as $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$, $CH_3NO_2^{-\cdot}$, and $HOCH_2NO_2^{-\cdot}$. The strongest spectrum was that of $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$; that of the aryl adduct was relatively weak and its lines were only just separated from those of the dinitro species, but the assignment was verified by independent generation of the species from [17] *p*-methoxybenzenediazonium ion and titanium(III). The hydroxy adduct doubtless arose from a small amount of hydrogen peroxide, since the peroxyacid, prepared from the acid chloride and alkaline hydrogen peroxide, was not purified extensively (*cf.* ref. 7). As expected, the ratio of the observed concentrations of the aroyloxyl and aryl adducts increased with increase in $[CH_2{:}NO_2^-]$. On the other hand, no signal could be detected when *p*-methoxybenzoate was oxidised by the titanium(III)–persulphate couple, either in the presence or in the absence of the trap.

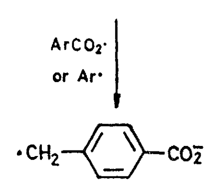
o-Methoxyperoxybenzoic acid behaved similarly with titanium(III) in giving the adduct of the aroyloxyl radical and $CH_2{:}NO_2^-$; had the aryl adduct been present, its resonances would have been obscured by those of $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$ if its splittings were *ca.* 2.6 (1N) and 1.1 mT (2H). However, no aroyloxyl or aryl adducts were detected with the *o*-methoxybenzoate–$SO_4^{-\cdot}$ system, although $O_2N{\cdot}CH_2CH_2{\cdot}NO_2^{-\cdot}$, $HOCH_2NO_2^{-\cdot}$, and $^-O_3SO{\cdot}CH_2NO_2^{-\cdot}$ were observed. No radicals were detected with the *m*-methoxybenzoate–$SO_4^{-\cdot}$ system.

Mechanisms of Reaction.—(i) *The aromatic peroxyacid–titanium*(III) *system.* The observations of aroyloxyl and aryl adducts with $CH_2{:}NO_2^-$, and the variation of their concentrations with $[CH_2{:}NO_2^-]$, are consistent with the sequence [7] in reaction (vi). There remains only the formation of the benzylic radicals (17) and (18) from *p*- and *o*-peroxytoluic acid.

$$\mathrm{ArCO_2OH \xrightarrow{Ti^{III}} ArCO_2\cdot \longrightarrow Ar\cdot + CO_2} \qquad \text{(vi)}$$

When *p*-toluate was oxidised with the PhN_2^+–Ti^{III} couple, a weak spectrum of the radical (17) was observed, indicating that the phenyl radical can abstract a hydrogen atom from the methyl group of toluate. Further, the weak signal of the radical (17) from the *p*-peroxytoluic acid–titanium(III) system was considerably intensified when *p*-toluate was included. We infer that *p*-toluate formed from the peroxyacid–titanium(III) system yields the radical (17) with the *p*-tolyl and/or the *p*-toluoyloxyl radical [reaction (vii; Ar = *p*-tolyl)].

The much stronger spectra of the radicals (19) and (18) from *o*-toluate, with and without the trap, compared with (16) and (17) respectively, strongly suggests the occurrence of intramolecular hydrogen-atom transfer in



(vii)

this case [reaction (viii)]. This is evidently a very rapid process since it competes effectively with the trapping of the acyloxyl radical, which is expected [7] to be fast, and it is also a more rapid process than decarboxylation, since there was no trace of the aryl adduct of $CH_2{:}NO_2^-$.

(ii) *The aromatic carboxylate*–$SO_4^{-\cdot}$ *system.* If radical-

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[16] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4857.

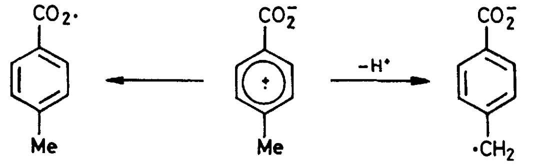
[17] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 403.

zwitterions related to (1) were simply canonical representations of aromatic acyloxyl radicals related to (2),

(viii)

the e.s.r. observations of the aromatic carboxylate–$SO_4^{-\cdot}$ system would have been essentially the same as those of the corresponding peroxyacid–titanium(III) system. The marked differences with *p*- and *o*-toluate and with *p*- and *o*-methoxybenzoate show that this cannot be so; * they are consistent with the occurrence of reaction (i) and also point to alternative reactions for radical-zwitterions such as (1).

The crucial observation in the oxidation of the *p*-toluate ion with $SO_4^{-\cdot}$ is that the relative observed concentrations of the adducts of the trap with the acyloxyl radical and with the benzylic radical (17) did not change with increase in $[CH_2{:}NO_2^-]$. This is in contrast to the behaviour shown by the *p*-peroxytoluic–titanium(III) system, and is not consistent with formation of the latter radical from the former. However, it is in accord with mediation of the radical-cation (20); the partitioning of this between conversion into the acyloxyl radical and deprotonation to yield the benzylic radical would be independent of $[CH_2{:}NO_2^-]$. The behaviour of *o*-toluate can be accounted for similarly.



(20)

When *p*-methoxybenzoate ion is oxidised by photolytically generated $SO_4^{-\cdot}$, the e.s.r. spectrum of its radical-cation is observed.[4] We should certainly have expected it to be formed under our conditions, and our failure to detect it could be the result of its being reduced back to *p*-methoxybenzoate ion by titanium(III) ion faster than it is converted into the trappable acyloxyl radical. It has been suggested that the anisole radical-cation is reduced efficiently by iron(II) in acid solution, accounting for the low yields of hydroxyanisoles from anisole and Fenton's reagent.[18,19]

We have identified, then, three possible fates for the radical-zwitterions from aromatic carboxylates: (*a*) reorganisation to give the acyloxyl radical, which was observed in all cases except for the methoxybenzoates; (*b*) one-electron reduction; (*c*) deprotonation (for methyl-substituted compounds) to give benzylic radicals. We have so far no evidence for a fourth fate, hydration, to yield a hydroxycyclohexadienyl radical, although this would be expected to occur since there is evidence that it does so in the case of the benzene radical-cation.[2] However, it is not yet possible fully to elucidate the factors which determine which path is preferred. In particular, why should the radical-zwitterion from *p*-methoxybenzoate preferentially undergo reduction? Possibly it fails to yield the acyloxyl radical rapidly because, compared with the other radical-zwitterions which do so, it is well stabilised by accommodation of the positive charge by the methoxy oxygen; and possibly it fails to yield a detectable concentration of the hydroxycyclohexadienyl radical because, for the same reason, hydration is slow. These suggestions are consistent with the relatively long-life of the species which is implied by its direct observation when it is generated in the absence of a reducing species.[5]

Kinetic Studies.—We have measured the rate constant for reaction (ii) at pH 9 [with titanium(III) complexed by EDTA] and pH 2.5. The method (*cf.* refs. 20 and 21) was to employ a compound which would react with $SO_4^{-\cdot}$ to give an observable radical, at such a concentration that scavenging of $SO_4^{-\cdot}$ was essentially complete, and then to vary the concentration of persulphate until that of the detected radical was maximised. Under these conditions,[20] $[S_2O_8^{2-}]_0 = 1/kt$, where $[S_2O_8^{2-}]_0$ is the initial concentration of persulphate, *k* is the desired rate constant, and *t* is the time between mixing and observation; *t* was measured independently [21] as 72 ms. For pH 9, acetate ion was used as the substrate, and the concentration of the resulting [13] methyl radical was determined; complete scavenging was found to occur with $\geqslant$3M-acetate, and $[S_2O_8^{2-}]_0$ for $[\cdot CH_3]_{max.}$ was determined as 0.17M, yielding *k* 82 ($\pm$16) dm^3 mol^{-1} s^{-1}. For pH 2.5, the system used was allyl alcohol (1M) and $[S_2O_8^{2-}]_0$ for [2] $[^-O_3SOCH_2\dot{C}HCH_2OH]_{max.}$ was estimated as 0.285M giving *k* 49 ($\pm$10) dm^3 mol^{-1} s^{-1}. As in the production of hydroxyl radicals from the titanium(III)–hydrogen peroxide couple, *k* increases with pH, but the rate constants are notably lower than in the peroxide system [22] (*e.g.* *k* 590 dm^3 mol^{-1} s^{-1} at pH 1 in sulphuric acid).

EXPERIMENTAL

Peroxybenzoic acid and *p*-methoxyperoxybenzoic acid were prepared by alkaline perhydrolysis of the parent acid chloride.[23] *o*-Methoxyperoxybenzoic acid [24] and *o*- and *p*-peroxytoluic acids [25] were prepared from the corresponding diaroyl peroxide. Benzene-1,2,4-tricarboxylic mono-

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* *Note added in proof.* In accord with this, recent work has indicated that the unpaired electron in the benzoyloxyl radical occupies an in-plane σ-orbital (M. B. Yim, O. Kikuchi, and D. E. Wood, *J. Amer. Chem. Soc.*, 1978, **100**, 1869), whereas $^{+\cdot}ArCO_2^-$ species are of π-type.

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peroxyacids were generated *in situ* using a method previously described.[7] Arenediazonium tetrafluoroborates were prepared by the previously reported method.[17] All other materials were obtained commercially and used without further purification.

E.s.r. spectra were recorded with a Varian E104 spectrometer in conjunction with a conventional flow system.[6] All solutions were purged with nitrogen before flowing and their pHs were adjusted with ammonia solution unless otherwise stated.

The titanium(III) ion reduction of peroxyacids was carried out by mixing one reagent stream containing a solution of the peroxyacid (0.02—0.05M), adjusted to pH 9 with sodium hydroxide solution, with a solution of titanium(III) chloride (*ca.* 0.01M) in the presence of EDTA (*ca.* 4 g l^{-1}). The pH of this solution was adjusted so that the pH after mixing was 9. Where $CH_2\dot{}NO_2^-$ was used as a trap, it was introduced in a third reagent stream containing nitromethane (0.5—24 $cm^3\ l^{-1}$) at pH 9.

Oxidation of carboxylic acids with $SO_4^{-}\cdot$ was carried out by mixing a solution of sodium persulphate (*ca.* 10 g l^{-1}) at pH 9 with a reagent stream containing a solution of titanium(III) chloride (*ca.* 0.01M) in the presence of EDTA (*ca.* 4 g l^{-1}) and the organic carboxylic acid (*ca.* 0.15M); the pH of the latter solution was adjusted to give pH 9 after mixing. When $CH_2\dot{}NO_2^-$ was used as a trap, it was introduced in a third reagent stream containing nitromethane (0.5—24 $cm^3\ l^{-1}$) at pH 9.

The generation of aryl radicals from diazonium salts was carried out by mixing a solution of the diazonium tetrafluoroborate (*ca.* 2 g l^{-1}) containing 1 drop of concentrated sulphuric acid, one containing nitromethane (*ca.* 3 $cm^3\ l^{-1}$) at pH 9, and one containing titanium(III) chloride (*ca.* 0.01M) and EDTA (*ca.* 4 g l^{-1}), together with sufficient ammonia solution to give a pH after mixing of 9—10.

For the kinetic study of the reaction of persulphate with titanium(III), three reagent streams were mixed. These contained sodium persulphate, titanium(III) chloride solution (10 ml l^{-1}) [containing EDTA (4 g l^{-1}) at pH 9], and the organic substrate [acetate (3.0M) at pH 9 or allyl alcohol (1.0M) at pH 2.5]. The pH of the solutions was adjusted, to either pH 9 or 2.5 as required, by addition of ammonia solution or concentrated sulphuric acid respectively.

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