Electron Spin Resonance Studies. Part 65.[1] The Selectivity of Radical Attack on Halogen-containing Compounds

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E.s.r. experiments with some carboxylic acid derivatives containing iodine (*e.g.* $CH_2ICO_2^-$) show that Ph·, ·OH, and $CO_2^{-\cdot}$ all react *via* iodine- rather than hydrogen-abstraction. Examples of bromine abstraction from related compounds (*e.g.* $MeCHBrCO_2^-$) by both Ph· and $CO_2^{-\cdot}$ are reported; these reactions are evidently facilitated by the presence of the electron-withdrawing carboxylate substituent adjacent to the halogen. With ·OH the exothermic hydrogen-atom abstraction appears to be preferred to the endothermic abstraction of bromine, though some examples of the latter are noted. For β-halogen-substituted radicals of the type $\cdot CHXCH_2Y$ ($X = CO_2^-$, CN, SO_3^-, Y = Br, and $X = CO_2^-$, Y = Cl) the results indicate the occurrence of a ready homolytic cleavage to give Y· and $CH_2{=}CHX$, which undergoes further reaction. Examples of oxidative decarboxylation by $SO_4^{-\cdot}$ are also described.

Product studies have shown that aryl radicals are capable of abstracting iodine and bromine atoms from a variety of compounds, including iodobenzene,[2] aliphatic iodides,[3] and some mono- and di-bromides.[4] Similarly, e.s.r. studies in conjunction with a continuous flow system have demonstrated[5] that Ph· abstracts the halogen atom from bromo- and iodo-ethanoate ions (to yield $\cdot CH_2CO_2^-$), though chloroethanoate reacts to give $\cdot CHClCO_2^-$. Other halogen-removal reactions monitored by e.s.r. include the reaction of $CO_2^{-\cdot}$ with bromides and iodides[6,7] and the reactions of these compounds with, *e.g.*, $Et_3Si\cdot$[8] and $Me_3Sn\cdot$[9] (both now widely employed for generating specific radicals in photolytic systems); hydroxyl radicals have also been found to remove iodine from, *e.g.*, iodoethanoic acid and iodoethanamide.[10]

We now report the results of a comparative study of the reactions of a series of halogen-containing substrates (chiefly carboxylic acids containing iodine, bromine, or chlorine substituents) with four radicals of widely different type, namely ·OH, an electrophilic radical, $SO_4^{-\cdot}$, a powerful one-electron oxidant, Ph·, a relatively nucleophilic species, and the one-electron reductant $CO_2^{-\cdot}$. In this way we have been able to study the competition between three types of process, hydrogen-atom abstraction, halogen-atom loss, and one-electron oxidation.

Structural and mechanistic studies of β-halogenoalkyl radicals are often complicated by the occurrence of rapid rearrangements [*e.g.*, the 1,2 shift, reaction (1)[11]] or fragmentations [*e.g.*, the homolysis reaction (2) and related examples,[12] and the heterolytic reaction (3)[13]].

$$\cdot CH_2CMe_2Cl \longrightarrow \cdot CMe_2CH_2Cl \qquad (1)$$

$$\cdot CH_2CH_2Br \longrightarrow CH_2{=}CH_2 + Br\cdot \qquad (2)$$

$$(MeO)_2\dot{C}CH_2Cl \longrightarrow (MeO)_2\overset{+}{C}{-}\dot{C}H_2 + Cl^- \qquad (3)$$

Investigation by e.s.r. is, additionally, often complicated by line-broadening associated with α- or β-halogen substituents, which may arise from the halogen nuclei's quadrupolar and anisotropic broadening, and, with Cl and Br, from the mixture of nuclear moments.† Accordingly we have carried out many of the reactions in the presence of the spin trap $CH_2{:}NO_2^-$; it was our intention in this way to corroborate, where possible, routes of abstraction reactions suggested by direct observation, to attempt to intercept short-lived species prone to fragmentation (and to gain information about the fate of such species as well as to distinguish between homolytic and heterolytic pathways), and to characterize adducts of α- and β-I-, Br-, and Cl-containing radicals.

Results and Discussion

The experiments involved the simultaneous mixing of three aqueous solutions *ca.* 60 ms before the passage of the combined solution through the cavity of an e.s.r. spectrometer. The first stream contained the substrate, the second contained titanium(III) (together with disodium ethylenediaminetetraacetate as sequestering agent and sufficient ammonia to achieve the required pH after mixing, typically *ca.* 6), and the third stream contained the other component of the redox couple in order that Ph·, ·OH, $SO_4^{-\cdot}$ [reactions (4)—(6), respectively], and $CO_2^{-\cdot}$ [reactions (5) and (7)] could be generated (*cf.* refs. 5, 6, 10, 15, and the Experimental section). In experiments in which the *aci*-anion of nitromethane was employed as a spin trap, nitromethane was included in the third stream and the pH was adjusted to either *ca.* 9.5 (for experiments with Ph·, ·OH, or $CO_2^{-\cdot}$) or the somewhat lower value of *ca.* 9.0 when $SO_4^{-\cdot}$ was employed (to reduce the extent of oxidation of OH^- to ·OH by $SO_4^{-\cdot}$).

$$Ti^{III} + PhN_2^+ \longrightarrow Ph\cdot + N_2 + Ti^{IV} \qquad (4)$$

$$Ti^{III} + H_2O_2 \longrightarrow \cdot OH + OH^- + Ti^{IV} \qquad (5)$$

$$Ti^{III} + S_2O_8^{2-} \longrightarrow SO_4^{-\cdot} + SO_4^{2-} + Ti^{IV} \qquad (6)$$

$$\cdot OH + HCO_2^- \longrightarrow CO_2^{-\cdot} + H_2O \qquad (7)$$

E.s.r. parameters of the radicals detected are collected in the Table. For many of these radicals the parameters are essentially as previously reported (see, *e.g.*, refs. 5 and 6 and, for the spin-trapped adducts, refs. 16 and 17). For radicals not previously described, or where ambiguities exist, justification will be presented here.

Reactions with Iodine-containing Compounds.—Reaction of

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† Attention may be drawn in particular to the controversies[14] which surround the identification of, *e.g.*, $\cdot CMe_2CH_2X$ (X = Br, I).

Table. E.s.r. parameters of radicals detected in reactions of Ph·, ·OH, $SO_4^{-\cdot}$, and $CO_2^{-\cdot}$ with halogen-containing compounds

Substrate	Trap (CH_2:NO_2^-)[a]	Radical	Method [A Ph·, B ·OH, C $SO_4^{-\cdot}$, D $CO_2^{-\cdot}$]	Hyperfine splittings (mT)[b]				g[c]
				a(N)	a(α-H)	a(β-H)	a(other)	
$ICH_2CO_2^-$	−	$\cdot CH_2CO_2^-$	A, B, D		2.12(2)			2.0032
	+	$^-O_2CCH_2CH_2NO_2^{-\cdot}$	A, B, D	2.60		1.00(2)	0.07(2)	2.0050
	+	$ICH_2CH_2NO_2^{-\cdot}$[d]	C	2.55		0.98(2)	0.065(2)	2.0050
ICH_2CONH_2	−	$\cdot CH_2CONH_2$	A, B, D		2.14(2)		0.18 (N) 0.22 (NH) 0.255 (NH)	2.0030
$ICH_2CH_2CO_2^-$	−	$\cdot CH_2CH_2CO_2^-$	A, B, D		2.225(2)	2.555(2)		2.0027
$BrCH_2CO_2^-$	−	$\cdot CH_2CO_2^-$	A, D			as above		
	+	$^-O_2CCHBrCH_2NO_2^{-\cdot}$	A, B	2.52		1.60(1) 0.505(1)	0.055(1)	2.0047
	+	$BrCH_2CH_2NO_2^{-\cdot}$	C	2.525		0.985(2)	0.065(2)	2.0050
$Br_2CHCO_2^-$	+	$^-O_2CCHBrCH_2NO_2^{-\cdot}$	A			as above		
$MeCHBrCO_2^-$	−	$\cdot CHMeCO_2^-$	A, D		2.02(1)	2.49(3)		2.0033
	+	$^-O_2CCHMeCH_2NO_2^{-\cdot}$	A, B, D	2.51		1.44(1) 0.68(1)	0.06(1)	2.0050
	+	$BrCHMeCH_2NO_2^{-\cdot}$	C	2.46		1.30(1) 0.66(1)	0.04(1)	2.0050
$EtCHBrCO_2^-$	−	$\cdot CHEtCO_2^-$	A, D		1.99(1)	2.35(2)		2.0033
	+	$^-O_2CCHEtCH_2NO_2^{-\cdot}$	A, D	2.51		1.42(1) 0.69(1)	0.055(1)	2.0050
$BrCH_2CH_2CO_2^-$	−	$\cdot CH(CO_2^-)CH_2Ph$	A		2.04(1)	2.30(2)		2.0033
	−	$\cdot CH(CO_2^-)CH_2OH$	B		2.05(1)	2.77(2)		2.0033
	−	$\cdot CH_2CH_2OSO_3^-$	C		2.21(2)	2.475(2)		2.0026
	+	$^-O_2CCH(CH_2Br)CH_2NO_2^{-\cdot}$	B	2.49		1.41(1) 0.58(1)	0.040(1)	2.0050
	+	$^-O_2CCH(CH_2OH)CH_2NO_2^{-\cdot}$	B	2.54		1.32(1) 0.78(1)	0.055(1)	2.0050
$BrCH_2CH_2CN$	−	$\cdot CH(CN)CH_2Ph$	A		2.015(1)	2.35(2)	0.34 (N)	2.0029
	−	$\cdot CH(CN)CH_2OH$	B		2.010(1)	2.83(2)	0.345 (N)	2.002 85
$BrCH_2CH_2SO_3^-$	−	$\cdot CH_2CH_2SO_3^-$	A, D		2.21(2)	1.865(2)		2.0027
	−	$\cdot CH(SO_3^-)CH_2Ph$	A		2.18(1)	2.42(2)		2.0025
	+	$^-O_3SCH_2CHBrCH_2NO_2^{-\cdot}$	B	2.52		1.525(1) 0.55(1)	0.05(1)	2.0050
$BrCH(CO_2^-)CH_2CO_2^-$	−	$\cdot CH(CO_2^-)CH_2CO_2^-$	A, B, D		2.02(1)	2.30(2)		2.003 25
	−	$\cdot CH(CO_2^-)CH(CO_2^-)Ph$	A		2.03(1)	1.09(1)		2.0033
	−	$\cdot CH(CO_2^-)CH(CO_2^-)OH$	B		2.02(1)	1.53(1)		2.0033

Table (*contd.*)

Substrate	Trap (CH_2:NO_2^-) [a]	Radical	Method [A Ph·, B ·OH, C $SO_4^{-\cdot}$, D $CO_2^{-\cdot}$]	Hyperfine splittings (mT) [b]				g [c]
				a(N)	a(α-H)	a(β-H)	a(other)	
$BrCH_2CHBrCO_2^-$	−	$\cdot CH(CO_2^-)CH_2Ph$	A			as above		
$BrCH(CO_2^-)CH(CO_2^-)Br$	−	$\cdot CH(CO_2^-)CH(CO_2^-)Ph$	A			as above		
	−	$\cdot CH(CO_2^-)CH(CO_2^-)OH$	B			as above		
	−	$\cdot CH(CO_2^-)CH(CO_2^-)_2$	D		2.01(1)	0.795(1)		2.0033
$ClCH_2CO_2^-$	−	$\cdot CHClCO_2^-$	A, B, C		2.00(1)		0.37 (^{35}Cl) 0.305 (^{37}Cl)	2.0064
	+	$^-O_2CCHClCH_2NO_2^{-\cdot}$	B	2.49		1.65(1) 0.41(1)	0.08(1)	2.0050
	+	$ClCH_2CH_2NO_2^{-\cdot}$	C	2.525		1.025(2)	0.055(2)	2.0051
$Cl_2CHCO_2^-$	−	$\cdot CCl_2CO_2^-$	A, B, C				0.29 (Cl)	2.0079
	−	$\cdot CHClCO_2^-$	D			as above		
	+	$^-O_2CCCl_2CH_2NO_2^{-\cdot}$	B, C	2.37		0.92(2)		2.0050
	+	$^-O_2CCHClCH_2NO_2^{-\cdot}$	D			as above		
$Cl_3CCO_2^-$	−	$\cdot CCl_2CO_2^-$	A, C			as above		
$MeCHClCO_2^-$	−	$\cdot CClMeCO_2^-$	A, B			2.11(3)	0.23 (Cl)	2.0059
	+	$^-O_2CCClMeCH_2NO_2^{-\bullet}$	B	2.495		1.455(1) 0.59(1)		2.0051
	+	$ClCHMeCH_2NO_2^{-\cdot}$	C	2.45		1.32(1) 0.65(1)	0.06(1)	2.0051
$ClCH_2CH_2CO_2^-$	−	$\cdot CH(CO_2^-)CH_2Cl$	A, B		2.045(1)	1.095(2)	1.415 (^{35}Cl) 1.19 (^{37}Cl)	2.002 85
	−	$\cdot CH(CO_2^-)CH_2Ph$	A			as above		
	−	$\cdot CH(CO_2^-)CH_2OH$	B			as above		
	−	$\cdot CH_2CH_2Cl$	C		2.19(2)	1.27(2)	1.865 (^{35}Cl) 1.60 (^{37}Cl)	2.0022
$ClCH_2CH_2CN$	−	$\cdot CH(CN)CH_2Ph$	A			as above		
	−	$\cdot CH(CN)CH_2OH$	B			as above		
$ClCH_2CH_2SO_3^-$	−	$\cdot CHClCH_2SO_3^-$	B		1.075(1)	1.825(2)	0.265 (Cl)	2.0059
$ClCH(CO_2^-)CH_2CO_2^-$	−	$\cdot CH(CO_2^-)CHClCO_2^-$	A, B		2.02(1)	0.64(1)	1.33 (^{35}Cl) 1.10 (^{37}Cl)	2.032
	−	$\cdot CH(CO_2^-)CH(CO_2^-)Ph$	A			as above		
	−	$\cdot CH(CO_2^-)CH(CO_2^-)OH$	B			as above		
	−	$\cdot CCl(CO_2^-)CH_2CO_2^-$	A, B			1.375(2)	0.235 (Cl)	2.0058

[a] In addition, in experiments with the trap, signals were detected from $PhCH_2NO_2^{-\cdot}$ (Ph·), $HOCH_2NO_2^{-\cdot}$ (·OH), $O_2NCH_2CH_2NO_2^{-\cdot}$ ($SO_4^{-\cdot}$), $^-O_3SOCH_2NO_2^{-\cdot}$ ($SO_4^{-\cdot}$), $^-O_2CCH_2NO_2^{-\cdot}$ ($CO_2^{-\cdot}$), and in some cases $CH_3NO_2^{-\cdot}$. [b] ±0.005 mT. [c] ±0.0001. [d] Tentative assignment; see text.

phenyl with each of the three iodine-containing substrates studied ($ICH_2CO_2^-$, $ICH_2CH_2CO_2^-$, and ICH_2CONH_2, at concentrations in the mixed stream of *ca.* 0.01M) led solely to the detection of the radicals resulting from iodine-atom abstraction: $\cdot CH_2CO_2^-$, $\cdot CH_2CH_2CO_2^-$, and $\cdot CH_2CONH_2$ (*cf.* also ref. 5). Similar results were obtained by reaction with[10] $\cdot OH$ and[6] $CO_2^{-\cdot}$, though for the latter radical the reactions should perhaps best be regarded as electron-transfer processes [*e.g.*, reaction (8)].

$$\cdot CO_2^- + ICH_2CO_2^- \longrightarrow CO_2 + I^- + \cdot CH_2CO_2^- \qquad (8)$$

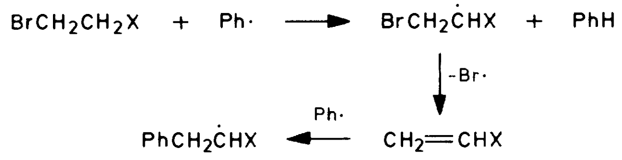
No evidence for hydrogen-atom abstraction was obtained in these experiments or when $CH_2{:}NO_2^-$ was included as a spin trap.

Reaction of $ICH_2CO_2^-$ with $SO_4^{-\cdot}$ gave no directly detectable signals. In the presence of $CH_2{:}NO_2^-$ at pH 9 signals were detected from $O_2NCH_2CH_2NO_2^{-\cdot}$ and $^-O_3SOCH_2NO_2^{-\cdot}$ (from reaction of $SO_4^{-\cdot}$ with the trap[18]) as well as weaker resonances from $HOCH_2NO_2^{-\cdot}$ and a signal with *a*(N) 2.55, *a*(2H) 0.98, *a*(2H) 0.065 mT, *g* 2.0050, which is tentatively attributed to the adduct formed with $\cdot CH_2I$. No evidence for the formation and trapping of $\cdot CH_2CO_2^-$ (*cf.* ref. 16) was obtained.

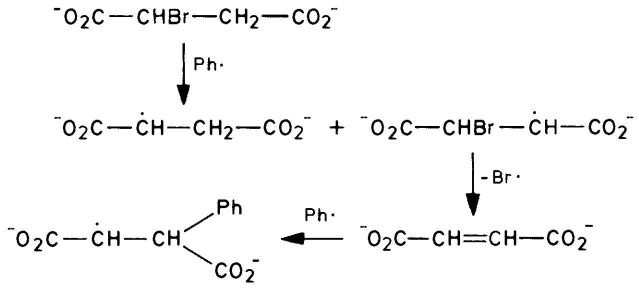
Reactions with Bromine-containing Compounds.—(a) Ph·. Reaction of phenyl with $BrCH_2CO_2^-$, $MeCHBrCO_2^-$, and $EtCHBrCO_2^-$ at pH *ca.* 8 gave strong signals from $\cdot CH_2CO_2^-$, $\cdot CHMeCO_2^-$, and $\cdot CHEtCO_2^-$, respectively, which shows that bromine-atom abstraction occurs readily. However, further findings for these and other substrates indicate that bromine loss both occurs less readily than iodine loss and is facilitated by the adjacent carboxy-group.

For example, reaction of Ph· with $BrCH_2CO_2^-$ in the presence of $CH_2{:}NO_2^-$ gave not only signals from $PhCH_2NO_2^{-\cdot}$ and $^-O_2CCH_2CH_2NO_2^{-\cdot}$, but also one with *a*(N) 2.52, *a*(1H) 1.60, *a*(1H) 0.505, *a*(1H) 0.055 mT, *g* 2.0047, and with the inner lines of the 1 : 1 : 1 : 1 quartet (attributed to the β-protons in the appropriate adduct) considerably broadened. This signal characterizes the trapping of a radical with three different substituents $XYZCCH_2NO_2^{-\cdot}$ (*i.e.* there is a chiral carbon atom attached to the carbon of the spin trap so that the β-protons are magnetically inequivalent), and it is attributed to $^-O_2CCHBrCH_2NO_2^{-\cdot}$ (see also ref. 17). The same spectrum was also detected during the reaction of Ph· with $CHBr_2CO_2^-$ in the presence of the trap, though in its absence no signals were detected. We conclude that $\cdot CHBrCO_2^-$ is formed from $CH_2BrCO_2^-$ (together with $\cdot CH_2CO_2^-$) and from $CHBr_2CO_2^-$, but that its e.s.r. signal is normally too broad for direct detection in aqueous solution.

Reaction of $MeCHBrCO_2^-$ and $EtCHBrCO_2^-$ in the presence of the trap gave signals from $MeNO_2^{-\cdot}$ and $PhCH_2NO_2^{-\cdot}$ and ones assigned to $CHMe(CO_2^-)CH_2NO_2^{-\cdot}$ and $CHEt(CO_2^-)CH_2NO_2^-$, respectively, which characterize the radicals resulting from bromine-atom abstraction. No lines attributable to the adducts of $\cdot CBrR(CO_2^-)$ (R = Me, Et) were detected; it is nevertheless possible that, as with bromoethanoate, hydrogen-atom abstraction to give α-bromo-substituted radicals occurs but that steric hindrance retards spin-trapping (*cf.* the variation in the rate constants for addition of Me· to a series of nitro *aci*-anions[19]).



Scheme 1.



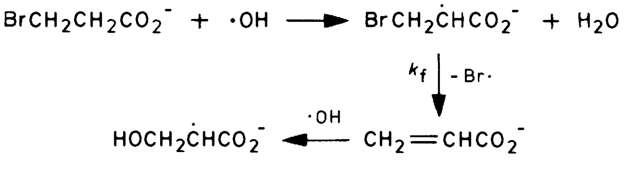
Scheme 2.

The results obtained with $BrCH_2CH_2CO_2^-$ and $BrCH_2CH_2CN$ (see Table), from which no sign of $\cdot CH_2CH_2CO_2^-$ or $\cdot CH_2CH_2CN$, respectively, could be discerned, indicate that bromine-atom abstraction does not occur at a significant rate with these substrates. The only signals detected had *a*(1H) 2.04, *a*(2H) 2.30 mT, *g* 2.0033 and *a*(1H) 2.015, *a*(2H) 2.35, *a*(N) 0.34 mT, *g* 2.0029. These are assigned to $\cdot CH(CO_2^-)CH_2Ph$ and $\cdot CH(CN)CH_2Ph$, respectively, and the assignments were confirmed by generating identical signals by addition of Ph· to $CH_2{:}CHCO_2^-$ and $CH_2{:}CHCN$ in separate experiments under identical conditions. In the case of analogous reactions initiated by ·OH, we were able to rule out the possibility that reaction occurs with alkenes present adventitiously in the sample of $BrCH_2CH_2CO_2H$ (see later), and we infer likewise here. It therefore seems likely that the radicals are generated *in situ via* abstraction of C(2)-H by phenyl, followed by rapid loss of the β-bromine atom (Scheme 1; X = CO_2^- or CN). Such an interpretation is consistent with the activation of C–H bonds adjacent to CO_2^- and CN groups as reported previously[5] for the (nucleophilic) phenyl radical and with the earlier suggestions[12] that β-bromoalkyl radicals undergo very rapid fragmentations.

Similar processes also appear to compete with bromine-atom abstraction in the reactions of $BrCH_2CH_2SO_3^-$ and $^-O_2CCHBrCH_2CO_2^-$ (see Table). For the former, the two radicals detected have parameters [*a*(2H) 2.21, *a*(2H) 1.865 mT, *g* 2.0027, and *a*(1H) 2.18, *a*(2H) 2.42 mT, *g* 2.0025] which are attributable to $\cdot CH_2CH_2SO_3^-$ and $\cdot CH(SO_3^-)CH_2Ph$ respectively, suggesting that both direct loss of a bromine atom and the sequence in Scheme 1 (X = SO_3^-) occur; and we infer that the sulphonate group is less effective than CO_2^- or CN in directing attack at C(2). For the latter, detection of $\cdot CH(CO_2^-)CH_2CO_2^-$ and $\cdot CH(CO_2^-)CH(CO_2^-)Ph$ (in the ratio *ca.* 1 : 2) can be explained in terms of two modes of reaction, namely loss of a bromine atom directly and attack at the methylene group (Scheme 2).

Analogous reactions involving the sequential loss of two bromine atoms appear to occur for $BrCH_2CHBrCO_2^-$ and $^-O_2CCHBrCHBrCO_2^-$ [which gave solely the signals from $\cdot CH(CO_2^-)CH_2Ph$ and $\cdot CH(CO_2^-)CH(CO_2^-)Ph$, respectively]. It is probable that, in the former case, it is the 2-bromo-substituent that is abstracted initially, owing to activation by the adjacent carboxylate ion; loss of the 3-bromo-group follows, to yield $CH_2{:}CHCO_2^-$. The rate of the appropriate fragmentation process will be discussed later.

(b) ·OH. No signals were directly detected in the reaction between ·OH and either $BrCH_2CO_2^-$ or $MeCHBrCO_2^-$. However, when reaction with the former was carried out in the presence of $CH_2{:}NO_2^-$, the spectrum of $BrCH(CO_2^-)CH_2$-



Scheme 3.

$NO_2^{-\cdot}$ (see earlier), as well as those of $HOCH_2NO_2^{-\cdot}$ and $MeNO_2^{-\cdot}$, was observed. When $MeCHBrCO_2^-$ was treated likewise, weak signals from $MeCH(CO_2^-)CH_2NO_2^{-\cdot}$ were characterized. This shows that bromine-atom abstraction occurs, but we believe that this represents only a minor pathway since $\cdot CHMeCO_2^-$ could not be *directly* detected (again, $\cdot CMeBrCO_2^-$ *may* be formed but its attack on $CH_2{:}NO_2^-$ may be hindered). These results suggest that, in contrast to reaction with Ph·, ·OH preferentially abstracts a hydrogen rather than a bromine atom.

Reaction with $BrCH_2CH_2CO_2^-$ gave $\cdot CH(CO_2^-)CH_2OH$ [with *a*(1H) 2.05, *a*(2H) 2.77 mT, *g* 2.0033]. We infer the sequence shown in Scheme 3 and we ruled out the possibility that the radical $\cdot CH(CO_2^-)CH_2OH$ arises from selective reaction of ·OH with alkene present adventitiously in the bromo-compound as follows.* The radicals $\cdot CO_2^-$ and ·SH show little propensity for hydrogen-atom abstraction but are known [6,20] to add readily to alkenes, including propenoate ion in particular. We found that the signal from $\cdot CO_2^-$ was not quenched or replaced by that from any other species when this radical was generated in the presence of 0.01M-$BrCH_2CH_2CO_2^-$. On the other hand, we found that $\cdot CO_2^-$ adds to $CH_2{:}CHCO_2^-$, with the latter in as low a concentration as 10^{-4}M, to give a readily detectable signal from $\cdot CH(CO_2^-)CH_2CO_2^-$. This places an upper limit of *ca.* 1% for the concentration of $CH_2{:}CHCO_2H$ in the sample of $BrCH_2CH_2CO_2H$ employed. (Analogous experiments with ·SH, from ·OH and SH^-, gave corresponding results.) Now reaction of ·OH with 10^{-4}M-$CH_2{:}CHCO_2^-$ was found to give only very weak signals from $\cdot CH(CO_2^-)CH_2OH$, much less intense than those observed with 10^{-2}M-$BrCH_2CH_2CO_2^-$, so we conclude that the radical is formed in the latter case, at least in large part, from $CH_2{:}CHCO_2^-$ formed as in Scheme 3.

When the reaction between ·OH and $BrCH_2CH_2CO_2^-$ was conducted at pH 10 in the presence of $CH_2{:}NO_2^-$, two adducts were detected (in addition to signals from $HOCH_2NO_2^{-\cdot}$ and $MeNO_2^{-\cdot}$). Their splittings [*a*(N) 2.54, *a*(1H) 1.32, *a*(1H) 0.78, *a*(1H) 0.055 mT (*g* 2.0050) and *a*(N) 2.49, *a*(1H) 1.41, *a*(1H) 0.58, *a*(1H) 0.040 mT (*g* 2.0050)] characterize them as of the type $XYHCCH_2NO_2^{-\cdot}$ (*i.e.* with a single γ-proton and chiral γ-carbon; *cf.* ref. 17). The concentration of the latter relative to that of the former increased with increase in $[CH_2{:}NO_2^-]$, and we suggest that they are, respectively, adducts of $\cdot CH(CO_2^-)CH_2OH$ and $\cdot CH(CO_2^-)CH_2Br$; their formation is then interpreted in terms of the competition between trapping of the first-formed radical $\cdot CH(CO_2^-)CH_2Br$ and its fragmentation to $CH_2{:}CHCO_2^-$ followed by addition of ·OH and spin-trapping. The fragmentation of $\cdot CH(CO_2^-)CH_2Br$ must occur at a rate comparable with that of its trapping at the concentrations of trap typically employed (*ca.* 0.01M); if we take *ca.* 10^8 dm^3 mol^{-1} s^{-1} as a realistic upper limit for the trapping reaction (*cf.* ref. 19 for the rate constant for reaction between Me· and $CH_2{:}NO_2^-$) then it follows that the upper limit for k_f is *ca.* 10^6 s^{-1}.

No signals could be detected directly from the reaction between ·OH and $BrCH_2CH_2SO_3^-$; the possibility that attack of the electrophilic hydroxyl is directed away from the methylene attached to the sulphonate group by the electron-withdrawing character of the latter is supported by the trapping of a radical thought to be $\cdot CHBrCH_2SO_3^-$ by the nitro *aci*-anion (as mentioned earlier, the lines from the α-bromo-radical itself may be too broad for detection).

Reaction of $BrCH_2CH_2CN$ led to the detection solely of the radical $\cdot CH(CN)CH_2OH$, evidently formed *via* loss of β-bromine from $\cdot CH(CN)CH_2Br$ (as outlined in Scheme 3 for the analogous radical from $BrCH_2CH_2CO_2^-$). Loss of both α-bromine (by abstraction) and β-bromine (*via* homolytic cleavage of the first-formed radical) is indicated by the detection of $\cdot CH(CO_2^-)CH(OH)CO_2^-$ from $^-O_2CCHBrCHBrCO_2^-$; with $^-O_2CCHBrCH_2CO_2^-$, reaction of ·OH gave $\cdot CH(CO_2^-)CH_2CO_2^-$ (presumably formed *via* bromine-atom abstraction) and, in much higher concentrations, $\cdot CH(CO_2^-)CH(OH)CO_2^-$ (evidently formed *via* attack at the methylene group and subsequent fragmentation as noted for related substrates).

(c) $SO_4^{-\cdot}$. No e.s.r. signals were detected when $SO_4^{-\cdot}$ was generated in the presence of either $BrCH_2CO_2^-$ or $MeCHBrCO_2^-$ at pH *ca.* 6. On the other hand when the reactions were carried out in the presence of $CH_2{:}NO_2^-$ at pH *ca.* 9, e.s.r. spectra were detected from $\cdot^-O_2NCH_2CH_2NO_2$ (from $SO_4^{-\cdot}$ and the *aci*-anion [18]) and one other radical in each case; their e.s.r. parameters [*a*(N) 2.525, *a*(2H) 0.985, *a*(2H) 0.065 mT, *g* 2.0050 and *a*(N) 2.46, *a*(1H) 1.30, *a*(1H) 0.66, *a*(1H) 0.04 mT, *g* 2.0050] characterize them as adducts from $\cdot CH_2Br$ and ·CHMeBr, respectively. They evidently derive from oxidative decarboxylation of the anions, as has been previously described for some related species.[16]

Reaction with $BrCH_2CH_2CO_2^-$ gave a signal with *a*(2H) 2.21, *a*(2H) 2.475 mT, *g* 2.0026, which is attributed to the radical $\cdot CH_2CH_2OSO_3^-$. This is presumably formed by oxidative decarboxylation to give $\cdot CH_2CH_2Br$, followed by rapid loss of Br· and addition of $SO_4^{-\cdot}$ to the ethene thus formed. In the presence of $CH_2{:}NO_2^-$, no signals attributable to adducts of $\cdot CH_2CH_2Br$ could be obtained.

No signals from substrate-derived radicals were observed in the reactions of $SO_4^{-\cdot}$ with $^-O_2CCHBrCH_2CO_2^-$ or $^-O_2CCHBrCHBrCO_2^-$, either in the presence or absence of $CH_2{:}NO_2^-$.

(d) $CO_2^{-\cdot}$. This radical-ion has been previously employed to effect debromination of a variety of compounds, including $BrCH_2CO_2^-$, $EtCHBrCO_2^-$, $Me_2CBrCO_2^-$, and $^-O_2CCHBrCH_2CO_2^-$; in each case the corresponding α-carboxy-radical was directly detected.[6] The reaction is believed to occur *via* electron transfer and subsequent loss of bromide ion. In contrast, we found that there is no reaction between $CO_2^{-\cdot}$ and $BrCH_2CH_2CO_2^-$; the signal from $CO_2^{-\cdot}$ remained unquenched. When $CH_2{:}NO_2^-$ was included, only signals from $HOCH_2NO_2^{-\cdot}$, $CH_3NO_2^{-\cdot}$, and $^-O_2CCH_2NO_2^{-\cdot}$ could be discerned. This indicates that the loss of bromine on reaction of 2-bromoalkanoate anions is assisted by the neighbouring carboxylate group.

Reaction of $CO_2^{-\cdot}$ with $^-O_2CCHBrCH_2CO_2^-$ gave, as expected, a strong signal from $\cdot CH(CO_2^-)CH_2CO_2^-$, formed by reductive elimination of Br^-. With $^-O_2CCHBrCHBrCO_2^-$ a weak signal was detected from $\cdot CH(CO_2^-)CH(CO_2^-)_2$ (verified by addition of $CO_2^{-\cdot}$ to $^-O_2CCH{:}CHCO_2^-$ in a separate experiment) suggesting that $^-O_2CCH{:}CHCO_2^-$ is formed *in situ* by successive loss of two bromines (first reductive elimination, then β-fragmentation).

With $BrCH_2CH_2CN$, the singlet from $CO_2^{-\cdot}$ was unquenched and no other signals were observed; with $BrCH_2CH_2SO_3^-$, $CO_2^{-\cdot}$ was detected along with weak signals from $\cdot CH_2CH_2SO_3^-$.

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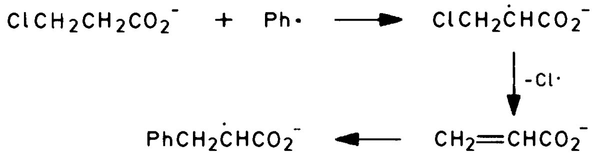
* Conventional analysis of the sample by ^{1}H n.m.r. under similar conditions did not reveal the presence of any propenoic acid.



Scheme 4.

Reactions with Chloro-compounds.—(a) Ph·. With one exception, the reaction of phenyl with 2-chloro-substituted alkanoates led to the detection solely of radicals derived by α-hydrogen abstraction: thus $ClCH_2CO_2^-$, $MeCHClCO_2^-$, and $CHCl_2CO_2^-$ gave $\cdot CHClCO_2^-$ (see ref. 5), $\cdot CClMeCO_2^-$, and $\cdot CCl_2CO_2^-$ respectively. (In trapping experiments only weak signals from the adducts of the above radicals to $CH_2{:}NO_2^-$ could be detected whereas strong signals from $PhCH_2NO_2^{-\cdot}$ were observed; the rate of hydrogen-atom abstraction is presumably much less than that of addition.) Reaction of $CCl_3CO_2^-$, however, gave $\cdot CCl_2CO_2^-$, which indicates that chlorine abstraction occurs in this case.

Reaction of Ph· with $ClCH_2CH_2CN$ and $ClCH_2CH_2CO_2^-$, as with the corresponding bromo-compounds, yielded $\cdot CH(CN)CH_2Ph$ and $\cdot CH(CO_2^-)CH_2Ph$, respectively. In addition, in the latter case, a spectrum was detected with *a*(1H) 2.045, *a*(2H) 1.095, *a*(^{35}Cl) 1.415, *a*(^{37}Cl) 1.19 mT, *g* 2.002 85, which is attributed to $\cdot CH(CO_2^-)CH_2Cl$ (which evidently [21] exists in a conformation in which the β-C–Cl bond eclipses the orbital of the unpaired electron, *cf.* $\cdot CH_2CH_2Cl$). The finding that increasing the flow-rate caused an increase in the ratio of concentrations of $\cdot CH(CO_2^-)CH_2Cl$ and $\cdot CH(CO_2^-)CH_2Ph$ is consistent with a mechanism (Scheme 4) in which the first-formed radical loses Cl· to give $CH_2{:}CHCO_2^-$ which accumulates down the flow-tube. Two particular points of interest emerge. First, loss of chlorine from $\cdot CH(CO_2^-)CH_2Cl$ is evidently slower than loss of bromine from the analogous β-bromo-radical (see earlier). {A rigorous analysis to give the rate constant for the loss of chlorine is not possible; however, if we assume that this process makes only a relatively minor contribution to decay of $\cdot CH(CO_2^-)CH_2Cl$ in competition with bimolecular termination, then taking [$\cdot CH(CO_2^-)CH_2Cl$] as *ca.* μM and $2k_t$ for this type of radical as *ca.* 10^9 dm^3 mol^{-1} s^{-1},[22] it follows that k_f must be of the order of 10^3 s^{-1}.} The second is that the β-C–Cl bond (as with β-C–Br) breaks *via* homolysis. Thus if the alternative fragmentation of the β-C–Cl bond had occurred in heterolytic manner [to give Cl^- and $\overbrace{CH_2{-}CHCO_2^-}^{+\cdot}$; *cf.* reaction of $\cdot CH(OMe)CH_2Cl$ and related species [13,23]] formation of $\cdot CH(CO_2^-)CH_2OH$, *via* hydration of the radical-cation, would have been expected.[23]

We suggest a mechanism analogous to that illustrated in Scheme 4 to account for the formation of both $\cdot CH(CO_2^-)CHClCO_2^-$ (see Table) and $\cdot CH(CO_2^-)CHPhCO_2^-$ [in addition to weak signals attributed to $\cdot CCl(CO_2^-)CH_2CO_2^-$] from the reaction of Ph· with $^-O_2CCHClCH_2CO_2^-$.

The spectrum detected during the reaction of Ph· with $ClCH_2CH_2SO_3^-$ was weak, with many ill resolved lines: a tentative analysis in terms of the presence of the signal from $\cdot CHClCH_2SO_3^-$ (see Table) is proposed.

(b) ·OH. Reaction of ·OH with some 2-chloroalkanoates led solely to the detection of radicals formed by hydrogen-atom abstraction from the carbon adjacent to the carboxylate function (see Table). No reaction with $CCl_3CO_2^-$ was observed. Oxidation of $ClCH_2CH_2CO_2^-$, as in the reaction with Ph·, gave $\cdot CH(CO_2^-)CH_2Cl$, together with the hydroxyl adduct of $CH_2{:}CHCO_2^-$ [$\cdot CH(CO_2^-)CH_2OH$], providing further evidence for the fragmentation depicted in Scheme 4. Similarly, reaction of $^-O_2CCHClCH_2CO_2^-$ gave both $\cdot CH(CO_2^-)CHClCO_2^-$ and $\cdot CH(CO_2^-)CH(OH)CO_2^-$, together with $\cdot CCl(CO_2^-)CH_2CO_2^-$ {with [$\cdot CH(CO_2^-)CHClCO_2^-$] : [$\cdot CCl(CO_2^-)CH_2CO_2^-$] *ca.* 1 : 1}.

The other chlorine-containing substrates studied in this way were $ClCH_2CH_2SO_3^-$ and $ClCH_2CH_2CN$; for the former the weak, complex, spectrum obtained is interpreted as that from $\cdot CHClCH_2SO_3^-$ (see Table), whereas the latter gave signals from $\cdot CH(CN)CH_2OH$ (as above for $BrCH_2CH_2CN$) and weak resonances ascribed to $\cdot CH(CN)CH_2Cl$.

(c) $SO_4^{-\cdot}$. With $CH_2ClCO_2^-$, the direct detection of $\cdot CHClCO_2^-$ and the trapping by $CH_2{:}NO_2^-$ of this as well as $\cdot CH_2Cl$ (see Table) suggests that hydrogen-atom abstraction competes with oxidative decarboxylation; the failure to detect $\cdot CH_2Cl$ directly probably reflects its ready oxidation by $S_2O_8^{2-}$. Direct hydrogen-atom abstraction was also observed for $CHCl_2CO_2^-$; only $\cdot CCl_2CO_2^-$ was detected, both directly and through trapping, and the failure to detect $\cdot CHCl_2$ suggests that decarboxylation is less important for $CHCl_2CO_2^-$ than for $CH_2ClCO_2^-$. With $CCl_3CO_2^-$ the signal from $\cdot CCl_2CO_2^-$ was detected. Successive chlorine substitution doubtless increasingly stabilises the carboxylate ion against one-electron oxidation.

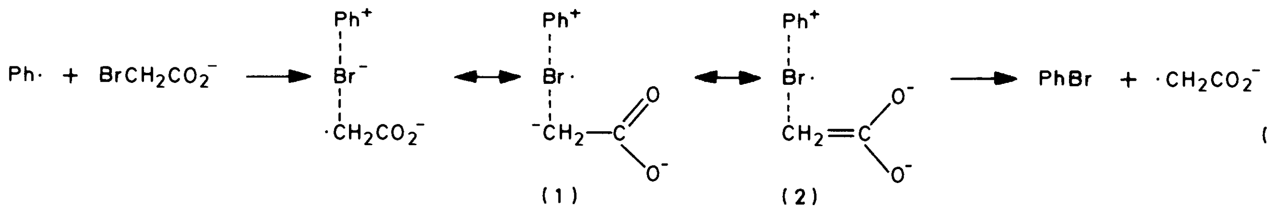
No signals were directly detected during the reaction of $MeCHClCO_2^-$, but the radical $\cdot CHMeCl$ was successfully trapped.

$ClCH_2CH_2CO_2^-$ was decarboxylated to give $\cdot CH_2CH_2Cl$, but, in contrast to the reaction of the bromo-analogue, $\cdot CH_2CH_2OSO_3^-$ was not detected, suggesting that loss of Br· from $\cdot CH_2CH_2Br$ is faster than loss of Cl· in $\cdot CH_2CH_2Cl$. No signals were obtained in the oxidation of $^-O_2CCHClCH_2CO_2^-$ (*cf.* attempted oxidation of the corresponding bromo-compound with $SO_4^{-\cdot}$).

(d) $CO_2^{-\cdot}$. Reductive elimination of Cl^- from chloro-compounds proved much more difficult than with the bromine-containing analogues. The signal from $CO_2^{-\cdot}$ remained unquenched with all substrates studied except $CHCl_2CO_2^-$ and $CCl_3CO_2^-$, where $\cdot CHClCO_2^-$ (as weak signals) and $\cdot CCl_2CO_2^-$ were detected respectively. Evidently introduction of further chlorine atoms facilitates loss of an α-chlorine.

Conclusions.—When the results for Ph·, ·OH, and $CO_2^{-\cdot}$ are compared it is apparent that, despite the differences in the polar and steric characteristics of the attacking radicals, similar trends in the reactivity of different halogen-containing compounds are revealed. We note, first, that iodine abstraction is clearly preferred to hydrogen-atom abstraction in all examples studied (*e.g.*, $\cdot CH_2CH_2CO_2^-$ is the only radical formed from $ICH_2CH_2CO_2^-$). Secondly, abstraction of bromine is evidently somewhat less ready, though examples of such reaction with Ph·, ·OH, and $CO_2^{-\cdot}$ have been noted. These reactions appear to be particularly effective in competition with hydrogen-abstraction for Ph· (*cf.*, *e.g.*, results for $BrCH_2CH_2SO_3^-$ and $BrCH_2CO_2^-$), and, as also with $CO_2^{-\cdot}$, the reaction appears to be aided by the presence of an adjacent carboxy-group (see below); for ·OH, however, bromine-atom abstraction, though possible, appears to be less favourable than hydrogen-atom abstraction. Thirdly, loss of chlorine by reaction with Ph· or reductive elimination with $CO_2^{-\cdot}$ appears to occur only when the process is assisted by the presence of two α-chlorine substituents and an α-carboxy-group (*i.e.* for $CCl_3CO_2^-$).

The overall trends presumably reflect the dominant influence of the carbon–halogen bond strength in the parent compounds (Cl > Br > I) in determining the activation energies and hence the rates of reaction. For the halogen-abstraction reactions by Ph· the removal of iodine or bromine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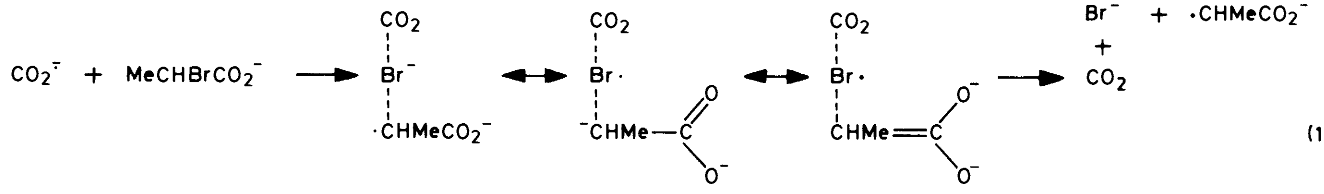
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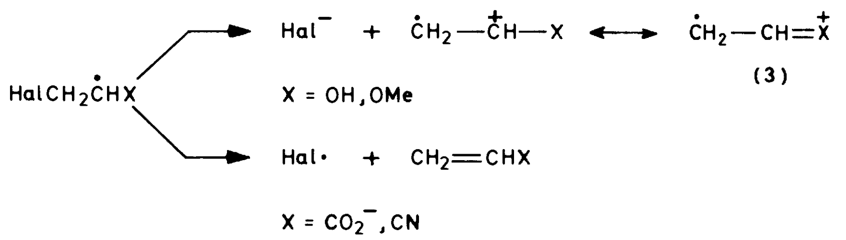
(11)

(12)

atoms which are not activated is nevertheless expected to be exothermic (by *ca.* 40 kJ mol^{-1}; *cf.* ref. 24); the activating effect of an α-CO_2^- group may reflect, in part, a radical-stabilizing effect of the carboxy-group (see below) or, more likely,[5] a polar effect in the transition state [*cf.* the contribution of structures (1) and (2) to the transition state of reaction (9)] which will encourage loss of α-Br or α-H in reactions of the nucleophilic phenyl radical. The preferential loss of I^- in reactions of $CO_2^{-\cdot}$ presumably reflects the good leaving-group ability of iodide in S_N2 reactions, and in the comparable (but slower) reactions of bromides polar effects may also assist loss of bromide from substrates with an α-carboxy-group [reaction (10)].

It is perhaps not surprising that the hydroxyl radical abstracts hydrogen in preference to chlorine or bromine. Thus, hydrogen-atom abstraction is calculated to be exothermic (ΔH *ca.* -90 kJ mol^{-1}), whereas abstraction of either Cl or Br should be endothermic (ΔH *ca.* 90 and 50 kJ mol^{-1}, respectively *); as is commonly the case, the more exothermic reaction occurs the faster (*i.e.*, the energy profiles do not cross). In contrast, the abstraction of iodine by hydroxyl, although slightly exothermic, is much less so than that of hydrogen and yet is the preferred reaction (*i.e.*, the energy profiles cross). Evidently the energy required for bond breaking (for the C–H bond at least) is of greater significance than that released in bond formation in determining the activation energy; additionally it is possible that a relatively low-energy intermediate adduct $HO\dot{I}R$ is formed in the iodine-abstraction process (*cf.* ref. 30).

Our results also provide further e.s.r. evidence for the efficacy of one-electron oxidation, and resultant decarboxylation, of carboxylate ions with the electrophilic $SO_4^{-\cdot}$. The only other reactions characterized are the loss of hydrogen from $CHCl_2CO_2^-$ (it seems likely that electron abstraction is retarded by the $-I$ effect of the chlorine substituent, whose $+M$ effect should encourage loss of α-hydrogen) and the loss of Cl from $CCl_3CO_2^-$.

Finally, we contrast the role of an α-methoxy- or α-hydroxy-group in encouraging *heterolytic* loss of a β-chlorine or bromine in the appropriate radicals [13,23] with the *homolytic* loss of these halogens in the examples encountered here, which possess α-CO_2^-, CN, or SO_3^- substituents (for Br loss) or α-CO_2^- or CN^- (for Cl loss). This presumably reflects the stabilization of the transition state leading to heterolysis in the former group of compounds by the $+M$ effect of the substituent [*cf.* structure (3), reaction (11)]; such a process would be much less likely when X is a $-M$ substituent and for these substrates it is perhaps not surprising that the alternative homolysis [reaction (12)] is favoured.

Experimental

A Varian E-104 e.s.r. spectrometer with 100 kHz modulation and an *X*-band klystron was employed; splitting constants were measured to within ± 0.005 mT and *g*-factors to within ± 0.0001 by comparison with the spectrum from Fremy's salt [a(N) 1.3091 mT,[31] g 2.0055 [32]]. Spectrum simulation with a program kindly supplied by Dr. M. F. Chiu was used to verify spectrum analysis and to determine relative radical concentrations. A mixing chamber was employed which allowed the simultaneous mixing of three reagents *ca.* 60 ms

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* These estimates are based on average bond-energy values and appropriate bond dissociation energies where these are available [24] (O–H, 497; O–Cl, 251; O–Br, 234; C–Cl, 340; C–Br, 284; C–H, 409 kJ mol^{-1}) which, in the cases of bonds to carbon, make no allowance for stabilisation of the corresponding radical by delocalisation of the unpaired electron on to α-substituents (CO_2^-, Br, Cl). The values are all likely, therefore, to be more exothermic (less endothermic) than quoted, and the differential between hydrogen and halogen-atom (X) abstraction from the fragment $-CHX-$ is likely to be still larger than suggested. The stabilizing effect of α-Cl or α-Br is likely to be less than that of α-OH [25] (*ca.* 32 kJ mol^{-1}) or α-NH_2 [26] (*ca.* 40 kJ mol^{-1}), but could still be significant; from the values of a(Me) for $\cdot CHMeCO_2^-$ and $\cdot CClMeCO_2^-$ we calculate [27] that the extent of delocalisation on to Cl is 15% (*cf.* a value of *ca.* 19% for Br in $\cdot CHBrCO_2H$ as deduced [28] from the solid-state spectrum of this species); likewise, the value for CO_2^- is estimated as 8%. On the other hand, radiolysis studies of the reaction of $\cdot OH$ with carboxylates indicate [29] that α- or β-substitution by either Cl or Br does not lead to a rate enhancement.

before passage through the cavity of the spectrometer. The flow was maintained with a Watson–Marlow 502S flow inducer positioned on the inlet tubing, and pH measurements were made with a Pye–Unicam PW 9410 pH meter (with the electrode inserted into the effluent stream of the flow system).

Solutions to be mixed (all deoxygenated prior to mixing by the passage of nitrogen) were as follows.

(a) *The* Ti^{III}–H_2O_2 *System* ($\cdot OH$).—The first stream contained titanium(III) chloride (0.008M), ethylenediaminetetra-acetic acid (3 g dm^{-3}), and concentrated ammonia solution to give the desired pH, the second stream contained hydrogen peroxide (0.033M), and the substrate was included in the third stream (with a concentration typically in the range 0.02—0.1M).

(b) *The* Ti^{III}–H_2O_2–HCO_2^- *System* ($CO_2^{-\cdot}$).—Concentrations similar to those in (a) were used, except that sufficient sodium formate was added to the first stream to give a concentration after mixing of at least 0.5M.

(c) *The* Ti^{III}–PhN_2^+ *System* ($Ph\cdot$).—Conditions used were as described in (a) above except that in the second stream hydrogen peroxide was omitted and replaced by a solution of benzenediazonium tetrafluoroborate (0.008M), prepared as described previously,[33] and one drop of concentrated sulphuric acid (at *ca.* 0 °C).

(d) *The* Ti^{III}–$S_2O_8^{2-}$ *System* ($SO_4^{-\cdot}$).—The first stream contained titanium(III) chloride (0.01—0.025M), ethylenediaminetetra-acetic acid (6 g dm^{-3}), and sufficient ammonia to give the desired pH, the second stream contained sodium persulphate (0.025M), and stream three was as in (a).

For the trapping experiments nitromethane (0.01M) was added to the third stream and the pH for the effluent stream was adjusted to *ca.* 9.

All material employed were commercially available samples, used as supplied.

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