J. Chem. Soc., Faraday Trans. 1, 1988, **84**(10), 3319–3330

Generation and Reactions of the Chlorine Atom in Aqueous Solution

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The chlorine atom ($Cl^{\bullet}$) has been generated in aqueous solution by reaction of Cl^- with $SO_4^{\bullet -}$ and $H_2PO_4^{\bullet}$, obtained by metal-catalysed decomposition of the appropriate peroxides. E.s.r. experiments in conjunction with a fast-flow method establish that $Cl^{\bullet}$ is highly reactive, readily undergoing rapid addition, hydrogen-abstraction and electron-transfer reactions ($k \approx 10^8$–10^9 dm^3 mol^{-1} s^{-1}). The factors which influence the observed selectivity (energetics and polar effects) are discussed.

The reactions of the chlorine atom ($Cl^{\bullet}$) in both organic solvents and the gas phase are relatively well understood,[1-3] but little is known of the reactivity of this species in aqueous solution. It is believed that $Cl^{\bullet}$ can be generated in water by oxidation of chloride with either[4] $SO_4^{\bullet -}$ or[5] $H_2PO_4^{\bullet}$ (both generated radiolytically) and rate constants for reactions (1) and (2)

$$SO_4^{\bullet -} + Cl^- \rightarrow Cl^{\bullet} + SO_4^{2-} \qquad (1)$$

$$H_2PO_4^{\bullet} + Cl^- \rightarrow Cl^{\bullet} + H_2PO_4^- \qquad (2)$$

of 3.1×10^8 and 2.2×10^6 dm^3 mol^{-1} s^{-1}, respectively, have been reported. However, in the presence of an excess of Cl^-, chlorine atoms are immediately scavenged[6] to give $Cl_2^{\bullet -}$ [reaction (3), $k_3 = 2.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 1 \times 10^5$ s^{-1}]

$$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet -} \qquad (3)$$

and this approach has been employed to explore the reactivity of this species: compared with, for example, $^{\bullet}OH$, $SO_4^{\bullet -}$ and $H_2PO_4^{\bullet}$, $Cl_2^{\bullet -}$ is believed to be relatively unreactive, at least towards hydrogen abstraction, although examples of relatively rapid reactions with alkenes (which result in β-chloroalkyl radicals) have been demonstrated.[7]

We have shown previously[8] that decomposition of peroxydisulphate with certain low-valence transition-metal ions (Ti^{III}, Fe^{II}, Cu^{I}) leads to the rapid generation of $SO_4^{\bullet -}$ [see *e.g.* reaction (4)]

$$Ti^{III} + S_2O_8^{2-} \rightarrow Ti^{IV} + SO_4^{\bullet -} + SO_4^{2-} \qquad (4)$$

and that reaction with chloride gives $Cl_2^{\bullet -}$[9] [*via* reactions (1) and (3)]. The experiments described here were designed so as to establish whether similar rapid decomposition of peroxymonosulphate ($HOOSO_3^-$) and peroxydiphosphate ($P_2O_8^{4-}$) could be induced and, in particular, whether conditions could be found (*e.g.* with $[Cl^-] < [RH]$) in which the direct reactions of the chlorine atom itself with organic substrates could be investigated:

$$Cl^{\bullet} + RH \rightarrow HCl + R^{\bullet}. \qquad (5)$$

Experimental

E.s.r. spectra were recorded on a Varian E-104 and Bruker ESP-300 spectrometer, each equipped with X-band klystron and 100 kHz modulation. Hyperfine splittings were measured directly from the field scan [with the ESP-300 by determination with an n.m.r.

gaussmeter ER 035M; with the E104 this was calibrated with an aqueous solution of Fremy's salt, *a*(N) 1.309 mT[10]; *g* values were determined by comparison with that for $^\bullet$CHMeOH ($g = 2.00321$[11]) obtained by reaction of $^\bullet$OH (Ti^{III}–H_2O_2) with ethanol. Relative radical concentrations were determined both by spectral simulation using a program supplied by Dr M. F. Chiu and by direct double integration (using the ESP-300).

For the flow experiments a mixing chamber was employed which allows simultaneous mixing of three reagent streams *ca.* 40 ms before passage through the cavity of the spectrometer. The flow was maintained using a Watson–Marlowe 502 peristaltic pump positioned on the inlet tubing. The solutions used were typically as follows: stream (i) contained titanium(III) sulphate (5×10^{-3} mol dm^{-3}) and concentrated sulphuric acid, stream (ii) contained the peroxide (at concentrations in the range 0.005–0.025 mol dm^{-3}: see later) and stream (iii) contained the substrate (at concentrations up to 1.5 mol dm^{-3}). Chloride ion was added as sodium chloride (0.01–1.0 mol dm^{-3}) to stream (iii) when required. pH Measurements were made using a Pye–Unicam pH meter PW9410 with the electrode inserted into the effluent stream. All solutions were deoxygenated both before and during use by purging with oxygen-free nitrogen.

In situ photolysis was carried out with the unfiltered radiation from an Hanovia 977B-1 1 kW mercury–xenon compact arc. Solutions containing $S_2O_8^{2-}$ (0.2 mol dm^{-3}) and the substrate (*ca.* 1.0 mol dm^{-3}) were slowly flowed through the cell.

The kinetic simulation program, executed on a DEC VAX computer, was kindly provided by Prof. D. J. Waddington. The chemicals employed were all commercial samples, used as supplied, except for potassium peroxymonosulphate (supplied as the triple salt $2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$) and potassium peroxydiphosphate ($K_4P_2O_8$), which were provided by Interox Chemicals Ltd.

Results and Discussion

Generation and Reactions of $SO_4^{\bullet -}$ and $H_2PO_4^\bullet$ in the Absence of Cl^-

In previous investigations we have shown that $SO_4^{\bullet -}$ can be generated by both *in situ* photolysis and decomposition with Ti^{III} of $S_2O_8^{2-}$ [reaction (4)] and that its subsequent reactions include addition to alkenes,[9] hydrogen abstraction (*e.g.* to give $^\bullet CH_2CMe_2OH$ and $Me^\bullet$, *via* $Me_3CO^\bullet$, from t-butyl alcohol) and overall electron transfer (from aromatic molecules and other electron-rich substrates.[12] Some typical substrates towards which its behaviour is known were chosen for initial studies of the viability of peroxymonosulphate ($HOOSO_3^-$) as an alternative source of $SO_4^{\bullet -}$ and of the possibility of generating the analogous phosphorus-containing radical ($H_2PO_4^\bullet$) for comparative purposes. Experiments with added chloride are described subsequently.

Reactions with Alkenes

Experiments with a variety of alkenes (see *e.g.* table 1) established that the Ti^{III}–peroxymonosulphate couple is an excellent source of $SO_4^{\bullet -}$: with typical conditions as follows, [Ti^{III}] [as titanium(III) sulphate] = 1.7×10^{-3} mol dm^{-3} and [HSO_5^-] = 5×10^{-3} mol dm^{-3},† it was found that strong signals of only $SO_4^{\bullet -}$ adducts to alkenes were detected [see table 1 and ref. (9)]. This indicates that reaction (6), rather than the alternative mode of decomposition, reaction (7), is preferred

$$Ti^{III} + HO{-}OSO_3^- \rightarrow Ti^{IV} + HO^- + SO_4^{\bullet -} \qquad (6)$$

$$Ti^{III} + HO{-}OSO_3^- \rightarrow Ti^{IV} + HO^\bullet + SO_4^{2-} \qquad (7)$$

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† Concentrations given hereafter in the text refer to those in the mixed stream.

(in contrast, one-electron reduction of peroxymonosulphate by pulse radiolysis yields[13] 80% $HO^{\cdot}$ and 20% $SO_4^{\cdot -}$). Kinetic analysis, using methods previously described,[8] leads to an estimate for the rate constant of the initiation reaction of 1.6×10^3 $dm^3\ mol^{-1}\ s^{-1}$ (*cf.* 2.0×10^2 $dm^3\ mol^{-1}\ s^{-1}$ for[8] Ti^{III}–$S_2O_8^{2-}$). This method was subsequently employed for generation of $SO_4^{\cdot -}$ for experiments with Cl^- (see below).

Experiments with Ti^{III} and peroxydiphosphate in which concentations and pH were varied were also employed in an attempt to establish conditions suitable for metal-catalysed generation of $H_2PO_4^{\cdot}$ (or $HPO_4^{\cdot -}$, $PO_4^{\cdot 2-}$). With alkenes and alkanols (see below) as substrates, we found that use of Ti^{III} (1.7×10^{-3} mol dm^{-3}, as the sulphate) and $H_2P_2O_8^{2-}$ (1.7×10^{-3} mol dm^{-3}) at pH 2 proved to be optimum conditions for the generation of phosphate-derived radicals:

$$Ti^{III} + H_4P_2O_8 \rightarrow Ti^{IV} + H_2PO_4^{\cdot} + H_2PO_4^{-} \qquad (8)$$

$$H_2PO_4^{\cdot} + HOCH_2CH{=}CH_2 \rightarrow HOCH_2\dot{C}H{-}CH_2OPO_3H^{-} + H^{+} \qquad (9)$$

(k_8 was estimated as 1×10^4 $dm^3\ mol^{-1}\ s^{-1}$). These conditions were subsequently employed in experiments with a range of alkenes in which the corresponding phosphate adducts were detected [in the monoprotonated form at this pH:[14] see table 1 and reaction (9)]. For some substrates (*e.g.* allyl alcohol or but-2-ene-1,4-diol) the detection of significant concentrations of allyl radicals indicates that, compared with $SO_4^{\cdot -}$, $H_2PO_4^{\cdot}$ has a greater propensity for hydrogen abstraction [see *e.g.* reaction (10)]:

$$H_2PO_4^{\cdot} + HOCH_2CH{=}CH_2 \rightarrow HO\dot{C}H{-}CH{=}CH_2 + H^{+} + H_2PO_4^{-}. \qquad (10)$$

Reactions with Alcohols and Acids

Reaction of $SO_4^{\cdot -}$ (with high [peroxymonosulphate]) with t-butyl alcohol was found, as expected,[12a] to give signals from both $^{\cdot}CH_2CMe_2OH$ and $^{\cdot}Me$, in the ratio 7:1:

$$SO_4^{\cdot -} + Me_3COH \begin{array}{l} \nearrow SO_4^{2-} + H^{+} + {}^{\cdot}CH_2CMe_2OH \qquad (11) \\ \searrow SO_4^{2-} + H^{+} + Me_3CO^{\cdot} \rightarrow Me_2CO + Me^{\cdot}. \qquad (12) \end{array}$$

With ethanol as substrate, detection of both α- and β-radicals ($^{\cdot}CHMeOH$ and $^{\cdot}CH_2CH_2OH$) was accompanied by signals from the methyl radical (especially at high [$HOOSO_3^-$]) the formation of which is attributed to subsequent oxidation of the first-formed radical, $^{\cdot}CHMeOH$, with the parent peroxide (the detailed mechanism of this reaction will be discussed elsewhere). Reactions of $H_2PO_4^{\cdot}$ with these substrates led to the detection solely of $^{\cdot}CH_2CMe_2OH$ from Bu^tOH and almost exclusively $^{\cdot}CHMeOH$ from EtOH:

$$H_2PO_4^{\cdot} + Me_3COH \rightarrow H_2PO_4^{-} + H^{+} + {}^{\cdot}CH_2CMe_2OH \qquad (13)$$

$$H_2PO_4^{\cdot} + EtOH \rightarrow H_2PO_4^{-} + H^{+} + Me\dot{C}HOH. \qquad (14)$$

The apparent increase in selectivity of $H_2PO_4^{\cdot}$ compared with $SO_4^{\cdot -}$ towards ethanol is perhaps surprising in terms of the greater rate of reaction reported for the former;[15] the failure to react *via* O—H abstraction with Bu^tOH may indicate its reluctance (relative to the more electrophilic $SO_4^{\cdot -}$) to react *via* electron transfer at oxygen.

With other alkanols comparable behaviour was observed. For example, propan-1-ol reacted with the Ti^{III}–$HOOSO_3^-$ couple to give signals from $^{\cdot}CHEtOH$, $^{\cdot}CHMeCH_2OH$ and $^{\cdot}CH_2CH_2CH_2OH$, as well as $Et^{\cdot}$ (evidently derived by further oxidation of $^{\cdot}CHEtOH$: see above). With $H_2PO_4^{\cdot}$ the dominant signal detected (*ca.* 80%) was from the α-radical $^{\cdot}CHEt(OH)$.

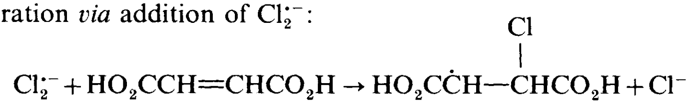
Reaction of Ti^{III} at pH 1.5 with either peroxymonosulphate or peroxydisulphate and Cu^{II} [*cf.* ref. (8)] in the presence of some simple aliphatic acids (*e.g.* ethanoic and propanoic acids) under the conditions described above did not lead to detectable signals from substrate-derived radicals. This is believed to reflect the relatively low reactivity of the electrophilic sulphate radical anion towards the acids themselves (in contrast to the much greater reactivity of the corresponding anions). However, as noted previously,[12a] photolytic decomposition of persulphate can be employed to establish that decarboxylation accompanies β-H attack: $EtCO_2H$ gives $^{\bullet}CH_2CH_2CO_2H$ ($k = 2 \times 10^5$ dm^3 mol^{-1} s^{-1}) and $Et^{\bullet}$ ($k = 7 \times 10^4$ dm^3 mol^{-1} s^{-1}), as well as $^{\bullet}CHMeCO_2H$, formed largely by subsequent reaction of the primary radicals with the high concentrations of parent compound employed (rather than direct abstraction). Ethanoic acid gives $^{\bullet}Me$ and $^{\bullet}CH_2CO_2H$ similarly, with the former present at higher concentrations (up to $[MeCO_2H] \approx 1.0$ mol dm^{-3}).

Reaction of $H_2PO_4^{\bullet}$ with ethanoic acid led to the detection of $^{\bullet}CH_2CO_2H$ (as the major radical) and $^{\bullet}Me$, indicating that both C—H and O—H abstraction occur, but that the less electrophilic $H_2PO_4^{\bullet}$ does not share the sulphate radical anion's reluctance for abstraction of the C—H next to the carboxyl group.

Reaction of $SO_4^{\bullet -}$ and $H_2PO_4^{\bullet}$ in the Presence of Cl^-

Reaction with Alkenes

When fumaric acid was employed as a substrate for $SO_4^{\bullet -}$ in the flow system, with the Ti^{III}–$HOOSO_3^-$ couple at pH ≈ 1.5, weak signals from $^{\bullet}CH(CO_2H)—CH(OSO_3^-)CO_2H$ were observed. On addition of Cl^- (0.005 mol dm^{-3}) to the system these signals were replaced by those assigned to (1) (see fig. 1 and table 1); the effect of increasing chloride ion on the concentration of this radical is shown in fig. 2. The marked decrease in the concentration of chlorine adduct above $[Cl^-]$ 0.02 mol dm^{-3} is apparently inconsistent with its generation *via* addition of $Cl_2^{\bullet -}$:



$$Cl_2^{\bullet -} + HO_2CCH{=}CHCO_2H \rightarrow HO_2C\dot{C}H{-}\overset{\overset{\displaystyle Cl}{|}}{C}HCO_2H + Cl^- \qquad (15)$$

(1)

as might have been expected, but could be explained if the radical largely results from direct addition of $Cl^{\bullet}$:

$$Cl^{\bullet} + HO_2CCH{=}CHCO_2H \rightarrow (1) \qquad (16)$$

[in competition with its scavenging by Cl^-, reaction (3)]. Similar, though less marked, trends were observed for citraconic acid ($HO_2CCH{=}CMeCO_2H$).

In contrast, reactions of $SO_4^{\bullet -}$ with a range of other alkenes (see table 1) in the presence of low concentrations of Cl^- (up to *ca.* 0.1 mol dm^{-3}) failed to reveal the presence of chlorine-atom adducts. We attribute this observation to the high reactivity of $SO_4^{\bullet -}$ towards alkenes lacking the two carboxylate substitutents: the rate constant of *ca.* 1.5×10^9 dm^3 mol^{-1} s^{-1} for reaction of $SO_4^{\bullet -}$ with allyl alcohol[15] suggests that in these cases the reaction with Cl^- is precluded, whereas the significantly lower rate constant expected for fumaric and maleic acid (the rate constant for fumarate ion is[16] 1.6×10^7 dm^3 mol^{-1} s^{-1}) is consistent with there being a significant contribution from reaction (16). In parallel experiments with $H_2PO_4^{\bullet}$, only in the case of fumaric (and maleic) acids did the addition of low concentrations of Cl^- lead to the detection of a chlorine adduct, which is taken to indicate the relatively low reactivity of these alkenes with $H_2PO_4^{\bullet}$, so that reactions (2) and (16) can compete effectively.

However, at considerably higher concentrations of added chloride ion, chlorine adducts (and in some cases hydroxyl adducts) can be detected from more reactive alkenes, *e.g.* allyl alcohol and 2-methylpropene (as already noted[9]): this observation is believed to reflect the reaction of these alkenes with $Cl_2^{\bullet -}$, rather than the chlorine atom.

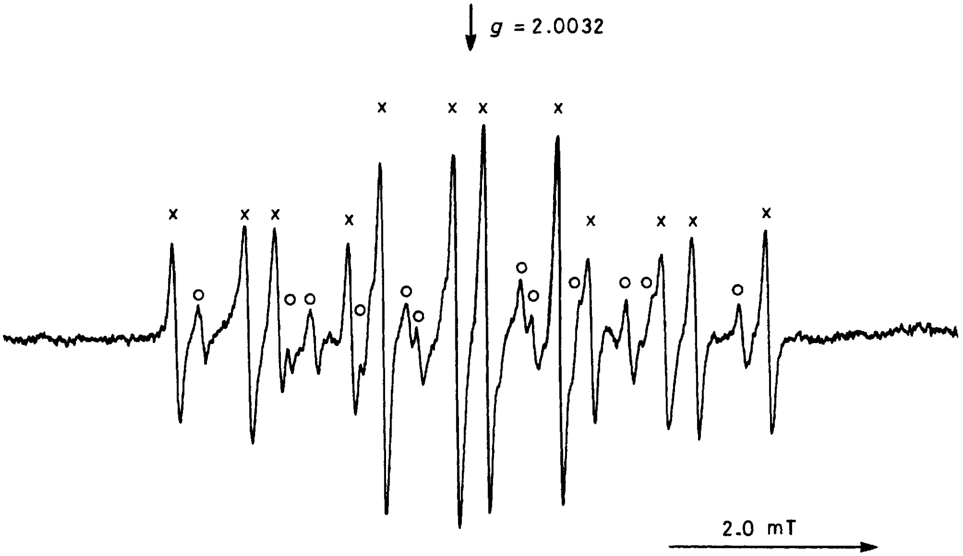


Fig. 1. E.s.r. spectra of the adducts of ^{35}Cl and ^{37}Cl (from Cl^- and $SO_4^{\bullet -}$) and fumaric acid (2.5×10^{-2} mol dm^{-3}), $^{\bullet}CH(CO_2H)$—$CHCl(CO_2H)$, at pH 1.5 ($[Cl^-] = 5 \times 10^{-3}$ mol dm^{-3}): ×, ^{35}Cl; o, ^{37}Cl.

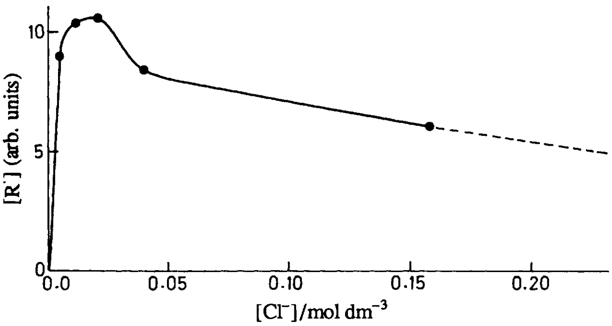


Fig. 2. Variation with $[Cl^-]$ of the concentration of the adduct $^{\bullet}CH(CO_2H)$—$CHCl(CO_2H)$ in experiments with fumaric acid (2.5×10^{-2} mol dm^{-3}), titanium(III) sulphate (1.7×10^{-3} mol dm^{-3}) and peroxymonosulphate (5×10^{-3} mol dm^{-3}) at pH 1.5.

Reaction with Alkanols and Acids

Addition of relatively low concentrations of chloride ion to experiments involving the reaction between $SO_4^{\bullet -}$ (from Ti^{III}–$HOOSO_3^-$) and Bu^tOH caused a dramatic enhancement of the concentrations of both $^{\bullet}CH_2CMe_2OH$ and $^{\bullet}Me$ with a correspondingly greater increase in the concentration of the latter (with $[Cl^-] = 0.005$ mol dm^{-3} the ratio is *ca.* 2:1: see table 2). At high concentrations of chloride, all signals were removed (see fig. 3). We interpret these observations, as with the related behaviour of alkenes, in terms of the reaction of $Cl^{\bullet}$ itself with Bu^tOH at low chloride concentrations [with a significant amount of O—H abstraction: reactions (17) and (18)] and its replacement at high $[Cl^-]$ by $Cl_2^{\bullet -}$, which is relatively unreactive towards hydrogen abstraction [it has been reported[7] that the rate constant for reaction between $Cl_2^{\bullet -}$ and

Table 1. E.s.r. parameters of radicals detected from alkenes in their reactions with $SO_4^{\cdot -}$, $H_2PO_4^{\cdot}$, $Cl^{\cdot}$ and $Cl_2^{\cdot -}$

substrate	attacking radical	radical formed	hyperfine splitting[a] $a(\alpha\text{-H})$	$a(\beta\text{-H})$	a(other)	g[b]
$HO_2CCH{=}CHCO_2H$	$SO_4^{\cdot -}$	$^{\cdot}CH(CO_2H)CH(OSO_3^-)CO_2H$	2.09	1.04	—	2.0032
	$H_2PO_4^{\cdot}$	$^{\cdot}CH(CO_2H)CH(OPO_3H^-)CO_2H$	2.07	1.14	—	2.0032
	$Cl^{\cdot}/Cl_2^{\cdot -}$	$^{\cdot}CH(CO_2H)CH(Cl)CO_2H$	2.08	0.73	1.03(^{35}Cl), 0.85(^{37}Cl)	2.0032
$HO_2CCH{=}CMeCO_2H$	$SO_4^{\cdot -}$	$^{\cdot}CMe(CO_2H)CH(OSO_3^-)CO_2H$	—	0.56, 2.34 (3)	—	2.0032
	$H_2PO_4^{\cdot}$	$^{\cdot}CMe(CO_2H)CH(OPO_3H^-)CO_2H$	—	0.66, 2.34 (3)	—	2.0032
	$Cl^{\cdot}/Cl_2^{\cdot -}$	$^{\cdot}CMe(CO_2H)CH(Cl)CO_2H$	—	0.42, 2.30 (3)	0.90(^{35}Cl), 0.75(^{37}Cl)	2.0032
$HO_2CCH{=}CHMe$	$SO_4^{\cdot -}$	$^{\cdot}CHMeCH(OSO_3^-)CO_2H$	2.19	1.42, 2.59 (3)	—	2.0025
		$^{\cdot}CH(CO_2H)CH(OSO_3^-)Me$	2.06	1.23	0.17 (3)	2.0031
	$H_2PO_4^{\cdot}$	$^{\cdot}CHMeCH(OPO_3H^-)CO_2H$	2.17	1.46, 2.58 (3)	—	2.0025
		$^{\cdot}CH(CO_2H)CH(OPO_3H^-)Me$	2.07	1.34	0.17 (3)	2.0031
	$Cl_2^{\cdot -}$	—[c]				
$HOCH_2CH{=}CH_2$	$SO_4^{\cdot -}$	$^{\cdot}CH(CH_2OH)CH_2OSO_3^-$	2.15	1.77 (2), 2.38 (2)	—	2.0025
		$^{\cdot}CH_2CH(OSO_3^-)CH_2OH$	2.12 (2)	2.05	—	2.0025
	$H_2PO_4^{\cdot}$	$^{\cdot}CH(CH_2OH)CH_2OPO_3H^-$	2.16	2.04 (2), 2.21 (2)	0.15(^{31}P)	2.0025
		$^{\cdot}CH(OH)CH{=}CH_2$	0.34, 1.38 (3)	—	—	2.0025
	$Cl_2^{\cdot -}$	$^{\cdot}CH(CH_2OH)CH_2Cl$	2.07	0.92 (2), 2.40 (2)	1.90(^{35}Cl), 1.56(^{37}Cl)	2.0027
$HOCH_2CH{=}CHMe$	$SO_4^{\cdot -}$	$^{\cdot}CHMeCH(OSO_3^-)CH_2OH$	2.15	1.35, 2.54 (3)	—	2.0025
		$^{\cdot}CH(CH_2OH)CH(OSO_3^-)Me$	2.18	1.45, 2.25 (2)	0.11 (3)	2.0025
	$H_2PO_4^{\cdot}$	$^{\cdot}CHMeCH(OPO_3H^-)CH_2OH$	2.17	1.61, 2.58 (3)	—	2.0025
		$^{\cdot}CH(CH_2OH)CH(OPO_3H^-)Me$	2.18	1.73, 2.21 (2)	0.10(3H, ^{31}P)	2.0025
	$Cl_2^{\cdot -}$	$^{\cdot}CHMeCH(OH)CH_2OH$	2.13	1.71, 2.51 (3)	—	2.0025
		$^{\cdot}CH(CH_2OH)CH(OH)Me$	2.17	1.75, 2.15 (2)	0.08 (3)	2.0025
$HOCH_2CH{=}CHCH_2OH$	$SO_4^{\cdot -}$	$^{\cdot}CH(CH_2OH)CH(OSO_3^-)CH_2OH$	2.16	1.41, 2.38, 2.31[d]	0.11(γ-H)	2.0025
	$H_2PO_4^{\cdot}$	$^{\cdot}CH(CH_2OH)CH(OPO_3H^-)CH_2OH$	2.21	1.61, 2.24 (2)	—	2.0025
		$^{\cdot}CH(OH)CH{=}CHCH_2OH$	0.37, 1.34 (2)	0.95 (2)	—	2.0025
	$Cl_2^{\cdot -}$	$^{\cdot}CH(CH_2OH)CH(Cl)CH_2OH$	2.21	0.95, 2.25 (2)	1.20(^{35}Cl), 1.00(^{37}Cl)	2.0025
$Me_2C{=}CH_2$	$SO_4^{\cdot -}$	$^{\cdot}CMe_2CH_2OSO_3^-$	—	1.17 (2), 2.31 (6)	—	2.0025
	$H_2PO_4^{\cdot}$	$^{\cdot}CMe_2CH_2OPO_3H^-$	—	1.35 (2), 2.35 (6)	0.37(^{31}P)	2.0025
	$Cl_2^{\cdot}$	$^{\cdot}CMe_2CH_2OH$	—	1.45 (2), 2.32 (6)	—	2.0025
$MeCH{=}CHMe$	$SO_4^{\cdot -}$	$^{\cdot}CHMeCH(OSO_3^-)Me$	2.18	1.43, 2.56 (3)	1.10 (3)	2.0025
	$H_2PO_4^{\cdot}$	$^{\cdot}CHMeCH(OPO_3H^-)Me$	2.10	1.65, 2.58 (3)	1.00 (3)	2.0025
	$Cl_2^{\cdot -}$	$^{\cdot}CHMeCH(OH)Me$	2.12	1.70, 2.50 (3)	—	2.0025

[a] +0.01 mT; coupling to 1 H unless indicated otherwise. [b] +0.0001. [c] Spectra not analysed. [d] Non-equivalent β-protons.

Table 2. Site selectivity of hydrogen abstraction from alkanols and acids by $Cl^{\bullet}$, $SO_4^{\bullet -}$ and $H_2PO_4^{\bullet}$

substrate	reagent	radicals formed[a]
Me_3COH	$SO_4^{\bullet -}$	$^{\bullet}CH_2CMe_2OH$ (86%), $CH_3^{\bullet}$ (14%)
	$H_2PO_4^{\bullet}$	$^{\bullet}CH_2CMe_2OH$ (100%)
	$Cl^{\bullet}$	$^{\bullet}CH_2CMe_2OH$ (67%), $CH_3^{\bullet}$ (33%)
EtOH	$SO_4^{\bullet -}$	$^{\bullet}CHMeOH$ (31%),[b] $^{\bullet}CH_2CH_2OH$ (10%), $CH_3^{\bullet}$ (59%)[b]
	$H_2PO_4^{\bullet}$	$^{\bullet}CHMeOH$ (97.5%), $^{\bullet}CH_2CH_2OH$ (2.5%)
	$SO_4^{\bullet -}/Cl^{\bullet}$[c]	$^{\bullet}CHMeOH$ (18%),[b] $^{\bullet}CH_2CH_2OH$ (43%), $CH_3^{\bullet}$ (39%)[b]
PrOH	$SO_4^{\bullet -}$	$^{\bullet}CH_2CH_2CH_2OH$ (13%), $^{\bullet}CHMeCH_2OH$ (38%), $^{\bullet}CHEtOH$ (9%), $Et^{\bullet}$ (40%)
	$H_2PO_4^{\bullet}$	$^{\bullet}CHMeCH_2OH$ (20%), $^{\bullet}CHEtOH$ (80)%)
	$SO_4^{\bullet -}/Cl^{\bullet}$[c]	$^{\bullet}CH_2CH_2CH_2OH$ (28%), $^{\bullet}CHMeCH_2OH$ (41%), $^{\bullet}CHEtOH$ (6%),[b] $Et^{\bullet}$ (25%)
$MeCO_2H$	[d]$SO_4^{\bullet -}$	$^{\bullet}CH_2CO_2H$ (33%),[e] $CH_3^{\bullet}$(67%)
	$H_2PO_4^{\bullet}$	$^{\bullet}CH_2CO_2H$(67%),[e] $CH_3^{\bullet}$(33%)
	$Cl^{\bullet}$	$^{\bullet}CH_2CO_2H$ (10%),[e] $CH_3^{\bullet}$ (90%)
$EtCO_2H$	[d]$SO_4^{\bullet -}$	$^{\bullet}CH_2CH_2CO_2H$ (60%), $^{\bullet}CHMeCO_2H$[e] (20%), $Et^{\bullet}$ (20%)
	$H_2PO_4^{\bullet}$	$^{\bullet}CH_2CH_2CO_2H$ (52%), $^{\bullet}CHMeCO_2H$ (30%), $Et^{\bullet}$ (18%)
	$Cl^{\bullet}$	$^{\bullet}CH_2CH_2CO_2H$ (60%), $^{\bullet}CHMeCO_2H$[e] (15%), $Et^{\bullet}$ (25%)
$(HO_2CCH_2)_2$	[d]$SO_4^{\bullet -}$	$^{\bullet}CH_2CH_2CO_2H$ (90%), $^{\bullet}CH(CO_2H)CH_2CO_2H$[e] (10%)
	$H_2PO_4^{\bullet}$	$^{\bullet}CH_2CH_2CO_2H$ (40%), $^{\bullet}CH(CO_2H)CH_2CO_2H$ (60%)
	$Cl^{\bullet}$	$^{\bullet}CH_2CH_2CO_2H$ (100%)
$MeCO_2Et$	[d]$SO_4^{\bullet -}$	$^{\bullet}CH_2CH_2OCOMe$ (100%)
	$H_2PO_4^{\bullet}$	$^{\bullet}CH_2CH_2OCOMe$ (57%), $^{\bullet}CHMeOCOMe$ (43%)
	$Cl^{\bullet}$	$^{\bullet}CH_2CH_2OCOMe$ (100%)

[a] Flow experiment (see text) except where indicated otherwise. [b] SO_4^{-} obtained from the reaction between Ti^{III} and $HOOSO_3^{-}$ (see text). $HOOSO_3^{-}$ is a powerful oxidant which dramatically reduces the α-radical concentration, leading to the formation of alkyl radicals (see text). [c] Since these substrates are very reactive towards $SO_4^{\bullet -}$, the ratios observed reflect the combined reactions of $SO_4^{\bullet -}$ and $Cl^{\bullet}$. [d] $SO_4^{\bullet -}$ generated by photolysis. [e] Some or all of these radicals are believed to result from reaction of first-formed organic radicals with the substrate (see text).

Bu^tOH is only 7×10^2 dm^3 mol^{-1} s^{-1}]. Photolytic experiments with Bu^tOH and $S_2O_8^{2-}$ in the presence of Cl^- led to the expected enhancement of [$Me^{\bullet}$] (for [Cl^-] 0.01 mol dm^{-3}) and the decrease of all signals for [Cl^-] > 0.4 mol dm^{-3}.

In an attempt to corroborate this interpretation we studied the effect of incorporation of Cl^- into the reaction between $H_2PO_4^{\bullet}$ and Bu^tOH (which yields only $^{\bullet}CH_2CMe_2OH$): as would be predicted on the basis of the occurrence of reactions (17) and (18):

$$Me_3COH + Cl^{\bullet} \begin{array}{l} \nearrow\ ^{\bullet}CH_2CMe_2OH + HCl \qquad (17) \\ \searrow\ HCl + Me_3CO^{\bullet} \rightarrow Me_2CO + Me^{\bullet} \qquad (18) \end{array}$$

with the latter somewhat more significant, signals from $^{\bullet}CH_2CMe_2OH$ were now accompanied by strong signals from $Me^{\bullet}$. At high [Cl^-], all signals were removed. A full kinetic analysis and further mechanistic discussion is presented below.

With ethanol as substrate for reaction with $SO_4^{\bullet -}$, addition of low concentrations of Cl^- (*ca.* 0.03 mol dm^{-3}) led to a dramatic enhancement of the signal from the β-radical, $^{\bullet}CH_2CH_2OH$, accompanied by a decrease in the concentrations of $^{\bullet}CHMeOH$ and $Me^{\bullet}$ (see table 2). Similarly, reaction of $H_2PO_4^{\bullet}$ with ethanol in the presence of chloride led to the detection of significant concentrations of the β-isomer (together with the α-radical generated by direct attack by $H_2PO_4^{\bullet}$). We conclude that $Cl^{\bullet}$ is a very reactive species,

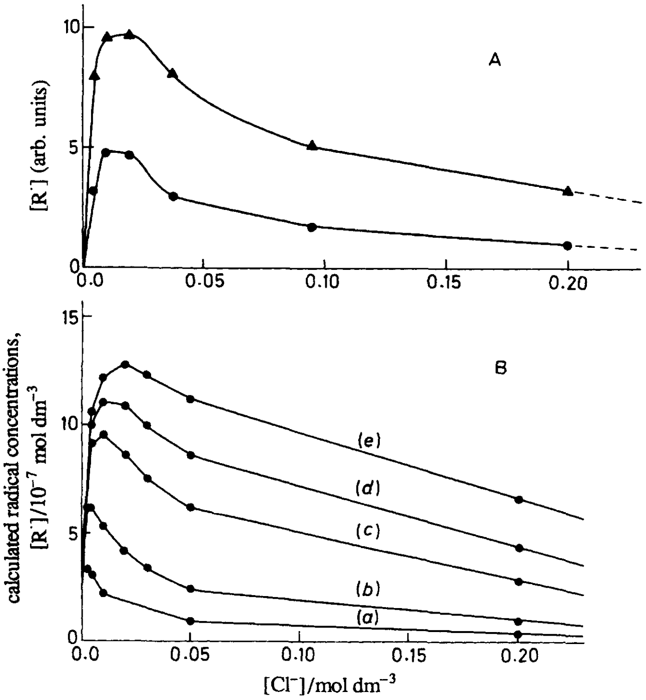


Fig. 3. (A) Variation with $[Cl^-]$ of $[R^\bullet]$ (●, methyl; ▲, $^\bullet CH_2CMe_2OH$) in experiments with Bu^tOH (3.3% v/v), titanium(III) sulphate (1.7×10^{-3} mol dm^{-3}) and peroxymonosulphate (5×10^{-3} mol dm^{-3}) at pH 2. (B) Kinetic simulations of the experimental results shown in (A) (total radical concentration), employing different values of the rate constant for attack of $Cl^\bullet$ on Bu^tOH (for details, see text): (*a*) 1×10^7, (*b*) 1×10^8, (*c*) 5×10^8, (*d*) 1×10^9 and (*e*) 2×10^9 dm^3 mol^{-1} s^{-1}.

which, compared with $SO_4^{\bullet -}$ and $H_2PO_4^\bullet$, is less discriminating between α- and β-positions: a kinetic analysis is presented below.

With propan-1-ol, addition of Cl^- (0.03 mol dm^{-3}) in $SO_4^{\bullet -}$ experiments caused a significant increase in the concentrations of $^\bullet CHMeCH_2OH$ and, especially, $^\bullet CH_2CH_2CH_2OH$, as expected on the basis of results for ethanol described above. Similar, but less marked, trends were observed for $H_2PO_4^\bullet$.

Addition of Cl^- (0.005 mol dm^{-3}) to experiments with Ti^{III}, $HOOSO_3^-$ and ethanoic acid led to the appearance of strong signals from $^\bullet Me$, accompanied by much smaller concentrations of $^\bullet CH_2CO_2H$ (in the ratio *ca.* 9:1): in related photolysis experiments, $[Me^\bullet]$ was also enhanced by addition of chloride. This suggests that $Cl^\bullet$ reacts rapidly with this substrate largely (or almost exclusively) *via* hydrogen abstraction from the carboxyl group, reaction (19) [formation of $^\bullet CH_2CO_2H$ is believed[12a] largely to be the result of reaction (20)]:

$$MeCO_2H + Cl^\bullet \rightarrow HCl + MeCO_2^\bullet \rightarrow Me^\bullet + CO_2 \tag{19}$$

$$Me^\bullet + MeCO_2H \rightarrow CH_4 + {^\bullet CH_2CO_2H}. \tag{20}$$

At high $[Cl^-]$ (*ca.* 0.2 mol dm^{-3}) no signals could be detected, presumably reflecting the low reactivity of $Cl_2^{\bullet -}$ towards ethanoic acid[7] ($k < 10^4$ dm^3 mol^{-1} s^{-1}). In related experiments with perphosphate alone, signals from $^\bullet CH_2CO_2H$ dominated those from $Me^\bullet$: addition of low chloride concentrations significantly enhanced signals from the latter, consistent with the interpretation of the persulphate/chloride experiments.

Table 3. Rate constants for reaction of $Cl^{\bullet}$ with organic substrates in water at 20 °C[a]

substrate	$k_{Cl^{\bullet}}/dm^3\ mol^{-1}\ s^{-1}$	$k_{Cl_2^{\bullet-}}/dm^3\ mol^{-1}\ s^{-1}$
Me_3COH	1.5×10^9 (C—H)[b] 7.0×10^8 (O—H)	7×10^2
EtOH	1.5×10^9 (α-H)[b] 7.5×10^8 (β-H)[b]	4.5×10^4
$MeCO_2H$	2×10^8 (CO_2H)	$< 1 \times 10^4$
$EtCO_2H$	2×10^8 (CO_2H) 6×10^8 (β-H)[b]	2.2×10^3
$HO_2CCH{=}CHCO_2H$	*ca.* 3×10^9	*ca.* 2×10^5

[a] Data for $Cl_2^{\bullet-}$ (for comparative purposes) taken from ref. (7). [b] Overall rate constant for reaction at this position.

In related experiments we showed that $Cl^{\bullet}$ (from both $SO_4^{\bullet-}$ and $H_2PO_4^{\bullet}$) reacts with propanoic acid to give $^{\bullet}CH_2CH_2CO_2H$ and $CH_3CH_2^{\bullet}$ (in the ratio *ca.* 2:1), with relatively weak signals detected from $^{\bullet}CHMeCO_2H$ [this probably results from hydrogen-atom abstraction by the primary radicals: see ref. (12*a*)]. Under similar conditions, succinic acid was exclusively decarboxylated to give $HO_2CCH_2{—}CH_2^{\bullet}$.

Reactions of ethyl ethanoate with $Cl^{\bullet}$ (carried out similarly) revealed the exclusive formation of the radical $^{\bullet}CH_2CH_2OC(O)Me$. No signals could be obtained from experiments involving the reaction of $Cl^{\bullet}$ with either acetonitrile or propanone; this presumably reflects the lack of reactivity of the highly electrophilic $Cl^{\bullet}$ towards a C—H bond adjacent to a substituent of the type —M.

Kinetic Analysis

A kinetic analysis of the proposed reaction of $Cl^{\bullet}$ with aliphatic substrates has been carried out using a kinetic simulation program to model the pseudo-steady-state conditions which are achieved in the cavity of the e.s.r. spectrometer in rapid-mixing experiment using Ti^{III}-peroxide redox couples.[16]

For example, the reaction between $Cl^{\bullet}$ (from $SO_4^{\bullet-}$) and Bu^tOH will involve (if correct mechanistic conclusions have been drawn) the generation of $SO_4^{\bullet-}$ [reaction (6), $k = 1.6 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$], oxidation of Cl^- [reaction (1),[4] $k = 3.1 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$] and subsequent attack on Bu^tOH [rate constant(s) to be determined]. Allowance must be made for the possibility that $Cl_2^{\bullet-}$ is formed [reaction (3), $k_3 = 2.1 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$, $k_{-3} = 1 \times 10^5\ s^{-1}$][6] and that $SO_4^{\bullet-}$ and $Cl_2^{\bullet-}$ can each react with the substrate[15] ($k = 4.0 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$ and $7 \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, respectively) and with Ti^{III} itself (k estimated to be *ca.* $2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ and $4.0 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$, respectively[15]). Allowance for radical oxidation by $HOOSO_3^-$ has also been made [*cf.* ref. (17)]. It was found that only by the incorporation of a rate constant for reaction of $Cl^{\bullet}$ with Bu^tOH of *ca.* $1 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ can the observed behaviour of the $SO_4^{\bullet-}/Cl^-/Bu^tOH$ system [fig. 3(*b*)] be reproduced (see also below): the calculations also indicate that the reduction of observed radical concentrations at high $[Cl^-]$ results from the increased occurrence of reaction (3), to generate $Cl_2^{\bullet-}$, the reactivity of which towards the substrate is lower. Similar analysis of the behaviour of aliphatic carboxylic acids leads to overall rates of attack by $Cl^{\bullet}$ of the order of $10^8\ dm^3\ mol^{-1}\ s^{-1}$, whereas the rate constant for addition to fumaric acid is *ca.* $3 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. Kinetic analysis of our results also confirms that, as suggested above, reactions of $Cl^{\bullet}$ are manifest most clearly when the first-formed radicals, $SO_4^{\bullet-}$ and $H_2PO_4^{\bullet}$, are relatively unreactive towards substrates (*e.g.*

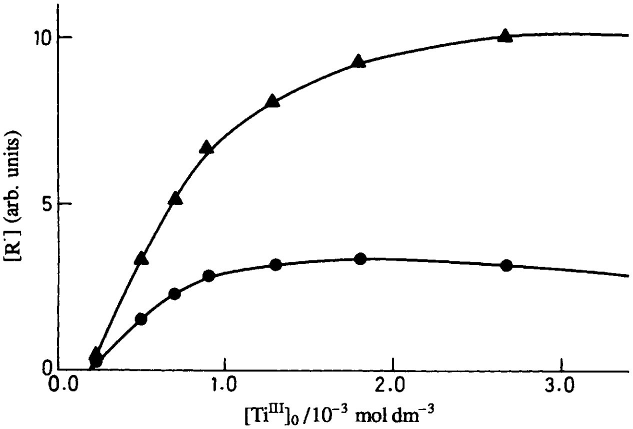


Fig. 4. Variation with [Ti^{III}] of [Me˙] (●) and [˙CH_2CMe_2OH] (▲) in experiments with Bu^{t}OH (10% v/v), titanium(III) sulphate, Cl^- (0.01 mol dm^{-3}) and $HOOSO_3^-$ (5×10^{-3} mol dm^{-3}) at pH 2.

acids, alkenic acids, unactivated alcohols, with $k \approx 10^5$–10^6 dm^3 mol^{-1} s^{-1}) to allow competitive attack on Cl^- at low [Cl^-] to take place (to avoid $Cl_2^{\cdot -}$ formation). Computed rate constants, chosen so as to optimize the agreement with observed behaviour, are collected together in table 3.

A more detailed study of the Ti^{III}/$HOOSO_3^-$/Cl^- system at pH 2 with Bu^{t}OH as substrate revealed an unexpected dependence of the ratio of [˙CH_2CMe_2OH]/[Me˙] on [Ti^{III}]; increase of the latter, other conditions being held constant, led to a significant increase in the ratio (see fig. 4). This is interpreted in terms of a rapid reaction of Bu^{t}O˙ with Ti^{III} (*cf.* the rapid reaction of Ti^{III} with ˙OH[18]), in competition with the generation of Me˙ in fragmentation (see scheme 1). Taking $k_{21} = 1.4\times10^6$ dm^3 mol^{-1} s^{-1}[19] and other rate constants as indicated above (*cf.* also table 3) we were able to simulate experimental observations, with a value for k_{22}, the rate constant for reduction of Bu^{t}O˙ by Ti^{III} of 6.0×10^8 dm^3 mol^{-1} s^{-1}.

$$\mathrm{Ti^{III} + HOOSO_3^- \rightarrow Ti^{IV} + HO^- + SO_4^{\cdot -}} \qquad (6)$$

$$\mathrm{SO_4^{\cdot -} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot}} \qquad (1)$$

$$\mathrm{Cl^{\cdot} + Me_3COH \rightarrow HCl + {}^{\cdot}CH_2CMe_2OH} \qquad (17)$$

$$\mathrm{Cl^{\cdot} + Me_3COH \rightarrow Me_3CO^{\cdot} + HCl} \qquad (18)$$

$$\mathrm{Me_3CO^{\cdot} \rightarrow Me^{\cdot} + Me_2CO} \qquad (21)$$

$$\mathrm{Me_3CO^{\cdot} + Ti^{III} \rightarrow Ti^{IV} + Me_3CO^-} \qquad (22)$$

$$\left.\begin{array}{r} \mathrm{Me^{\cdot} + Me^{\cdot} \rightarrow} \\ \mathrm{Me^{\cdot} + {}^{\cdot}CH_2CMe_2OH \rightarrow} \\ \mathrm{{}^{\cdot}CH_2CMe_2OH + {}^{\cdot}CH_2CMe_2OH \rightarrow} \end{array}\right\} \begin{array}{c}\text{non-radical}\\ \text{products}\end{array} \qquad \begin{array}{r}(23)\\(24)\\(25)\end{array}$$

Scheme 1.

Conclusions

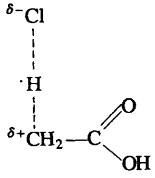
Our results demonstrate that conditions can readily be established in which oxidation of chloride ion by the one-electron oxidants $SO_4^{\cdot -}$ and $H_2PO_4^{\cdot}$ (formed from metal–peroxide reaction or, in the former case, photolytically) can produce the very reactive chlorine atom (rather than $Cl_2^{\bullet-}$). The reactions exhibited by $Cl^{\bullet}$ include addition to alkenes (see tables 1 and 3) as well as rapid hydrogen-atom abstraction from C—H bonds in acids and alcohols (table 2).

Like the hydroxyl radical, $Cl^{\bullet}$ reacts with ethanol at an overall rate which is close to the diffusion-controlled limit ($k_{OH} \approx 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1}),[18] which is an indication of the extreme reactivity of this electrophilic species (and which presumably also reflects the exothermicity of the reaction). However, compared with $^{\bullet}OH$ attack, for which attack is predominantly of the α-position ($\alpha/\beta = 13$),[20] the chlorine atom leads to a significant amount of β-abstraction ($\alpha/\beta \approx 2$).† This apparent lack of selectivity is consistent with the greater reactivity of $Cl^{\bullet}$ and an earlier transition state, with less bond-breaking and contribution from resonance stabilisation of α-abstraction in the transition state (*cf.* comparable behaviour for $Cl^{\bullet}$ in organic solvents[22, 23]).

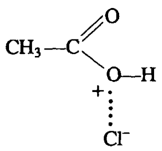
The chlorine atom shows a preference for O—H rather than C—H abstraction (per C—H bond) in its reaction with Bu^tOH ($SO_4^{\bullet-}$ shows similar but less marked behaviour: $^{\bullet}OH$ and $H_2PO_4^{\bullet}$ undergo exclusively C—H abstraction). Although consideration of the bond strengths involved [C—H = 401, O—H = 440 and H—Cl = 433 kJ mol^{-1}: *cf.* ref. (24), (25) and (1), respectively] would suggest that C—H bond abstraction should be favoured (reaction of MeOH in the gas phase[26] gives only C—H abstraction with $Cl^{\bullet}$), the overall exothermicity in aqueous solution is presumably increased by the dissociation of HCl and solvation of the H^+ and Cl^- ions. It is also likely that the overall O—H abstraction reaction proceeds *via* an electron-transfer mechanism, as shown in reaction (26) (a process in which the aqueous environment would be expected to stabilize the incipient charges):

$$Me_3COH + Cl \rightarrow [Cl^- + Me_3C\overset{\cdot+}{O}H] \rightarrow Me_3CO^{\bullet} \rightarrow Me^{\bullet} + Me_2CO. \qquad (26)$$

The reactivity of $Cl^{\bullet}$ at the carboxyl group, rather than the C—H position, of the alkanoic acids studied is believed to reflect two features of its reactivity. The first is that for such an electrophilic species polar effects are important in the transition state: although attack of the α-position leads to a stabilized free radical (*e.g.* $^{\bullet}CH_2CO_2H$), nevertheless its formation will evidently be discouraged because of the relatively high energy of the appropriate transition state (**2**). On the other hand (and as with Bu^tOH), overall O—H abstraction (as observed) *via* electron transfer provides a route with significant assistance from solvation of incipient charges (**3**).



(2)



(3)

Finally we note that although $SO_4^{\bullet-}$ oxidizes Cl^- to $Cl^{\bullet}$ [and is hence expected to be a more effective one-electron oxidant than the latter: $E(SO_4^{\bullet-}/SO_4^{2-})$ 2.5–3.0 V, $E(Cl^{\bullet}/Cl^-) = 2.4$ V[27]] the order of reactivity of these radicals in formal electron-transfer reactions (*e.g.* with acids) is reversed: the observed order matches instead their leaving-group abilities [$Cl^- > SO_4^{2-}$, as measured by the pK_a values[27] of HCl (−7) and HSO_4^- (1.9)]. This suggests that the overall electron-transfer process proceeds *via* an addition–elimination sequence rather than *via* an outer-sphere mechanism.

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† We cannot rule out the occurrence of O—H abstraction (*cf.* Bu^tOH) to give $EtO^{\bullet}$, which would be followed by a rapid 1,2-shift to give $^{\bullet}CHMeOH$ [ref. (21)].

We thank Interox Chemicals Ltd for support and Mr W. R. Sanderson and Dr M. Jeff for helpful comments.

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Paper 8/01171K; *Received* 24*th March*, 1988