Mechanisms of Peroxide Decomposition. EPR Studies of the One-electron Oxidation of the Peroxymonosulphate Anion ($HOOSO_3^-$) and the Reactions of $SO_5^{\bullet -}$

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Continuous-flow EPR studies of the reaction between Ce^{IV} and the peroxymonosulphate anion $HOOSO_3^-$ at low pH enable the isotropic EPR spectrum of $SO_5^{\bullet -}$ to be characterized, and provide kinetic information on the formation and reaction of this radical. Alkylperoxyl radicals ($RO_2^{\bullet}$) detected when the reaction is carried out in the presence of alkenes (*e.g.* methyl methacrylate) are shown to arise from reactions of $SO_4^{\bullet -}$ (derived from self-reaction of $SO_5^{\bullet -}$) with the alkene, and subsequent addition of oxygen (also formed from $SO_5^{\bullet -}$).

Widespread interest in the chemistry of sulphur–oxygen radicals $SO_n^{\bullet -}$ ($n = 3, 4, 5$) has been stimulated, at least in part, by the suggestion that the oxidation of atmospheric SO_2 to sulphuric acid (acid rain) involves chain oxidation of HSO_3^- in the aqueous phase of cloud droplets (see refs. 1 and 2 and references therein): the mechanism which has been proposed involves $SO_3^{\bullet -}$, whose reaction with oxygen generates $SO_5^{\bullet -}$, for which self-termination is believed to give rise to $SO_4^{\bullet -}$.[1,3] We have previously described[4,5] the use of EPR spectroscopy to study the decomposition of the peroxymonosulphate anion ($HOOSO_3^-$) with some one-electron reductants: Ti^{III}, Fe^{II} and certain organic radicals lead to the production of $SO_4^{\bullet -}$ and OH^- [reaction (1)][4] whereas Cu^I (like pulse radiolysis) gives $^{\bullet}OH$ and SO_4^{2-} [reaction (2)].[5] Unlike the *sulphur*-centred species $SO_3^{\bullet -}$, $SO_4^{\bullet -}$ is not detectable in fluid solution by EPR spectroscopy (though its reactions have been thoroughly investigated with this approach):[6] on the other hand the radical $SO_5^{\bullet -}$ should possess a *peroxy*-structure ($^{\bullet}OOSO_3^-$) which should render this species detectable in aqueous solution (*n.b.* it has been suggested[7] that a radical pair with g_x, g_y, g_z *ca.* 2.031, 2.008, 2.006, respectively, formed in irradiated potassium persulphate[8] is characteristic of $SO_5^{\bullet -}$ rather than $SO_4^{\bullet -}$ pairs).

Accordingly we have attempted to detect $SO_5^{\bullet -}$ *via* the one-electron oxidation of the peroxymonosulphate anion with Ce^{IV} [reaction (3)], a reaction described by Edwards and his co-workers:[9] our approach has involved the use of a continuous-flow system in conjunction with EPR spectroscopy. We also wished to explore the ease of formation of $SO_5^{\bullet -}$ by other routes [*e.g. via* reactions (1) and (4), again studied with a flow system] and to determine, with EPR, the fate of $SO_5^{\bullet -}$ both in the presence and absence of other substrates (chosen so as to reveal parallel reactions of $SO_4^{\bullet -}$). In particular we intended to determine the rate constants for the generation of $SO_5^{\bullet -}$ [*via* reactions (3), directly, or (1) and (4)] and especially for the two self-termination routes proposed for this species [reactions (5) and (6)], for which conflicting claims have been made.[2,9] With this aim in mind we have also carried out stopped-flow experiments, kinetic analysis of continuous-flow experiments as a function of flow-rate and photolysis experiments with intermittent illumination.

$$Ti^{III} + HOOSO_3^- \longrightarrow Ti^{IV} + OH^- + SO_4^{\bullet -} \tag{1}$$

$$Cu^{I} + HOOSO_3^- \longrightarrow Cu^{II} + SO_4^{2-} + {}^{\bullet}OH \tag{2}$$

$$Ce^{IV} + HOOSO_3^- \longrightarrow Ce^{III} + H^+ + SO_5^{\bullet -} \tag{3}$$

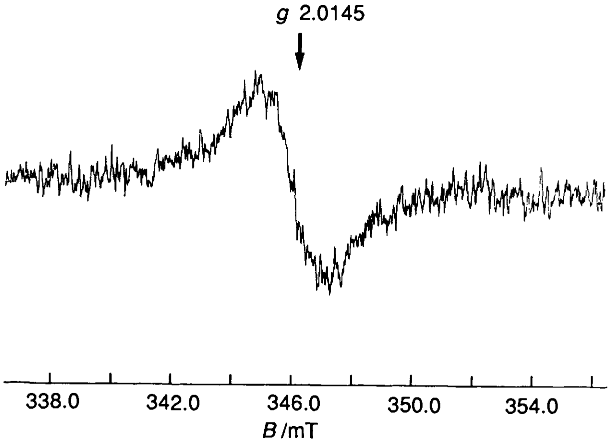

Fig. 1 EPR spectrum (at high magnetic field modulation, 1.0 mT) of $SO_5^{\bullet -}$ obtained from the reaction between Ce^{IV} and $HOOSO_3^{\bullet -}$ in the presence of $HClO_4$ using a continuous-flow system (at pH 1.2, 20 °C and with $[Ce^{IV}]_0$ 10^{-2} mol dm^{-3}, $[HOOSO_3^-]_0$ 5×10^{-2} mol dm^{-3}; mixing time *ca.* 36 ms)

$$SO_4^{\bullet -} + SO_5^{2-} \longrightarrow SO_4^{2-} + SO_5^{\bullet -} \tag{4}$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow S_2O_8^{2-} + O_2 \tag{5}$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow 2SO_4^{\bullet -} + O_2 \tag{6}$$

Results and Discussion

(1) *Continuous-flow EPR Experiments*.—(i) *The* Ce^{IV}–$HOOSO_3^-$ *reaction.* Initial experiments involved the use of a continuous-flow system, in which three streams were mixed shortly before passage through the cavity of an EPR spectrometer (with time between mixing and observation in the range 20–100 ms).

When cerium(IV), as ammonium ceric nitrate, was mixed in this way with a solution of peroxymonosulphate, as the triple salt OXONE [each acidified with $HClO_4$ (0.1 mol dm^{-3})], to give a solution with concentrations $[Ce^{IV}]$ 1×10^{-2} mol dm^{-3} and $[HOOSO_3^-]$ 5×10^{-2} mol dm^{-3} (at pH *ca.* 1.0 and 20 °C, with a mixing time of 20–100 ms, and with acidified water in the third stream) a very broad singlet was detected with ΔB *ca.* 2.0 mT, g 2.0145 (see Fig. 1).† This spectrum, which was obtained

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† Concentrations given in the text (except where stated otherwise) refer to the mixed stream.

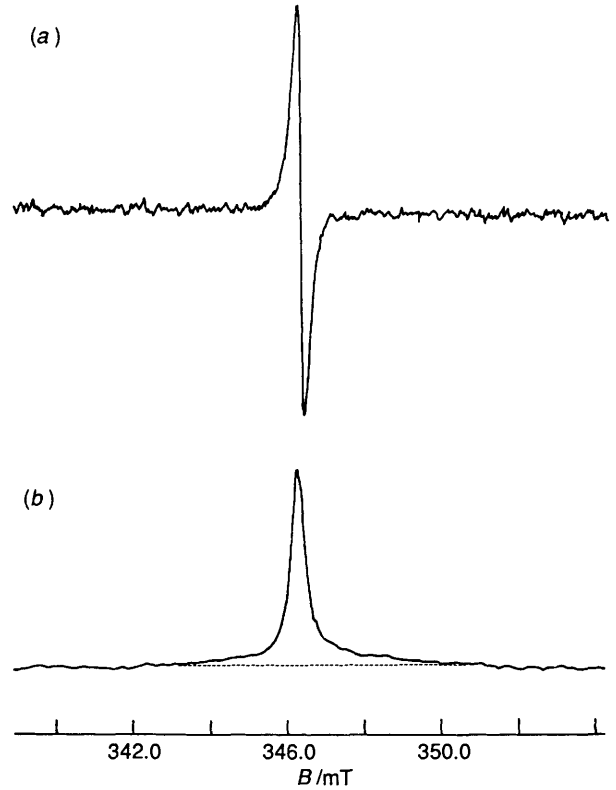


Fig. 2 (*a*) EPR spectrum (at low magnetic field modulation, 0.2 mT) of the peroxyl radical $^{-}O_3SOCH_2CMe(CO_2H)O_2^{\bullet}$ obtained in a continuous-flow study of the reaction between Ce^{IV} and $HOOSO_3^-$ in the presence of $HClO_4$ and methacrylic acid (conditions as for Fig. 1, with $[CH_2{=}CMeCO_2H]$ 3×10^{-2} mol dm^{-3}). (*b*) Integral of spectrum (*a*) showing broad line attributed to presence of $SO_5^{\bullet -}$.

irrespective of whether or not the solution had been deoxygenated, is assigned to $SO_5^{\bullet -}$: although to our knowledge the isotropic spectrum of this species has not previously been reported, the anisotropic parameters of $SO_5^{\bullet -}$ obtained from irradiated potassium persulphate[7,8] give an isotropic *g*-value (2.015) close to that obtained here. As would be anticipated, this is typical of a peroxyl radical (*cf.* $Bu^tO_2^{\bullet}$), as is the large line-width.[10] The determination of the rate constants for reactions (3), (5) and (6) is described below.

When these experiments were repeated with lower concentrations of Ce^{IV} and $HOOSO_3^-$, weaker signals were obtained: the need for high concentrations in the experiments described above (compared with those typically employed for successful studies of metal–peroxide reactions of this type)[4,5] is believed to reflect both the relatively large line-width of the signal from $SO_5^{\bullet -}$ and the fact that the rate constant for oxidation of $HOOSO_3^-$ by Ce^{IV} is significantly lower than those for the reduction of peroxymonosulphate by Ti^{III}, Fe^{II} and Cu^{I}. It has also been suggested that the reaction between Ce^{IV} and $HOOSO_3^-$ in H_2SO_4 is significantly slower than that in $HClO_4$:[9] in accord with this we found that much weaker signals from $SO_5^{\bullet -}$ were obtained when sulphuric acid, rather than perchloric acid, was employed to adjust the pH to *ca.* 1.

(ii) *The reaction of* Ce^{IV} *with* $HOOSO_3^-$ *in the presence of substrates.* In an attempt to employ EPR spectroscopy to gain further information concerning the reactions of $SO_5^{\bullet -}$, the experiments described above were extended *via* the inclusion of alkenes as substrates for possible further reactions.

For example, reaction of ammonium ceric nitrate (10^{-2} mol dm^{-3}) and peroxymonosulphate (5×10^{-2} mol dm^{-3}) with methacrylic acid (3×10^{-2} mol dm^{-3}) at pH *ca.* 1 (achieved with $HClO_4$), under nitrogen and with mixing time *ca.* 20 ms, led to the detection of a narrow intense line (line-width 0.2 mT) with *g* 2.0145, characteristic of an alkylperoxyl radical; the broad (weak) signal from $SO_5^{\bullet -}$ was still detectable [see Fig. 2: the underlying signal from $SO_5^{\bullet -}$ is clearly visible in derivative spectra for which the magnetic field modulation is high (1 mT), but then the signal from the alkylperoxyl radical is severely over-modulated]. With methyl methacrylate, similar spectra were obtained, together with a weak alkyl-radical spectrum: only some groups of lines were observed, and these were identical with those in the spectra of radicals detected during the reaction of $SO_4^{\bullet -}$ with methyl methacrylate and attributed to the corresponding monomer/dimer radical-adducts (see below).[11]

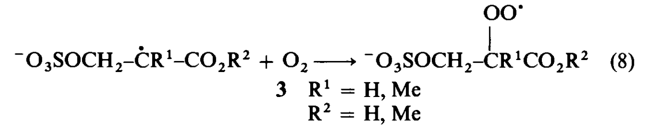
When experiments were conducted with lower concentrations of reagents (typically $[Ce^{IV}]$ 5×10^{-4}, $[HOOSO_3^-]$ 5×10^{-3} and [alkene] 10^{-3}–10^{-2} mol dm^{-3}) signals from the (sharper) alkylperoxyl radicals were still detectable. Other peroxyl radicals detected in this way included those from fumaric acid, acrylic acid and methyl acrylate [each of which gave a weak doublet, with *a*(H) 0.46 mT, ΔB 0.2 mT, *g* 2.0145] and allyl alcohol, for which a broad singlet was observed (ΔB 0.9 mT, *g* 2.0145); the hyperfine splitting detectable for the former group is within the range of values reported for a range of other secondary alkylperoxyl radicals.[12]

$$Ce^{IV} + HOOSO_3^- \longrightarrow Ce^{III} + H^+ + SO_5^{\bullet -} \qquad (3)$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow S_2O_8^{2-} + O_2 \qquad (5)$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow 2SO_4^{\bullet -} + O_2 \qquad (6)$$

$$\underset{\substack{\mathbf{1}\\ R^1 = H, Me;\ R^2 = H, Me}}{SO_4^{\bullet -} + CH_2{=}CR^1CO_2R^2} \longrightarrow \underset{\substack{\mathbf{2}\\ R^1 = H, Me;\ R^2 = H, Me}}{^{-}O_3SOCH_2\text{–}\dot{C}R^1CO_2R^2} \qquad (7)$$



$$\underset{\substack{\mathbf{3}\ \ R^1 = H, Me\\ R^2 = H, Me}}{^{-}O_3SOCH_2\text{–}\dot{C}R^1\text{–}CO_2R^2} + O_2 \longrightarrow {^{-}O_3SOCH_2\text{–}}\overset{\overset{\displaystyle OO^{\bullet}}{|}}{C}R^1CO_2R^2 \qquad (8)$$

Scheme 1

When these experiments were repeated in the presence of air (*i.e.* without deoxygenation), the same peroxyl radicals were observed at comparable intensity and, perhaps surprisingly, traces of the alkyl-radical spectrum from addition to methyl methacrylate were still observed.

A plausible mechanism to account for these observations (to be tested in experiments described below) is shown in Scheme 1. Reaction of Ce^{IV} with $HOOSO_3^-$ to give $SO_5^{\bullet -}$ is followed by the occurrence of reactions (5) and (6), to give oxygen and $SO_4^{\bullet -}$. Reaction of $SO_4^{\bullet -}$ thus produced with the alkenes **1** would be expected to proceed very rapidly[6,13] to give alkyl-radical adducts **2** (one example of which, from methyl methacrylate was detectable: see earlier): these adducts then react with oxygen (produced from $SO_5^{\bullet -}$) to give peroxyl radicals **3**. The latter possess relatively narrow EPR spectra with a detectable extra doublet splitting when they possess a β-proton (*e.g.* acrylic acid, methyl acrylate).

Comparison of the line-width of these species (*ca.* 0.2 mT) with the much greater line-widths for *e.g.* $Bu^tO_2^{\bullet}$ (1.4 mT at room temperature)[10] and that from allyl alcohol (discussed above) suggests that this feature is a property of the free radical conferred by the possession of a β-CO_2R group.

In order to confirm these assignments and interpretation, experiments were carried out in which $SO_4^{\bullet -}$ was generated directly from the Ti^{III}–$HOOSO_3^-$ couple, in the presence of the alkenes discussed above.

(iii) *Reactions of* Ti^{III} *and* $HOOSO_3^-$ *in the presence and*

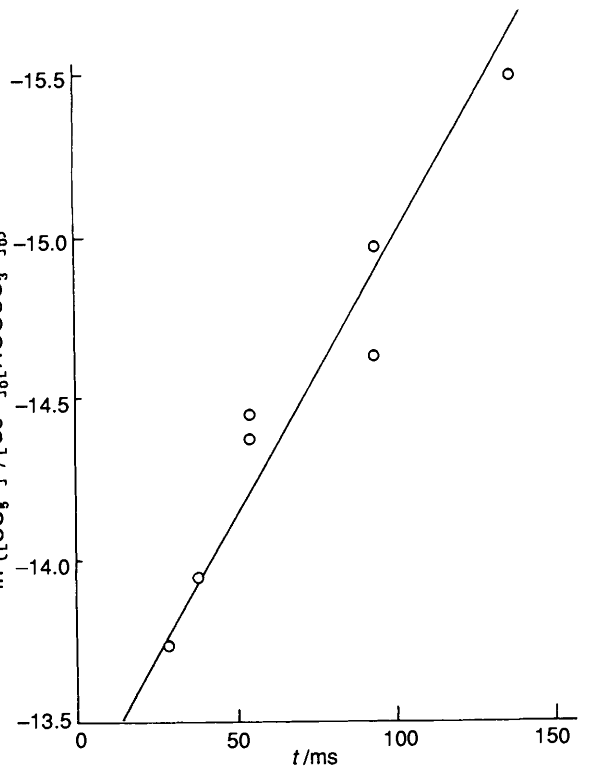


Fig. 3 Variation of ln([$SO_5^{\bullet -}$]^2/[$HOOSO_3^-$]$_0$[Ce^{IV}]$_0$) with time after mixing (t) in continuous-flow experiments with [Ce^{IV}]$_0$ = 10^{-2} mol dm^{-3} and [$HOOSO_3^-$]$_0$ = 5 × 10^{-2} mol dm^{-3} in $HClO_4$ (0.1 mol dm^{-3})

absence of added substrates. In continuous-flow experiments involving Ti^{III} (1.7 × 10^{-3} mol dm^{-3}) and $HOOSO_3^-$ (10^{-2} mol dm^{-3}) at pH 2 (in deoxygenated solution and with mixing time *ca.* 30 ms: *cf.* ref. 4), no signals from $SO_5^{\bullet -}$ were detectable. Since it has previously been established[4] that reaction (1), to give $SO_4^{\bullet -}$, proceeds rapidly under these circumstances we can conclude that oxidation of $HOOSO_3^-$ by $SO_4^{\bullet -}$ is not an effective route to $SO_5^{\bullet -}$ (it has previously been suggested[14] that k_4 is $\leqslant 10^5$ dm^3 mol^{-1} s^{-1}).

However, when this experiment was repeated in the presence of methyl methacrylate (at concentrations similar to those employed in the experiment with Ce^{IV} described above) we were able to detect not only the alkyl radicals observed earlier but also, when oxygen was not excluded, the peroxyl radical described above (3, $R^1 = R^2$ = Me): under these conditions the other alkenes with carboxyl groups (*e.g.* fumaric acid) also gave signals from peroxyl radicals identical to those obtained earlier. Since this system does not serve as an effective source of $SO_5^{\bullet -}$, but rather of $SO_4^{\bullet -}$, we believe that these observations strongly support our assertion that the peroxyl radicals observed derive from the prior generation of $SO_4^{\bullet -}$ followed by reaction of the sulphate adduct with oxygen.

Careful examination of the Ti^{III}/$HOOSO_3^-$/methyl methacrylate reaction in deoxygenated conditions by EPR as a function of the alkene concentration revealed that the alkyl radicals detected are mainly the monomer adduct **4** [a(β-CH_3) 2.33, a(β-CH_2) 1.69, 1.85, a(δ-CH_3) 0.14 mT] and a small amount of the dimeric species **5** [a(β-CH_3) 2.25, a(β-CH_2) 0.95, 1.38, a(δ-CH_3) 0.14 mT] formed by addition of **4** to the parent alkene [reaction (9)].

$$\underset{\mathbf{4}}{^-O_3SOCH_2\dot{C}MeCO_2Me} + CH_2{=}CMeCO_2Me$$

$$\longrightarrow \underset{\mathbf{5}}{^-O_3SOCH_2CMe(CO_2Me)CH_2\dot{C}MeCO_2Me} \quad (9)$$

(b) *Kinetic studies* via *EPR.*—Because of the large line-width of the EPR signal of $SO_5^{\bullet -}$ the signal-to-noise ratio of its spectrum was poor, even at concentrations obtained in the steady-state experiments (estimated to be *ca.* 10^{-5} mol dm^{-3}). It was not possible to employ a stopped-flow method to follow the kinetics of the growth and decay of $SO_5^{\bullet -}$ (an attempted stopped-flow experiment did show, however, that the rate of disappearance of $SO_5^{\bullet -}$ was very fast); a steady-state analysis of variation of [$SO_5^{\bullet -}$] with flow-rate was therefore attempted (see below).

On the other hand, most of the alkylperoxyl radicals formed by reaction of $SO_4^{\bullet -}$ in the presence of alkenes have relatively sharp lines (*ca.* 0.2 mT), with the result that both continuous- and stopped-flow methods could be employed for kinetic measurements. Most of the experiments were conducted in solutions acidified with $HClO_4$, as the rate of reaction between Ce^{IV} and $HOOSO_3^-$ is much faster than in solutions acidified with H_2SO_4.

(i) *EPR continuous-flow studies of* [$SO_5^{\bullet -}$]. Using the continuous-flow system the steady-state concentration of $SO_5^{\bullet -}$ was monitored at various flow rates which provided flow-times (the time between mixing and observation) in the range 20–200 ms. Typical values of [$SO_5^{\bullet -}$] were in the range (3–10) × 10^{-6} mol dm^{-3} for solutions acidified with $HClO_4$ and initial concentrations of reactants [Ce^{IV}] 10^{-3}–10^{-2} mol dm^{-3} and [$HOOSO_3^-$] 10^{-2}–5 × 10^{-2} mol dm^{-3}.

$$Ce^{IV} + HOOSO_3^- \rightleftharpoons Ce^{III} + SO_5^{\bullet -} + H^+ \quad (3)$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow S_2O_8^{2-} + O_2 \quad (5)$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow 2SO_4^{\bullet -} + O_2 \quad (6)$$

$$SO_4^{\bullet -} + SO_4^{\bullet -} \longrightarrow S_2O_8^{2-} \quad (10)$$

$$SO_4^{\bullet -} + Ce^{III} \longrightarrow Ce^{IV} + SO_4^{2-} \quad (11)$$

Scheme 2

Our initial steady-state analysis is based on the assumption that the mechanism of reaction involves reactions (3) (5), (6) and (10) as set out in Scheme 2 [the effect of incorporation of reaction (11) is discussed later]: the reverse of reaction (3), the oxidation of Ce^{III} by $SO_5^{\bullet -}$ can be neglected because it will not become significant until the later stages of the reaction when [Ce^{III}] has built up. It can then be shown that the predicted variation of [$SO_5^{\bullet -}$] with time after mixing (t) is given by eqn. (12).

$$\ln([SO_5^{\bullet -}]_t^2/[HOOSO_3^-]_0[Ce^{IV}]_0) = -k_3[HOOSO_3^-]_0t - \ln\left(\frac{2k_5 + 2k_6}{k_3}\right) \quad (12)$$

A plot of ln([$SO_5^{\bullet -}$]$_t^2$/[$HOOSO_3^-$]$_0$[Ce^{IV}]$_0$) against t for experiments carried out with $HClO_4$ is shown in Fig. 3; the predicted behaviour is observed. We derive values of k_3 = 94 dm^3 mol^{-1} s^{-1} and ($2k_5 + 2k_6$) = 7.4 × 10^8 dm^3 mol^{-1} s^{-1} in $HClO_4$. The value of ($2k_5 + 2k_6$) is close to that derived from the results given by Huie and Neta ($2k_5$ 1.4 × 10^8, $2k_6$ 6 × 10^8 dm^3 mol^{-1} s^{-1}).[3]

If, on the other hand, we incorporate reaction (11) rather than reaction (10) as the dominant mode of termination of $SO_4^{\bullet -}$ [it has been proposed by Edwards and co-workers[9] that reaction (11) has k_{11} = 1.4 × 10^8 dm^3 mol^{-1} s^{-1}, which would certainly ensure that this is justified], then the predicted relationship between [$SO_5^{\bullet -}$] and t is given by eqn. (13).

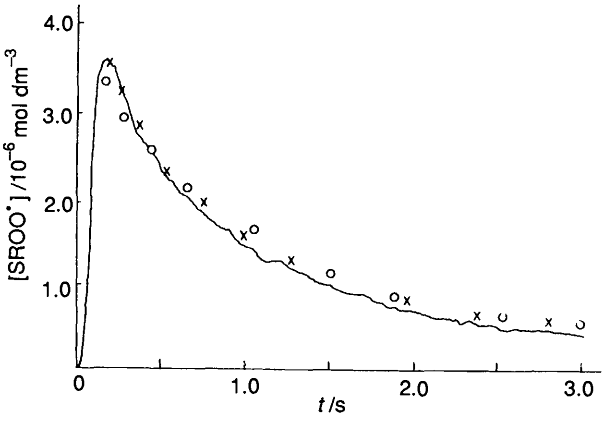


Fig. 4 Variation of $[^-O_3SOCH_2CMe(CO_2H)O_2^{\bullet}]$ with time after mixing in a stopped-flow experiment with Ce^{IV}, $HOOSO_3^-$ and methacrylic acid, each acidified with H_2SO_4 (9.2×10^{-2} mol dm^{-3}): initial concentrations of reagents in the mixed stream were 2.4×10^{-3}, 1.1×10^{-2} and 1.2×10^{-2} mol dm^{-3}, respectively. Solid line, experimental results; ×, simulated behaviour, using $k_3 = 150$, $k_{18} = 2.4 \times 10^8$ dm^3 mol^{-1} s^{-1}; ○, simulated behaviour, using $k_3 = 150$, $k_{18} = 1 \times 10^7$, $k_{20} = 2.5 \times 10^8$ dm^3 mol^{-1} s^{-1}.

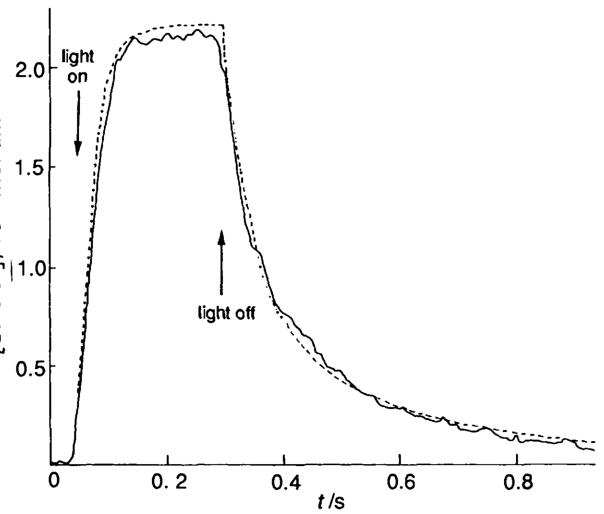


Fig. 5 Growth and decay of the EPR signal from $^-O_3SOCH_2CMe(CO_2H)O_2^{\bullet}$ obtained on photolysis of an aqueous solution of methacrylic acid (6×10^{-2} mol dm^{-3}) and potassium peroxydisulphate (5.3×10^{-2} mol dm^{-3}) in the presence of propanone (0.3 mol dm^{-3}) and oxygen. The dashed curve is that simulated from a simple kinetic model incorporating $2k_t$ 1×10^7 dm^3 mol^{-1} s^{-1} for the rate constant of termination of the peroxyl radical.

$$\ln([SO_5^{\bullet-}]_t^2/[HOOSO_3^-]_0[Ce^{IV}]_0) = \frac{-2k_3k_5[HOOSO_3^-]_0 t}{2k_5 + 2k_6} - \ln\left(\frac{2k_5 + 2k_6}{k_3}\right) \qquad (13)$$

As shown in Fig. 3, the observed linear variation of $\ln([SO_5^{\bullet-}]^2/[HOOSO_3^-]_0[Ce^{IV}]_0)$ with t is consistent with this mechanism and analysis, and we have used this interpretation to derive values of k_3, k_5 and k_6. For experiments at high concentrations of $HClO_4$ (>0.25 mol dm^{-3}, to be in considerable excess over the concentration of SO_4^{2-} derived from the peroxide employed) we find that k_1 is 8500 dm^3 mol^{-1} s^{-1}, with $2k_5$ and $2k_6$ 7.0×10^8 and 4.3×10^9 dm^3 mol^{-1} s^{-1} [the individual values being derived from the value of the ratio of $2k_6/2k_5$ (6.5) proposed by Edwards[9]]. It was found that at lower $[HClO_4]$ the calculated rate of the initiation reaction (1) decreased markedly (possibly on account of increased complexation by sulphate), but $2k_5$ and $2k_6$ did not alter. These values of $2k_5$ and $2k_6$ are much higher than those indicated by the kinetic measurements of Huie and Neta (1.4 and 10^8 and 6.0×10^8 dm^3 mol^{-1} s^{-1}, respectively). Edwards[15] comments that the rate of the reverse reaction (−3) can be comparable to that of the forward reaction and so cannot be neglected. If we assume values of $2k_5$ 1×10^8 dm^3 mol^{-1} s^{-1} and $2k_6$ 6.5×10^8 dm^3 mol^{-1} s^{-1}, which are in reasonable agreement with those given by Huie and Neta,[3] and the ratio $2k_6/2k_5$ 6.5, as found by Edwards,[9] then it is possible to obtain a good fit to the experimental results with $k'_{-3} = 1 \times 10^7$ dm^3 mol^{-1} s^{-1}.*

The much weaker signal from $SO_5^{\bullet-}$ observed in experiments with H_2SO_4 (maximum $[SO_5^{\bullet-}]$ *ca.* 2.5×10^{-6} mol dm^{-3}) could not be studied effectively in the same manner; however, an alternative approach involving the peroxyl radical(s) derived from $SO_5^{\bullet-}$ proved a satisfactory alternative (see below).

(ii) *EPR continuous- and stopped-flow studies of the peroxyl radicals from sulphate-adducts.* We have shown earlier that in the presence of an effective excess of appropriate alkene (to scavenge $SO_4^{\bullet-}$, from $SO_5^{\bullet-}$) and oxygen, the EPR signal from $SO_5^{\bullet-}$ is replaced by that from the peroxyl radical derived from the sulphate adducts. In a separate set of experiments we have monitored the steady-state concentration of the peroxyl radical **3** from methacrylic acid after reaction times in the range 20–250 ms (typically with $[Ce^{IV}]$ 6.8×10^{-4}, $[HOOSO_3^-]$ 3.4×10^{-3} and [methacrylic acid] $(5–12) \times 10^{-3}$ mol dm^{-3} at pH 1 in the presence of $HClO_4$): continuous-flow and stopped-flow methods have been employed. Analysis for $RO_2^{\bullet}$ in terms of the rate of radical generation (k_3) and removal [now the bimolecular termination rate constant ($2k_t$) for $RO_2^{\bullet}$] leads to values of k_3 1×10^4 and $2k_t$ 2×10^8 dm^3 mol^{-1} s^{-1}.

Related studies of the reaction in H_2SO_4 by stopped-flow (see *e.g.* Fig. 4) lead to values of k_3 150 dm^3 mol^{-1} s^{-1} and $2k_t$ ($RO_2^{\bullet}$) 2.5×10^8 dm^3 mol^{-1} s^{-1}. (Preliminary optical measurements of Ce^{IV} in a stopped-flow system confirm k_3 150 dm^3 mol^{-1} s^{-1} and indicate that k'_{-3} is *ca.* 3×10^5 dm^3 mol^{-1} s^{-1} in H_2SO_4). The value of the rate constant $2k_t$ for the mutual termination of the peroxyl radical seems very high for a tertiary alkylperoxyl (*e.g.* $2k_t$ for $Bu^tO_2^{\bullet}$ is 2.0×10^4 dm^3 mol^{-1} s^{-1} under comparable conditions).[16] To check this result we have generated the same radical photochemically (see below).

(iii) *EPR photolytic determination of* $2k_t$ *for* $RO_2^{\bullet}$. *In situ* photolysis of solutions containing $S_2O_8^{2-}$ (5.3×10^{-2} mol dm^{-3}) and methacrylic acid or methyl methacrylate (*ca.* 6×10^{-2} mol dm^{-3}) (with 0.3 mol dm^{-3} propanone as a photosensitizer) in the presence of oxygen does lead to the detection of the EPR signals of the alkylperoxyl radicals described above. Growth and decay curves were recorded in an experiment with a shutter (see Fig. 5). The decay curves for the peroxyl radicals were close to second-order giving in each case an overall rate constant for termination, $2k_t$, of 1.0×10^7 dm^3 mol^{-1} s^{-1}.

This value is much lower than that determined from flow experiments in which the peroxyl radical is generated from Ce^{IV} and $HOOSO_3^-$ *via* $SO_4^{\bullet-}$ but it is still very much higher than that for the *tert*-butylperoxyl radical ($2k_t = 2 \times 10^4$ dm^3 mol^{-1} s^{-1} at room temperature). The reason for this enhanced rate of mutual termination is not clear, but it appears that there must be an alternative route for the formation of products to that normally encountered for tertiary alkylperoxyl radicals.

Possible reasons for the difference in $2k_t$ for the peroxyl radical measured from the photolytic experiments and the flow experiments are discussed below.

(iv) *Full reaction scheme and kinetic modelling of* $[RO_2^{\bullet}]_{ss}$. The reaction scheme leading to the formation of the peroxyl radical and its subsequent destruction is complex (see Scheme

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* It should be noted that reaction (−3) is strictly a third-order process; k'_{-3} is the appropriate psuedo-second-order rate constant under these conditions ($k'_{-3} = k_{-3}[H^+]$).

$$\mathrm{Ce^{IV} + HOOSO_3^- \rightleftharpoons Ce^{III} + SO_5^{\bullet -} + H^+} \qquad (3)$$

$$\mathrm{SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow S_2O_8^{2-} + O_2} \qquad (5)$$

$$\mathrm{SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow 2SO_4^{\bullet -} + O_2} \qquad (6)$$

$$\mathrm{SO_4^{\bullet -} + SO_4^{\bullet -} \longrightarrow S_2O_8^{2-}} \qquad (10)$$

$$\mathrm{SO_4^{\bullet -} + Ce^{III} \longrightarrow Ce^{IV} + SO_4^{2-}} \qquad (11)$$

$$\mathrm{SO^{4\bullet -} + Alkene \longrightarrow SR^\bullet\ (adduct)} \qquad (14)$$

$$\mathrm{SR^\bullet + O_2 \longrightarrow SROO^\bullet} \qquad (15)$$

$$\left.\begin{array}{l} \mathrm{SR^\bullet + SR^\bullet \longrightarrow} \\ \mathrm{SROO^\bullet + SR^\bullet \longrightarrow} \end{array}\right\}\text{non-radical products} \qquad \begin{array}{r}(16)\\(17)\end{array}$$

$$\mathrm{SROO^\bullet + SROO^\bullet \longrightarrow O_2 + \text{non-radical products}} \qquad (18)$$

$$\mathrm{SROO^\bullet + SROO^\bullet \rightleftharpoons SROOOORS} \qquad (19)$$

$$\mathrm{SROO^\bullet + SO_5^{\bullet -} \longrightarrow O_2 + \text{non-radical products}} \qquad (20)$$

Scheme 3

3), and involves $SO_5^{\bullet -}$, $SO_4^{\bullet -}$ and $SR^\bullet$ (the sulphate adduct of the alkene) as intermediate free-radical species (the peroxyl species is represented as $SROO^\bullet$ in the Scheme). We have taken the value of k_{14} as 8×10^8 dm^3 mol^{-1} s^{-1},[13] and thus, in the presence of an excess of alkene, reaction of $SO_4^{\bullet -}$ *via* reactions (10) and (11) will be insignificant. Values of $k_{15} = 1 \times 10^9$ dm^3 mol^{-1} s^{-1} and $2k_{16} = 2 \times 10^9$ dm^3 mol^{-1} s^{-1} have been used, which are typical for alkyl radicals. For k_{18} we used the value obtained in our photolysis experiments (1.0×10^7 dm^3 mol^{-1} s^{-1}). We estimate $k_{17} = 2 \times 10^8$ dm^3 mol^{-1} s^{-1}, which is close to the geometric mean of the mutual reactions ($\sqrt{4k_{16}k_{18}} = 1.4 \times 10^8$ dm^3 mol^{-1} s^{-1}). However, in the presence of a reasonable concentration of oxygen ($[O_2] = 2.4 \times 10^{-4}$ mol dm^{-3}) this rate (k_{17}) has little effect on the overall concentration of $SROO^\bullet$. The values for k_3 and k'_{-3} are those determined above, namely 1.0×10^4 and 1.0×10^7 dm^3 mol^{-1} s^{-1} in $HClO_4$ and 150 and 3×10^5 dm^3 mol^{-1} s^{-1} in H_2SO_4, while $2k_5$ and $2k_6$ are taken as 1.0×10^8 and 6.5×10^8 dm^3 mol^{-1} s^{-1} in both media.

Use of these values and a model based on reactions (3), (5), (6), (10), (11) and (14)–(18) (see Scheme 3) leads to the predicted concentrations of $[SROO^\bullet]$ approximately five times those actually observed for solutions acidified with either $HClO_4$ or H_2SO_4. Clearly this proposed reaction mechanism is inadequate and additional reactions involving $SROO^\bullet$ or the precursor radicals must be included to account for the lower concentrations of $SROO^\bullet$ observed experimentally. Depletion of oxygen would lead to the reduction of the concentration of the peroxyl radical $[SROO^\bullet]$ relative to that of the alkyl radical $[SR^\bullet]$. However, no difference in $[SROO^\bullet]$ is observed for solutions which are saturated in oxygen: the concentration of oxygen increases during the reaction, and when the oxygen initially present is removed by bubbling nitrogen through the solutions, the peroxyl radical is still the only radical observed.

If a considerable fraction of the peroxyl radicals exist as the appropriate tetraoxide [see reaction (19)] then the observed concentration of $[SROO^\bullet]$ would indeed be lower than that predicted. However, the equilibrium constants for other peroxyl–tetraoxide equilibria are such that there is only a small amount of the tetraoxide ($< 1\%$) present at room temperature.[17] It is reasonable to assume that the same behaviour is exhibited for the peroxyl radicals ($SROO^\bullet$) studied here. The existence of tetraoxide should also be evident in the photolytic experiments.

A plausible alternative is the inclusion of an additional termination reaction between $SO_5^{\bullet -}$ and $RSOO^\bullet$ [reaction (20)]. In comparison with other cross-termination reactions between peroxyl radicals the ratio constant is likely to be well above (5–20 times) that given by $k_{20} = \sqrt{4k_5k_{18}}$ *i.e.* 3×10^7 dm^3 mol^{-1} s^{-1}. Inclusion of this reaction with $k_{20} = 3 \times 10^8$ dm^3 mol^{-1} s^{-1} gives a reasonable fit to the experimental results (for $[SROO^\bullet]$ with time) in solutions acidified with either $HClO_4$ or H_2SO_4 (see *e.g.* Fig. 4).

Finally, use of the simulation program together with the rate constants given above and the reactions shown in Scheme 3 allowed us to verify that in continuous-flow experiments with Ce^{IV}, $HOOSO_3^-$ and methacrylic acid both $SO_5^{\bullet -}$ and $SROO^\bullet$ should be detectable (as observed), with relative concentrations typically *ca.* 4×10^{-6} and *ca.* 1×10^{-5} mol dm^{-3} (see Fig. 2).

Conclusions

We have shown by kinetic EPR studies that the reaction between Ce^{IV} and peroxymonosulphate at low pH leads to the production of $SO_5^{\bullet -}$ and that the reaction is much faster in $HClO_4$ than H_2SO_4; data have also been obtained for the rapid oxidation of Ce^{III} by $SO_5^{\bullet -}$ under these conditions.

Self-reaction of $SO_5^{\bullet -}$ leads to $SO_4^{\bullet -}$ and oxygen, as well as $S_2O_8^{2-}$, and the inclusion of alkenes in the continuous-flow EPR experiments leads to the detection of peroxyl radicals formed from $SO_4^{\bullet -}$ adducts. Kinetic analysis of our results leads to values of *ca.* 10^7 dm^3 mol^{-1} s^{-1} for the rate constant for the self-termination of the peroxyl radicals and a rate constant of 3×10^8 dm^3 mol^{-1} s^{-1} for the cross-termination reaction between $^-O_2SOCH_2CMe(CO_2H)O_2^\bullet$ and $SO_5^{\bullet -}$ in aqueous solution at room temperature.

Experimental

EPR spectra were recorded on a Varian E-104 and a 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 NMR Gaussmeter ER 035M; with the E-104 the field scan was calibrated with an aqueous solution of Fremy's salt, *a*(N) 1.309 mT];[18] *g* values were determined by comparison with that for $^\bullet CHMeOH$ ($g = 2.003\,21$)[19] obtained from the reaction of $^\bullet OH$ (from Ti^{III}–H_2O_2) with ethanol. Relative radical concentrations were determined both by spectrum simulation using a program supplied by Dr. M. F. Chiu and by direct double integration (using the ESP-300); absolute radical concentrations were determined by comparison of doubly integrated signals with those from a standard solution of vanadyl sulphate. Flow experiments were conducted by pumping three reagent streams through a mixer which allowed simultaneous mixing *ca.* 20–200 ms before passage through the cavity of the spectrometer (using a Watson–Marlow 502 peristaltic pump). pH Measurements were made using a Pye–Unicam pH meter PW 9410 with the electrode inserted into the effluent stream.

Stopped-flow measurements were made with a simple two-syringe system. The solutions were contained in 1 cm^3 syringes, which were driven by a piston actuated by compressed air. Mixing times were *ca.* 20 ms and the stop time for the solution in the aqueous sample cell was also *ca.* 20 ms. These times were sufficiently fast for accurate measurement of the reactions of peroxyl radicals. The growth and decay curves of the concentration of peroxyl radicals were recorded by feeding the output of the EPR spectrometer into a Datalab DL 4000 Signal Averager. The signal averager was triggered by a signal from the syringe-drive unit. Between 1 and 16 separate curves were accumulated depending on the signal-to-noise ratio and the averaged curve was plotted on an X–Y recorder.

The photolysis experiments were carried out using a 100 W mercury compact-arc lamp, which was focussed into the sample cavity of the EPR spectrometer by a fused silica lens (focal length 50 mm). Exposure times were controlled by a magnetic shutter placed in front of the cavity. The growth and decay curves of the concentration of peroxyl radicals were recorded in the same manner as that used for the stopped-flow experiments. Up to 128 separate curves were accumulated and averaged, depending on the signal-to-noise ratio.

When necessary the values of the rate constants were determined from the experimental curves by mathematical modelling of the reaction. The kinetic simulation program, SIMULA, is based on CHEKIN, developed for handling linked-reaction schemes by computer.[20]

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