Mechanisms of Peroxide Decomposition. An ESR Study of the Reactions of the Peroxomonosulphate Anion ($HOOSO_3^-$) with Ti^{III}, Fe^{II}, and α-Oxygen-substituted Radicals

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It is shown that decomposition of the peroxymonosulphate anion ($HOOSO_3^-$) in aqueous solution with the low-valence metal ions Ti^{III} and Fe^{II} proceeds *via* one-electron transfer to yield $SO_4^{-\bullet}$ and OH^- (rather than SO_4^{2-} and $^{\bullet}OH$), with rate constants in the range $10^2 - 10^5$ dm^3 mol^{-1} s^{-1}. A variety of subsequent reactions of $SO_4^{-\bullet}$ with added substrates has been demonstrated.

ESR results also reveal the efficacy of $HOOSO_3^-$ as an oxidant for carbon-centred radicals generated *in situ*. In addition to the occurrence of rapid one-electron oxidation of alkyl radicals (*e.g.* $Et^{\bullet}$, with k 3.8×10^5 dm^3 mol^{-1} s^{-1}) it is also established that certain oxygen-conjugated radicals undergo a novel oxidation reaction involving oxygen-transfer and subsequent fragmentation ($^{\bullet}CHMeOH$ gives $Me^{\bullet}$, with k 1.1×10^6 dm^3 mol^{-1} s^{-1}).

The formation of free radicals during the decomposition of various peroxides by certain transition-metal ions has been effectively demonstrated by continuous-flow ESR experiments which provide information on the first-formed radicals, the kinetics of their formation, and subsequent radical reactions.[1–4] Examples recently described include the Fenton reaction and its analogues[3] [reaction (1), $M^{n+} = Fe^{II}, Ti^{III}$] and related decomposition of the peroxydisulphate anion[4] [reaction (2), $M^{n+} = Fe^{II}, Ti^{III}, Cu^{I}$]. Steady-state analysis (coupled, for example, with computer simulation) also leads to kinetic information on the initiation reactions and the oxidation or reduction of free radicals with metal ions[3,4] [see *e.g.* reactions (3) and (4)] as well as the oxidation of relatively nucleophilic free radicals with peroxides [see *e.g.* reaction (5)].[2]

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+1)+} + HO^{\bullet} + HO^- \quad (1)$$

$$M^{n+} + S_2O_8^{2-} \longrightarrow M^{(n+1)+} + SO_4^{-\bullet} + SO_4^{2-} \quad (2)$$

$$^{\bullet}CHMeOH + Fe^{III} \longrightarrow Fe^{II} + H^+ + MeCHO \quad (3)$$

$$^{\bullet}CH_2CMe_2OH + Fe^{II} \longrightarrow Fe^{III} + CH_2{=}CMe_2 + OH^- \quad (4)$$

$$^{\bullet}CHMeOH + H_2O_2 \longrightarrow H^+ + MeCHO + HO^{\bullet} + HO^- \quad (5)$$

In the work to be described here we set out to investigate the ease with which the low-valent transition-metal ions Ti^{III} and Fe^{II} react with the peroxomonosulphate ion $HO\text{–}OSO_3^-$ and, in particular, to determine the effect on these reactions of the ligands co-ordinated to the metal. We have previously established that for Ti^{III}, Ti^{III}–EDTA and Fe^{II}–EDTA the reaction of hydrogen peroxide is normally considerably faster than that of peroxydisulphate [for example, for Ti^{III} k is *ca.* 2×10^3 dm^3 mol^{-1} s^{-1} compared with 200 dm^3 mol^{-1} s^{-1}][4] and have also noted, however, how certain ligands (*e.g.* diethylenetriaminepenta-acetic acid, DTPA) inhibit the Ti^{III}–H_2O_2 but not the Fe^{II}–H_2O_2 reaction.[3]

Transition-metal decomposition of $HOOSO_3^-$ has been reported to initiate radical polymerization[5,6] although there is little evidence to indicate whether the initial reaction proceeds *via* reaction (6) or (7). Although the reaction with Co^{II} is believed[7] to occur *via* reaction (7), to give $SO_4^{-\bullet}$, pulse radiolysis studies[8] lead to the conclusion that in this case reaction proceeds almost exclusively (*ca.* 80%) to give the hydroxyl radical [reaction (6)]. Our aim has been to employ ESR spectroscopy to determine whether one-electron transfer to $HOOSO_3^-$ from a low-valent metal ion parallels that achieved by pulse-radiolysis, to measure the rates of such reactions, and to establish the efficacy and mechanism of oxidation of organic radicals by the peroxide [*cf.* reaction (5)].

$$HOOSO_3^- \xrightarrow{e^-} HO^{\bullet} + SO_4^{2-} \quad (6)$$

$$HOOSO_3^- \xrightarrow{e^-} HO^- + SO_4^{-\bullet} \quad (7)$$

Results and Discussion

Our experiments typically involved the use of a continuous-flow system in which three solutions were mixed shortly (*ca.* 30 ms) prior to flowing through a sample cell in the cavity of an ESR spectrometer. The three solutions normally contained, respectively, (i) the metal ion (Ti^{III}, Fe^{II}), in some cases with added complexing agent (*e.g.* EDTA), (ii) the peroxymonosulphate anion, and (iii) the substrate (see the Experimental section for details). The pH was adjusted by addition of sulphuric acid, ammonia, or sodium hydroxide to streams (i) or (iii), and in certain experiments hydrogen peroxide was also added to streams (ii) or (iii).

(a) *The Reaction between* $HOOSO_3^-$ *and Metal Ions* (Ti^{III}, Fe^{II}).—To determine whether $SO_4^{-\bullet}$ or $^{\bullet}OH$ (or both) result from reaction between Ti^{III} and Fe^{II} we carried out experiments in the presence of several alkenes for which the $^{\bullet}OH$ and $SO_4^{-\bullet}$ adducts (obtained from separate experiments with[9] H_2O_2 and[10,11] $S_2O_8^{2-}$ respectively) are distinguishable by virtue of their ESR parameters. In the reaction of $HOOSO_3^-$ with Ti^{III} at pH *ca.* 2 [in the absence or presence of suitable complexing agents EDTA and NTA (nitrilotriacetic acid)] the addition of a variety of alkenes led to the detection of relatively intense and well-resolved ESR spectra which establish unambiguously that $SO_4^{-\bullet}$ adducts alone are formed[10,11] [see reactions (8) and (9), Figure 1 and Table 1]: no $^{\bullet}OH$ adducts were detectable [a limit of *ca* 5% can be placed on the contribution from reaction (6)]. Further support for this conclusion is provided by results for other substrates (see also Table 1), notably the characteristic oxidative decarboxylation of carboxylate anions[12] ($^{\bullet}OH$ reacts

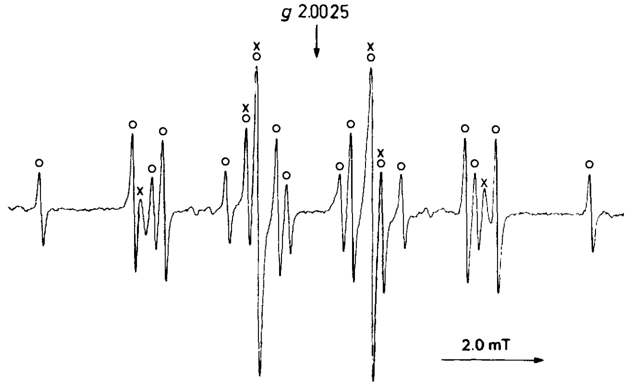


Figure 1. ESR spectra of the adducts of $SO_4^{-\bullet}$ and allyl alcohol, detected during the reaction of $Ti^{III}/HOOSO_3^-$ and $HOCH_2CH{=}CH_2$ at pH 2: ○, $^\bullet CH(CH_2OH)CH_2OSO_3^-$; ×, $^\bullet CH_2CH(OSO_3^-)CH_2OH$.

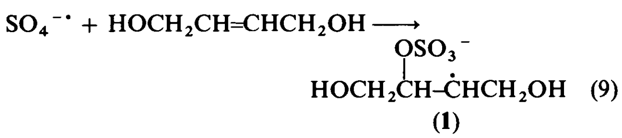
Table 1. Radicals detected by ESR in the reaction of the $Ti^{III}/HOOSO_3^-$ couple with aliphatic alkenes and carboxylic acids.[a,b]

Substrate	Radicals detected
$HOCH_2CH{=}CH_2$	$^\bullet CH(CH_2OH)CH_2OSO_3^-$, $^\bullet CH_2CH(OSO_3^-)CH_2OH$
$HOCH_2CH{=}CHMe$	$^\bullet CHMeCH(OSO_3^-)CH_2OH$, $^\bullet CH(CH_2OH)CH(OSO_3^-)Me$
$HOCH_2CMe{=}CH_2$	$^\bullet CMe(CH_2OH)CH_2OSO_3^-$
$HOCH_2CH{=}CHCH_2OH$	$^\bullet CH(CH_2OH)CH(OSO_3^-)CH_2OH$
$Me_2C{=}CH_2$	$^\bullet CMe_2CH_2OSO_3^-$
$MeCH{=}CHMe$	$^\bullet CHMeCH(OSO_3^-)Me$
$HO_2CCH{=}CHMe$	$^\bullet CHMeCH(OSO_3^-)CO_2H$, $^\bullet CH(CO_2H)CH(OSO_3^-)Me$
$HO_2CCH{=}CHCO_2H$	$^\bullet CH(CO_2H)CH(OSO_3^-)CO_2H$
$HO_2CCH{=}CMeCO_2H$	$^\bullet CMe(CO_2H)CH(OSO_3^-)CO_2H$
$MeCO_2H$	$^\bullet Me$, $^\bullet CH_2CO_2H$
$EtCO_2H$	$^\bullet CH_2CH_2CO_2H$, $^\bullet Et$, $^\bullet CHMeCO_2H$
Me_2CHCO_2H	$^\bullet CMe_2CO_2H$, $^\bullet CH_2CHMeCO_2H$, $^\bullet CHMe_2$
Me_3CCO_2H	$^\bullet CH_2CMe_2CO_2H$

[a] Experiments conducted at pH 2–2.5. [b] ESR parameters as previously reported: refs. 10–12.

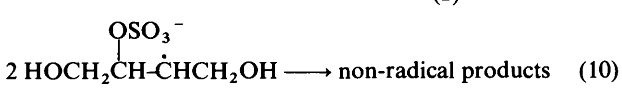
via hydrogen-atom abstraction rather than electron-transfer) and the formation of the methyl radical (*via* $Bu^tO^\bullet$) from Bu^tOH.[11,12]

$$Ti^{III} + HOOSO_3^- \longrightarrow Ti^{IV} + HO^- + SO_4^{-\bullet} \quad (8)$$



$$SO_4^{-\bullet} + HOCH_2CH{=}CHCH_2OH \longrightarrow HOCH_2\overset{OSO_3^-}{\overset{|}{C}}H\text{-}\dot{C}HCH_2OH \quad (9)$$

(1)



$$2\,HOCH_2\overset{OSO_3^-}{\overset{|}{C}}H\text{-}\dot{C}HCH_2OH \longrightarrow \text{non-radical products} \quad (10)$$

The rate constants for reaction (8) for a variety of Ti^{III} complexes were determined *via* a steady-state kinetic analysis and measurement of the concentration of radicals [*e.g.* (**1**)] formed by the scavenging of $SO_4^{-\bullet}$ with appropriate concentrations of suitable substrates [*e.g. via* reaction (9)].[2,13] It has been shown[13] that for effective scavenging of an intermediate (primary) radical to give a radical [*e.g.* (**1**)] which is not itself either oxidized or reduced, and which decays simply *via* bimolecular termination [reaction (10)], kinetic analysis of the resulting pseudo steady-state condition achieved in the cavity (*i.e.* after time *t*) leads to two important equations.* The first indicates that the observed radical concentration should vary with $[HOOSO_3^-]_0$ in such a way that it is a maximum for the value of $[HOOSO_3^-]_0$ indicated in equation (11); the second relates the observed radical concentration to time after mixing (and hence to the flow-rate)

$$[HOOSO_3^-]\ (\text{for } [R^\bullet]_{max}) = \frac{1}{k_8 t} \quad (11)$$

$$\ln[R^\bullet] = \text{const.} - \frac{k_8[HOOSO_3^-]t}{2} \quad (12)$$

In an initial series of experiments the steady-state concentrations of $SO_4^{-\bullet}$ adducts (to both allyl alcohol and butene-1,4-diol) were monitored as a function of $[HOOSO_3^-]_0$ {for fixed $[Ti^{III}]_0$ and *t*, and with $[HOOSO_3^-]_0 \gg [Ti^{III}]_0$, to ensure that the concentration of the former remains constant, and with alkene concentrations† *ca.* 0.1 mol dm^{-3} (to ensure scavenging)}, and as a function of flow-rate (and hence *t*), all other conditions and concentrations being held fixed. The results confirmed the behaviour expected on the basis of the kinetic analysis (a 'peaking' in $[R^\bullet]$ as a function of $[HOOSO_3^-]_0$ and a linear dependence of $\ln[R^\bullet]$ on *t*: see ref. 3). Data from both types of experiment were analysed to yield values for k_8 (the initiation rate constant for reaction with Ti^{III}) for different complexes (see Table 2; the reaction of the Ti^{III}–DTPA complex was evidently too slow to follow using these techniques (only weak signals from organic radicals at high $[HOOSO_3^-]$ could be detected) and the value for the rate constant given in Table 2 was derived by monitoring the pseudo first-order decay of the ESR signal (*g ca.* 1.965) from Ti^{III}–DTPA itself both when the flow was stopped (see ref. 3) and *via* experiments with allyl alcohol at different flow-rates.

Comparison of results for a variety of peroxides (see Table 2) show that for most complexes studied (and for the complexed ion) the rate constants are similar for $HOOSO_3^-$ and H_2O_2[3] (and somewhat greater than for[4,10] $S_2O_8^{2-}$). For both $HOOSO_3^-$ and H_2O_2 (but more markedly with the latter[3]) the use of DTPA leads to a significant reduction in the rate of electron-transfer.

Detailed information on the redox potentials of the full range of metal complexes employed is not apparently available but it might be anticipated that the $E^\ominus$ values for these should not differ greatly:[14] the variation in k_8, *e.g.* the acceleration with NTA and the retardation with DTPA, therefore suggests that steric factors are more important than electronic factors in controlling the reaction. In particular, we note that the DTPA complex, the reaction of which is slow, is more crowded than that of EDTA.[15] This observation coupled with the finding that the reaction yields $SO_4^{-\bullet}$ rather than $^\bullet OH$ (in contrast with pulse radiolysis results)[8] suggests that electron-transfer proceeds *via* an inner-sphere mechanism and decomposition of a metal–peroxide complex.‡

Reaction between Fe^{II}–EDTA, Fe^{II}–NTA, and Fe^{II}–DTPA also yielded $SO_4^{-\bullet}$, as judged by the detection of signals from the appropriate adducts. That the relative weakness of the signals under typical flow system conditions reflects the rapidity of the initiating reaction (13) was confirmed by kinetic analysis as indicated above [k_{13} *ca.* 3×10^4 dm^3 mol^{-1} s^{-1}]

$$Fe^{II} + HOOSO_3^- \longrightarrow Fe^{III} + HO^- + SO_4^{-\bullet} \quad (13)$$

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* See refs. 1, 2, and 13 for derivation and for kinetic applications in metal-peroxide systems.

† Here and elsewhere in the text, the concentrations referred to are those after mixing.

‡ The finding[16] that $SO_4^{-\bullet}$ reacts readily with OH^- to give $^\bullet OH$ (*k ca.* 5×10^7 dm^3 mol^{-1} s^{-1}) indicates that production of $^\bullet OH$ and SO_4^{2-} from peroxymonosulphate is thermodynamically preferred.

Table 2. Rate constants (k/dm^3 mol^{-1} s^{-1}) for the reactions between Ti^{III} complexes and both $HOOSO_3^-$ and H_2O_2.[a,b]

Complex	$HOOSO_3^-$	H_2O_2
Ti^{III}(aq)[c]	7.0×10^2	2.1×10^3
Ti^{III}–EDTA	3.5×10^2 (pH 2) 1.3×10^3 (pH 8–9)	4.5×10^3 (pH 3–7)
Ti^{III}–DTPA	1.5×10^2	5
Ti^{III}–NTA	1.0×10^4	*ca.* 1×10^4

[a] At room temperature and at pH 2 unless indicated otherwise: estimated error in k ± 15%. For abbreviations see text. [b] Rate constants for H_2O_2 are taken from ref. 3 except for Ti^{III}–NTA (determined in this study). [c] Contrast rate constants for Ti^{III} with $H_2P_2O_8^{2-}$ (2×10^4 dm^3 mol^{-1} s^{-1}: ref. 11) and $S_2O_8^{2-}$ (2×10^2 dm^3 mol^{-1} s^{-1}: ref. 4).

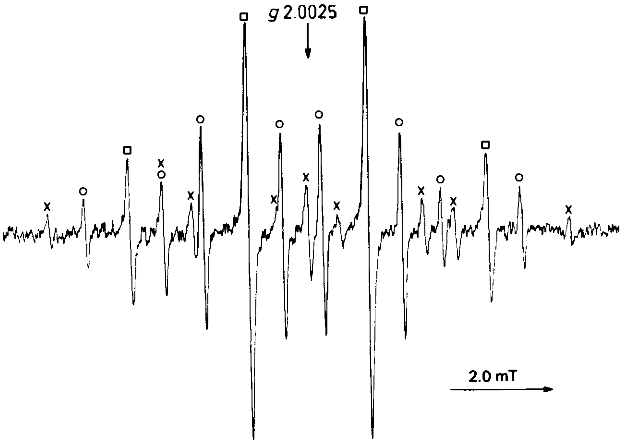
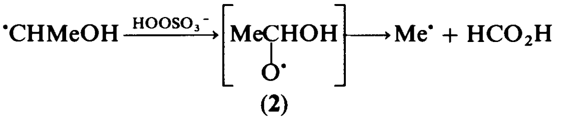


Figure 2. ESR spectra obtained from the reaction of the Ti^{III}/$HOOSO_3^-$ couple with ethanol ([Ti^{III}SO$_4$] 1.7×10^{-3} mol dm^{-3}, [$HOOSO_3^-$] 1.0×10^{-2} mol dm^{-3}, [EtOH] 0.5 mol dm^{-3}, pH 2): o, $^{\cdot}$CHMeOH; x, $^{\cdot}CH_2CH_2OH$; □ Me$^{\cdot}$.

(b) *The Oxidation of Radicals by* $HOOSO_3^-$.—When ethanol was employed as substrate with the Ti^{III}–$HOOSO_3^-$ couple, three radicals were detected, namely the α- and β-radicals $^{\cdot}$CHMeOH and $^{\cdot}CH_2CH_2OH$, respectively, and the methyl radical (see Figure 2). As the concentration of $HOOSO_3^-$ was increased, a decrease in the concentration of $^{\cdot}$CHMeOH was matched by a marked increase in [Me$^{\cdot}$] [see Figure 3(*a*).]. This leads to the suggestion that Me$^{\cdot}$ is formed by oxidation of the α-radical by the peroxide, for example as depicted in reaction (14); this is in contrast with a formal electron-transfer process [*cf.* reactions (15*a*) or (15*b*), a reaction-type established for radicals of the type $^{\cdot}CR^1R^2OH$ with[2] H_2O_2 and[17] $S_2O_8^{2-}$ (see *e.g.* reaction (5)]. The suggested involvement of an α-hydroxyalkoxyl radical (2) in the novel decomposition is supported in part by the observation[18] that such species fragment rapidly to alkyl radicals: other evidence was sought *via* the experiments described below.

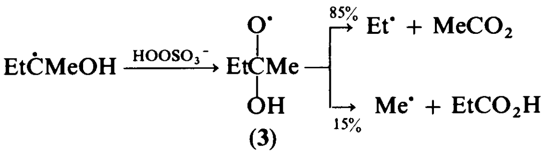


$$^{\cdot}\text{CHMeOH} \xrightarrow{\text{HOOSO}_3^-} \left[\text{Me}\underset{\text{O}^{\cdot}}{\text{CHOH}}\right] \longrightarrow \text{Me}^{\cdot} + \text{HCO}_2\text{H} \quad (14)$$

(2)

$$^{\cdot}\text{CHMeOH} + \text{HOOSO}_3^- \longrightarrow \begin{cases} \text{MeCHO} + \text{H}^+ + \text{HO}^- + \text{SO}_4^{-\cdot} & (15a) \\ \text{MeCHO} + \text{H}^+ + \text{HO}^{\cdot} + \text{SO}_4^{2-} & (15b) \end{cases}$$

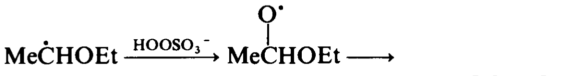
(i) *Reactions of Other Oxygen Conjugated Radicals.*—Results for a number of alcohols and and ethers with the Ti^{III}/$HOOSO_3^-$ couple (see Table 3) show behaviour parallel to that for ethanol. For example, propan-2-ol gave both $^{\cdot}CMe_2OH$ and $^{\cdot}CH_2CHMeOH$ as well as strong signals from Me$^{\cdot}$, which grew at the expense of $^{\cdot}CMe_2OH$ for increased [$HOOSO_3^-$]: the higher ratio of [Me$^{\cdot}$]/[$^{\cdot}CMe_2OH$] than [Me$^{\cdot}$]/[$^{\cdot}$CHMeOH] (for ethanol) for given [$HOOSO_3^-$] is consistent with a more ready fragmentation of the intermediate for propan-2-ol. Reaction of propan-1-ol and pentan-3-ol led to the detection of the ethyl radical, as well as radicals expected from $SO_4^{-\cdot}$ attack on the substrates. Reaction with butan-2-ol (for which $SO_4^{-\cdot}$ itself gives largely $^{\cdot}$CMeEtOH) produced Et$^{\cdot}$ and Me$^{\cdot}$, with the former in significantly higher concentration [as might be anticipated from preferential fragmentation of the intermediate (3) to give the more stable alkyl radical, reaction (16*a*)]. The ratio [Et$^{\cdot}$]/[Me$^{\cdot}$] was somewhat dependent upon [$HOOSO_3^-$] in a manner that suggests that the former is itself more readily oxidized by the peroxide (see later). Other examples of C–C cleavage in radicals obtained from alkanols and diols are included in Table 3.



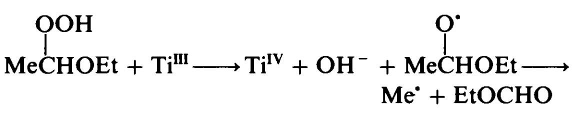
$$\text{Et}\dot{\text{C}}\text{MeOH} \xrightarrow{\text{HOOSO}_3^-} \text{Et}\overset{\text{O}^{\cdot}}{\underset{\text{OH}}{\text{C}}}\text{Me} \longrightarrow \begin{cases} \xrightarrow{85\%} \text{Et}^{\cdot} + \text{MeCO}_2 & (16a) \\ \xrightarrow{15\%} \text{Me}^{\cdot} + \text{EtCO}_2\text{H} & (16b) \end{cases}$$

(3)

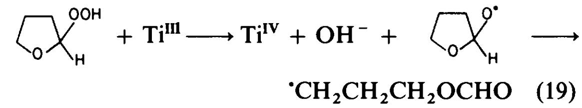
Reaction of both diethyl and di-isopropyl ethers also gave strong signals from Me$^{\cdot}$ in addition to $^{\cdot}$CHMeOEt and $^{\cdot}CMe_2OCHMe_2$, respectively (and weaker signals from the appropriate β-radicals): again, [Me$^{\cdot}$] increased as [$HOOSO_3^-$] was increased. Tetrahydrofuran gave the ring-opened radical (4). These observations lend considerable support to the proposal that an alkoxy intermediate is involved [see *e.g.* reaction (17)] since it has previously been shown that decomposition of the hydroperoxides derived from these ethers by one-electron transfer from Ti^{III} leads to the fragmentation identical with that observed in the reactions described here [see reactions (18) and (19)].[18] These findings strongly suggest that alcohols and ethers react in analogous fashion and that the reactions of the former to give alkyl radicals are not a consequence of direct oxidation of the OH groups to give alkoxyl radicals.



$$\text{Me}\dot{\text{C}}\text{HOEt} \xrightarrow{\text{HOOSO}_3^-} \text{Me}\overset{\text{O}^{\cdot}}{\text{C}}\text{HOEt} \longrightarrow \text{Me}^{\cdot} + \text{EtOCH=O} \quad (17)$$



$$\text{Me}\overset{\text{OOH}}{\text{C}}\text{HOEt} + \text{Ti}^{III} \longrightarrow \text{Ti}^{IV} + \text{OH}^- + \text{Me}\overset{\text{O}^{\cdot}}{\text{C}}\text{HOEt} \longrightarrow \text{Me}^{\cdot} + \text{EtOCHO} \quad (18)$$



+ Ti^{III} ⟶ Ti^{IV} + OH$^-$ + ⟶ $^{\cdot}CH_2CH_2CH_2OCHO$ (19)

(4)

Reaction of 3-phenylpropan-1-ol led to the detection of $^{\cdot}CH_2CH_2Ph$, evidently formed *via* oxidation of $^{\cdot}$CH(OH)-CH_2CH_2Ph (which is obtained from $SO_4^{-\cdot}$ in a manner previously described[19]). Reaction of 2-methylpropan-1-ol led to the detection of the anticipated α-, β-, and γ-radicals but, perhaps surprisingly there was only a trace of the prop-2-yl radical, the presence of which would have been expected in terms of the mechanism outlined above. No trace of Bu$^{t\cdot}$ could be

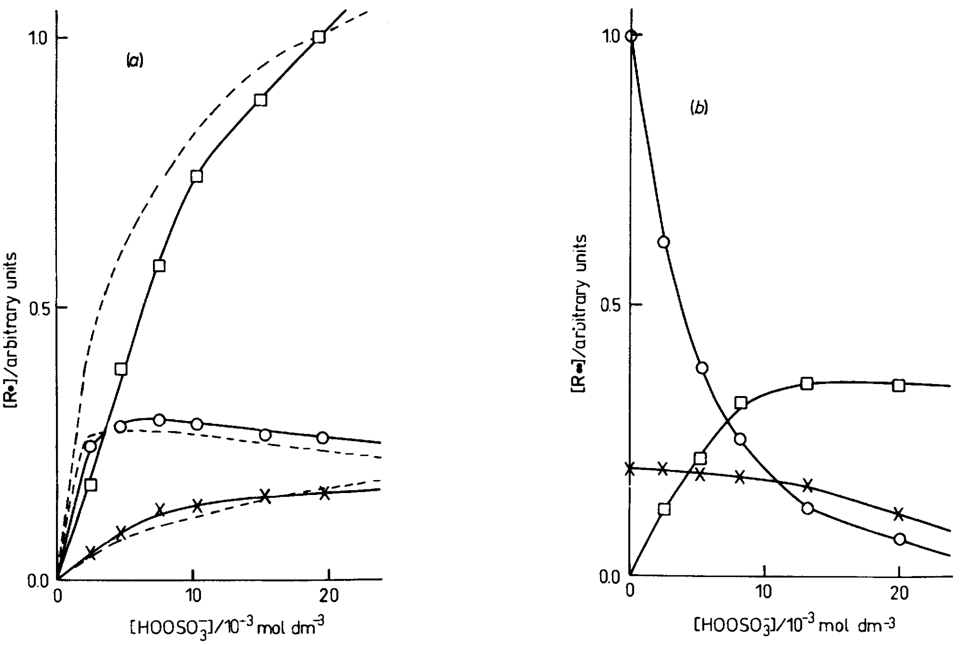
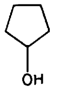
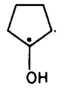
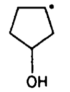
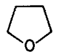
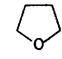
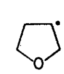
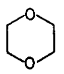
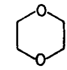


Figure 3. (*a*) Variation of relative radical concentration with [$HOOSO_3^-$] in the reaction of EtOH with $Ti^{III}/HOOSO_3^-$ at pH 2 with mixing time 0.03 s (for conditions see Figure 2), together with simulations based on the kinetic Scheme given in the text, and values for k_{24} and k_{25} given in Table 4; ○ $^{\bullet}CHMeOH$, X $^{\bullet}CH_2CH_2OH$, □ $Me^{\bullet}$, (*b*) Variation in the concentrations of radicals derived from $^{\bullet}OH$ (from Ti^{III}-EDTA and H_2O_2) and EtOH with [$HOOSO_3^-$] ([Ti^{III}] = [EDTA] = 1.7 × 10^{-3} mol dm^{-3}, [H_2O_2] = 1.7 × 10^{-2} mol dm^{-3}, [EtOH] = 0.5 mol dm^{-3}, pH 2): ○, $^{\bullet}CHMeOH$; ×, $^{\bullet}CH_2CH_2OH$; □ $Me^{\bullet}$.

Table 3. Radicals detected from reaction of the $Ti^{III}/HOOSO_3^-$ couple with aliphatic alcohols and ethers.[a]

Substrate	$R^{1\bullet}$ (α-radical)	$R^{2\bullet}$ (derived from reaction of $R^{1\bullet}$)	Other radicals detected
Me_3COH	—	—	$^{\bullet}CH_2CMe_2OH$ $^{\bullet}Me$
MeOH	$^{\bullet}CH_2OH$	—	—
EtOH	$^{\bullet}CHMeOH$	$Me^{\bullet}$	$^{\bullet}CH_2CH_2OH$
Me_2CHOH	$^{\bullet}CMe_2OH$	$Me^{\bullet}$	$^{\bullet}CH_2CHMeOH$
PrOH	$^{\bullet}CHEtOH$	$Et^{\bullet}$	$^{\bullet}CHMeCH_2OH$ $^{\bullet}CH_2CH_2CH_2OH$
Et_2CHOH	$^{\bullet}CEt_2OH$	$Et^{\bullet}$	$^{\bullet}CH_2CH_2CHEtOH$ $^{\bullet}CHMeCHEtOH$
EtCHMeOH	$^{\bullet}CEtMeOH$	$Et^{\bullet b}$ $Me^{\bullet}$	$^{\bullet}CH_2CH_2CHMeOH$ $^{\bullet}CHMeCHMeOH$ $^{\bullet}CH_2CHEtOH$
		$^{\bullet}CH_2CH_2CH_2CH_2CO_2H$	
$HOCH_2CH_2CH_2CH_2OH$	$^{\bullet}CH(OH)CH_2CH_2CH_2OH$	$^{\bullet}CH_2CH_2CH_2OH$	$^{\bullet}CH(CH_2OH)CH_2CH_2OH$
Me_2CHCH_2OH	$^{\bullet}CH(OH)CHMe_2$	$^{\bullet}CHMe_2{}^{c}$	$^{\bullet}CMe_2CH_2OH$ $^{\bullet}CH_2CHMeCH_2OH$
Me_3CCH_2OH	$^{\bullet}CH(OH)CMe_3$	—	$^{\bullet}CH_2CMe_2CH_2OH$
$PhCH_2CH_2CH_2OH$	$^{\bullet}CH(OH)CH_2CH_2Ph$	$^{\bullet}CH_2CH_2Ph$	—
EtOEt	$^{\bullet}CHMeOEt$	$Me^{\bullet}$	$^{\bullet}CH_2CH_2OEt$
$Me_2CHOCHMe_2$	$^{\bullet}CMe_2OCHMe_2$	$Me^{\bullet}$	$^{\bullet}CH_2CHMeOCHMe_2$
		$^{\bullet}CH_2CH_2CH_2OCHO$	
		—	—
$MeOCH_2CH_2OH$	$^{\bullet}CH_2OCH_2CH_2OH$ $^{\bullet}CH(OMe)CH_2OH$	—	$^{\bullet}CH_2CH(OH)OMe$ $^{\bullet}CH_2CHO$
$MeOCH_2CH_2OMe$	$^{\bullet}CH_2OCH_2CH_2OMe$ $^{\bullet}CH(OMe)CH_2OMe$	—	—
$HOCH_2CH_2OH$	—	—	$^{\bullet}CH_2CHO$

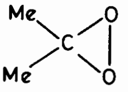
[a] pH 2. [b] [$Et^{\bullet}$]/[$Me^{\bullet}$] *ca.* 7 for [$HOOSO_3^-$] 6 × 10^{-3} mol dm^{-3}. [c] Only a trace of this radical detected.

detected during the reaction of $Ti^{III}/HOOSO_3^-$ with 2,2-dimethylpropan-1-ol (neopentyl alcohol). We believe that secondary and tertiary radicals are more readily oxidized by $HOOSO_3^-$ than methyl and ethyl radicals [as would be expected on the basis of their ionization potentials[20] ($Me^{\bullet}$ 9.34, $Et^{\bullet}$ 8.30, $Pr^{i\bullet}$ 7.55, $Bu^{t\bullet}$ 6.93 eV) and as already noted[17] for $S_2O_8^{2-}$] so that their steady-state concentrations are reduced to, or below, that required for detection. Consistent with this, it was shown that when $Et^{\bullet}$ and $Pr^{\bullet}$ were generated by oxidative decarboxylation of the appropriate acids with $Ti^{III}/HOOSO_3^-$, signals from the former, but more markedly the latter, were reduced as $[HOOSO_3^-]$ was increased: no signals from $Bu^{t\bullet}$ were obtained from Bu^tCO_2H, presumably on account of the more rapid oxidation of the tertiary radical.

No radicals resulting from fragmentation were observed from some 1,2-diols and related α,β-dioxygen-substituted compounds (see Table 3) including ethane-1,2-diol, 1,4-dioxane, 1,2-dimethoxyethane, and 2-methoxyethanol. This appears to reflect the effect of a β-oxygen substituent in retarding oxidation of an α-oxygen-substituted radical.[21]

(ii) *Reactions of* Ti^{III}/H_2O_2 *in the Presence of* $HOOSO_3^-$.—In order to distinguish oxidation of free radicals by peroxymonosulphate from the generation of radicals by $SO_4^{-\bullet}$ (from $HOOSO_3^-$) we utilized the faster rate of reaction of Ti^{III}–EDTA with H_2O_2 than $HOOSO_3^-$ (by a factor of *ca.* 10) to generate free radicals from $^{\bullet}OH$ and study their subsequent oxidation in experiments with mixed peroxides (these being in separate streams) with $[H_2O_2] \gg [HOOSO_3^-]$. As Figure 3(*b*) indicates, reaction of $^{\bullet}OH$ with EtOH gives $^{\bullet}CHMeOH$ (the major species) and $^{\bullet}CH_2CH_2OH$: when $[HOOSO_3^-]$ is increased, removal of the former and production of $^{\bullet}Me$ is clearly established. However, we also note that the rate of decrease in $[^{\bullet}CHMeOH]$ is faster than the increase in $[^{\bullet}Me]$, which suggests that oxidation to give $[Me^{\bullet}]$ is accompanied by direct oxidation [probably *via* reaction (15*a*) or (15*b*)]. A full kinetic analysis is described later but we note that in experiments with MeOH (0.6 mol dm^{-3}) and fumaric acid (0.02 mol dm^{-3}) as well as Ti^{III} and $HOOSO_3^-$, no $^{\bullet}OH$ adducts of the alkene were observed, suggesting that reaction (15*a*), rather than (15*b*), is preferred.

(iii) *Oxidation of Other Possible Intermediates.*—The possibilities that the methyl radical (from ethanol) could result from further oxidation of ethanal [formed, *e.g. via* reactions (15*a*) or (15*b*)] was ruled out in rapid-flow experiments in which it was shown that this substrate is unreactive towards $HOOSO_3^-$ (and Ti^{III}) under these conditions. Similarly, propanone (which is believed to be formed by one-electron oxidation of $^{\bullet}CMe_2OH$) failed to react under our conditions; this also rules out the possibility that reactions involved here proceed *via* a dioxirane intermediate [*e.g.* (**5**)], the formation of which has been invoked[22] in the (non-radical) reaction between $HOOSO_3^-$ and ketones. Addition of Fe^{III}, to encourage one-electron oxidation of $^{\bullet}CHMeOH$,[3] led to reduction in its concentration and a reduction, rather than increase in $[^{\bullet}Me]$, which rules out reaction of $^{+}CHMeOH$ with peroxymonosulphate as the source of the latter.



(**5**)

(iv) *Photolysis Experiments.*—*in situ* photolytic decomposition of $HOOSO_3^-$ (which gives[23] $HO^{\bullet}$ and $SO_4^{-\bullet}$) in the presence of ethanol by the radiation from a 1 kW mercury–xenon lamp also led to the detection of $^{\bullet}CHMeOH$, $^{\bullet}CH_2CH_2OH$, and $Me^{\bullet}$ (the last of which is not detected in comparable experiments with H_2O_2 and $S_2O_8^{2-}$ above). This establishes that metal ions are not required for the unusual oxidation reaction to give alkyl radicals.

(v) *Other Experiments.*—Investigation of the effect of pH on the Ti^{III}–EDTA/$HOOSO_3^-$/EtOH reaction established that relatively low radical concentrations are detected at low pH (possibly on account of the low rate of reaction between $HOOSO_3^-$ and Ti^{III}–EDTA in acid) whereas above pH *ca.* 10 $[^{\bullet}CHMeOH]$ decreased rapidly, accompanied by an increase in $[Me^{\bullet}]$. There are at least two possible explanations for the latter behaviour, namely that the ionized counterpart $^{\bullet}CHMeO^-$ [pK_a ($^{\bullet}CHMeOH$) is[24] 11.6] is more easily oxidized or that the anion $^-OOSO_3^-$ [pK_a ($HOOSO_3^-$) 9.3: ref. 25] is a more effective oxidant, or both. The observation that for $^{\bullet}CHMeOEt$ (from diethyl ether) there is little decrease in the concentration of the radical or increase in $[Me^{\bullet}]$ above pH 10 suggests that the behaviour of $^{\bullet}CHMeOH$ is attributable to an increased rate of oxidation of the (unprotonated) ketyl radical.

Experiments in which $[Ti^{III}]$ was increased ($\geqslant 1.7 \times 10^{-3}$ mol dm^{-3}) led to a reduction in the concentration of alkyl radicals derived by fragmentation (*e.g.* $^{\bullet}Me$ from $^{\bullet}CHMeOH$). Since alkyl radicals themselves are not effectively reduced by Ti^{III} under these conditions (but see ref. 26) and, as we have also shown, alkoxy radicals are readily reduced (with[11] k 6×10^8 dm^3 mol^{-1} s^{-1}), we regard this as further support for the proposal that alkoxy radicals are indeed generated in the reactions investigated here.

In experiments with Ti^{III}, $HOOSO_3^-$, and ethanol, addition of acetonitrile to the solvent (33% v/v) led to an increase in $[^{\bullet}CHMeOH]$ and decrease in $[Me^{\bullet}]$ (to *ca.* 25% of its value in the absence of MeCN). This suggests that the route to the formation of methyl may involve an intermediate in which charge separation is stabilized by solvent polarity or in which hydrogen-bonding confers stability. Alternatively, the intermediate alkoxy radical may be intercepted by acetonitrile, *via* a hydrogen-transfer reaction.

Finally, analysis of the reaction mixture from Ti^{III}/$HOOSO_3^-$/Pr^iOH by GLC indicated that propanone and ethanoic acid are formed in comparable (though low) yields, suggesting that the two (competing) oxidation pathways for $^{\bullet}CMe_2OH$ [reactions (20) and (21)] are of similar importance under the conditions employed here.

$$^{\bullet}CMe_2OH + HOOSO_3^- \longrightarrow H^+ + Me_2CO + HO^{\bullet} + SO_4^{2-} \quad (20a)$$

$$^{\bullet}CMe_2OH + HOOSO_3^- \longrightarrow H^+ + Me_2CO + HO^- + SO_4^{-\bullet} \quad (20b)$$

$$^{\bullet}CMe_2OH + HOOSO_3^- \longrightarrow SO_4^{2-} + H^+ + Me_2C{<}\begin{matrix}O^{\bullet}\\OH\end{matrix} \longrightarrow Me^{\bullet} + MeCO_2H \quad (21)$$

(vi) *Kinetic Analysis.*—In an attempt to determine kinetic parameters both for oxidation of radicals by (formal) one-electron transfer to $HOOSO_3^-$ [*e.g.* reactions (15*a*) and (15*b*)] and for the effective oxygen-transfer [which results in the production of alkyl radicals *via* fragmentation, *e.g.* reaction (14)] we have employed both steady-state analysis (as above) as well as computer simulation. Most of our experiments have involved use of the Ti^{III}–EDTA/H_2O_2 couple to generate $^{\bullet}OH$ and addition of $HOOSO_3^-$ to study the reaction of first-formed radicals with this substrate. The reactions to be included in the analysis are (22)–(28), reactions (24) and (25) representing the competing modes of oxidation (*n.b.* the formation of minor

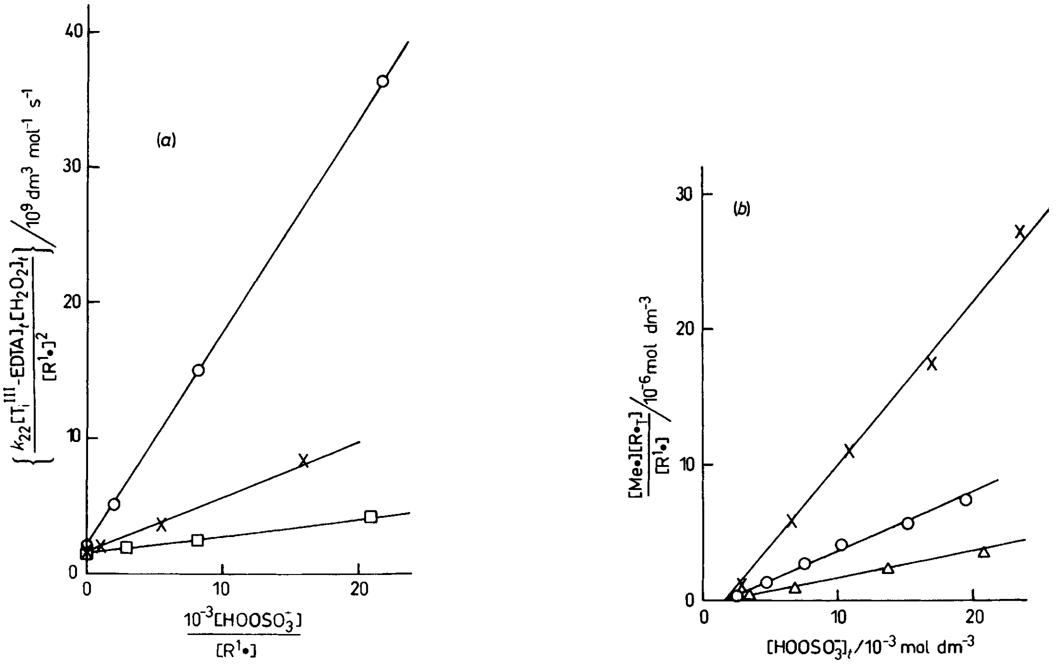


Figure 4. (*a*) Variation of $k_{22}[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t[\mathrm{R^1}]^{-2}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ with $[\mathrm{HOOSO_3^-}][\mathrm{R^1}]^{-1}$ in experiments in which $\mathrm{HOOSO_3^-}$ is added to the $\mathrm{Ti^{III}/H_2O_2/RH}$ system; ○ $^•\mathrm{CH_2OH}$ (from MeOH), □ Me$^•$ (from $\mathrm{Me_2SO}$), X Et$^•$ (from $\mathrm{Et_2SO}$). (*b*) Variation of $[^•\mathrm{Me}][\mathrm{R^•}]_\mathrm{T}[\mathrm{R^{1•}}]^{-1}$ with $[\mathrm{HOOSO_3^-}]_t$ [see equation (30)] in experiments in which $^•$Me was generated by reaction of $\mathrm{R^{1•}}$ with $\mathrm{HOOSO_3^-}$; $\mathrm{R^{1•}}$: x, $^•\mathrm{CMe_2OH}$ (from $\mathrm{Me_2CHOH}$); o, $^•$CHMeOH (from EtOH); △, $^•$CHMeOEt (from EtOEt).

radicals by attack of $\mathrm{SO_4^{-•}}$ on β-hydrogens is ignored at this stage).

$$\mathrm{Ti^{III}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Ti^{IV}} + \mathrm{HO^-} + {}^•\mathrm{OH} \quad (22)$$

$$\mathrm{HO^•} + \mathrm{R^1H} \longrightarrow \mathrm{R^{1•}} + \mathrm{H_2O} \quad (23)$$

$$\mathrm{R^{1•}} + \mathrm{HOOSO_3^-} \longrightarrow \mathrm{R^{1+}} + \mathrm{HO^-} + \mathrm{SO_4^{-•}} \quad (24)$$

$$\mathrm{R^{1•}} + \mathrm{HOOSO_3^-} \longrightarrow \mathrm{R^{2•}} \quad (25)$$

$$\left.\begin{array}{ll} \mathrm{R^{1•}} + \mathrm{R^{1•}} \longrightarrow & (26) \\ \mathrm{R^{1•}} + \mathrm{R^{2•}} \longrightarrow & (27) \\ \mathrm{R^{2•}} + \mathrm{R^{2•}} \longrightarrow & (28) \end{array}\right\} \text{non-radical products}$$

Initial experiments involved kinetic analysis of experiments in which the substrates MeOH, $\mathrm{Me_2SO}$, and $\mathrm{Et_2SO}$ (each of which gives only a single radical $\mathrm{R^{1•}}$) were studied separately: signals from $^•\mathrm{CH_2OH}$, Me$^•$, and Et$^•$ decreased steadily as $[\mathrm{HOOSO_3^-}]$ was increased. Appropriate reactions for steady-state analyses for these substrates and under these conditions are equations (22)–(24) and (26): reaction of $\mathrm{Ti^{III}}$–EDTA with $\mathrm{HOOSO_3^-}$ is negligible (as predicted and also established experimentally). Steady-state analysis for [HO$^•$] and $[\mathrm{R^{1•}}]$ leads to equation (29), which indicates that if the kinetic analysis is correct, then a plot of $k_{22}\ [\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t/[\mathrm{R^{1•}}]^2$ against $[\mathrm{HOOSO_3^-}]/[\mathrm{R^{1•}}]$ should be linear, with a gradient k_{24} and intercept $2k_t$. As illustrated in Figure 4(*a*) the observed behaviour is consistent with that predicted on this basis (in particular, the values of $2k_t$ which result are *ca.* $2 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, which is as expected for small uncharged aliphatic radicals [27]).

The resulting rate constants for oxidation of $^•\mathrm{CH_2OH}$, Me$^•$, and $^•$Et by $\mathrm{HOOSO_3^-}$ (see Table 4) are in accord with expectation based on the relative ionization potentials of these radicals, and are also greater than the corresponding rates of the analogous reactions with $\mathrm{H_2O_2}$ and $\mathrm{S_2O_8^{2-}}$. The failure, noted above, to detect significant concentrations of $\mathrm{Pr^{i•}}$ and $\mathrm{Bu^{t•}}$ in the presence of $\mathrm{HOOSO_3^-}$ is understandable if the rate constants for oxidation of these radicals are $\geqslant$ *ca.* $1 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$

$$k_{22}[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t = 2k_t[\mathrm{R^{1•}}]^2 + k_{24}[\mathrm{HOOSO_3^-}][\mathrm{R^{1•}}] \quad (29)$$

For the corresponding reactions of ethanol, diethyl ether, and propan-2-ol, for which there is not only the complication of a small extent of β-radical formation but also as the generation of Me$^•$ [*via* reaction (25)] the above approach was employed (at low $[\mathrm{HOOSO_3^-}]$) simply to provide estimates for the rate constants for destruction of the first-formed radicals (k_{24}) in the range 2–3 × $10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$; these values were refined by computer simulation (see below).

Information on the oxygen-transfer reaction [reaction (25)] for the latter substrates was found by a steady-state analysis for $[\mathrm{R^{2•}}]$ (*i.e.* [Me$^•$]): this leads to equation (30), in which $[\mathrm{R^•}]_\mathrm{T}$ is the total radical concentration (including $\mathrm{R^{1•}}$, $\mathrm{R^{2•}}$, and any β-radical detected: allowance has also been made for termination reactions involving the last-named). Following experiments with $\mathrm{Ti^{III}}$–EDTA–$\mathrm{H_2O_2}$, with added $\mathrm{HOOSO_3^-}$, and also $\mathrm{Ti^{III}_{aq}}$–$\mathrm{HOOSO_3^-}$, in the presence of EtOH, Pr^{i}OH, and EtOEt it was demonstrated that, as expected on the basis of equation (30), $[\mathrm{R^{2•}}][\mathrm{R^•}]_\mathrm{T}/[\mathrm{R^{1•}}]$ varies linearly with $[\mathrm{HOOSO_3^-}]_t$* [Figure 4(*b*)]. Estimates for k_{25} can be obtained from the gradient (taking k_t as $2 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$); these values were also refined by computer simulation.

$$k_t[\mathrm{R^{2•}}][\mathrm{R^•}]_\mathrm{T} = k_{25}[\mathrm{R^{1•}}][\mathrm{HOOSO_3^-}]_t \quad (30)$$

Experimental results for both the $\mathrm{Ti^{III}}$–EDTA–$\mathrm{H_2O_2}$–RH–$\mathrm{HOOSO_3^-}$ and $\mathrm{Ti^{III}_{aq}}$–$\mathrm{HOOSO_3^-}$–RH systems were satisfactorily simulated with a kinetic program which incorporated

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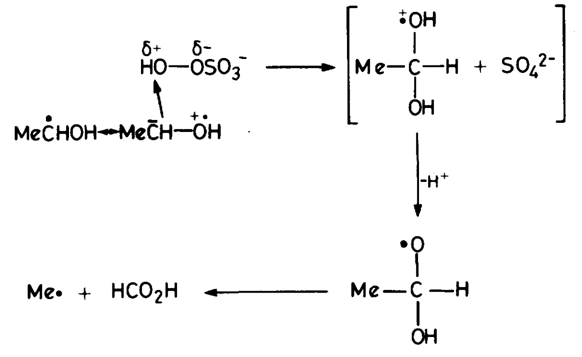
* In these experiments, $[\mathrm{Ti^{III}}]_0$ was kept low ($< 10^{-3}$ mol dm^{-3}) to minimize the occurrence of reduction of the intermediate alkoxyl radical by $\mathrm{Ti^{III}}$ (see earlier).

Table 4. Rate constants (k/dm^3 mol^{-1} s^{-1}) for the oxidation of aliphatic radicals by $HOOSO_3^-$, $S_2O_8^{2-}$, and H_2O_2.[a]

	Oxidant			
	$HOOSO_3^-$		$S_2O_8^{2-}$	H_2O_2
Radical	k_{24}	k_{25}	k_{24}	k_{24}
$Me^{\bullet}$	1.2×10^5		3.3×10^4	
$Et^{\bullet}$	3.8×10^5		7.4×10^4	
$^{\bullet}CH_2OH$	1.8×10^6		1.3×10^5	3×10^4
$^{\bullet}CHMeOH$	2.1×10^6	1.1×10^6	6.9×10^5	1.5×10^5
$^{\bullet}CHMeOEt$	2.0×10^6	5.5×10^5	7.5×10^5	5.5×10^4
$^{\bullet}CMe_2OH$	3.0×10^6	3.4×10^6	7.1×10^5	5.0×10^5
$^{\bullet}CMe_2OCHMe_2$	6.0×10^6	1.9×10^6		
	*ca.* 1.8×10^6	*ca.* 8.0×10^5		3×10^4

[a] Estimated error $k \pm 20\%$: data for $S_2O_8^{2-}$ taken from ref. 17 and for H_2O_2 taken from ref. 2. [b] Calculated on the assumption that the intermediate alkoxyl radical is not reduced by Ti^{III} (see the text). Values for k_{25} may be regarded as a lower limit.

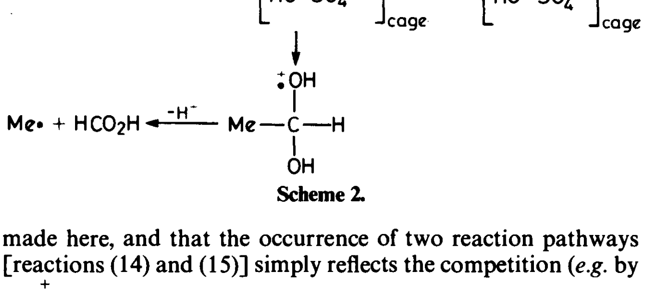


Scheme 1.

the appropriate reactions (22)–(28) (with established rate constants) and other reactions where necessary. For example, for Ti^{III}–EDTA–H_2O_2–EtOH system (with added $HOOSO_3^-$) we employed[3] k_{22} 4.5×10^3 dm^3 mol^{-1} s^{-1}, $k(^{\bullet}OH + EtOH)$[28] 1.7×10^9 dm^3 mol^{-1} s^{-1} (for α-attack) and 1.6×10^8 dm^3 mol^{-1} (for β-attack), with[27] cross-termination k_t 2×10^9 dm^3 mol^{-1} s^{-1}; allowance was made for oxidation of $^{\bullet}CHMeOH$ by Ti^{IV}–EDTA (k 6×10^8 dm^3 mol^{-1} s^{-1}) and the removal of Ti^{IV}–EDTA by H_2O_2 (k 2×10^6 dm^3 mol^{-1} s^{-1}: *cf.* ref. 29), as well as the oxidation of $Me^{\bullet}$ by $HOOSO_3^-$ (k 1.2×10^5 dm^3 mol^{-1} s^{-1}). The best fit to experimental results was obtained with k_{24} and k_{25}, the rate constants for oxidation of $^{\bullet}CHMeOH$ by $HOOSO_3^-$ to give $Me\overset{+}{C}HOH$ and $Me^{\bullet}$, as 2.1×10^6 and 1.1×10^6 dm^3 mol^{-1} s^{-1}, respectively. These values were also incorporated into analogous calculations to simulate the behaviour of α- and β-radicals and $Me^{\bullet}$ from Ti^{III}–$HOOSO_3^-$–EtOH, employing[16] $k(SO_4^{-\bullet} + EtOH)$ as 1.7×10^7 dm^3 mol^{-1} s^{-1} (α-attack) and 5×10^5 dm^3 mol^{-1} s^{-1} (β-attack), respectively. Again, good agreement was obtained [see Figure 3(*a*)]. Similar analysis for $R^{1\bullet}$ and $R^{2\bullet}$ in the reactions of Et_2O and Pr^iOH led to the values for k_{24} and k_{25} shown in Table 4.

(c) *Summary and Mechanistic Conclusion.*—It has been shown that reaction of Ti^{III} and Fe^{II} complexes with peroxymonosulphate anion generates $SO_4^{-\bullet}$ rather than $^{\bullet}OH$ ($\geqslant 95\%$). The steric inhibition of this reaction by DTPA and the contrast with pulse radiolysis suggests that the overall electron transfer may proceed *via* an inner-sphere mechanism.

Our results also indicate that $HOOSO_3^-$ is a more powerful one-electron oxidant of radicals than $S_2O_8^{2-}$ and H_2O_2 and, as would be expected, the rates of reaction increases with decrease in the ionization potential of the appropriate radicals. Although data on $E^{\ominus}$ for the one-electron reduction of $HOOSO_3^-$ are not known, these results are certainly not inconsistent with this reaction being an outer-sphere electron-transfer process (governed by Marcus theory).[30] We have also established that for certain oxygen-conjugated radicals an alternative and competing mode of oxidation yields alkyl radicals (*e.g.* $Me^{\bullet}$ from $^{\bullet}CHMeOH$), probably *via* intermediate alkoxyl radicals. This reaction is best envisaged, we believe, in terms of a 2-electron oxidation (Scheme 1) involving nucleophilic attack of the radical on the peroxide (*cf.* the well-established heterolytic reaction of amines and sulphides with peroxides to yield *N*-oxides and sulphoxides, respectively[31]): the resultant α-hydroxyalkoxy radical intermediate would be expected to fragment rapidly, as indicated.* A similar oxygen-centred radical has been postulated[32] in the oxidation by $S_2O_8^{2-}$ of the radical-adduct from 1,3-dimethyluracil, though in this case the mechanism proposed involved reaction of a carbonium ion with $SO_4^{-\bullet}$ in a solvent cage. It is of course possible that such a reaction mechanism (Scheme 2) accounts for the observations made here, and that the occurrence of two reaction pathways [reactions (14) and (15)] simply reflects the competition (*e.g.* by $Me\overset{+}{C}HOH$) between deprotonation and in-cage trapping by $^{\bullet}OH$. Although our evidence does not point conclusively to either mechanism, the absence of similar reactions with either H_2O_2 or $S_2O_8^{2-}$ (even when these oxidations proceed rapidly), the difference in the ratios of the two modes of oxidation with structure (*e.g.* alcohol-derived radicals *vs.* ether-derived



Scheme 2.

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* We have also considered the possibility that the α-hydroxyalkoxy-radical is the product of reaction of the first-formed oxygen-conjugated radical with $SO_5^{-\bullet}$ (from oxidation of $HOOSO_3^-$ by $SO_4^{-\bullet}$ or $^{\bullet}OH$). We have dismissed the involvement of $SO_5^{-\bullet}$ on a kinetic basis (the rate constant for reaction $SO_4^{-\bullet}$ with $HOOSO_3^-$ is reported[8] as being less than 10^5 dm^3 mol^{-1} s^{-1}).

analogues), and the widespread occurrence of related oxidation pathways *via* oxygen transfer lends support to the suggestion that Scheme 1 is the more appropriate representation. The observed rate constants (Table 4) could certainly be explained on the basis of Scheme 1: ethers would be expected to react somewhat slower than the corresponding alcohols on the basis of increased steric hindrance, whereas the increase in rate on α-alkylation (*e.g.* $^{\bullet}\mathrm{CHMeOH}$ to $^{\bullet}\mathrm{CMe_2OH}$ is consistent with the expected increase in nucleophilicity).

Experimental

ESR 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 this was calibrated with an aqueous solution of Fremy's salt, *a*(N) 1.309 mT[33]]; *g*-values were determined by comparison with that for $^{\bullet}\mathrm{CHMeOH}$ (*g* 2.003 21[34]) obtained from the reaction of $^{\bullet}\mathrm{OH}$ (from $\mathrm{Ti^{III}–H_2O_2}$) 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.* 30 ms before passage through the cavity of the spectrometer (using a Watson–Marlowe 502 peristaltic pump). The solutions used were typically as follows: stream (i) contained titanium(III) sulphate (typically $[\mathrm{Ti^{III}}]$ 0.005 mol dm^{-3}) in some cases with added sequestering agent (EDTA, DTPA, NTA), stream (ii) contained $\mathrm{HOOSO_3^-}$ at concentrations in the range 0.006–0.06 mol dm^{-3} and stream (iii) contained the substrate (at concentrations up to 1.5 mol dm^{-3}). The pH was adjusted by addition of sulphuric acid, ammonia or sodium hydroxide to streams (i) or (iii), and in certain experiments hydrogen peroxide (0.05 mol dm^{-3}) was added to streams (ii) or (iii). pH Measurements were made using a Pye-Unicam pH meter PW 9410 with the electrode inserted into the effluent stream. All solutions were deoxygenated both before and during use by purging with oxygen-free nitrogen.

Photolysis experiments were carried out with the unfiltered radiation from an Hanovia 9778-1 1 kW mercury–xenon compact arc lamp. Solutions containing $\mathrm{HOOSO_3^-}$ (*ca.* 0.03 mol dm^{-3}) and the substrate (*ca.* 1.0 mol dm^{-3}) were slowly flowed (at a rate of *ca.* 2 cm^3 min^{-1}) through the cell during photolysis.

A product study was performed *via* the addition of titanium(III) chloride solution (0.4 mol dm^{-3}) to an aqueous solution of propan-2-ol and $\mathrm{HOOSO_3^-}$ (both 0.05 mol dm^{-3}). Analysis was carried out by flame-ionization GLC *via* injection of the aqueous reaction mixture onto an 80/100 Carbopack C/0.1% sp-1000 column and identification *via* retention times.

The kinetic simulation program, executed on a DEC VAX computer was kindly provided by Professor D. J. Waddington.

The source of the peroxymonosulphate anion was the triple salt $\mathrm{2KHSO_5{\cdot}K_2SO_4{\cdot}KHSO_4}$, kindly provided by Interox Chemicals Ltd. Other chemicals employed were commercial samples (used as supplied) except for diethyl sulphoxide which was generated *in situ* as described previously.[17]

Acknowledgements

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