Mechanisms of Peroxide Decomposition. An EPR Investigation of the Reactions between some Transition Metal Ions ($\mathrm{Ti^{III}}$, $\mathrm{Fe^{II}}$, $\mathrm{Cu^{I}}$) and Monoperoxyphthalic Acid and its Anion

Bruce C. Gilbert,[*,a] **(the late) Jonathan K. Stell,**[a] **Adrian C. Whitwood,**[a] **Carol Halliwell**[a] **and William R. Sanderson**[b]
[a] *Department of Chemistry, University of York, Heslington, York YO1 5DD, UK*
[b] *Interox Chemicals Ltd., PO Box 51, Moorfield Road, Widnes, Cheshire, WA8 0FE, UK*

Continuous-flow and spin-trapping experiments have been employed in conjunction with EPR spectroscopy to investigate the metal-ion induced decomposition of magnesium monoperoxyphthalate (MMPP) in aqueous solution (at pH *ca.* 2 and 6). As with the corresponding reactions of peroxymonosulphate ($\mathrm{HOOSO_3^-}$) it is shown that the behaviour of $\mathrm{Cu^I}$ (which leads to the formation of $\mathrm{^{\bullet}OH}$ and $\mathrm{ArCO_2^-}$, Ar = $\mathrm{2\text{-}C_6H_4CO_2H}$) is in complete contrast with that of $\mathrm{Ti^{III}}$ and $\mathrm{Fe^{II}}$, both of which bring about electron transfer to give $\mathrm{ArCO_2^{\bullet}}$ and $\mathrm{OH^-}$. Some subsequent reactions of $\mathrm{ArCO_2^{\bullet}}$ and $\mathrm{Ar^{\bullet}}$, formed by rapid decarboxylation, have been studied.

We have previously established[1] that the peroxymonosulphate anion ($\mathrm{HOOSO_3^-}$) reacts with a number of $\mathrm{Ti^{III}}$ and $\mathrm{Fe^{II}}$ complexes in aqueous solution to form the sulphate radical anion [reaction (1)], whereas, in complete contrast, its reaction with $\mathrm{Cu^I}$ gives exclusively the hydroxyl radical [reaction (2)]:[2] pulse-radiolysis experiments establish[3] that reaction with the hydrated electron leads predominantly to the latter mode of decomposition. These findings have been rationalized in terms of an inner-sphere reaction mechanism for $\mathrm{Ti^{III}}$ and $\mathrm{Fe^{II}}$ in which the dominant interaction is that between the small, 'hard' metal centre and the nucleophilic (hydroxyl) oxygen of the peroxide; in contrast, the copper-catalysed decomposition more closely resembles an outer-sphere electron-transfer reaction to give the thermodynamically-preferred products ($\mathrm{SO_4^{2-}}$, $\mathrm{^{\bullet}OH}$).

$$\mathrm{Ti^{III} + HOOSO_3^- \longrightarrow Ti^{IV} + OH^- + SO_4^{\bullet -}} \quad (1)$$

$$\mathrm{Cu^{I} + HOOSO_3^- \longrightarrow Cu^{II} + SO_4^{2-} + {}^{\bullet}OH} \quad (2)$$

One-electron reduction of percarboxylic acids, as with peroxymonosulphate, might also be expected to proceed in one or both of two possible ways, namely to produce the carbonyloxyl radical and hydroxide ion [reaction (3)] or the carboxylate anion and the hydroxyl radical [reaction (4)]. The former mode of decomposition is believed to occur in the reduction of a number of peracids by $\mathrm{Ti^{III}}$ (these have been studied using an EPR flow technique[4]), and $\mathrm{Co^{II}}$,[5] and also in the reduction of some peracids by nucleophilic radicals [see reaction (5)].[6] In contrast, the reaction of 4-nitroperbenzoic acid with the hydrated electron is reported to give the hydroxyl radical,[7] in a reaction which appears to be parallel to that invoked to account for the well-known Kharasch reaction between $\mathrm{Cu^I}$ and peresters[8] [see *e.g.* reaction (6)].

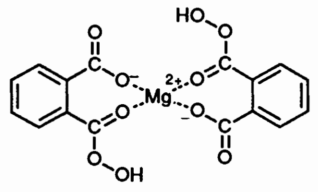
$$\mathrm{RCO_2OH \xrightarrow{1e} RCO_2^{\bullet} + OH^-} \quad (3)$$

$$\mathrm{RCO_2OH \xrightarrow{1e} RCO_2^- + {}^{\bullet}OH} \quad (4)$$

$$\mathrm{R^1CO_2OH + R^{2\bullet} \longrightarrow R^1CO_2^{\bullet} + R^2OH} \quad (5)$$

$$\mathrm{Cu^{I} + MeC(O)OOBu^{\mathit{t}} \longrightarrow MeCO_2^- + Cu^{II} + {}^{\bullet}OBu^{\mathit{t}}} \quad (6)$$

In this paper, we report the results of an investigation of the one-electron reduction of the commercially-available, water-soluble, peroxide magnesium monoperoxyphthalate (MMPP) (**1**): a variety of low-valent transition-metal ions has been employed, as well as some organic radicals for which ready oxidation might be envisaged. EPR spectroscopy (in conjunction with continuous-flow and spin-trapping techniques) has been employed to explore the mechanism of these reactions and to determine kinetic parameters where possible.



1

Results and Discussion

(a) *Reactions of Metal Ions in the Absence of Substrate: Continuous Flow EPR Experiments.*—Continuous flow EPR experiments were initially performed on the reaction between $\mathrm{Ti^{III}}$ and MMPP, using a three-way mixer (with water in the third stream) in which the solutions were mixed *ca.* 30 ms before the combined streams entered the cavity of an EPR spectrometer (see Experimental section and refs. 1–4).

The reaction between $\mathrm{Ti^{III}}$ (as $[\mathrm{Ti^{III}SO_4^+}]$; 1.7×10^{-3} mol dm^{-3}) and MMPP (10^{-1}–10^{-3} mol dm^{-3}) at pH *ca.* 2 led to the detection of a complicated spectrum (which is evidently from a mixture of signals);† an example is shown in Fig. 1. Related experiments in which the peracid concentration was varied, with mixing time 40 ms, showed that optimum signal intensity was obtained with [MMPP] 0.04 mol dm^{-3}. It has previously been shown that in reactions of this type, in which short-lived radicals are produced in metal-peroxide systems studied by flow techniques, a pseudo steady-state is achieved in the cavity.[9] Further analysis shows that the maximum radical concentration is achieved at a *peroxide* concentration given by eqn. (7), in which k_{in} is the rate constant for the reaction in which radicals are first generated, and t is the time between

---

† Concentrations given in the text are those *after* mixing, unless stated otherwise.

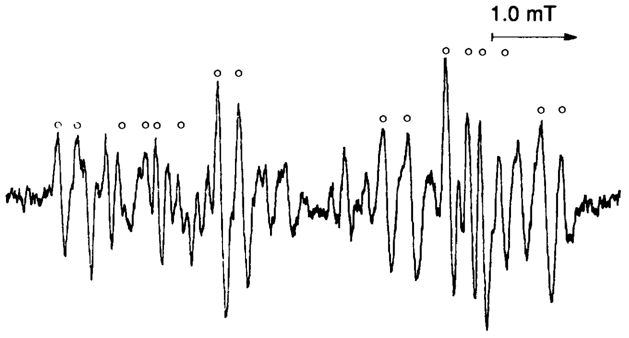


Fig. 1 EPR spectrum observed from the reaction between titanium(III) (as $TiSO_4^+$, 1.7×10^{-3} mol dm^{-3}) and magnesium monoperoxyphthalate, MMPP (4×10^{-2} mol dm^{-3}), at pH 2.0. (Continuous-flow: time between mixing and observation 40 ms).

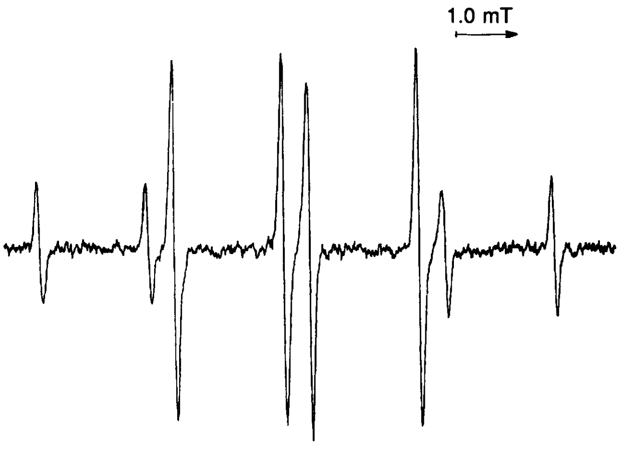


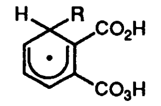
Fig. 2 EPR spectrum of $^{\bullet}CHMeCO_2H$ formed in the reaction between Ti^{III} and MMPP in the presence of propanoic acid at pH 2. $[TiSO_4^+]_0$ 1.7×10^{-3}, [MMPP] 4×10^{-2} mol dm^{-3}, $[EtCO_2H]_0$ 5% v/v.

mixing and observation. Analysis of our results in terms of eqn. (7) gives a value of *ca.* 6×10^2 dm^3 mol^{-1} s^{-1} for the reaction between Ti^{III} and MMPP under these conditions.

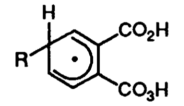
$$[\text{Peroxide}]_{\text{max}} = \frac{1}{k_{\text{in}}t} \qquad (7)$$

The radicals detected are believed to be of the cyclohexadienyl type, with a characteristic large doublet splitting of *ca.* 3.9 mT, as well as the readily observable small *meta*-proton splitting of *ca.* 0.25 mT: a series of dominant lines (marked ○) is clearly associated with a radical with EPR parameters *a*(1 H) 3.87, 1.20, 0.82, 0.25 mT (and *g* 2.0030). The possibilities include radicals **2** and **3**, in which first-formed hydroxyl, arenecarbonyloxyl **4** and aryl **5** radicals (from decarboxylation of the arenecarbonyloxyl precursor) have added rapidly to the parent peracid.

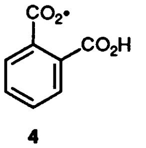
Although EPR data for peroxide-derived radicals **2** and **3** are not available, we anticipate that the parameters for these adducts would closely resemble those for corresponding adducts of phthalic acid (see *e.g.* refs. 10 and 11). On this basis, we conclude that the major adduct detected in our experiments (see Fig. 1) is of type **2** rather than **3** (*cf.* in particular, the *ortho-* and *para*-splittings of 0.82 and 1.20 mT, respectively) and, from the magnitude of the large proton splitting, that this is typical of an *aryl* adduct to a di-carboxyl-substituted benzene ring rather than an hydroxyl adduct.[10] Radical **2c** (and/or the analogue with the CO_2H and CO_3H groups interchanged) is therefore believed to be the dominant species formed under the conditions described in Fig. 1: this assertion is justified below.



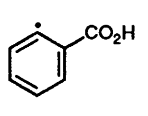
2a R = OH
2b R = OC(O)(2-$C_6H_4CO_2H$)
2c R = 2-$C_6H_4CO_2H$



3a R = OH
3b R = OC(O)(2-$C_6H_4CO_2H$)
3c R = 2-$C_6H_4CO_2H$

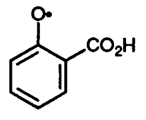


4



5

Related experiments were also carried out in an attempt to determine whether evidence could similarly be obtained for the homolytic decomposition of MMPP with Fe^{II} and Cu^{I}, though results were less clear cut than for Ti^{III}. For example, when solutions of Fe^{II}–EDTA and MMPP were flowed together at pH 7 (with concentrations after mixing of 8×10^{-4} and 1×10^{-2} mol dm^{-3}, respectively) the only EPR signal detected had the following parameters: *a*(1 H in each case), 0.998, 0.639, 0.184 and 0.178 mT, *g* 2.0045. This is identified as the phenoxyl radical **6** (*cf.* ref. 12), presumably formed *via* oxidation of the first-formed aryl radical **5**; possible mechanisms are discussed below. When Cu^{II} (at concentrations up to 2×10^{-4} mol dm^{-3}) was included in flow-system experiments at pH 2 employing Ti^{III} and H_2O_2 (to generate Cu^{I} in the cavity) the only signal detected was a singlet with *g* 2.0134, presumably associated with a peroxyl radical.



6

(b) *Reactions of Metal Ions with MMPP in the Presence of Substrates.*—A series of flow-system experiments was next performed with organic substrates present in excess of the MMPP concentration (up to a concentration of *ca.* 1.5 mol dm^{-3}) in an attempt to eliminate complications from the reaction of the first-formed radicals with the parent peracid. In order to distinguish, in particular, between the formation of hydroxyl radical and the arenecarbonyloxyl (and aryl) radicals [see reactions (3) and (4)] from the reaction between MMPP and Ti^{III}, propanoic acid was chosen as substrate. This substrate is known to have different reactivity towards electrophilic and nucleophilic radicals:[13] nucleophilic radicals (such as aryl radicals) are believed to react solely (or at least predominantly) at the α-position to give $^{\bullet}CHMeCO_2H$ [an attack governed both by the relative weakness of the α C–H bond and the presence of the adjacent carboxyl group (–M,–I) which helps stabilize incipient negative charge in the transition state], whereas the electrophilic hydroxyl radical gives mainly $^{\bullet}CH_2CH_2CO_2H$.

Reaction of a freshly-prepared solution of MMPP with Ti^{III} and propanoic acid at pH 2 led to the detection of, almost exclusively, $^{\bullet}CHMeCO_2H$ (see Fig. 2);* similar observations were made for the reaction of Ti^{III}–EDTA at pH *ca.* 8 and in experiments at very high concentration of propanoic acid (up to

---

* EPR parameters for radicals which have previously been reported (see *e.g.* ref. 10) are not repeated here.

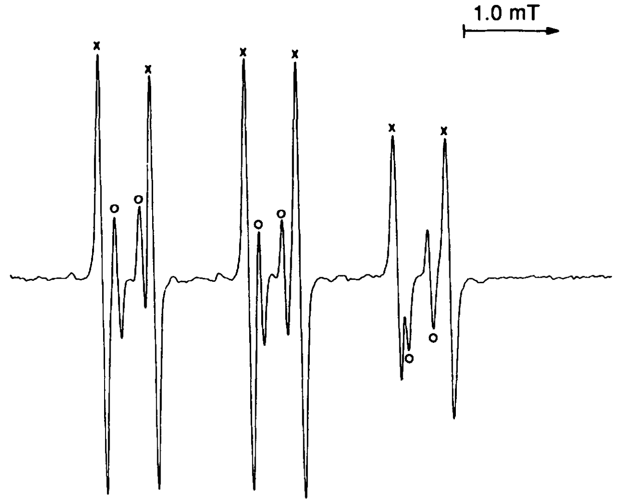
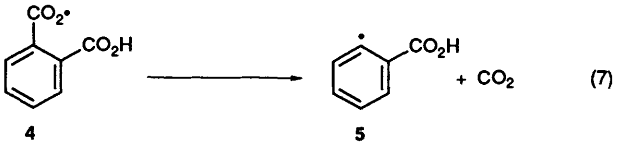
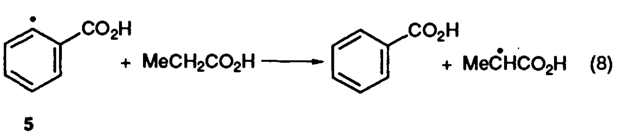


Fig. 3 EPR spectra of PBN spin-adducts formed by the reaction of MMPP (1.7×10^{-3} mol dm^{-3}), Ti^{III}-EDTA (1.7×10^{-3} mol dm^{3}) and PBN (3.4×10^{-2} mol dm^{-3}) at pH 6. Spectra recorded several minutes after mixing. ×, aryl adduct **9**; ○, hydroxyl adduct **10**.

10% v/v). The selectivity observed is consistent with the rapid production of the appropriate aryl radical **5**, presumably *via* very rapid decarboxylation of the initial carbonyloxyl radical **4**, as indicated in reactions (7) and (8).

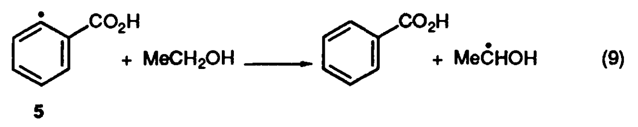
In contrast, different results were obtained when the peroxide-containing solution was allowed to stand for a period of *ca.* 10 min prior to flowing: the spectrum of $^{\bullet}CHMeCO_2H$ was then accompanied by that from $^{\bullet}CH_2CH_2CO_2H$ (the concentration of the latter grew to be *ca.* 40% of the former after standing for 2 h). This is believed to reflect the formation of $^{\bullet}OH$, *via* reaction of Ti^{III} with H_2O_2 produced by decomposition of MMPP.[14]

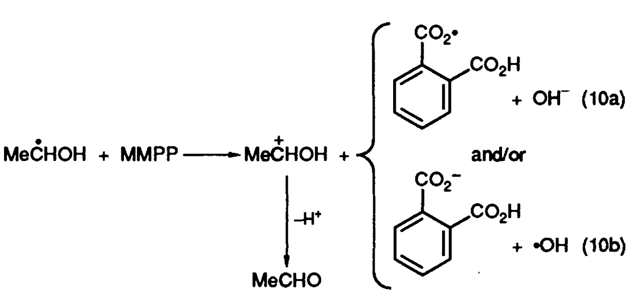




Reaction of Ti^{III} and MMPP at pH 2 in the presence of fumaric acid led to the detection of a signal [with a(α-H) 2.09, a(β-H) 1.47 mT, g 2.0032] assigned to the aryl-radical adduct, rather than the hydroxyl-radical adduct (*cf.* refs. 1, 2, 10), and reaction in the presence of 2-methylpropan-2-ol gave signals from $^{\bullet}CH_2CMe_2OH$ together with cyclohexadienyl adducts resulting from attack on the parent compound (as noted earlier): clearly in the latter case there is a relatively low rate of reaction between the aryl radical and the substrate.

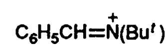
Experiments with ethanol led to the detection of weak signals from the α- and β-radicals $^{\bullet}CHMeOH$ and $^{\bullet}CH_2CH_2OH$, respectively, together with weak signals from cyclohexadienyl adducts. Now both $^{\bullet}OH$ and the aryl radical would be expected to lead to preferential abstraction of the α-hydrogen atom [reaction (9); see *e.g.* refs. 1 and 15, respectively]: our observation of a low steady-state concentration of the isomer $^{\bullet}CHMeOH$ is consistent with the rapid destruction of this radical *via* oxidation by the peroxide itself [reaction (10)], a type of reaction which has been demonstrated to occur for oxygen-conjugated carbon-centred radicals in the presence of, *e.g.* H_2O_2, $S_2O_8^{2-}$ and $HOOSO_3^{-}$.[1,2] A rate constant of *ca.* 10^6 dm^3 mol^{-1} s^{-1} may be estimated for reaction (10).





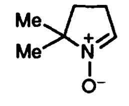
Related experiments were carried out with other metal ions but, again, less clear-cut results were obtained. For example, reaction of Fe^{II} and MMPP at pH 7 in the presence of either ethanol or propanoic acid (as above) led solely to the detection of the phenoxyl radical **6**, as noted earlier, and in the reaction of Ti^{III} and MMPP in the presence of propanoic acid with Cu^{II}, signals from a peroxyl species were again observed (though with EtOH a weak spectrum from $^{\bullet}CHMeOH$ was discerned). The implications of these observations are described below.

(c) *Spin Trapping Experiments.*—A series of experiments was carried out using the spin traps α-phenyl-*N*-*tert*-butylnitrone [PBN (**7**)] and 5,5-dimethylpyrroline *N*-oxide [DMPO (**8**)], in an attempt to gain further information on the metal-catalysed decomposition of the peroxide. Initially, the study involved transfer to the EPR cavity of mixed, deoxygenated solutions of the metal, peroxide and nitrone in an aqueous sample cell (see Experimental section). Subsequent experiments involved use of the continuous rapid-flow system employed, as described earlier, to mix solutions at the entrance to the sample cell held in the cavity (with time between mixing and observation typically 30 ms). Photolytic decomposition was also employed, to provide confirmation for the correct assignment of splittings to adducts.



$C_6H_5CH{=}\overset{+}{N}(Bu^t)O^-$

7



8

(i) *Conventional spin-trapping experiments.* Fig. 3 shows the EPR spectra of nitroxide spin-adducts obtained from an experiment with Ti^{III}-EDTA, MMPP and PBN at pH 6 (for concentrations employed, see Fig. 3): the spectrum was recorded in the period 2–10 min after mixing. The signals are assigned, as indicated in the caption and Table 1, to the aryl adduct **9** [a(N) 1.56, a(H) 0.56 mT, g 2.0060] and the hydroxyl adduct **10**, [a(N) 1.54, a(H) 0.26 mT, g 2.0060]; these assignments are based on accepted values for aryl adducts (see *e.g.* ref. 16) as well as reported values for the $^{\bullet}OH$ adduct (an identical signal was also obtained from Ti^{III}/H_2O_2 under these conditions) and the results of photolysis experiments described below. Extra weak signals which were detected under certain conditions [a(N) 1.51, a(H) 0.275 mT, g 2.0060] may be associated with the arenecarbonyloxyl-radical adduct **11** (*cf.* ref. 16). As can be seen from Fig. 3 the aryl-radical adduct is the dominant signal. The signals from the hydroxyl adduct were observed to be somewhat greater in intensity, compared with other signals, when [PBN]

Table 1 Hyperfine splittings in the EPR spectra of nitroxide spin-adducts from MMPP[a,b]

Spin Trap	Addend	Radical adduct	a(N)[c]	a(β-H)[c]
PBN	**5**	**9**	1.560	0.560
PBN	˙OH	**10**	1.540	0.260
DMPO	**4**	**15**	1.375	1.025
DMPO	**5**	**12**	1.575	2.400
DMPO	˙OH	**13**	1.475	1.475

[a] In water: pH 6–7. [b] g 2.0060, ±0.0001. [c] mT, ±0.005.

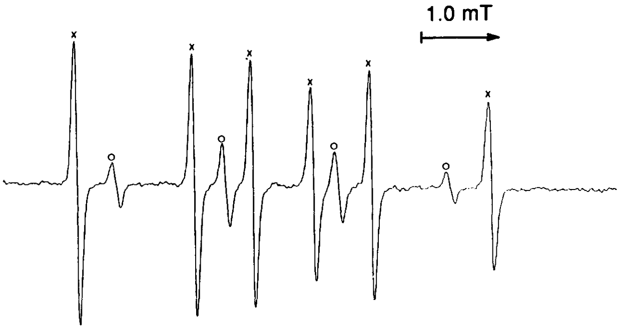
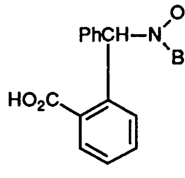
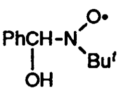


Fig. 4 EPR spectra of DMPO spin-adducts obtained in the reaction between Ti^{III} (1.7 × 10^{-3} mol dm^{-3}) and MMPP (1.7 × 10^{-3} mol dm^{-3}) in the presence of the spin trap (1.7 × 10^{-2} mol dm^{-3}) at pH 2. The spectrum was recorded several minutes after mixing. ×, aryl adduct **12**; O, hydroxyl adduct **13**.

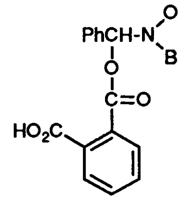
was increased; the ˙OH-adduct also appeared to increase as a function of time, as the other adducts decayed. Similar results were obtained at pH 2.



9

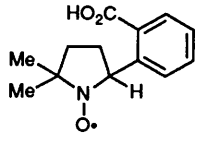


10

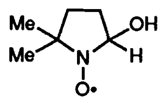


11

Similar experiments with DMPO and the Ti^{III}/MMPP system led to the observation of signals from both the aryl- and hydroxyl-adducts **12** and **13** (see Fig. 4 and Table 1). As with the PBN experiments, increase in the spin-trap concentration led to the detection of increased intensity from the ˙OH adduct.



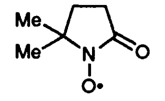
12



13

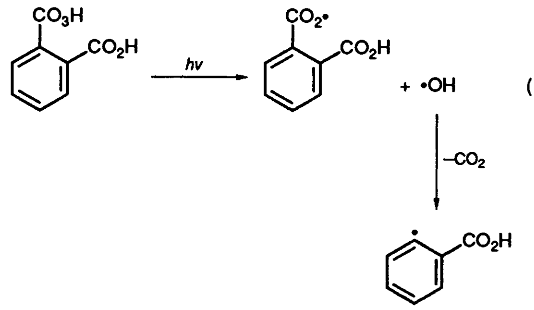
Experiments were also conducted with Cu^{I} (from Cu^{II} and Ti^{III} at low pH) and Fe^{II}. With Cu^{I}, typically at concentrations of *ca.* 5 × 10^{-4} mol dm^{-3}, use of both spin traps PBN and DMPO led to the detection of strong signals from the *hydroxyl* adducts, with traces of signals assigned to the aryl-radical adducts in each case.

With Fe^{II} (at initial concentrations of *ca.* 10^{-2} mol dm^{-3}) two unusual observations were made. In experiments with PBN a radical was detected with parameters [a(N) 1.46, a(1 H) 0.225 mT, g 2.0060] unlike any of those radicals detected previously. With DMPO the spectrum was dominated by a signal with a(N) 0.71, a(2 H) 0.40 mT, g 2.0060, assigned to the radical **14**, evidently formed by oxidation (proably by Fe^{III}) of the hydroxyl-radical adduct of the trap.[16]



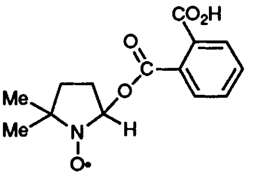
14

(ii) *Photolysis experiments. In situ* photolysis of an aqueous solution of MMPP (1.7 × 10^{-3} mol dm^{-3}) and PBN (1.7 × 10^{-2} mol dm^{-3}) at pH 7 with the unfiltered radiation from a 100 W mercury lamp led to the detection of signals from both the aryl- and hydroxyl-adducts **9** and **10**, respectively (in similar concentrations), which is as expected on the basis of the homolysis of the peroxide bond followed by rapid decarboxylation [reaction (11)]. At higher spin-trap concentrations, the relative concentration of the ˙OH adduct was enhanced, though in all experiments this adduct also decreased somewhat in intensity, with respect to the other adduct, as a function of time. Similar results were obtained at low pH (*ca.* 2).



(11)

With the spin trap DMPO all three possible adducts were detected. With relatively low concentrations of spin-trap (< *ca.* 1 × 10^{-3} mol dm^{-3}) the EPR spectrum showed signals characteristic of a mixture (*ca.* 50:50) of the ˙OH and aryl adducts (as for PBN). However, for higher concentrations of the trap (see *e.g.* Fig. 5) additional signals assigned to the arene-carboxyl adduct **15** were clearly seen (note the low β-hydrogen splitting and further proton splittings[16] typical of such species), with a consequent reduction in the observed intensity of the signal from the corresponding aryl radical. Evidently under these conditions the rate of addition of the former to the trap competes effectively with its fragmentation to the aryl radical.



15

(iii) *Spin-trapping with a rapid-mixing system.* A variety of experiments was conducted with aqueous solutions of the spin trap PBN, using the conventional rapid-mixing system. The spectrum recorded from the reaction between Ti^{III} and MMPP at pH 2 (after *ca.* 30–40 ms) is similar to that shown in Fig. 3 but is even more clearly dominated by the adduct of the aryl radical **9** (only a trace of the hydroxyl adduct **10** was detected). The addition of Cu^{II} (at a concentration of *ca.* 10^{-4} mol dm^{-3}), to enable the reaction between Cu^{I} and MMPP to be studied, brought about a dramatic change in the relative signal intensities: it is clear that hydroxyl radical formation is dominant under these conditions (see Fig. 6). These results,

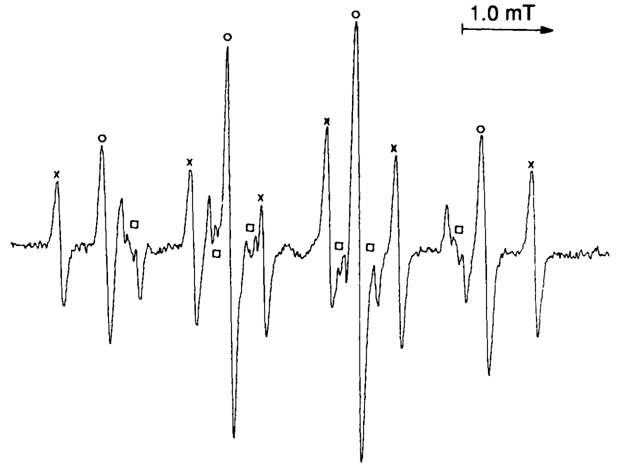
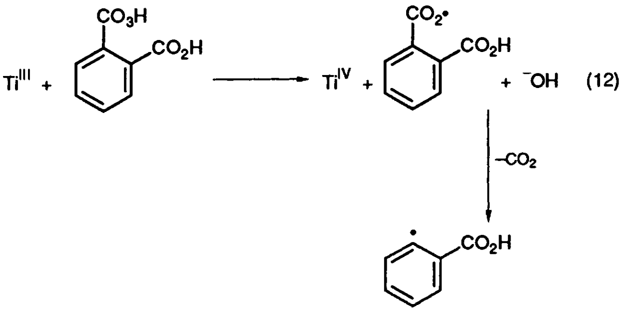
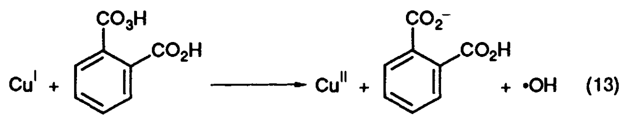


Fig. 5 EPR spectra of DMPO spin-adducts obtained during *in situ* photolysis of MMPP (1.7 × 10^{-3} dm^{-3}) in the presence of DMPO (1.7 × 10^{-2} mol dm^{-3}) at pH 7. ×, aryl radical adduct **12**; □, arenecarboxyloxyl adduct **15**; ○, hydroxyl adduct **13**

obtained a very short time after mixing, strongly suggest that the major routes for homolytic decomposition of MMPP by Ti^{III} and Cu^{I} are different (as for HOOSO$_3^-$), as outlined in reactions (12) and (13), respectively.*



(12)



(13)

In the corresponding flow-experiments with Fe^{II} at pH 7, EPR signals were dominated by those from the aryl-radical adduct and that noted above [with a(N) 1.46, a(1 H) 0.225 mT, g 2.0060]. Though our conclusions must remain tentative (in particular, oxidation reactions by Fe^{III} may be implicated), the reduction of the peracid by Fe^{II} appears to involve, in major part, the formation of carbonyloxyl and aryl radicals [*cf.* Ti^{III}, reaction (12)].

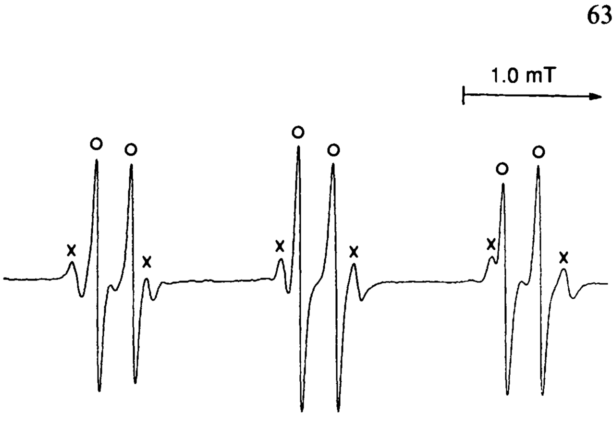


Fig. 6 EPR spectra of **9** and **10** obtained in a flow-system study of the reaction between Cu^{I} and MMPP at pH 2 in the presence of PBN (with [MMPP] 1 × 10^{-2} mol dm^{-3}, [PBN] 2.3 × 10^{-2} mol dm^{-3}, and [Ti^{III}] 1.7 × 10^{-3} mol dm^{-3}) with the addition of CuSO$_4$ to the PBN stream to give an overall concentration [Cu^{II}]$_0$ 10^{-4} mol dm^{-3}

Conclusions

The results of spin-trapping experiments, particularly those conducted under flow-system conditions, strongly suggest that the hydroxyl radical is generated predominantly from the reaction of Cu^{I} and peroxymonophthalic acid whereas with Ti^{III} and Fe^{II} the corresponding aryl radical is obtained, *via* the arenecarbonyloxyl radical.

The detection of the spin-adduct of the latter in photolytic experiments with DMPO but not with PBN may reflect, in part, the more rapid addition of ArCO$_2$• to the cyclic trap [though the nature of the spectra, dominated by the large a(β-H) of DMPO, allow oxy-radical adducts to the cyclic trap to be more easily distinguished]. Although detailed kinetic conclusions from our work are not possible our interpretation of the behaviour of the carbonyloxyl radical from MMPP is at least consistent with the results of kinetic studies[17–19] of the reactions of other arenecarbonyloxyl radicals. Thus it has been reported that the rate of decarboxylation of C$_6$H$_5$CO$_2$• is[18] 10^6 s^{-1} in CCl$_4$ (at 24 °C) and $\leqslant 2.5 \times 10^5$ s^{-1} in water,[4] and the rate constant for addition to PBN under similar conditions is[18] 3 × 10^7 dm^3 mol^{-1} s^{-1} (*cf.* also ref. 19). Given similar rate constants for reaction of ArCO$_2$• (Ar = 2-CO$_2$H–C$_6$H$_4$) then in the presence of DMPO at a concentration as given in Fig. 5 (1.7 × 10^{-2} mol dm^{-3}), the rate of spin-trapping of ArCO$_2$• should, as observed, be broadly comparable with the rate of fragmentation (to give Ar•, which is also trapped); this suggests that k_7 is *ca.* 5 × 10^5 s^{-1}.

The interpretation of the EPR spectra from flow experiments in terms of aryl-radical attack on added substrates, rather than reaction of the arenecarbonyloxyl radical, is again consistent with reported kinetic parameters for related reactions. For example, it has been shown[11] that the rate constants for attack of 4-MeOC$_6$H$_4$CO$_2$• on tetrahydrofuran and diethyl ether are only *ca.* 7 × 10^5 dm^3 mol^{-1} s^{-1}, and reaction with propanoic acid should be slower. Even at the substrate concentrations employed it is likely that decarboxylation (with $k > 10^5$ dm^3 mol^{-1} s^{-1}) would be favoured, with subsequent reactions of the aryl radical. Again, although rate constants for addition of ArCO$_2$• to benzene are in the range 2 × 10^6 to 2 × 10^8 dm^3 mol^{-1} s^{-1}, it seems likely that for the addition to the peracid itself (*cf.* Fig. 1) the carboxyl and percarboxyl groups will retard attack of the electrophilic radical, so that fragmentation occurs leading to addition of the appropriate aryl radical, as observed.

As with the parallel metal-catalysed decomposition of HOOSO$_3^-$, it appears then that reactions of Ti^{III} and Cu^{I} with MMPP [reactions (12 and 13)] are governed by different factors. We suggest that, for the former (and, probably, Fe^{II}) the reaction is inner-sphere in type, and dominated by the penetration into the coordination sphere of the metal of the nucleophilic hydroxyl group followed by formation of a metal-oxygen bond. In contrast the reaction of the less highly charged,

---

* The observation of significant concentrations of the hydroxyl adduct in experiments with Ti^{III} in the static spin-trapping experiments described earlier suggests that other pathways to this adduct are available: these might include hydrolysis of first-formed carbonyloxyl adducts, reaction of hydrogen peroxide formed by hydrolysis of MMPP, and, most likely, nucleophilic attack of HO$^-$ on the nitrone followed by oxidation of the anionic adduct. These observations also illustrate the care which should be exercised in the interpretation of spin-trapping results, and the importance of studying the reactions a short-time after mixing.

'softer' Cu^I ion may proceed *via* outer-sphere electron transfer to give the thermodynamically-preferred products $ArCO_2^-$ and $^{\bullet}OH$.

Our failure to detect significant concentrations of carbon-centred radicals (*e.g.* of the cyclohexadienyl type) in the flow-system studies involving iron and copper as catalysts for peroxide decomposition is perhaps not surprising in view of the ease with which Fe^{III} and Cu^{II} bring about free-radical oxidation and the rapidity with which Cu^I, especially, reduces alkyl radicals (see *e.g.* refs. 20 and 21). The unexpected detection of the phenoxy radical **6** during the Fe^{II}-catalysed decomposition of MMPP suggests that the corresponding phenol is formed, presumably *via* oxidation of the corresponding aryl-radical intermediate by Fe^{III}, and that subsequent oxidation (by *e.g.* Fe^{III} or radicals derived from the peroxide) is rapid: this may not reflect a major reaction pathway since the phenoxyl radical may well have a longer lifetime than the carbon-centred radicals involved in the reactions. We believe that direct one-electron transfer from the aryl radical by Fe^{III} (with subsequent hydration of an aryl cation) would be unlikely to be rapid enough to account for our observations but note that direct ligand-transfer of hydroxyl from iron to the aryl radical might be possible: thus it has been shown[22,23] that phenyl radicals react readily with iron(II) chloride *via* ligand transfer, and evidence has been obtained that, at least with Cu^{II} as oxidant, water transfer can compete effectively with halide transfer.[24]

Experimental

EPR spectra were recorded on Varian E-104 and Bruker ESP-300 spectrometers, each equipped with an X-band Klystron and 100 kHz modulation (see refs. 1, 2 and 4).

In the continuous-flow EPR experiments, a three-way mixer was employed which allowed simultaneous mixing of three reagent streams, *ca.* 30 ms before their passage through the cell in the EPR cavity. Flow was maintained with a Watson Marlow 502 peristaltic pump positioned on the inlet tubing. pH measurements were made using a Pye-Unicam PW9410 pH meter, with a glass electrode positioned in the effluent stream. All solutions were made up in deionised water and were deoxygenated before, and during, use by purging with oxygen-free nitrogen. The three streams typically contained the metal ion and chelate, where necessary, (1.6×10^{-3} mol dm^{-3}), MMPP (1.0×10^{-2} mol dm^{-3}) and, where applicable, the organic substrate (0.01–1.0 mol dm^{-3}), respectively. In experiments with copper, copper(II) sulphate, (typically 10^{-4} mol dm^{-3}) was added to the third stream. pH was adjusted by addition of either H_2SO_4 or ammonia (*d* 0.880; 20 mol dm^{-3}) to the metal-containing stream.

A typical spin-trapping (static) experiment involved the mixing of equal quantities of three solutions, as follows. Firstly, solutions of MMPP (1.6×10^{-3} mol dm^{-3}) and spin-trap (either PBN or DMPO, 1.6×10^{-2} mol dm^{-3}) were mixed, and the metal-ion solution (1.6×10^{-3} mol dm^{-3}) was then added. The resulting solution was then transferred to an aqueous-solution sample-cell and the EPR spectrum recorded (the field scan was normally begun *ca.* 2 min after mixing). Continuous-flow spin-trapping experiments involved use of the flow system as described earlier. In these experiments, the third stream contained the spin trap, PBN, at a concentration of 2.3×10^{-3} mol dm^{-3}.

Spin-trapping studies of radicals produced by the photolytic decomposition of MMPP were carried out *in situ* by irradiation of a solution containing MMPP (1.7×10^{-3} mol dm^{-3}) and either PBN or DMPO (3.4×10^{-2} mol dm^{-3}) with the unfiltered radiation of an Hanovia 100 W mercury arc lamp.

Titanium(III) sulphate (15%) was obtained from Fisons PLC. All other chemicals were obtained from Aldrich and were used without further purification, except for the spin traps DMPO and PBN. Aqueous solutions of the traps were treated with decolourising charcoal prior to use.

Acknowledgements

We thank Interox Chemicals Ltd. for support of the work (for a studentship to J. K. S.).

References

1 B. C. Gilbert and J. K. Stell, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1281.
2 B. C. Gilbert and J. K. Stell, *J. Chem. Soc., Faraday Trans.*, 1990, 3261.
3 W. Roebke, M. Renz and A. Henglein, *Int. J. Radiat. Phys. Chem.*, 1969, **1**, 39; P. Maruthamuthu and P. Neta, *J. Phys. Chem.*, 1977, **81**, 937.
4 B. C. Gilbert, R. G. G. Holmes, P. D. R. Marshall and R. O. C. Norman, *J. Chem. Res.*, 1977, (*S*) 172; (*M*) 1949.
5 V. A. Lunenok-Burmakina, G. G. Lerzina, V. B. Emel'yanov and A. G. Miroshnichenko, *Zh. Fiz. Khim.*, 1977, **51**, 2831. [*Russ. J. Phys. Chem.* (*Engl. Trans.*), 1977, **51**, 1650].
6 D. Lefort, J. Fossey, M. Gruselle, J-Y. Nedelec and J. Sorba, *Tetrahedron*, 1985, **41**, 4237.
7 E. Heckel, *J. Phys. Chem.*, 1976, **80**, 1274.
8 See *e.g.* R. A. Sheldon and J. K. Kochi, *Oxid. Combust. Rev.*, 1973, **5**, 135.
9 G. Czapski, *J. Phys. Chem.*, 1971, **75**, 2957; B. C. Gilbert, R. O. C. Norman and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2174.
10 *Magnetic Properties of Free Radicals*, New Series, Group II, vol. 9, part b, Landolt–Börnstein, Springer Verlag, Berlin, 1977.
11 K. Eiben and R. H. Schuler, *J. Chem. Phys.*, 1975, **62**, 3093.
12 P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.
13 See *e.g.* B. Ashworth, B. C. Gilbert and R. O. C. Norman, *J. Chem. Res.*, 1977, (*S*) 94; (*M*) 1101.
14 See *e.g.* P. Jones, M. L. Haggett, D. Holden, P. J. Robinson, J. O. Edwards, S. J. Bachofer and Y. T. Hayden, *J. Chem. Soc., Perkin Trans. 2*, 1989, 443.
15 E. G. Janzen, D. E. Nutter, Jr. and C. A. Evans, *J. Phys. Chem.*, 1975, **79**, 1983.
16 G. R. Buettner, *Free Rad. Biol. Med.*, 1987, **3**, 259.
17 J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2877.
18 J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2886.
19 V. E. Zubarev, V. N. Beleuskii and L. T. Bagaenko, *Uspekhii Khimii*, 1979, **48**, 1361; *Russ. Chem. Rev.* (*Engl. Trans.*), 1979, **48**, 729.
20 J. Grodkowski, P. Neta, C. J. Schlesener and J. K. Kochi, *J. Phys. Chem.*, 1985, **89**, 4373.
21 B. C. Gilbert, J. K. Stell and M. Jeff, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1867.
22 Y. Nakatani, *Tetrahedron Lett.*, 1970, 4455.
23 J. K. Kochi, *J. Am. Chem. Soc.*, 1957, **79**, 2942.
24 T. Cohen, A. G. Dietz, Jr. and J. R. Miser, *J. Org. Chem.*, 1977, **42**, 2053.

Paper 0/05450J
Received 4*th December* 1990
Accepted 16*th January* 1991