Electron Spin Resonance Studies of the Effect of Copper(II) and Copper(I) on the Generation and Reactions of Organic Radicals formed from the Fenton Reaction and the Ti^{III}–H_2O_2 and Ti^{III}–$S_2O_8{}^{2-}$ Redox Couples

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Kinetic analysis of the intensity of steady-state e.s.r. signals from Ti^{III} and organic radicals in a Ti^{III}–Cu^{II}–H_2O_2–RH reaction system suggests that one-electron transfer from Ti^{III} to Cu^{II} (k *ca.* 10^6 dm^3 mol^{-1} s^{-1}) is followed by extremely rapid reaction of Cu^I with organic radicals (produced by $^{\bullet}OH$). For some substrates, *e.g.* ethanol, a chain reaction occurs involving reduction of Cu^{II} (by $^{\bullet}CHMeOH$) and oxidation of Cu^I (by $^{\bullet}CH_2CH_2OH$). The decomposition of $S_2O_8{}^{2-}$ by Ti^{III} or Cu^{II} is dramatically accelerated when both metal ions are present: the rate constant for reaction between Cu^I and $S_2O_8{}^{2-}$ is estimated as 10^6 dm^3 mol^{-1} s^{-1}.

The use of e.s.r. spectroscopy in conjunction with a rapid-mixing system provides a direct and sensitive method for characterizing free radicals formed in the decomposition of peroxides (see *e.g.* ref. 1). It has been shown for example that the reaction between Ti^{III} and H_2O_2 leads to the rapid formation of $^{\bullet}OH$,[1] as does the Fenton reaction between Fe^{II} and H_2O_2 (both at pH 7 in the presence of a chelating reagent such as EDTA and at pH 2 in their absence).[2,3] Detailed kinetic analysis, involving the study of steady-state radical concentrations, yields rate constants for the initiation reactions as well as processes such as radical rearrangements and reactions involving metal ions (*e.g.* reduction of $^{\bullet}CH_2CHO$ by[4] Ti^{III} and oxidation of oxygen-conjugated radicals by[3] Fe^{III}).

It is generally accepted that Cu^{II} in aqueous solution is an effective oxidant for organic radicals (though somewhat less selective than Fe^{III}: see refs. 5—7) and rate constants have been reported for the very rapid reaction (k 10^9—10^{10} dm^3 mol^{-1} s^{-1}) between Cu^I and some β-hydroxyalkyl radicals;[6,8] in some reactions organo-copper intermediates are believed to be involved.[5,7,9] Our interest in these reactions and in the metal-catalysed decomposition of peroxides led us to employ e.s.r. spectroscopy to explore the effect of added copper ions in Fenton (and related) systems[10] and in the decomposition of the peroxydisulphate ion.[11]

Results and Discussion

E.s.r. and Spectrophotometric Results.—The experimental arrangement for e.s.r. studies typically involved the mixing of three aqueous solutions *ca.* 30 ms before the passage of the mixed solution through the cavity of the e.s.r. spectrometer. The solutions normally contained the transition metal ion (Ti^{III} or Fe^{II}, together with a chelating reagent in some cases), the peroxide (H_2O_2 or $S_2O_8{}^{2-}$), and the substrate, respectively; the pH was varied by the addition of sulphuric acid, hydrochloric acid, or ammonia. Copper ions (as Cu^{II}) were normally added to the substrate-containing stream, except where the effect of pre-mixing with the other transition metal was to be investigated.

(i) *The* Ti^{III}–H_2O_2 *reaction.* Initial experiments were conducted by the addition of relatively small amounts of copper sulphate (in the third stream) to flow-system investigations of the Ti^{III}–H_2O_2 reaction in the presence of organic substrates each of which gives only a single radical with $^{\bullet}OH$ [Bu^tOH, dimethyl sulphoxide, and methanol: reactions (1)—(4)].† Experiments normally involved the use of $TiCl_3$ at pH *ca.* 2 (adjusted to this value with HCl); similar results were obtained with $Ti_2(SO_4)_3$ at the same pH (adjusted with H_2SO_4), which rules out any contributions from reactions of $^{\bullet}OH$ with Cl^-.

$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + HO^{\bullet} + OH^- \quad (1)$$

$$^{\bullet}OH + Me_3COH \longrightarrow H_2O + {}^{\bullet}CH_2CMe_2OH \quad (2)$$

$$^{\bullet}OH + Me_2SO \longrightarrow Me^{\bullet} + MeSO_2H \quad (3)$$

$$^{\bullet}OH + MeOH \longrightarrow H_2O + {}^{\bullet}CH_2OH \quad (4)$$

In all cases the observed steady-state radical concentrations (compared *via* peak heights, since the line widths remained unchanged) decreased significantly in the presence of low concentrations of Cu^{II} (typically 10^{-4}—10^{-5} mol dm^{-3})‡ as shown in Figure 1. With ethanol as substrate, addition of Cu^{II} led to the rapid decrease in the intensity of the signal from the minor (β) radical $^{\bullet}CH_2CH_2OH$, that of the major radical $^{\bullet}CHMeOH$ being relatively insensitive to the presence of copper (see also Figure 1). The two analogous radicals from propan-2-ol ($^{\bullet}CH_2CHMeOH$ and $^{\bullet}CMe_2OH$) behaved similarly. A relatively small decrease, *ca.* 6% for $[Cu^{II}]_0$ 4×10^{-5} mol dm^{-3}, was observed for the radical $^{\bullet}CMe_2CH_2OH$ obtained by addition of $^{\bullet}OH$ to $CH_2{=}CMe_2$.

In comparable experiments with Bu^tOH in which Cu^{II} was added to the Ti^{III}-containing stream (to give, typically, $[Cu^{II}]_0$ *ca.* 1×10^{-4} mol dm^{-3}), a considerable decrease in initial signal intensity was observed, the extent of which depended upon the length of time elapsed between pre-mixing and the recording of the spectrum: after 1 minute, the signal intensity had been reduced to *ca.* 10% of its initial value (*i.e.* in the absence of copper). After several minutes pre-mixing, no signals were detectable (and deposition of a red-brown solid, presumably copper, was observed on the walls of the containing vessel).

The differences in behaviour of the various radicals studied in the initial experiments (*i.e.* without pre-mixing) suggest that our

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† E.s.r. parameters of the organic radicals have been previously reported[12] and will not be repeated here.

‡ Concentrations given are those after mixing.

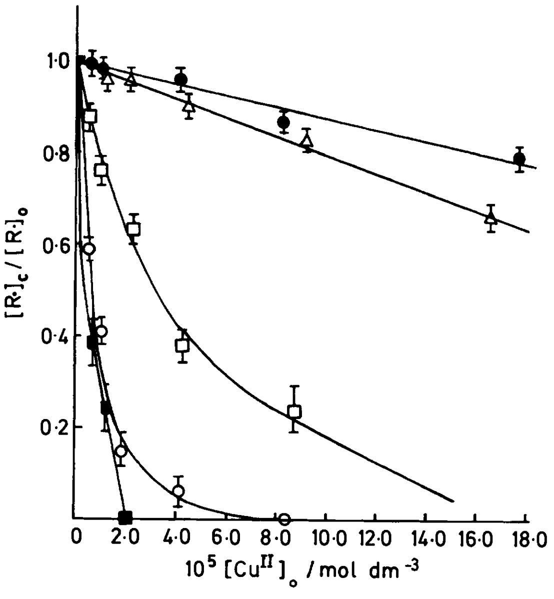

Figure 1. Variation of relative radical concentrations with the initial concentration of Cu^{II} in experiments with Ti^{III} and H_2O_2 ($[Ti^{III}]_0$ 1.7×10^{-3}, $[H_2O_2]_0$ 1.33×10^{-2} mol dm^{-3}, $[RH]_0$ 3% v/v, pH 2, mixing time 0.03 s): ○, $^{\bullet}Me$ (from dimethyl sulphoxide); □, $^{\bullet}CH_2CMe_2OH$ (from Bu^tOH); △, $^{\bullet}CH_2OH$ (from methanol); ●, $^{\bullet}CHMeOH$ (from ethanol); ■, $^{\bullet}CH_2CH_2OH$ (from ethanol). Subscripts c and o refer to radical concentrations detected in the presence and absence of Cu^{II}, respectively

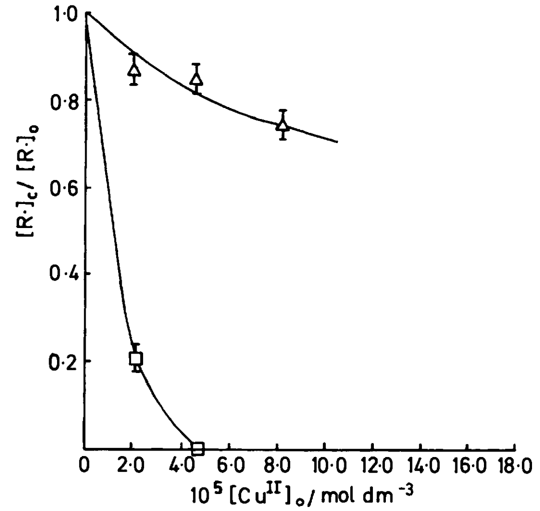

Figure 2. Variation of relative radical concentrations (□, $[^{\bullet}CH_2CMe_2OH]$, △, $[^{\bullet}CH_2OH]$) with the initial concentration of Cu^{II} in experiments with Ti^{III} and $[H_2O_2]$ in the presence of Bu^tOH and MeOH. $[Ti^{III}]_0$ 2×10^{-3}, $[H_2O_2]_0$ 1.33×10^{-2}, $[Bu^tOH]_0 = [MeOH]_0 = 0.2$ mol dm^{-3}, pH *ca.* 1.8. Subscripts c and o refer to radical concentrations detected in the presence and absence of Cu^{II}, respectively

observations do not reflect significant changes in the rate of generation of $^{\bullet}OH$, since addition of Cu^{II} would then be expected to have the same effect for all substrates investigated. Indeed, since the rates of reaction of both Cu^{II} and Cu^{I} with H_2O_2 are not believed to be higher than that between Ti^{III} and H_2O_2 under comparable conditions,[13] and since much lower concentrations of copper than titanium are employed, the rate of the initiation reaction (1) should not be significantly affected. Instead, it is believed that the decreases in radical concentration are due to alternative decay pathways involving the reaction of first-formed organic radicals with a copper species. If this is so then the observed order for the decrease of $[R^{\bullet}]$ with $[Cu^{II}]_0$ (*e.g.* $^{\bullet}CH_2CMe_2OH > {}^{\bullet}CH_2OH$ and $^{\bullet}CH_2CH_2OH > {}^{\bullet}CHMeOH$) and, in particular, the efficiency of removal of β-hydroxyalkyl radicals, suggests that the reactive species is Cu^{I} [formed in reaction (5)] rather than Cu^{II}. Thus it has been proposed[6] that reduction of $^{\bullet}CH_2CH_2OH$ by Cu^{I} in aqueous solution [reaction (6)] has a rate constant of 1.9×10^{10} dm^3 mol^{-1} s^{-1}, which is close to the diffusion-controlled limit; for the ethanol-derived radicals $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CHMeOH$ the rate constants for reaction with Cu^{II} are reported to be[6] 2.2×10^7 and[7] 9.2×10^7 dm^3 mol^{-1} s^{-1} respectively [see *e.g.* reaction (7)]. The slower rate of decrease with copper concentration in $[^{\bullet}CMe_2CH_2OH]$ than either $[^{\bullet}CH_2CMe_2OH]$ or $[^{\bullet}CH_2CH_2OH]$ may then reflect either or both the electron-donating effect of the two methyl groups at the radical centre or a steric effect which retards formation of a copper-bonded intermediate.[5,7]

$$Ti^{III} + Cu^{II} \longrightarrow Ti^{IV} + Cu^{I} \qquad (5)$$

$$Cu^{I} + {}^{\bullet}CH_2CH_2OH \longrightarrow Cu^{II} + CH_2{=}CH_2 + {}^{-}OH \qquad (6)$$

$$Cu^{II} + {}^{\bullet}CHMeOH \longrightarrow Cu^{I} + MeCHO + H^+ \qquad (7)$$

The occurrence of reaction (5) as the source of Cu^{I} is consistent with the redox potentials of the Ti^{IV}/Ti^{III} and Cu^{II}/Cu^{I} couples, 0.1 and 0.15 V respectively,[14] with our observations in the pre-mixing experiments (metallic copper presumably results from further reduction of Cu^{I} by Ti^{III} or *via* disproportionation of Cu^{I}), and with previous studies of this equilibrium (for which K has been reported[15] as 4.2×10^6 at 25 °C). It has been shown, for example, that copper(II) chloride catalyses the oxidation of titanium(III) chloride with molecular oxygen, evidently *via* reaction (5).[15] Further evidence for the occurrence of this process was sought *via* spectrophotometric and e.s.r. investigations (see below).

From the results presented in Figure 1 it can be seen that the concentration of $^{\bullet}CH_2CH_2OH$, from ethanol, decreases more rapidly on addition of Cu^{II} than does that of $^{\bullet}CH_2CMe_2OH$, from Bu^tOH, whereas it is claimed[6] that rate constants for reduction of $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CH_2CMe_2OH$ by Cu^{I} are similar. A possible rationale for this apparent anomaly is that the reaction of $^{\bullet}OH$ with ethanol leads to the production not only of the readily reducible β-hydroxyalkyl radical but also of the major radical $^{\bullet}CHMeOH$ whose ready oxidation by Cu^{II} would be expected (see above); this would bring about more rapid regeneration of Cu^{I} and hence more effective destruction of $^{\bullet}CH_2CH_2OH$.

To investigate this possibility further, variation of $[R^{\bullet}]$ with $[Cu^{II}]_0$ was investigated for mixed substrate systems where both an oxidizable and reducible radical are present; we employed a mixture of the radicals $^{\bullet}CH_2OH$ and $^{\bullet}CH_2CMe_2OH$ (from methanol and Bu^tOH, respectively) and also $^{\bullet}CH_2OH$ and $^{\bullet}Me$ (from methanol and dimethyl sulphoxide, respectively). The results for the former system are shown in Figure 2. It can be seen that, for example for the MeOH–Bu^tOH system, the concentration of $^{\bullet}CH_2CMe_2OH$ decreases much more rapidly with added Cu^{II} in the presence of $^{\bullet}CH_2OH$ than in its absence (contrast Figure 1), and that the decrease in $[^{\bullet}CH_2OH]$ is also more marked, as would be predicted. The MeOH–Me_2SO system behaved similarly. We conclude that for the former system, for example, the interconversion of Cu^{II} and Cu^{I} is brought about not only by Ti^{III} but also by $^{\bullet}CH_2CMe_2OH$ and $^{\bullet}CH_2OH$; we propose a scheme for the generation and destruction of radicals including reactions (1), (2), and (4) as well as (5) and (8)—(12).

Since $^{\bullet}Me$ is apparently removed more rapidly than

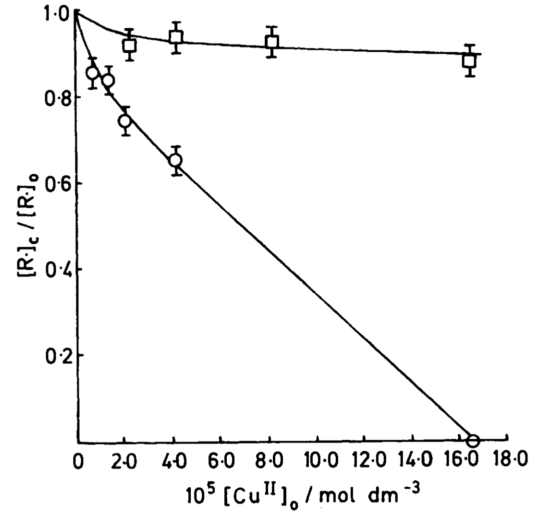

Figure 3. Variation in relative radical concentrations (○, [$^\bullet$Me], □, [$^\bullet CH_2CMe_2OH$]) with the initial concentration of Cu^{II} in experiments with Fe^{II}–EDTA and H_2O_2 in the presence of dimethyl sulphoxide or Bu^{t}OH respectively. ($[Fe^{II}]_o$ = $[EDTA]_o$ 8.3×10^{-4}, $[H_2O_2]$ 3.33×10^{-3} mol dm^{-3}, $[RH]_o$ 3% v/v solution; pH *ca.* 7). Subscripts c and o refer to radical concentrations detected in the presence and absence of Cu^{II}, respectively

$^\bullet CH_2CMe_2OH$ in the single-substrate systems (see Figure 1), despite the likelihood that its reduction by Cu^I cannot be significantly faster (it cannot exceed the diffusion-controlled limit), it seems likely that methyl is itself oxidized rapidly by Cu^{II} (see later).

$$Cu^I + {}^\bullet CH_2CMe_2OH \longrightarrow Cu^{II} + CH_2{=}CMe_2 + OH^- \quad (8)$$

$$Cu^{II} + {}^\bullet CH_2OH \longrightarrow Cu^I + CH_2{=}O + H^+ \quad (9)$$

$$\left.\begin{array}{ll} {}^\bullet CH_2OH + {}^\bullet CH_2OH \longrightarrow & (10) \\ {}^\bullet CH_2OH + {}^\bullet CH_2CMe_2OH \longrightarrow & (11) \\ {}^\bullet CH_2CMe_2OH + {}^\bullet CH_2CMe_2OH \longrightarrow & (12) \end{array}\right\} \text{non-radical products}$$

The effect of the presence of the complexing agent EDTA has been explored *via* experiments (*e.g.* with Bu^{t}OH as substrate) in which either Ti^{III} or both Ti^{III} and Cu^{II} were complexed prior to mixing in the e.s.r. cavity.

When both metal ions were complexed to EDTA there was found to be only a very slight reduction in [$^\bullet CH_2CMe_2OH$] as $[Cu^{II}]_o$ was increased both at pH 2 and pH 9 (with *ca.* 10% decrease for $[Cu^{II}]_o$ 4×10^{-4} mol dm^{-3}). This is a marked contrast with results for the uncomplexed ions and suggests either that the generation of Cu^I [reaction (5)] is significantly retarded (see next section) or that Cu^I–EDTA is a less effective radical reductant. Experiments with Ti^{III}–EDTA and initially uncomplexed copper showed intermediate but variable behaviour; results were independent of pH but dependent critically upon [EDTA]. With $[EDTA] \leqslant [Ti^{III}]_o$ behaviour as with uncomplexed titanium was observed ([R$^\bullet$] decreasing rapidly with $[Cu^{II}]_o$), but with even a slight excess of EDTA over Ti^{III}, this effect was dramatically and progressively eliminated; we conclude that uncomplexed EDTA rapidly binds [Cu^{II}] and that the resulting Cu^{II}–EDTA complex is relatively resistant to reduction.

(ii) *The* Ti^{III}–Cu^{II} *reaction.* In order to provide further support for the occurrence of a rapid reaction between Cu^{II} and Ti^{III}, spectrophotometric changes following mixing were examined. Acidic aqueous solutions of $TiCl_3$ have $\lambda_{max.}$ 500 nm (with ε 0.39 m^2 mol^{-1}), and similar solutions of $CuSO_4$ show an absorption from Cu^{II} with $\lambda_{max.}$ 800 nm (ε 1.13 m^2 mol^{-1}), with no effective absorption at 800 and 500 nm, respectively. Experiments were conducted by measuring the absorbance of a mixed solution of Cu^{II} and Ti^{III} (initial concentrations 2.25×10^{-3} mol dm^{-3} and 2.11×10^{-2} mol dm^{-3}, respectively), as soon after mixing as possible. The disappearance of the absorbance at 800 nm *ca.* 50 s after mixing indicated that Cu^{II} had been completely removed; measurements at 500 nm indicated a decrease in the Ti^{III} concentration of 3×10^{-3} mol dm^{-3} in a similar period. This suggests that the reaction is effectively complete in *ca.* 1 minute, as indicated by the corresponding e.s.r. results.

An attempt to determine the rate constant for the forward reaction by a corresponding stop-flow technique was thwarted by the need for relatively concentrated solutions to be employed and by the build up of a solid deposit (of copper) on the walls of the cell. Two alternative approaches were thus employed.

In the first, we used a continuous-flow system to monitor the effect of increasing [Cu^{II}] on the concentration of the Ti^{III}–EDTA complex at pH *ca.* 9, determined *via* its e.s.r. signal (*g* 1.954) [the corresponding signals from $Ti(H_2O)_6^{3+}$ and $Ti(SO_4)^+$ at low pH are broadened beyond detection].

A series of experiments was conducted in which solutions of Ti^{III}–EDTA and Cu^{II} (both with and without EDTA) were mixed and flowed through the e.s.r. cavity, [Ti^{III}–EDTA] being monitored as a function of flow rate (and hence the time between mixing and observation, calibrated by study of the Fe^{3+}–thiocyanate reaction[16]). The reaction between Ti^{III}–EDTA and Cu^{II}–EDTA was found to be much slower than that involving uncomplexed copper (as suggested above). For example, in experiments with $[Cu^{II}]_o \gg [Ti^{III}\text{–EDTA}]$ (*e.g.* 1.7×10^{-3} and 1.7×10^{-4} mol dm^{-3}, respectively), scarcely any decrease in [Ti^{III}–EDTA] was observed *ca.* 0.04 s after mixing with Cu^{II}–EDTA, indicating that the rate constant of reaction (13) has an upper limit of 4×10^2 dm^3 mol^{-1} s^{-1}; on the other hand, under these conditions, mixing of Cu^{II} (uncomplexed) and Ti^{III}–EDTA led to complete removal of the signal from the latter on the same time scale. Further experiments were carried out using a series of equimolar solutions of Ti^{III}–EDTA and Cu^{II}_{aq} (typically *ca.* 2.5×10^{-4} mol dm^{-3}) and in which the decrease in [Ti^{III}–EDTA] was monitored between 0.02—0.05 s after mixing: second-order analysis of the results led to measurement of the rate constant for reaction (14) as $1 \pm 0.5 \times 10^6$ dm^3 mol^{-1} s^{-1} (at 20 °C).

$$Ti^{III}\text{–EDTA} + Cu^{II}\text{–EDTA} \longrightarrow Ti^{IV}\text{–EDTA} + Cu^{I}\text{–EDTA} \quad (13)$$

$$Ti^{III}\text{–EDTA} + Cu^{II}_{aq} \longrightarrow Ti^{IV}\text{–EDTA} + Cu^{I}_{aq} \quad (14)$$

A second approach to the estimation of the rate constant for the reduction of Cu^{II} by Ti^{III} (in the absence of added chelate) involved use of a kinetic simulation program.[17] Steady-state calculations of [$^\bullet CH_2CMe_2OH$] (as formed from Bu^{t}OH in the Ti^{III}–H_2O_2 system) were performed in an attempt to match experimental observations in both the absence of copper [allowing for the occurrence of reactions, (1), (2), and (12)] and in the presence of added Cu^{II} [when the additional occurrence of reactions (5), (8), and (15) must be incorporated]. Accepted values were chosen for the rate constants for reactions (1),[3] (2),[18] and (12)[19] (2×10^3 dm^3 mol^{-1} s^{-1}, 1.9×10^9 dm^3 mol^{-1} s^{-1}, and 2×10^9 dm^3 mol^{-1} s^{-1}, respectively) which in the absence of copper gives [$^\bullet CH_2CMe_2OH$] 3×10^{-6} mol dm^{-3} for a 30 ms mixing time (as observed). Values for the oxidation and reduction of $^\bullet CH_2CMe_2OH$ by Cu^{II} and Cu^I respectively [reactions (15) and (8), respectively] were taken

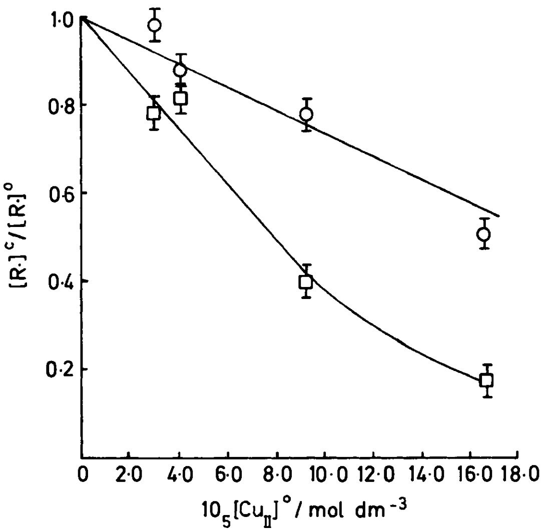

Figure 4. Variation in relative radical concentrations of $^{\cdot}CHMeOH$ (○) and $^{\cdot}CH_2CH_2OH$ (□) with $[Cu^{II}]$ in the Fenton system (for conditions, see Figure 3).

as[7] 3.2×10^6 and[6] 2.6×10^{10} $dm^3\ mol^{-1}\ s^{-1}$, as has been previously claimed.

$$^{\cdot}CH_2CMe_2OH + Cu^{II} \xrightarrow{H_2O} HOCH_2CMe_2OH + H^+ + Cu^I \quad (15)$$

Optimum agreement between experimental behaviour {as judged by the initial slope of the variation of $[^{\cdot}CH_2CMe_2OH]$ with $[Cu^{II}]_0$ (see Figure 1)} and simulation on this basis was obtained for a value of k_5 of *ca.* 1×10^6 $dm^3\ mol^{-1}\ s^{-1}$. Using this value, simulation of the dependence of $[^{\cdot}CH_2OH]$ on $[Cu^{II}]_0$ with the inclusion of the reported[6] rate of oxidation as 1.6×10^8 $dm^3\ mol^{-1}\ s^{-1}$, yields a rate constant for the overall removal of this radical by reaction with Cu^I as 1.5×10^7 $dm^3\ mol^{-1}\ s^{-1}$ (pulse radiolysis results suggest that an intermediate is first formed). The particularly rapid removal of $^{\cdot}Me$ (Figure 1) could only be effectively simulated if rapid oxidation of that radical was also incorporated; with a diffusion-controlled rate of reduction (k *ca.* 2×10^{10} $dm^3\ mol^{-1}\ s^{-1}$) a rate constant of oxidation of $Me^{\cdot}$ by Cu^{II} of 1×10^8 $dm^3\ mol^{-1}\ s^{-1}$ was required (contrast a value of 7.4×10^5 $dm^3\ mol^{-1}\ s^{-1}$ previously reported[20]).

Further support for the overall mechanisms and the postulated rate constant for production of Cu^I was obtained by satisfactory simulations of observed behaviour of systems with mixtures of radicals, both from $MeOH/Bu^tOH$ and from EtOH. For the former system rate constants as noted above were used for oxidation and reduction, by Cu^{II} and Cu^I respectively of both $^{\cdot}CH_2OH$ and $^{\cdot}CH_2CMe_2OH$; for the latter system, we incorporated literature values for the oxidation by Cu^{II} of $^{\cdot}CH_2CH_2OH$ and $^{\cdot}CHMeOH$ (2.2×10^7 and 9.2×10^7 $dm^3\ mol^{-1}\ s^{-1}$, respectively[6,7]) and the Cu^I reduction of $^{\cdot}CH_2CH_2OH$[6] (1.9×10^{10} $dm^3\ mol^{-1}\ s^{-1}$), and obtained optimum matching using an overall rate of removal of $^{\cdot}CHMeOH$ by Cu^I of 7×10^6 $dm^3\ mol^{-1}\ s^{-1}$.

(iii) *The* Fe^{II}/Cu^{II}–H_2O_2 *system.* Experiments were carried out in an analogous manner to those described for the Ti^{III}–H_2O_2 system, except that an Fe^{II}–EDTA solution replaced $TiCl_3$ and the pH was adjusted to 7 rather than 2; these conditions were chosen since the initiation rate of the Fenton system [to give $^{\cdot}OH$, reaction (16)] is then high enough (*ca.* 10^4 $dm^3\ mol^{-1}\ s^{-1}$) to ensure that for most substrates a high steady-state concentration of derived radicals can be generated [though, as noted previously,[2,3] the relatively low concentrations of readily oxidizable radicals detected reflects their ease of oxidation by Fe^{III}: see *e.g.* reaction (17)]

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + HO^{\cdot} + OH^- \quad (16)$$

$$^{\cdot}CHMeOH + Fe^{III} \longrightarrow Fe^{II} + MeCHO + H^+ \quad (17)$$

Addition of Cu^{II} to experiments with the Fenton system and Bu^tOH led, in contrast to the Ti^{III} system, to only a very small decrease in $^{\cdot}CH_2CMe_2OH$ (up to values of $[Cu^{II}]_0$ *ca.* 2×10^{-4} mol dm^{-3}, see Figure 3). Similar results were obtained with $^{\cdot}CH_2CHMeOH$ (the dominant radical from propan-2-ol in the presence of iron) and $^{\cdot}Me$: however, the decrease in the concentration of the latter is more significant than the other radicals, but considerably less marked than in the presence of Ti^{III}. The concentration of the radical $^{\cdot}CH_2OH$ from methanol was scarcely affected by the addition of Cu^{II} (though it must be recalled that the steady-state concentration of this radical is low even in the absence of Cu^{II}, since Fe^{III} is an effective oxidant).

These results suggest that Cu^I is not produced in significant amounts in the Fe^{II}/Cu^{II}–H_2O_2 system; the smaller decreases in $[R^{\cdot}]$ presumably then reflect either the radicals' oxidation by Cu^{II} or the somewhat less effective reduction when only traces of Cu^I are generated.

With ethanol as substrate both $^{\cdot}CH_2CH_2OH$ and $^{\cdot}CHMeOH$ decrease somewhat faster than $[^{\cdot}CH_2CMe_2OH]$ or $[^{\cdot}CH_2OH]$ (in experiments with separate substrates). These observations can be understood in terms of the presence together of an oxidizable and a reducible radical; then reaction (7), whereby $^{\cdot}CHMeOH$ is readily oxidized by Cu^{II}, generates Cu^I which is recycled *via* ready reaction with the reducible radical $^{\cdot}CH_2CH_2OH$ [reaction (6)]. To confirm this interpretation we observed that when a mixture of methanol and t-butyl alcohol was oxidized by $^{\cdot}OH$ in the Fenton system, both radical concentrations decreased much more rapidly than when generated independently (see Figure 4).

The much faster decrease in $[Me^{\cdot}]$ than for other radicals in the $Fe^{II}/Cu^{II}/H_2O_2$ system (see Figure 3) is entirely consistent with the claim made earlier that this radical is rapidly oxidized by Cu^{II}; a value of the rate constant of 5×10^7 $dm^3\ mol^{-1}\ s^{-1}$ leads to satisfactory simulation. This is encouragingly close to that suggested by analysis of the more complex $Ti^{III}/Cu^{II}/H_2O_2$ system.

That Fe^{II}–EDTA, unlike Ti^{III}, does not reduce Cu^{II} in the $Fe^{II}/Cu^{II}/H_2O_2$ system appears somewhat unexpected in view of the standard electrode potentials of the Fe^{III}/Fe^{II}–EDTA and Cu^{II}/Cu^I couples (0.12 and 0.15 V, respectively). This appears to be the result of rapid complexation of Cu^{II} with EDTA (presumably thereby stabilizing the higher oxidation state); evidence that this occurs derives from the observation of strong u.v. absorption at *ca.* 720 nm (from Cu^{II}–EDTA) as well as ~850 nm (Fe^{II}–EDTA) when solutions of Fe^{II}–EDTA and Cu^{II} are mixed.

(iv) *The reaction between* Cu^I *and other peroxides and related compounds.* The generation of Cu^I in aqueous solution from the reaction between Cu^{II} and Ti^{III} suggests, in principle at least, a method of the study of the one-electron reduction by Cu^I of other peroxides. We here present the results of a study of the reaction of Cu^I with Bu^tOOH, NH_2OH, and $S_2O_8^{2-}$, all of which react readily with Ti^{III} (to give $Bu^tO^{\cdot}$, $^{+\cdot}NH_3$, and $SO_4^{-\cdot}$, respectively).

In experiments with $[Ti^{III}]_0$ 1.7×10^{-3} mol dm^{-3} and $[Bu^tOOH]_0$ 1.3×10^{-2} mol dm^{-3} at pH *ca.* 2, signals from $^{\cdot}Me$ are detected; this is believed to result from one-electron reduction of the peroxide [reaction (18)] followed by rapid fragmentation [reaction (19)].[1] Addition of Cu^{II} to the flow system (as above) simply led to a steady decrease in $[^{\cdot}Me]$ (with

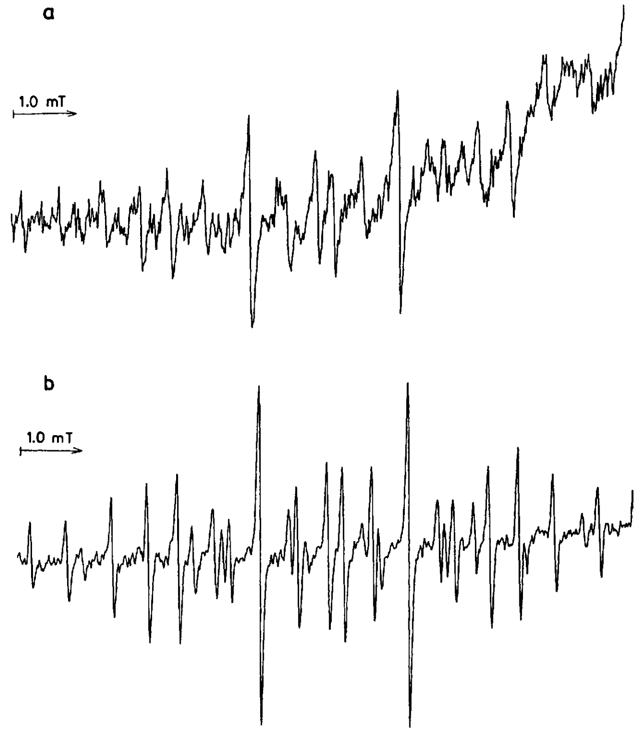

Figure 5. E.s.r. spectrum of $^{\bullet}CMe(CH_2OH)CH_2OSO_3^-$ generated from the reaction between $SO_4^{-\bullet}$ and 2-methylprop-2-en-1-ol: (a) Ti^{III}–EDTA–$S_2O_8^{2-}$, pH 7.5 (with $[Ti^{III}] = [EDTA] = 1.7 \times 10^{-3}$ mol dm^{-3}, $[S_2O_8^{2-}]$ 8.3×10^{-3} mol dm^{-3}); (b) As (a), but with inclusion of Cu^{II} (2×10^{-4} mol dm^{-3})

$[Cu^{II}]_0$ 10^{-4} mol dm^{-3} the signal was totally removed), exactly as in the Ti^{III}/H_2O_2/DMSO reaction (see above). This observation strongly suggests that reaction of Cu^I with Bu^tOOH is relatively slow.

$$Ti^{III} + Bu^tOOH \longrightarrow Ti^{IV} + Bu^tO^{\bullet} + OH^- \quad (18)$$

$$Bu^tO^{\bullet} \longrightarrow Me^{\bullet} + Me_2CO \quad (19)$$

Similar experiments were also carried out with Ti^{III} (2.7×10^{-3} mol dm^{-3}) and NH_2OH (0.15 mol dm^{-3}), with ethanol (0.6 mol dm^{-3}) as substrate at pH 2 [one-electron-transfer at low pH gives $^{+\bullet}NH_3$, whose reaction with ethanol leads solely to the detection of the α-radical, $^{\bullet}CHMeOH$,[21] reactions (20) and (21)]. Addition of Cu^{II} resulted in a relatively small decrease in the observed radical concentration (*e.g.* of *ca.* 25% for $[Cu^{II}]_0$ 1.7×10^{-4} mol dm^{-3}). The extent of this change (which presumably reflects the reaction of the radical with Cu^{II} or Cu^I: *cf.* Figure 1) suggests that there is no significant reaction between hydroxylamine and Cu^I.

$$Ti^{III} + NH_2OH \xrightarrow{H^+} Ti^{IV} + {}^{+\bullet}NH_3 + OH^- \quad (20)$$

$${}^{+\bullet}NH_3 + EtOH \longrightarrow NH_3 + H^+ + {}^{\bullet}CHMeOH \quad (21)$$

Two methods have previously been employed for the generation of $SO_4^{-\bullet}$ for e.s.r. studies, namely the use of a flow system[22,23] employing Ti^{III}–EDTA and $S_2O_8^{2-}$ (usually at pH *ca.* 7) and photolysis[23] of a slowly flowing solution of $S_2O_8^{2-}$ (in some cases with propanone added as photosensitizer). For the former system the spectra are generally of low intensity (contrast the Ti^{III}–H_2O_2 system, for example), which is believed to reflect, at least in part, the relatively low rate of reaction (22) (*ca.* 200 dm^3 mol^{-1} s^{-1}:[22] *cf. k ca.* 2×10^3 dm^3 mol^{-1} s^{-1} for Ti^{III}–H_2O_2 and *ca.* 10^4 dm^3 mol^{-1} s^{-1} for Fe^{II}–EDTA–H_2O_2).

$$Ti^{III} + S_2O_8^{2-} \longrightarrow Ti^{IV} + SO_4^{-\bullet} + SO_4^{2-} \quad (22)$$

In contrast to the results described for Bu^tOOH and NH_2OH, e.s.r. signals detected from the Ti^{III}–$S_2O_8^{2-}$ couple under certain circumstances were considerably enhanced on addition of small amounts of Cu^{II}. Most of these experiments involved alkenes (whose rapid reactions with $SO_4^{-\bullet}$ have previously been described in detail[24]).

For example, reaction of Ti^{III}–EDTA [5.3×10^{-3} mol dm^{-3}, from titanium(III) chloride or sulphate] and $S_2O_8^{2-}$ (8.3×10^{-3} mol dm^{-3}) with 2-methylprop-2-en-1-ol at pH 7 gave a weak spectrum of the adduct $^{\bullet}CMe(CH_2OH)CH_2OSO_3^-$, together with a signal from Ti^{III}–EDTA (*g* 1.954) consistent with the relatively slow formation of $SO_4^{-\bullet}$ and subsequent addition to the least substituted terminus of the double bond. Addition of uncomplexed Cu^{II} (with $[Cu^{II}]_0$ 1.7×10^{-4} mol dm^{-3}) resulted in a dramatic increase in the observed concentration of the adduct, together with a considerable reduction in the concentration of the Ti^{III}-complex (see Figure 5). The observations are consistent with a significantly increased rate of production of $SO_4^{-\bullet}$ *via* reaction (14) followed by reaction (23). No enhancement was observed when Cu^{II} was pre-complexed with EDTA [as would be expected, since we have shown that reaction (13) is slow], but enhancement was observed at low pH in the absence of EDTA, as predicted from the kinetic results described above. No enhancement was observed for the Fe^{II}–EDTA–$S_2O_8^{2-}$ system on the addition of copper(II), which is as expected if Cu^I is not produced in this system.

$$Cu^I + S_2O_8^{2-} \longrightarrow Cu^{II} + SO_4^{-\bullet} + SO_4^{2-} \quad (23)$$

A similar degree of enhancement to that noted above was observed in experiments between pH 3 and 9 with Ti^{III}–EDTA, $S_2O_8^{2-}$ and Cu^{II} with a variety of substrates including methanol (to give $^{\bullet}CH_2OH$), $CH_2{=}CHOEt$ (to give both hydroxy adducts, evidently *via* hydration of the radical cation[25]), $PhCH_2CH_2CO_2^-$ (to give[26] $PhCH_2CH_2^{\bullet}$), $S(CH_2CH_2CO_2H)_2$ [to give $^{\bullet}CH(CH_2CO_2H)SCH_2CH_2CO_2H$], $CH_3CH_2CO_2^-$ (to give[27] $^{\bullet}Et$, *via* electron-transfer and decarboxylation, and $^{\bullet}CHMeCO_2^-$), as well as $CH_2{=}CMe_2$ (to give[24] $^{\bullet}CMe_2CH_2OSO_3^-$ and weaker signals from $^{\bullet}CMe_2CH_2OH$) and Bu^tOH (to give $^{\bullet}CH_2CMe_2OH$ as well as $^{\bullet}CMe_2CH_2OSO_3^-$ and traces of the signal from $^{\bullet}CMe_2CH_2OH$, see later). In all cases the most intense signals were obtained for $[Cu^{II}]_0$ *ca.* 10^{-4} mol dm^{-3}; for concentrations of copper greater than this it seems likely that reaction (23) is largely complete between mixing and observation (though an additional factor is presumably the facility with which Cu^I, especially, removes organic radicals).

The spectra detected from the variety of substrates described above are entirely consistent with the straightforward generation of $SO_4^{-\bullet}$ [*via* reaction (23)], with two notable exceptions. We consider first the reaction of Bu^tOH to give $^{\bullet}CMe_2CH_2OSO_3^-$ as the major radical in addition to $^{\bullet}CH_2CMe_2OH$. This secondary radical is believed to be formed (see Scheme) *via* addition of $SO_4^{-\bullet}$ to the alkene $CH_2{=}CMe_2$ generated *in situ via* reactions (24) and (8) (*cf.* refs. 5 and 6). In accord with this, in experiments in which slower flow rates were employed [to allow reaction (8) to proceed to a greater extent], a significant increase was observed in the concentration in this adduct.

To test the validity of this interpretation, *via* kinetic simulation of the observed behaviour, we determined the rate constant of reaction (23). This was achieved *via* experiments at pH 2 with Ti^{III}–Cu^{II} and $S_2O_8^{2-}$ in the presence of methanol to give $^{\bullet}CH_2OH$, a radical with a relatively low rate of reaction with Cu^I. The concentration of $^{\bullet}CH_2OH$ was monitored as a

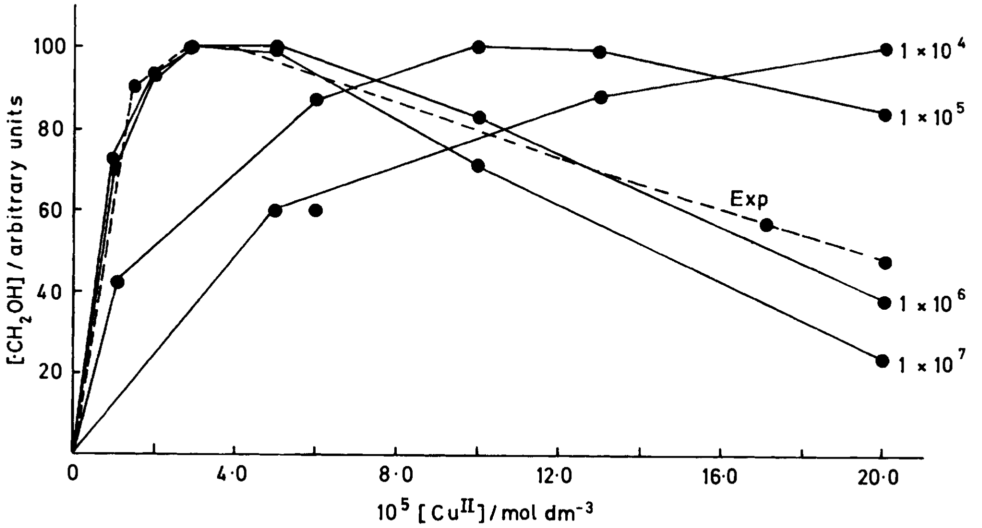

Figure 6. Variation in the concentration of $\cdot CH_2OH$ (arbitrary units) with the concentration of Cu^{II} in experiments with Ti^{III} and $S_2O_8^{2-}$ in the presence of MeOH at pH 1.9 with mixing time 0.03 s ([Ti^{III}], as titanium sulphate, 1.7×10^{-3}, [$S_2O_8^{2-}$] 8.3×10^{-3} mol dm^{-3}, [MeOH] 3% v/v), together with simulations based on the kinetic scheme given in the text [for various values of $k(23)$]

function of [$S_2O_8^{2-}$] (with [Ti^{III}], [Cu^{II}], MeOH, and the mixing time held constant) and also as a function of Cu^{II} (the other parameters being held constant: see Figure 6). The kinetic scheme employed for simulation was based on the generation of Cu^I [reaction (5), k 1.0×10^6 dm^3 mol^{-1} s^{-1}] and hence $SO_4^{-\cdot}$ [reaction (23)], followed by generation of $\cdot CH_2OH$ (k 2.0×10^7 dm^3 mol^{-1} s^{-1}; *cf.* ref. 28) and its oxidation and reduction by Cu^{II} and Cu^I, respectively (with[6] k 1.6×10^8 dm^3 mol^{-1} s^{-1} and 1.5×10^7 dm^3 mol^{-1} s^{-1}) as well as oxidation[23] with $S_2O_8^{2-}$ (k 1.3×10^5 dm^3 mol^{-1} s^{-1}). Good agreement with the observed behaviour [see *e.g.* Figure 6] and the maximum steady-state concentration of $\cdot CH_2OH$ of 3×10^{-6} mol dm^{-3} was obtained with a rate constant for the reaction between Cu^I and $S_2O_8^{2-}$ of 10^6 dm^3 mol^{-1} s^{-1}.

Furthermore, incorporation of this rate constant together with accepted values for the rate constants for reactions involved in the $Ti^{III}/Cu^{II}/S_2O_8^{2-}/Bu^tOH$ reaction (Scheme) led to the prediction *via* simulation of [$\cdot CMe_2CH_2OSO_3^-$] > [$\cdot CH_2CMe_2OH$], {typically *ca.* 3:1 in the range [Cu^{II}] (0.2—1.5) × 10^{-4} dm^3 mol^{-1} s^{-1}}, exactly as observed experimentally.

$$Ti^{III} + Cu^{II} \longrightarrow Ti^{IV} + Cu^{I} \qquad (5)$$

$$Cu^{I} + S_2O_8^{2-} \longrightarrow Cu^{II} + SO_4^{-\cdot} + SO_4^{2-} \qquad (23)$$

$$SO_4^{-\cdot} + Bu^tOH \longrightarrow HSO_4^- + \cdot CH_2CMe_2OH \qquad (24)$$

$$\cdot CH_2CMe_2OH + Cu^{I} \longrightarrow Cu^{II} + OH^- + CH_2{=}CMe_2 \qquad (8)$$

$$CH_2{=}CMe_2 + SO_4^{-\cdot} \longrightarrow \cdot CMe_2CH_2OSO_3^- \qquad (25)$$

Scheme.

A second exception to the expected behaviour is provided by the alkene $CH_2{=}CMe_2$ itself which appears to give the corresponding hydroxy adduct as a minor component as well as the $SO_4^{-\cdot}$ adduct (only the latter is formed from $S_2O_8^{2-}$ at pH 7—8 *). The proportion of the $\cdot OH$ adduct grew from *ca.* 30% to *ca.* 60% of the total radical concentration detected as [Cu^{II}]$_0$ was increased from 2×10^{-4} to 7×10^{-4} mol dm^{-3}. Our observation would be consistent with the generation and hydration of an alkene radical cation [a reaction of $SO_4^{-\cdot}$ demonstrated for some related alkenes with an increased number of alkyl substituents, though not for $CH_2{=}CMe_2$ itself; $Cl_2^{-\cdot}$ also brings about this conversion,[24] though its participation here was ruled out *via* the observation that the same adduct was detected from titanium(III) sulphate]. This suggests either that the metal ion can accelerate the hydrolysis of the first formed radical [reaction (26)] or that the reaction between either $SO_4^{-\cdot}$ or $S_2O_8^{2-}$ and Cu^{II} produces a one-electron oxidant (*e.g.* Cu^{III}) which subsequently oxidizes the alkene [reactions (27) and (28)]. Since no signals were detected in the presence of Cu^{II} and $S_2O_8^{2-}$ alone, we rule out reaction of the persulphate itself.

$$\cdot CMe_2CH_2OSO_3^- \xrightarrow[Cu^{II}]{H_2O} \cdot CMe_2CH_2OH + HOSO_3^- \qquad (26)$$

$$Cu^{II} + SO_4^{-\cdot} \longrightarrow SO_4^{2-} + Cu^{III} \qquad (27)$$

$$Cu^{III} + CH_2{=}CMe_2 \longrightarrow Cu^{II} + {}^{+\cdot}CH_2{-}CMe_2 \xrightarrow{H_2O} HOCH_2CMe_2\cdot \qquad (28)$$

Conclusions

We have demonstrated that the rapid reaction between Ti^{III} and Cu^{II} (k *ca.* 10^6 dm^3 mol^{-1} s^{-1}) serves as an effective means for generation of Cu^I in aqueous solution.

Our results provide further spectroscopic and kinetic evidence for the rapidity of the reaction between Cu^I and, especially, β-hydroxyalkyl radicals (which give rise to alkenes) and the methyl radical. As with these reductions, the rate constants of the oxidation of radicals by Cu^{II} (*e.g.* 5×10^7 dm^3 mol^{-1} s^{-1} and 3×10^7 dm^3 mol^{-1} s^{-1} respectively, for $\cdot Me$ and $\cdot CH_2CH_2OH$, which are comparable to the value[6] of 9×10^7 dm^3 mol^{-1} s^{-1} for the electron-rich radical $\cdot CHMeOH$) are best interpreted in terms of inner-sphere reactions, probably involving organo-copper complexes, rather than outer-sphere electron-transfer reactions.

Our observation of the enhanced rate of generation of $SO_4^{-\cdot}$ in the Ti^{III}–Cu^{II}–$S_2O_8^{2-}$ system is interpreted in terms of the rapid reaction of Cu^I with persulphate (in contrast to the much slower reaction between Cu^I and H_2O_2); this provides a

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* $Ti^{III}/S_2O_8^{2-}$ also gives the $\cdot OH$ adduct at pH > 9 *via* oxidation of OH^- by $SO_4^{-\cdot}$ (see ref. 28).

convincing rationale of the catalytic effect of Cu^{II} in persulphate induced oxidations (see *e.g.* ref. 29). A chain process is presumably involved in which the oxidation by Cu^{II} of organic radicals regenerates Cu^{I} and hence $SO_4^{-\bullet}$ (see above). Our suggestion that Cu^{III} may also be formed as a one-electron oxidant, though more tentative, finds support from the recent claim[30] that this electron-transfer process is involved in the oxidation of aryl-substituted alkenes with Cu^{II}–peroxydisulphate in ethanoic acid.[30]

Experimental

E.s.r. spectra were recorded with Varian E-104 and Bruker ESP-300 spectrometers, each equipped with X-band Klystron and 100 kHz modulation. Relative radical concentrations were obtained from measurements of peak heights (where the appropriate line widths were the same) or by double integration (either with a Datalab DL4000 microcomputer interfaced with the E-104 or directly with the ESP-300). In the continuous-flow e.s.r. experiments the flow was maintained with a Watson-Marlowe 502 peristaltic pump and a mixing chamber employed which allowed simultaneous mixing of three reagent streams *ca.* 30 ms before passage through the cavity of the spectrometer. The compositions of solutions to be mixed in experiments with $^{\bullet}OH$ (from Ti^{III}) were as follows: stream (i) contained titanium(III) chloride or titanium(III) sulphate (0.005 mol dm^{-3}), stream (ii) contained hydrogen peroxide (0.05 mol dm^{-3}), and stream (iii) contained the substrate. Copper(II) sulphate was normally added to stream (iii) (to give a concentration in this stream of between 10^{-5}—10^{-3} mol dm^{-3}). For reactions above pH 2.5 the disodium salt of ethylenediaminetetra-acetic acid was added to stream (i) (0.005 mol dm^{-3}) and the pH was altered by the addition of ammonia solution (*d* 0.880) to stream (i). In experiments with the Fenton system, conditions were the same as above except that stream (i) contained iron(II) sulphate (0.0025 mol dm^{-3}) together with the disodium salt of EDTA (0.0025 mol dm^{-3}).

Experiments with $SO_4^{-\bullet}$ involved the mixing of three streams, typically as follows: stream (i) contained titanium(III) chloride or sulphate (as above), together with the disodium salt of EDTA (as above), stream (ii) contained sodium peroxydisulphate (0.025 mol dm^{-3}) and ammonia (when required), and the third stream contained the substrate and copper(II) sulphate when required, as described above.

pH Measurements were made using a Pye-Unicam PW9410 pH meter with the electrode inserted into the effluent stream. All solutions were degassed both before and during use by purging with oxygen-free nitrogen.

The mixing times (*i.e.* the times between mixing and observations) for the e.s.r. flow experiments were determined for the variety of flow rates employed *via* experiments with a Pye-Unicam SP8-500 u.v.-visible spectrometer which had been modified to accept the e.s.r. cell and mixer. The portion of the flat e.s.r. cell which is normally in the centre of the e.s.r. cavity was positioned such that it was directly in the path of the light beam; a series of experiments was conducted in which changes in optical density at 460 nm (from $FeNCS^{2+}$) were monitored during the reaction between $Fe(ClO_4)_3$ and KSCN, with the former in excess, in $HClO_4$ (see ref. 16). Measurement of absorbance (A_t) at a given flow rate (and hence t) leads *via* knowledge of A_∞, $[Fe^{III}]$, and $[H^+]$, as well as $k(Fe^{III} + SCN^-)$[16] to the determination of t.

Kinetic simulations were carried out using a program derived by Dr. A. Protheroe (Shell Research Ltd), modified by Dr. T. M. F. Salmon and Mr. M. Brown and kindly provided by Professor D. J. Waddington.

The chemicals employed were commercial samples, used as supplied.

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