Effect of iron(II), cerium(IV) and manganese(III) in the reaction between thallium(III) and hydrogen peroxide in aqueous perchloric acid

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The otherwise slow reaction between Tl(III) and H₂O₂ goes to completion in a few seconds in the presence of 10⁻⁶ mol dm⁻³ Fe(II). The reaction involves a cycle of steps with reactive intermediates such as Tl(II) and H₂O₂, [Fe(III)] > 1 x 10⁻⁴ mol dm⁻³ is very effective and [Fe(III)] < 1 x 10⁻⁵ mol dm⁻³ has no effect at all on the reaction. Cerium(IV) and Mn(III) induce Tl(III) → H₂O₂ reaction and the extent of reduction of Tl(III) depends on the absolute and relative concentrations of the reactants. Ag(II) and Cr(III) are without any effect, but vanadium(IV) induces the reaction.

Small amounts (~ 10⁻⁶ mol dm⁻³) of iron(II) have been employed as initiator or pre-reductor for the determination¹ of H₂O₂ with Tl(III). The reaction, Tl(III) + Fe(II) → Tl(II) + Fe(III) is said to initiate²,³ the oxidation of H₂O₂, but the forward reaction⁴ is slow and has a second order rate constant of 4.6 x 10⁻² mol⁻¹ dm³ s⁻¹ at 25° (or 1.39 x 10⁻² mol⁻¹ dm³ s⁻¹ at 23° found by Dodson and coworkers⁵) and hence initiation by this step seems to be less likely. An alternative initiating reaction⁶ could be Fe(II) + H₂O₂ → Fe(III) + OH⁻ + OH⁻ which has a second order rate constant of 53 mol⁻¹ dm³ s⁻¹ (see ref. 6). Such conflicting reports necessitate a thorough kinetic study of Tl(III)-H₂O₂ reaction in the presence of Fe(II). Further the effect of various metal ions, e.g. Ce(IV), Mn(III), Ag(II) etc. which could oxidize H₂O₂, and of Cr(III), VO²⁺ etc. which could reduce H₂O₂, has also been investigated.

**Materials and Methods**

Thallium(III) solutions were prepared as described earlier⁷ and standardised iodometrically. Stock solutions of H₂O₂ were always prepared afresh by dilution of 30% H₂O₂ (E. Merck) and standardised cerimetrically using ferroin as indicator. Lithium perchlorate was prepared by dissolving Li₂CO₃ (AR Sisco) in 70% HClO₄. CO₂ was removed by gentle heating and pH of the solution adjusted to 6.7-7.0. Solutions of ceric sulphate were prepared by dissolving ammonium Ce(IV) pentanitrate in 1.0 mol dm⁻³ H₂SO₄. Ceric perchlorate was prepared by precipitating Ce(IV) as hydroxide by the addition of dilute ammonia and then dissolving the precipitate in 1.0 mol dm⁻³ HClO₄. Mn(III) sulphate solution was prepared⁸ by dissolving Mn(III) acetate (Aldrich) in 6.0 mol dm⁻³ H₂SO₄ in the presence of 0.1 mol dm⁻³ Mn(II) sulphate (E. Merck). Ag(II) solution was prepared⁹,¹⁰ by dissolving AgO (Aldrich) in 4.0 mol dm⁻³ HClO₄ in the presence of 0.2 mol dm⁻³ AgClO₄. Vanadium(IV) solution was prepared by dissolving VOSO₄ (AR, BDH) in water and standardised iodometrically. Ferric perchlorate (E. Merck) was employed for Fe(III) and Fluka chromium(III) nitrate for Cr(III).

**Kinetic Procedure**

Experiments were conducted in stoppered conical flasks immersed in a thermostated water bath at (20 ± 0.1)° unless mentioned otherwise. The reaction was initiated by adding a known volume of Fe(II) solution to a temperature pre-equilibrated (20 ± 0.1°) mixture containing required amounts of Tl(III), H₂O₂ and HClO₄. Since the reaction goes to completion within 1-2 minutes, the usual kinetic procedure of sampling was not adopted. For each experiment, 7-8 identical reaction mixtures were prepared and allowed to react for different predetermined times. Ice cold 5% KI solutions (10ml) was added to each flask and liberated iodine was titrated below 5° (see ref. 11) against standard thiosulphate while shaking continuously. Separate experiments with mixtures of H₂O₂ and KI without Tl(III) showed that no iodine is liberated in about 3 min. If [HClO₄] < 1.0 mol dm⁻³, Initial rates (ir) were determined by the plane mirror method¹² and these were reproducible within ±15%. Larger concentrations of reactants could not be employed since the reaction becomes too fast for conventional method of analysis.

Concentrations of metal ions employed were of the order 10⁻³ mol dm⁻³ and hence did not matter.
in iodometric estimation of Tl(III). Even otherwise metal ions are rapidly reduced by H_2O_2 and there is no interference from them in the iodometric estimation of Tl(III). [V(IV)] employed was of the order of ~10^{-4} mol dm^{-3} and this interfered with the iodometric estimation of Tl(III), and hence the latter was determined by ascorbic acid. A known excess of ascorbic acid was added to the reaction mixture. The reaction^{10} of ascorbic acid and Tl(III) is fast and unreacted ascorbic acid was determined iodimetrically. Vanadium(V) also reacts^{14} with ascorbic acid and hence an amount of iodine equivalent to V(V) was subtracted from the total titre of iodine.

Results

Stoichiometry of Tl(III) - H_2O_2 reaction

Several mixtures with different concentrations of reactants at constant [HClO_4] = 0.5 mol dm^{-3} and at I = 1.0 mol dm^{-3} and temp = 30° were allowed to react. Excess of Tl(III) was determined iodimetrically and excess H_2O_2 was determined cerimetricaly^{15}. From several experiments an average value of Δ[Tl(III)]/Δ[H_2O_2] was found to be 0.99 ± 0.01.

Order of mixing the reactants and kinetic results

There are two ways of initiating the reaction. Tl(III) and H_2O_2 can be mixed and reaction may be initiated by the addition of Fe(II) in the end. Alternatively Tl(III) and Fe(II) may be mixed and then H_2O_2 added to initiate the reaction. The rates under identical conditions are about two times larger in the latter case. Reaction, however, cannot be initiated by adding Tl(III) in the end since Fe(II) is completely oxidised to Fe(III) which in small amounts has no effect. In the second way of initiation, Fe(II) and Fe(III) are in equilibrium(I) and Fe(II) is not oxidised completely.

\[ \text{Tl}(\text{III}) + \text{Fe}(\text{II}) \rightarrow \text{Tl}(\text{II}) + \text{Fe}(\text{III}) \]  

(1)

Reaction initiated by Fe(II): Thallium(III) and H_2O_2 dependences

The [Tl(III)] was varied in the range (3.0 × 10^{-4} - 11.8 × 10^{-4}) mol dm^{-3} at two different [H_2O_2], other conditions being as shown in Fig. 1. The order in Tl(III) is thus one. The first order rate constants for [H_2O_2] = 3.6 × 10^{-4} mol dm^{-3} and 5.5 × 10^{-4} mol dm^{-3} were found to be 0.714 × 10^{-2} s^{-1} and 1.66 × 10^{-2} s^{-1} respectively. The third order rate constants of 5.51 × 10^{4} and 5.48 × 10^{4} mol^{-2} dm^{6} s^{-1} obtained by dividing the first order rate constants by [H_2O_2]^2 show that order in H_2O_2 is two. This is further supported by a plot of rate versus [H_2O_2]^2 (Fig. 1).

Iron(II) dependence

The initial rates versus [Fe(II)] plot shows increase in rate which tends to be limiting with increase in [Fe(III)]. The third order rate constant under limiting conditions was found to be 1.4 × 10^{5} mol^{-2} dm^{6} s^{-1} at 20°. The order in [Tl(III)] and [H_2O_2], and dependence on [Fe(II)] suggest a rate law of the following type.

\[-d[Tl(III)]/dt = \frac{A[Tl(III)][H_2O_2]^2[Fe(II)]}{B + C[Fe(II)]} \]  

(2)

where A, B and C are constants.

Reaction initiated by H_2O_2

The variations of [Tl(III)] and [H_2O_2] have been shown in Fig. 1. Again the order in Tl(III) and H_2O_2 were one and two respectively and the third order rate constants for [Fe(II)] = 5.0 × 10^{-6} mol dm^{-3} were found to be 9.4 × 10^{4} mol^{-2} dm^{6} s^{-1} and 9.3 × 10^{4} mol^{-2} dm^{6} s^{-1} in the two cases respectively. The effect of varying [Fe(II)] at three different [H_2O_2] is shown in Fig. 2. The third order rate constants (mol^{-2} dm^{6} s^{-1}) under limiting conditions were 2.85 × 10^{5}, 2.80 × 10^{5} and 2.90 × 10^{5} for [H_2O_2] = 3.0 × 10^{-4} mol dm^{-3}, 4.5 × 10^{-4} mol dm^{-3} and 6.0 × 10^{-4} mol dm^{-3} respectively. Thus the nature of the results under the two conditions of order of mixing is similar, but the rates are about
two times high in the case \( \text{H}_2\text{O}_2 \) is added in the end. It is appropriate to study the kinetics by the addition of Fe(II) since Ti(III) - \( \text{H}_2\text{O}_2 \) reaction is extremely slow.

**Effect of \([\text{H}^+]\) and ionic strength**

Variation in \([\text{H}^+]\) (0.2 to 1.0) mol dm\(^{-3}\) keeping \([\text{Ti}(\text{III})]=4.0 \times 10^{-4}\) mol dm\(^{-3}\), \([\text{H}_2\text{O}_2]=5.0 \times 10^{-4}\) mol dm\(^{-3}\), \([\text{Fe}(\text{II})]=1.0 \times 10^{-5}\) mol dm\(^{-3}\) and \(I=1.0\) mol dm\(^{-3}\) did not affect the rate. Similarly variation in ionic strength (LiClO\(_4\)) at \([\text{H}^+]=0.5\) mol dm\(^{-3}\) keeping the other concentrations as above (except ionic strength) does not affect the rate.

**Effect of Fe(III) and Ti(II) on the rate**

Added Ti(II) has no effect on the rate of reaction and Fe(III) alone at a concentration of \(1.0 \times 10^{-5}\) mol dm\(^{-3}\) or less has no effect (Table 1). However, in the presence of iron(II), \(1 \times 10^{-5}\) mol dm\(^{-3}\) Fe(III) had some effect on the rate. Fe(III) at a concentration of \(1 \times 10^{-4}\) mol dm\(^{-3}\) in the presence or absence of Fe(II) made the reaction to go to completion instantaneously. The previous finding\(^6\) that Fe(III) is without any effect on the rate, is a sweeping statement and is valid if \([\text{Fe}(\text{III})]<1.0 \times 10^{-5}\) mol dm\(^{-3}\). Thus Fe(III) may not be effective for the reaction when present in low concentrations, but it is as effective as Fe(II) if the concentrations is \(1 \times 10^{-4}\) mol dm\(^{-3}\) or more.

**Reaction of Ti(III) with UV irradiated \( \text{H}_2\text{O}_2 \)**

Since the reaction is said to be accompanied by the formation of intermediate free radicals\(^3\)\(^,\)\(^6\) from \( \text{H}_2\text{O}_2 \), it is likely that irradiation of \( \text{H}_2\text{O}_2 \) solution might generate these radicals and initiate the otherwise slow reaction. \( \text{H}_2\text{O}_2 \) was irradiated with UV lamp in a box for 5 min and then added to Ti(III) solution. The third order rate constant with irradiated \( \text{H}_2\text{O}_2 \) was found to be \(4 \times 10^4\) mol\(^{-2}\) dm\(^6\) s\(^{-1}\) at 29.5\(^\circ\)C, and \([\text{HClO}_4]=0.5\) mol dm\(^{-3}\). This rate constant with unirradiated \( \text{H}_2\text{O}_2 \) was found to be about \(12\) mol\(^{-2}\) dm\(^6\) s\(^{-1}\) at 30\(^\circ\)C and \([\text{HClO}_4]=0.5\) mol dm\(^{-3}\). The value found earlier\(^2\) was between 10-15 mol\(^{-2}\) dm\(^6\) s\(^{-1}\) under the same conditions. Thus there is more than thousand fold increase in the rate for the irradiated \( \text{H}_2\text{O}_2 \).

**Ti(III) - \( \text{H}_2\text{O}_2 \) reaction in the presence of Ce(IV)**

The reaction of Ce(IV) and \( \text{H}_2\text{O}_2 \) is quite fast\(^1\)\(^7\)\(^-\)\(^9\) and it is over within the time of mixing. The first isometric analysis for Ti(III) could be done only after 5 seconds and thereafter no change occurred if the concentration of reactants is of the order of \(\sim 10^{-4}\) mol dm\(^{-3}\). This gave an estimate of reduction of Ti(III) on account of induced reaction. It may also be noted that at \([\text{Ce}(\text{IV})]<1 \times 10^{-4}\) mol dm\(^{-3}\) the induced reaction is a little slower. The previous works\(^1\)\(^6\)\(^-\)\(^9\) have shown the reduction on account of induced reaction to be equivalent (or half molar) to Ce(IV). Our results show that this is partly true, and that for smaller concentrations (\(\sim 10^{-5}\) mol dm\(^{-3}\)) of Ce(IV) employed, there is always larger reduction of Ti(III) than expected and that at large (>\([\text{H}_2\text{O}_2]\))

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**Table 1 - Effect of Ti(II) and Fe(III) on the rate of Ti(III) - \( \text{H}_2\text{O}_2 \) reaction**

<table>
<thead>
<tr>
<th>([\text{Ti}(\text{III})]=4.1 \times 10^{-4}) mol dm(^{-3}); [( \text{H}_2\text{O}_2]=6.25 \times 10^{-4}) mol dm(^{-3}); [( \text{HClO}_4]=0.5) mol dm(^{-3}); [( \text{LiClO}_4]=1.0) mol dm(^{-3}); ([\text{Fe}(\text{II})]=4.0 \times 10^{-6}) mol dm(^{-3}); (25^\circ)C</th>
<th>(10^4[\text{Ti}(\text{III})]/\text{mol dm}^{-3})</th>
<th>(10^4[\text{Ti}(\text{III})]/\text{mol dm}^{-3})</th>
<th>([\text{Fe}(\text{II})]=0.0)</th>
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\(^a\)No Fe(II) added, only in the presence of Fe(III). \(^b\)No reaction even after six hr.
Ce(IV), the amount of Ti(III) reduced is always much less than the expected amount. The results are quite complicated and depend on the relative and absolute [Ti(III)], [H₂O₂] and [Ce(IV)]. As a matter of fact if [Ti(III)] > [H₂O₂] > [Ce(IV)], the reduction of Ti(III) is always more than that on the basis mentioned above. Table 2 shows such results. For certain [Ce(IV)], the whole of H₂O₂ is oxidised and the amount of Ti(III) reduced is equal to {1/[Ce(IV)] + [H₂O₂]−[Ce(IV)]}.

**Ti(III) − H₂O₂ reaction in the presence of Mn(III)**

The reaction of Mn(III) with H₂O₂ is also known to be fast and the free radicals HO₂ are formed which are likely to induce Ti(III) − H₂O₂ reaction. The results are more or less similar to the reaction in the presence of Ce(IV).

Silver(II) is another oxidant similar to Ce(V) and Mn(III) that reacts with H₂O₂ and yields HO₂ radicals and which is expected to initiate or induce Ti(III) − H₂O₂ reaction. However, Ag(II) is not at all effective for promoting Ti(III) − H₂O₂ reaction.

**Ti(III) and H₂O₂ reaction in the presence of V(IV) and Cr(III)**

Vanadium(IV) was employed in view of the fact that it is oxidised with H₂O₂. These results show that vanadium(IV) does induce the slow reaction of Ti(III) − H₂O₂. Estimation of Ti(III) in the presence of vanadium(IV) is complicated and hence it was not pursued. Chromium(III) has no effect on the Ti(III) − H₂O₂ reaction.

**Spectrophotometric results**

These measurements were made on Hitachi model U2000. HO₂ radical is known to have an absorption maximum at 230 nm. Ti(III) and Fe(II) do not absorb, and H₂O₂ absorbs little at 230 nm. Ti(I) has molar extinction coefficient of about 54 mol⁻¹ cm⁻¹ and hence 0.001 mol dm⁻³ Ti(III) on reduction would give an absorption of only 0.054 due to Ti(I). An absorption of 0.5 of the reaction mixture ([Ti(III)] = 4.8 × 10⁻⁴ mol dm⁻³, [H₂O₂] = 1.0 × 10⁻³ mol dm⁻³; [Fe(II)] = 1.0 × 10⁻⁵ mol dm⁻³, [HClO₄] = 1.0 mol dm⁻³) must be due to some intermediate, most probably HO₂.

**Discussion**

The empirical rate law (2) can be explained on the basis of the reactions (3) and (4).

\[
\text{Ti}^3+ + 2 \text{H}_2\text{O}_2 \rightarrow \text{Ti}^2\text{(H}_2\text{O}_2\text{)}^2^+ \quad \text{(3)}
\]

\[
\text{Ti}^2\text{(H}_2\text{O}_2\text{)}^2^+ + \text{Fe}^2^+ \rightarrow \text{Ti}^2^+ + \text{Fe}^{3+} + 2 \text{H}_2\text{O}_2 \quad \text{(4)}
\]

As a matter of fact step (4) is followed by several fast steps involving reactive intermediates like Ti(II), HO₂ and OH radicals. Based on steps (3) and (4), rate law (5) can be derived.

\[
-d[\text{Ti(III)}]/dt = \frac{k_1 k_3 [\text{Ti(III)}] [\text{H}_2\text{O}_2] [\text{Fe}^{2+}]}{k_2 + k_3 [\text{Fe}^{2+}]} \quad \text{(5)}
\]

This is identical with (2) with A = k₁k₃, B = k₂ and C = k₃. From a plot of (ir)⁻¹ versus [Fe(II)]⁻¹ (Figs 3 and 4). k₁ and k₂/k₃ have been calculated and these
are given in Table 3. The experimentally found \( k_0 \)
(third order rate constant) is in good agreement with
the calculated value (see Table 3). It is not possible
to separate \( k_2 \) and \( k_3 \). The value of \( k_1/k_2 \) is
5 \( \times 10^5 \). It will be seen later that \( k_3 \) cannot be less
than \(-10^4 \) (100 times the rate constant for reaction
6) and it cannot be more than \(-10^8 \) since it cannot
be diffusion controlled. \( k_1/k_2 \) would then be be-
tween \( 10^3 \) and unity and since \( k_1 \) is \(-10^5 \), \( k_2 \) would
be between unity and \( 10^7 \). There is no kinetic evid-
ence for complex \( \text{TI}^{II} \text{H}_2 \text{O}_2 \) and since \([\text{TI}^{III}] \) and
\([\text{H}_2 \text{O}_2] \) employed are of the order of \(-10^{-4} \) mol
\( \cdot \) dm\(^{-3} \), the equilibrium constant
\((k_1/k_2)\) could have any value from \( 10^6 \) downwars. This is in line with
the conclusion drawn above. Unfortunately \([\text{H}_2 \text{O}_2] \) larger than \(-10^{-3} \) mol \( \cdot \) dm\(^{-3} \) could not be employ-
ed to obtain kinetic evidence for the complex since
the reaction is too fast for conventional method of
analysis.

Complex formation between \( \text{TI}^{III} \) and \( \text{H}_2 \text{O}_2 \)
which has been discussed at length in the previous
paper\(^1\), is quite possible even though there is no di-
rect evidence. However, more important is the fact
that the order in \( \text{H}_2 \text{O}_2 \) is two and in no case less than
two for even the lower concentration range of \( \text{H}_2 \text{O}_2 \)
and this fact points to the existence of a dimer of
\( \text{H}_2 \text{O}_2 \) in the system. Such dimerization of \( \text{H}_2 \text{O}_2 \) by
hydrogen bonding in concentrated solutions, has
been indicated from NMR\(^2\) and Raman\(^3\) studies in
the past. It is possible that this dimer may complex
with \( \text{TI}^{III} \). The facts that a kinetic study of the
reaction by conventional method was possible only
with low \((\sim 10^{-4} \) mol \( \cdot \) dm\(^{-3} \)) concentrations of
\( \text{H}_2 \text{O}_2 \) and the determination\(^4\) of \( \text{H}_2 \text{O}_2 \) (immediate
reaction with \( \text{TI}^{III} \)) can be made only if
\([\text{H}_2 \text{O}_2] > 10^{-3} \) mol \( \cdot \) dm\(^{-3} \), show how effective is the
concentration for dimerization and the redox reac-
tion between \( \text{TI}^{III} \) and \( \text{H}_2 \text{O}_2 \).

The two reactants, \( \text{TI}^{III} \) and \( \text{H}_2 \text{O}_2 \) involve two
reactive radical intermediates, \( \text{TI}^{II} \) and \( \text{HO}_2 \) and
the role of \( \text{Fe}^{II} \) can be explained by generating
one of them through one of the following reactions
(i-iv).

\[
\text{TI}^{III} + \text{Fe}^{II} \rightarrow \text{TI}^{II} + \text{Fe}^{III} \quad \ldots (i)
\]

The rate constant\(^5\) for the forward reaction is
\( \sim 10^{-2} \) mol\(^{-1} \) \( \cdot \) dm\(^3 \) \( \cdot \) s\(^{-1} \) and the equilibrium constant is
\( 3 \times 10^{-8} \) at \( 25^\circ \).

\[
\text{Fe}^{II} + \text{H}_2 \text{O}_2 \rightarrow \text{Fe}^{III} + \text{OH}_2 + \text{OH}^- \quad \ldots (ii)
\]

The second order rate constant\(^6\) for this reaction
is reported to be \( 53 \) mol\(^{-1} \) \( \cdot \) dm\(^3 \) \( \cdot \) s\(^{-1} \) at \( 25^\circ \). The sub-
sequent reaction produces radicals \( \text{HO}_2 \).

\[
\text{OH} + \text{H}_2 \text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2 \text{O} \quad \ldots (iii)
\]
This reaction is reported\(^2\) to be rapid. The reaction of Fe(II) and OH is also rapid, but this does not seem to occur as compared to reaction (iii), since otherwise the main reaction between Tl(III) and H\(_2\)O\(_2\) would not occur.

\[
\text{[H}_2\text{O}_2\text{]}^2+ \text{Fe}^{2+} \rightarrow \text{Tl(II)} \text{or H}_2\text{O}_2 \text{+ other products} \quad \ldots \text{(iv)}
\]

The rate constant for this reaction is not known, but one can compare the rate of this reaction with those of other two reactions under similar conditions. For \([\text{Tl(III)}]=4 \times 10^{-4} \text{ mol dm}^{-3},\) \([\text{H}_2\text{O}_2]=4 \times 10^{-4} \text{ mol dm}^{-3}\) and \([\text{Fe(II)}]=5 \times 10^{-6} \text{ mol dm}^{-3}\), the rate for \(\text{Tl(III)} - \text{Fe(II)}\) reaction would be \(10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}\) and the rate for \(\text{H}_2\text{O}_2 - \text{Fe(II)}\) reaction would be \(10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}\). The overall rate for the present reaction is \(10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}\). Thus it is obvious that the present reaction is initiated by reaction (iv) which can be regarded as a combination of steps (i) and (ii). Optimum concentrations of H\(_2\)O\(_2\) and Tl(II) generate a cycle of following reactions till one of the reactants is exhausted.

\[
\text{Tl(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Tl(I)} + \text{H}_2\text{O}_2 + \text{H}^+ \quad \ldots \text{(v)}
\]

\[
\text{Tl(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Tl(II)} + \text{H}^+ + \text{O}_2 \quad \ldots \text{(vi)}
\]

The possible reactions that may occur in the solvent cage are (ii), (iii) and (v) in that order. The second order rate constant for reaction (v) has been reported\(^4\) to be \(3.0 \times 10^6 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}\) at 25°. The rate constant for reaction (vi) is not known, but immediate reduction of Tl(III) (possibly by H\(_2\)O\(_2\)) in the presence of Ce(IV) shows that this is rapid.

Cerium(IV) and manganese(II) have limited role in promoting Tl(III) - H\(_2\)O\(_2\) reaction and H\(_2\)O\(_2\) radicals are responsible for initiating the reaction as shown below.

\[
\text{Ce(IV)/Mn(III) + H}_2\text{O}_2 \rightarrow \text{Ce(III)/Mn(II) + HO}_2 + \text{H}^+ \quad \ldots \text{(6)}
\]

\[
\text{Ce(IV)/Mn(III) + HO}_2 \rightarrow \text{Ce(III)/Mn(II) + H}^+ + \text{O}_2 \quad \ldots \text{(7)}
\]

\[
\text{Tl(III)} + \text{HO}_2 \rightarrow \text{Tl(II)} + \text{H}^+ + \text{O}_2 \quad \ldots \text{(8)}
\]

There is competition between Ce(IV)/Mn(III) and Tl(III) and hence [Tl(II)] would depend on the relative concentrations of Tl(III) and the other oxidant. Unless an optimum concentration of Tl(II) is formed, the main cycle of reactions would not be triggered. Our results show that Mn(III) is not so effective as an inductor as Ce(IV). The second order rate constant for reaction (6) is \(1 \times 10^6 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}\) (for Ce(IV))\(^2\) and \(5 \times 10^4 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}\) (for Mn(III))\(^2\) at 25° and hence equilibrium concentration of HO\(_2\) is likely to be smaller in case of Mn(III). Then the induction would also depend on the relative reactivities of Ce(IV) and Mn(III) towards HO\(_2\). These are not known presently.

Ag(II) is not effective for induction. Though reaction (6) is fast\(^9\) (first order rate constant is 80 s\(^{-1}\) at 20°), reaction (7) appears to be much faster than (8) and hence no HO\(_2\) is available for induction. Cr(III) does not induce Tl(III) - H\(_2\)O\(_2\) reaction at all. It is also obvious by the relative reactivities of several of the oxidants towards H\(_2\)O\(_2\) lying in the following order\(^2\), and Tl(III) would probably occupy a position between Fe(III) and Cr(III).

\[
\text{Ce(IV)} > \text{Mn(III)} > \text{Ag(II)} > \text{Co(II)} > \text{Fe(III)} > \text{Cr(III)}
\]

The role of Fe(III) requires a special mention. Large concentrations of Fe(III) (\(> 1 \times 10^{-4} \text{ mol dm}^{-3}\)) affect the reaction significantly. The mechani-
ism involves a reaction (9) similar to (6) producing \( \text{HO}_2 \) radicals, but this is a slow process:

\[
\text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2 + \text{H}^+ \quad \ldots (9)
\]

with a rate constant\(^{29}\) of less than \(10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\) at 25\(^\circ\), the optimum concentration of \(\text{HO}_2\) to induce cycle of reactions, is not generated. It is Fe(II), however, which is formed as a product which can participate in reaction (iv) to generate \([\text{TI}^{II}]\) to induce the cycle of reactions (v) and (vi). A reaction (10) with a rate constant\(^{6}\) of \(1.2 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\) has not been considered since both \([\text{HO}_2]\) and \([\text{Fe(III)}]\) would be small.

\[
\text{HO}_2 + \text{Fe(III)} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \quad \ldots (10)
\]

All the oxidants mentioned above are similar in their action in producing first \(\text{HO}_2\) radical, but Fe(II) is different in that it first generates \(\text{OH}\) and then \(\text{HO}_2\). Vanadium(IV) was employed to support this mechanism. The results do show an induction of \([\text{TI}^{II}] - \text{H}_2\text{O}_2\) reaction and it should be through \(\text{OH}\) radicals since V(IV) - \(\text{H}_2\text{O}_2\) reaction yields \(\text{OH}\) radical.

We could not verify the order between two and three with respect to \(\text{H}_2\text{O}_2\) as found by Csanay and co-workers\(^{5}\) since we could not employ \([\text{H}_2\text{O}_2]\) larger than \(1 \times 10^{-3} \text{ mol dm}^{-3}\) to avoid interference in iodometric determination. However, we did not observe the slightest trend for increase in the order even at the largest concentration of \(\text{H}_2\text{O}_2\) employed.

References