There is a competition between reactions (2) and (3) and when excess of H_3PO_3 is present, reactions (1) and (3) occur, while reaction (2) is masked. Under this condition the limiting value of unity for the induction factor is obtained.

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Ce(IV)–induced Reduction of Tl(III) by Hydrogen Peroxide

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The reduction of Tl(III) perchlorate by H_2O_2 is a slow process but in the presence of Ce(IV) it becomes fast. The induction factor has a value of one. A mechanism has been suggested for the induced reduction of Tl(III). It is further observed that cerimetric estimation of H_2O_2 can be carried out even in the presence of Tl(III), if a large excess of Ce(IV) (20-fold) is used.
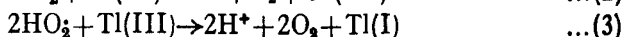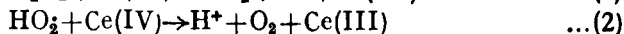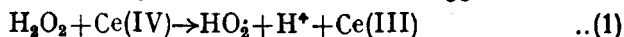
THE reduction[1] of Tl(III) perchlorate by hydrogen peroxide is slow, but that of Ce(IV) sulphate and perchlorate is fast[2-4]. If, however, Tl(III) and Ce(IV) are mixed and H_2O_2 added, both metal ions are reduced simultaneously. It is, therefore, a case of induced reduction. H_2O_2, Ce(IV) and Tl(III) are respectively actor, inductor and acceptor.

Tl(III) perchlorate was prepared by dissolving Tl(III) oxide in 60% perchloric acid and filtering through a sintered glass crucible to remove undissolved material. It was standardized iodometrically[5]. 0·01M solution was prepared from this by dilution. Ce(IV) sulphate was prepared by dissolving ammonium Ce(IV) pentanitrate in 1·0M sulphuric acid to yield 0·01M solution and standardized[6] against diammonium iron(II) bis-sulphate solution.

H_2O_2 solution (0·01M) was prepared by dilution of 20 or 30% w/v H_2O_2 and standardized[7] against a Ce(IV) solution using ferroin as indicator. Several mixtures containing 0·5-10 ml of Tl(III) and 8 ml of Ce(IV) solution were prepared. 10 ml of H_2O_2 solution were added to each of the mixtures. Tl(III) in the reaction mixtures was determined iodometrically in the following way. The mixtures were cooled in ice and then 5 ml of 10% solution of KI were added. The liberated iodine was titrated with constant and vigorous shaking against a standard thiosulphate (0·01M). The temperature throughout the titration was kept low so as to eliminate a reaction[8] between H_2O_2 (in the reaction mixture) and the iodine (liberated). For this reason in any other reaction mixture larger concentrations of H_2O_2 had to be avoided. In any reaction mixture the conditions were maintained such that $[H_2O_2] > [Ce(IV)]$ and $[Tl(III)] > [Ce(IV)]$. From the Tl(III) so determined millimoles of Tl(III) consumed were calculated.

The results presented in Fig. 1 reveal that the maximum and limiting quantity of Tl(III) consumed is approximately 4 millimoles. It does not become constant owing to a slow reaction between Tl(III) and H_2O_2. Since each mole of Tl(III) involves two electrons for reduction, the equivalents of Tl(III) consumed is eight. The same is the amount of Ce(IV) consumed and hence the limiting value of induction factor is one.

Following mechanism has been suggested[1]:

$$H_2O_2 + Ce(IV) \rightarrow HO_2^- + H^+ + Ce(III) \qquad ..(1)$$

$$HO_2^- + Ce(IV) \rightarrow H^+ + O_2 + Ce(III) \qquad ...(2)$$

$$2HO_2^- + Tl(III) \rightarrow 2H^+ + 2O_2 + Tl(I) \qquad ...(3)$$

One could also write $H_2O_2^+$ in place of $(HO_2^- + H^+)$ in the above mechanism. As soon as reaction (1) occurs, there is a competition between Ce(IV) and Tl(III) for HO_2^- radical. If a large excess of Tl(III) is employed, reaction (2) can be suppressed and reaction (3) only occurs. Thus the induction factor, the ratio of the equivalents of acceptor reduced to the equivalents of inductor reduced has a limiting value of one.
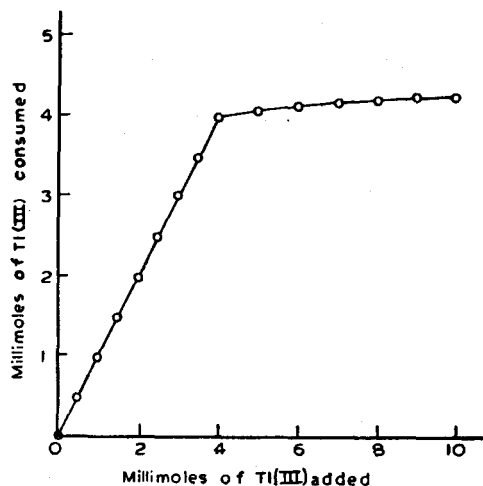

Fig. 1 — Induced reduction of Tl(III) by H_2O_2 [Ce(IV) added = 8 millimoles; H_2O_2 added = 10 millimoles]
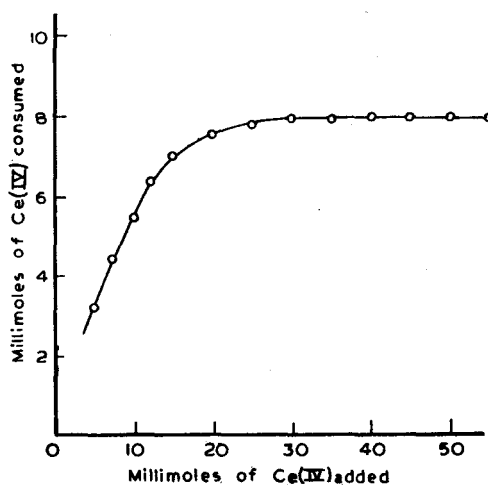

Fig. 2 — Determination of H_2O_2 by Ce(IV) in presence of Tl(III) [Tl(III) added = 2 millimoles; H_2O_2 added = 4 millimoles]

The reactions (2) and (3) have comparable rates, which was proved by the determination of H_2O_2 with Ce(IV) in the presence of Tl(III). Solutions of H_2O_2 were added to a mixture containing a known excess of Ce(IV) and a fixed amount of Tl(III). Excess of Ce(IV) was determined[6] with Fe(II). The results are shown in Fig. 2. It follows that cerimetric estimation of H_2O_2 can be carried out even in the presence of Tl(III) without any interference, provided sufficient excess [more than twenty times Tl(III)] of Ce(IV) is used. In other words, reaction (3) is suppressed in the presence of large excess of Ce(IV).

A comparison of Figs. 1 and 2 further reveals that the ratio Ce(IV): Tl(III) required to make reaction (2) predominant is larger than the ratio Tl(III): Ce(IV) required to make reaction (3) predominant. This suggests that reaction (3) is faster than reaction (2).

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Kinetics of Ag(I)-catalysed Oxidation of Methyl Mandelate by Peroxydisulphate

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Contrary to the general observation that the rate of silver-catalysed oxidation by peroxydisulphate is independent of the [substrate], it has now been found that the rate of oxidation of methyl mandelate is dependent on the concentration of substrate. Michaelis and Menten type of rate dependence on the [substrate] has been observed and this suggests a reversible formation of a complex between the ester and silver ions. The reaction products identified are benzaldehyde and methanol. This is in contrast to the keto acids isolated in earlier studies.

CONTRARY to the general observation[1,2] that Ag(I)-catalysed peroxydisulphate oxidations are independent of [substrate], it has been found in the present study that the rate of silver-catalysed peroxydisulphate oxidation of methyl mandelate depends on the [substrate]. This observation has implications from the mechanistic point of view.

Methyl mandelate required for the study was prepared by the literature method[3]. Silver nitrate (BDH) and potassium peroxydisulphate (E. Merck) used were of Analar grades. All other chemicals used were chemically pure. Potassium peroxydisulphate solution was freshly prepared and its concentration checked by iodometry. The ionic strength was kept constant at 0·2M (NaOAc).

Procedure — The rate of reaction in acetic acid-water (1:1, v/v) was followed by taking out aliquots of the reaction mixture at different intervals of time determining the concentration of peroxydisulphate left unreacted by the method of Bartlett and Cotman[4]. Duplicate rate measurements were reproducible to ±5%. The reactions were carried out at 35° keeping [Ag(I)] = $7·5 \times 10^{-4}M$, [$S_2O_8^{2-}$] = $2·0 \times 10^{-3}M$ and [NaOAc] = $0·2M$ (Table 1).

The reaction of peroxydisulphate proceeded at the same rate in the dark and in diffused light. Hence rates were measured in the diffused light. Since Ag(I)-catalysed oxidation of various substrates follows the same rate laws both in the presence and absence of oxygen[5-7], no attempt was made to exclude oxygen from the system.

Following conclusions can be drawn from the results of the present study:

(i) The reaction follows 1:1 stoichiometry up to 90% completion giving benzaldehyde, identified as 2,4-DNP derivative and methanol, identified by the chromotropic acid method[8].

(ii) The reaction is first order with respect to [peroxydisulphate]. There is no significant change even by changing the initial [peroxydisulphate]. The values of k were obtained from Eq. (1) employing the method of least squares.

$$\frac{d[S_2O_8^{2-}]}{dt} = k[S_2O_2^{-}] \qquad ...(1)$$

(iii) An increase in [substrate] increased the rate constant (Table 1).

(iv) The rate of reaction is proportional to [Ag(I)] (Table 2).

(v) The rate constant increased with increasing acetic acid percentage in the medium. A plot of log k versus $1/D$ is linear at low [CH$_3$COOH] having a positive slope.

TABLE 1 — EFFECT OF VARYING CONCENTRATION OF METHYL MANDELATE

[Substrate], M	$k \times 10^4$ (sec^{-1})
1·00	5·76
0·44	4·99
0·22	3·84
0·10	2·61
0·05	1·92
0·03	1·42
0·02	1·16

TABLE 2 — EFFECT OF VARYING {[Ag(I)] [SUBSTRATE]=$2·0 \times 10^{-2}M$}

[Ag(I)] $\times 10^4$ M	$k \times 10^4$ sec^{-1}	$K = \dfrac{k}{[Ag(I)]}$
7·5	1·15	0·15
10·0	1·35	0·13
15·0	1·93	0·13
20·0	2·30	0·15