Kinetics & Mechanism of Silver(I) Catalyzed Oxidation of Hypophosphorous Acid by Cerium(IV) in Perchloric Acid Solutions

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Spectrophotometric evidence is presented to show the existence of six complexes, viz., I: 1, I: 2, I: 3, I: 4, I: 5 and I: 6 of Ce(IV) with H₃PO₂ in Ag(I) catalyzed Ce(IV) oxidation of H₃PO₂ in aqueous perchloric acid medium. Catalysis by Ag(I) operates through complex formation with a cerium(IV) complex, and also through Ag(I)/Ag(II) cycle depending on the ratio of [H₃PO₂]/[Ce(IV)]. The latter operates preferably at large ratios of [H₃PO₂]/[Ce(IV)]. The effect of ionic strength on the rate is of two types depending on the ratio of [cerium(IV)]/[H₃PO₂]. Based on the kinetic data two mechanisms, one for the uncatalyzed path and the other for the catalyzed path have been suggested.

Silver(I) is generally used as a catalyst for peroxydisulphate and peroxydiphosphate oxidations. Higginson and coworkers reported its catalytic activity in the oxidation of Hg²⁺ and thallium(I) by cerium(IV). Ag(I)/Ag(II) cycle is reported to be operative in these oxidations with Ag(II) as the potential oxidant. However, in the Ag(I) catalyzed oxidation of H₃PO₂ by vanadium(V), direct oxidation with Ag(I) through Ag(I)/Ag(0) cycle has also been reported. Again in Co(III) oxidation of Cr(III), Ag(I) is reported to be operative through Ag(I)/Ag(II) cycle. Another interesting example of Ag(I) catalysis has been observed in the oxidation of molecular hydrogen. In this reaction Ag(I) acts by forming a complex with molecular hydrogen. It thus becomes obvious that the catalysis by silver(I) is rather complex. Silver(I) catalysis was indicated in the Ce(IV) oxidation of H₃PO₂ and this appeared to us to be an ideal system for a thorough kinetic study to unravel Ag(I) catalysis. The uncatalyzed H₃PO₂ oxidation has been studied by Mishra and Gupta, Carroll and Thomas, and Treindl and Hatala.

Materials and Methods

A stock solution of cerium(IV) perchlorate was prepared as follows: Ceric ammonium nitrate (E. Merck) was dissolved in water and to this solution was added ammonium hydroxide when ceric hydroxide precipitated out. The precipitate was allowed to settle for 48 hr, the supernatant decanted, precipitates leached several times with water, and finally dissolved in perchloric acid. The solution was filtered and standardized against ferrous ammonium sulphate using N-phenylanthranilic acid as an indicator. Cerous perchlorate was also prepared likewise from cerous sulphate (BDH).

Sodium hypophosphite (May and Baker) and perchloric acid (Riedel, 70%) were used. Other chemicals employed were either AR(BDH) or GR(E. Merck) grade. Doubly distilled conductivity water was used through out.

Reactions, carried out at 30 ± 0.05°C, were initiated by adding an equilibrated solution of ceric perchlorate to a solution containing the desired amounts of hypophosphite, perchloric acid and silver nitrate. The kinetics were followed by removing aliquots (10 ml each) at regular time intervals and quenching the reaction by adding it to a known excess of ferrous ammonium sulphate solution. The excess reagent was determined against standard silver solution using N-phenyl-anthranilic acid as an indicator. Initial rates were obtained by the plane mirror method and the rate constants were reproducible within ±5%.

For dilute solutions (< 0.001 mol dm⁻³) of Ce(IV) the kinetics were followed by determining Ce(IV) colorimetrically at 350 nm. The complex formation was studied spectrophotometrically employing a Beckman UV spectrophotometer in 1 cm matching quartz cells.

To find out whether Ag(I)/Ag(II) cycle operates or not, a knowledge about Ce(IV) + Ag(I) and Ag(I) + H₃PO₂ reactions was considered essential. Hence a study of the forward reaction of equilibrium (1)

Ce(IV) + Ag(I) ⇌ Ce(III) + Ag(II) \[ \text{... (1)} \]

was made by precipitating Ag(II) in the reaction mixture with 2, 2'-bipyridyl, centrifuging and determining the remaining cerium(IV) by any of the methods mentioned above. The reproducibility of the rate constants was within ±10%. The reaction of Ag(II) with H₃PO₂ has been studied recently in 4.0 mol dm⁻³ HClO₄ and the second order rate
constant was found to be $7.6 \times 10^2 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ at 30°.

The reaction of Ag(I) with H$_3$PO$_2$ has also been recently studied$^{14}$ and it was not found to be as simple as reported earlier$^{15}$. The rate dependence on [Ag(I)], [H$_3$PO$_2$] and [H$^+$] followed complex kinetics. However, under the condition [Ag(I)]/[H$_3$PO$_2$]//[H$^+$], the orders were nearly one. Typical rate constant of this reaction at [Ag(I)] = 0.02 mol dm$^{-3}$, [H$_3$PO$_2$] = 0.04 mol dm$^{-3}$, [HClO$_4$] = 0.5 mol dm$^{-3}$ and 30° was found to be 0.1 dm$^3$ mol$^{-1}$ s$^{-1}$. Freshly prepared Ag(0) reacted with Ce(IV) almost instantaneously, hence the systematic study could not be made.

In acid solutions hypophosphate would exist partly as H$_3$PO$_2$ and partly as H$_2$PO$_2^-$ since the acid dissociation constant$^{16}$ of H$_3$PO$_2$ is 0.135 at 25°, but hereafter hypophosphate has been used for the total analytical concentration of all such species.

Results

Stoichiometry

Hypophosphate, ceric perchlorate and silver nitrate in perchloric acid solutions of different concentrations were kept at room temperature for about 24 hr. Excess Ce(IV) was estimated$^{10}$ with ferrous ammonium sulphate and excess hypophosphate by Ce(IV) method$^{17}$. The results conform to the stoichiometry given by Eq. (2), similar to that found earlier for the uncatalyzed reaction.

$$2\text{Ce(IV)} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow 2\text{Ce(III)} + \text{H}_3\text{PO}_3$$

$$+ 2\text{H}^+ \quad \ldots (2)$$

Cerium(IV) dependence

The concentration of cerium(IV) was varied in the range $1 \times 10^{-4}$ to $5 \times 10^{-2}$ mol dm$^{-3}$ at three different [hypophosphate]. Rate depends on the ratio [Ce(IV)]/[H$_3$PO$_2$]. It is nearly constant for the ratio 0.1 and it decreases and attains a limiting value with increasing [Ce(IV)] for ratios > 5. The observed constant initial rates for, [Ce(IV)]/[H$_3$PO$_2$] ratio of 0.1 are $15.3 \times 10^{-7}$, $7.0 \times 10^{-7}$ and $3.0 \times 10^{-7}$ (mol dm$^{-3}$ s$^{-1}$) at [H$_3$PO$_2$] = 0.01, 0.005 and 0.002 mol dm$^{-3}$, respectively. The limiting initial rates are $2.5 \times 10^{-7}$, $1.3 \times 10^{-7}$ and $0.6 \times 10^{-7}$ (mol dm$^{-3}$ s$^{-1}$) for the same concentrations of H$_3$PO$_2$.

Hypophosphite dependence

The [hypophosphate] was varied in the range $5.0 \times 10^{-4}$ to $1.0 \times 10^{-2}$ mol dm$^{-3}$ for four different [Ce(IV)]. The plots of rate versus [H$_3$PO$_2$] are shown in Fig. 1.

Effect of simultaneously varying [Ce(IV)] and [hypophosphate]

Since the rate depends on the relative [Ce(IV)] and [hypophosphate], these were varied at fixed ratios of 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6 and the results are plotted in Fig. 2. For any fixed ratio, the rate is proportional to [Ce(IV)] and the linear plots pass through the origin.
Ag(I) dependence

The [Ag(I)] was varied from $5.0 \times 10^{-5}$ to $5 \times 10^{-4}$ mol dm$^{-3}$ at six different ratios of $[\text{Ce(IV)}]/[\text{H}_3\text{PO}_2]$ and the results are plotted in Fig. 3. The order in Ag(I) is one but the linear plot of rate versus $[\text{Ag(I)}]$ has an intercept on the rate axis suggesting that the uncatalyzed reaction also occurs. The uncatalyzed reaction has also been studied and the rates, in general, are found to correspond to the intercepts of the linear plots shown in Fig. 3; the rate data are given in Table 1. The slopes of the linear plots which represent catalyzed reaction are found to be $0.76 \times 10^{-3}$, $2.7 \times 10^{-3}$, $5.8 \times 10^{-3}$, $8.3 \times 10^{-3}$, $11.2 \times 10^{-3}$ and $12 \times 10^{-3}$ (dm$^6$ mol$^{-2}$ s$^{-1}$) for $[\text{Ce(IV)}]/[\text{H}_3\text{PO}_2] = 1:1, 1:2, 1:3, 1:4, 1:5$ and $1:6$ respectively. Thus another important feature of Ag(I) catalysis is its significant role only for smaller ratios of $[\text{Ce(IV)}]/[\text{H}_3\text{PO}_2]$.

Effect of ionic strength

The ionic strength was varied by adding lithium perchlorate at fixed $[\text{H}^+]$ and different ratios of the reactants. For $[\text{Ce(IV)}]/[\text{H}_3\text{PO}_2] = 0.002/0.005$ the salt effect is negative and for this ratio equal to 1 or above salt effect is positive. These results are presented in Table 2. It is obvious that at least two different mechanisms are operating in the system depending on the ratio of the reactants.

Effect of hydrogen ion

The $[\text{H}^+]$ at different ratios of reactants and at constant ionic strength of 3.0 mol dm$^{-3}$ (lithium perchlorate) was varied by adding perchloric acid. The rates increase with the increase in $[\text{H}^+]$ and the plots of rate versus $[\text{HClO}_4]$ at different ratios of the reactants are linear passing through the origin.

Table 1 — Comparison of Calculated and Observed Rates for Some Selected Concentrations of Ce(IV) and $\text{H}_3\text{PO}_2$

<table>
<thead>
<tr>
<th>$10^3[\text{Ce(IV)}]_T$ (mol dm$^{-3}$)</th>
<th>$10^3[\text{H}_3\text{PO}_2]_T$ (mol dm$^{-3}$)</th>
<th>$10^3[\text{Ce(IV)}]_f$ (mol dm$^{-3}$)</th>
<th>$10^3[\text{H}_3\text{PO}_2]_f$ (mol dm$^{-3}$)</th>
<th>$10^7$ Rate (mol dm$^{-3}$ s$^{-1}$)</th>
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</tr>
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<tr>
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<td>$2.10 \times 10^{-6}$</td>
<td>$9.223$</td>
<td>6.5</td>
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* These values were not determined, but calculated on the basis of other determined values.

† Rates were calculated from Eq. (17) with $k_1, k_2, k_3$ and $k_4$ equal to $5.4 \times 10^3, 1.65 \times 10^4, 2.05 \times 10^4$ and $2.5 \times 10^3$ respectively, and $\beta_1, \beta_2, \beta_3,$ and $\beta_4$ equal to $3.65 \times 10^4, 7.85 \times 10^6, 11.8 \times 10^6$ and $11.2 \times 10^2$ respectively; $k$ was $0.1$ dm$^3$ mol$^{-1}$ s$^{-1}$.

Suffixes T and f mean total and free concentrations respectively.
Table 2—Effect of Ionic Strength on Ag(I) Catalyzed Oxidation of H₃PO₂ by Ce(IV)

| [Ag(I)] = 5.0 x 10⁻² mol dm⁻³ | [HClO₄] = 0.5 mol dm⁻³ | [Ce(IV)] = 2.0 x 10⁻² mol dm⁻³; temp. = 30° C
<table>
<thead>
<tr>
<th>[LiClO₄] (mol dm⁻³)</th>
<th>10⁻¹(μ)(mol dm⁻³ s⁻¹) at</th>
<th>[H₃PO₂]/[Ce(IV)] ratios</th>
</tr>
</thead>
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<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
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</tr>
<tr>
<td>1.0</td>
<td>0.875</td>
<td>0.875</td>
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</tr>
<tr>
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</tr>
<tr>
<td>2.5</td>
<td>2.65</td>
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</tr>
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</table>

Thermodynamic parameters

Reactions with different reactant ratios were studied at 35°, 40° and 45° C. The energies of activation for [Ce(IV)]/[H₃PO₂] = 4:1, 1:1, 1:2, 1:2.5, 1:3 and 1:4 are 90, 75, 71, 74, 75 and 74.0 kJ mol⁻¹ respectively with an average deviation of ±2 kJ mol⁻¹.

Reaction of Ce(IV) with Ag(I)

This reaction has been studied by precipitating Ag(II) as 2,2'-bipyridyl complex, centrifuging and determining [Ce(IV)]. The orders with respect to Ce(IV) and Ag(I) are found to be one, and the second order rate constant is found to be 4 x 10⁻³ dm³ mol⁻¹ s⁻¹ for [HClO₄] = 0.5 mol dm⁻³ at 30° C.

Complex formation

The absorption spectra of ceric perchlorate, and different mixtures of Ce(IV) and H₃PO₂ in perchloric acid solutions are shown in Fig. 4. The absorbance of the mixture increases with the increase in [H₃PO₂]. Since H₃PO₂ does not absorb in the wavelength region shown, it is obvious that various complexes of Ce(IV) and H₃PO₂ are formed. Absorbance of 8.0 x 10⁻³ mol dm⁻³ Ce(IV) in mixtures with different concentrations of H₃PO₂ in 0.5 mol dm⁻³ HClO₄ were measured at 285 nm at 30° C, and from this successive formation constants for Ce(IV) complexes were calculated by Yatsimirskii's method. They were found to be: K₁ = 3.65 x 10³; K₂ = 2.15 x 10³; K₃ = 1.50 x 10³; K₄ = 9.5 x 10²; K₅ = 1.3 x 10²; and K₆ = 60 dm³ mol⁻¹ (all values within a precision of ±10-15%). Spectrophotometric measurements made on the mixtures of Ag(I) and H₃PO₂ in perchloric acid solutions also indicated weak complex formation between Ag(I)-and H₃PO₂.

Discussion

The results show that the rate is a complex function of [H₃PO₂]/[Ce(IV)] ratio. It is thus difficult to give a comprehensive rate-law and the mechanism covering all the features of the reaction. Hydrogen ion dependence is simple. Silver(I) dependence is clear cut and significant mechanistically. On the basis of [Ag(I)] and [H⁺] dependences only and at fixed [Ce(IV)] and [H₃PO₂] the empirical rate law (3) holds.

\[-d[Ce(IV)]/dt = A[H⁺] + B[H⁺][Ag(I)] \]  

where A and B are complex rate constants involving Ce(IV) and H₃PO₂. Further evidence for such a rate law is provided by the similarities in values of intercepts of plots in Fig. 3 and the rates of uncatalyzed reactions determined independently under identical conditions. Another fact of mechanistic importance is the plots in Fig. 2. If one disregards the variation of [H₃PO₂] and considers only the variation of [Ce(IV)], it is obvious that the apparent order in Ce(IV) is one since the linear plots in Fig. 2 pass through the origin. However, it must be noted that Ce(IV) is present in the form of complexes with H₃PO₂. Thus the empirical rate law (3) can be put in a more precise form (4)

\[-d[Ce(IV)]/dt = (\Sigma[Ce(IV) complex]) [H⁺] (k + k₂[Ag(I)]) \]  

The values of k and k₂ are given in Table 3. The values of \((k + k₂[Ag(I)])\) obtained from Fig. 2 are 1.64 x 10⁻⁴, 4.3 x 10⁻⁴, 7.1 x 10⁻⁴, 10.8 x 10⁻⁴, 13.6 x 10⁻⁴ and 17.2 x 10⁻⁴ dm³ mol⁻¹ s⁻¹ for [Ce(IV)]/[H₃PO₂] = 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6 respectively. The corresponding calculated values obtained from the
data in Table 3 are $1.6 \times 10^{-4}$, $4.8 \times 10^{-4}$, $8.7 \times 10^{-4}$, $12 \times 10^{-4}$, $16 \times 10^{-4}$ and $18 \times 10^{-4} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$. Thus there is internal consistency so far as [Ag(I)] dependence and limited [Ce(IV)] and [H$_3$PO$_3$] dependences are concerned.

The values of $(k + k_e[\text{Ag(I)}])$ obtained from the linear plots of initial rate versus [H$^+$] are $1.9 \times 10^{-4}$, $2.6 \times 10^{-4}$ and $3 \times 10^{-4} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 30$^\circ$C and $I = 3.0 \text{mol dm}^{-3}$ for [Ce(IV)]/[H$_3$PO$_3$] = 1:1, 1:2 and 1:3 respectively. The value $1.9 \times 10^{-4} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ obtained from [H$^+$] variation data for 1:1 ratio is slightly larger than that (1.64 x $10^{-4}$) obtained from Fig. 2 or Fig. 3, because the ionic strength is larger in the [H$^+$] variation. The values $2.6 \times 10^{-4}$ and $3.0 \times 10^{-4}$ obtained from [H$^+$] variation data for 1:2 and 1:3 ratios are smaller than the corresponding values (4.3 x $10^{-4}$ and 7.1 x $10^{-4}$) obtained from Fig. 2, again in line with the ionic strength dependence. The variation of the effect of ionic strength on the rate with the variation in the composition of the complex is somewhat unusual because there appears to be no difference in the charge on the activated complex under the two situations.

It may now be worthwhile to discuss the various species participating in the reaction. Carroll and Thomas$^8$ have reported at least three complexes of Ce$^{3+}$ with H$_3$PO$_3$. Treindl and Hatala$^9$ have indicated six complexes from solubility and spectrophotometric measurements and all the formation constants are reported to be large. Our spectrophotometric data also show the formation of six complexes, 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6. Similarly there is kinetic and spectrophotometric evidence for a complex between Ag(I) and H$_3$PO$_3$ and a formation constant of 138 has been reported$^{14}$.

The catalysis by Ag(I) in the present investigation operates preferably through its complex AgH$_3$PO$_3$. This conclusion is corroborated by the results of Fig. 3 wherein catalysis by Ag(I) becomes significant only for larger ratios of [H$_3$PO$_2$]/[Ce(IV)] because more free [H$_3$PO$_2$] is available at high total [H$_3$PO$_3$]. Catalysis by Ag(I) has been explained by complex formation; also in the oxidations of isopropyl alcohol$^{19,20}$ and other oxygen containing compounds$^{21}$.

At this juncture two facts have to be considered. Only four complexes (as will be seen later) of Ce(IV) with H$_3$PO$_2$, viz., 1:1, 1:2, 1:3 and 1:4 have been found to be reactive. If this is so, the rate should decrease with the formation of 1:5 and 1:6 complexes at higher H$_3$PO$_2$ and fixed [Ce(IV)], or low [Ce(IV)] and fixed [H$_3$PO$_3$]. While limiting rates are obtained at low [Ce(IV)], no such behaviour is observed at large [H$_3$PO$_3$] (see Fig. 1). This is probably due to the fact that at large [H$_3$PO$_3$], the free [H$_3$PO$_3$] becomes large enough to make the reaction of Ag(I) and H$_3$PO$_2$ significant, and Ce(IV) is used up in the rapidly operating Ag(O)/Ag(I) cycle. Similarly for the reactions having [Ce(IV)]/[H$_3$PO$_3$] ratio of 0.1, the reason for the constant rate is the significant contribution from (Ag(I) + H$_3$PO$_2$) reaction and Ce(IV) is involved in a fast step.

For large [Ce(IV)], the rate is constant since 1:1 complex is the only one which is predominantly formed for ([Ce(IV)]/[H$_3$PO$_3$]) > 2 and this only contributes to the rate. Since [H$_3$PO$_3$] is fixed, the concentration of the complex is almost fixed and the rate is constant. Thus the contribution from equilibrium (I) should be negligible since the rate constant for the forward reaction is only $4 \times 10^{-3} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$.

The hydrogen ion effect is positive and this is one more example of tautomeric equilibrium$^{22}$ involving normal and active forms of H$_3$PO$_2$ participating in such systems, though there is no direct evidence. The catalysis by [H$^+$] increases with the increase of the ratio [H$_3$PO$_2$]/[Ce(IV)], presumably because larger free [H$_3$PO$_2$] is available. Hydrogen ion can have a role through the dissociation of H$_3$PO$_2$ also. Since its dissociation constant$^{16}$ is 0.135 at 25$^\circ$C and $I = 1.0 \text{mol dm}^{-3}$, and hence both undissociated molecule and the anion of H$_3$PO$_2$ would exist under the acid conditions employed. The positive [H$^+$] effect on the rate through the two forms of H$_3$PO$_2$ would be possible only if the rate increases and attains a limiting value. No such effect is noticed. Also UV spectra of mixtures of Ce(IV) and H$_3$PO$_3$ in aqueous perchloric acid media (0.1 to 2 mol dm$^{-3}$ HClO$_4$) are similar and hence complex formation is not influenced by the variation in the concentration of two species of H$_3$PO$_2$. Thus both the forms of H$_3$PO$_2$ seem to be capable of complexing with Ce(IV) and hydrogen ion has a role in the transformation of normal form to active form of H$_3$PO$_2$.

Thus the results for ([H$_3$PO$_3$]/[Ce(IV)]) $\approx$ 10.0 to 0.2 can be satisfactorily explained and the following mechanism may be suggested.

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Table 3 – Values of $k$ and $k_e$ of the Ag(I) Catalyzed Reaction of Ce(IV) with H$_3$PO$_2$ at 30$^\circ$C from the Variation of Ag(I) at Different [Ce(IV)]/[H$_3$PO$_2$] Ratios

<table>
<thead>
<tr>
<th>[Ce(IV)]/[H$_3$PO$_2$] Ratios</th>
<th>$10^5$[H$_3$PO$_2$] (mol dm$^{-3}$)</th>
<th>$10^4 k$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$k_e$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
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</table>
Path 1 (uncatalyzed)

\[ Ce^{4+} + mH_3PO_2 \rightleftharpoons [Ce(IV)(H_3PO_2)_m]^{4+} \tag{5} \]

where \( m = 1, 2, 3 \) or 4

\[ ([H_3PO_2]_mCe(IV)(H_3PO_2)_a]^{4+} + H^+ \rightleftharpoons \tag{6} \]

where \( (H_3PO_2)_m \) and \( (H_3PO_2)_a \) are normal and active forms respectively.

\[ ([H_3PO_2]_mCe(IV)(H_3PO_2)_a]^{4+} + H^+ \rightarrow \text{products} \tag{7} \]

Path 2 (catalyzed) (a) and (b)

(a)

\[ Ag^+ + H_3PO_2 \rightleftharpoons AgH_3PO_2^+ \tag{8} \]

\[ [Ce(IV)(H_3PO_2)_m]^{3+} + AgH_3PO_2^+ \rightleftharpoons [([H_3PO_2]_mCe(IV)(H_3PO_2)_Ag]^{3+} \tag{9} \]

\[ ([H_3PO_2]_mCe(IV)(H_3PO_2)_a]^{5+} + H^+ \rightleftharpoons \tag{10} \]

\[ ([H_3PO_2]_mCe(IV)(H_3PO_2)_Ag]^{5+} + H^+ \rightarrow \text{products} \tag{11} \]

(b)

\[ Ag(II) + H_3PO_2 \rightarrow Ag(O) + H_3PO_2^+ \tag{12} \]

\[ Ag(II) + H_3PO_2^+ + H_2O \rightarrow Ag(O) + H_3PO_3 + 2H^+ \tag{13} \]

\[ Ag(O) + Ce(IV) \rightarrow Ag(I) + Ce(III) \tag{14} \]

The hydrogen ion catalysis may operate before step (9) via complex \([Ce(IV)(H_3PO_2)_m]^{5+}\) or \(AgH_3PO_2^+\) alone. A dinuclear complex of \(Ce^{4+}\) and \(Ag^+\) as shown in equilibrium (9), may be formed with two molecules of hypophosphite, one of which may be in the active form. Such a formation may facilitate electron transfer from \(H_3PO_2\) to Ce(IV) through Ag(I).

If \(K_{m}\) and \(K_{a}\) are small compared to \(K_{m}\), \(k\), \(k_{-m}[H^+]\times k_{-m}[Ce(IV)\text{ complex}],\) and \(k_{-10}[H^+]\times k_{11}[Ce(IV)(H_3PO_2)Ag(II)\text{ complex}],\) the rate law (15) may be obtained assuming a steady state for \([H_3PO_2]_m\).

\[ -\frac{d[Ce(IV)]}{dt} = \frac{k_7 \times k_6}{k_{-6}} [Ce(IV)(H_3PO_2)_m][H^+] \]

\[ + \frac{k_8 \times k_{10} \times k_{11}}{k_{-10}} [Ce(IV)(H_3PO_2)_m][H^+] \times [Ag^+] \times [H_3PO_2] \]

\[ + k[Ag(II)][H_3PO_3] \tag{15} \]

\[ = [Ce(IV)(H_3PO_2)_m][H^+] \]

\[ (k_m + k_{-m}[Ag^+][H_3PO_2]) \]

\[ + k[Ag(II)][H_3PO_3] \tag{16} \]

In Eqs. (15) and (16) \([H_3PO_2]_m\) represents free \([H_3PO_2]_m\) and all other species represent total analytical concentrations. The empirical rate law corresponding to (16) has already been verified at constant \([Ce(IV)]\) and \([H_3PO_2]_m\) or at constant \([Ce(IV)]/[H_3PO_2]_m\) ratio.

Since the mechanism of uncatalyzed reaction is already known and its rate can be determined independently, it can be put separately in the rate law and then writing all the probable steps of the catalyzed reaction, we get.

\[ -\frac{d[Ce(IV)]}{dt} = \text{uncatalyzed rate} \]

\[ + [Ce(IV)]_\text{free}[H_3PO_2]_\text{free} \]

\[ + k_3[Ag(II)][H_3PO_3]_\text{free} \]

\[ + k_4[Ag(II)][H_3PO_3]_\text{free} \]

\[ + k[Ag(II)][H_3PO_3] \tag{17} \]

where \(k_1, k_2, k_3\) and \(k_4\) are rate constants and \(\beta_1, \beta_2, \beta_3\) and \(\beta_4\) are gross formation constants of 1:1, 1:2, 1:3 and 1:4 Ce(IV)-H_3PO_2 complexes respectively. The concentrations of free \([H_3PO_2]_m\) and various Ce(IV) species were calculated by successive approximations from the equilibrium and mass balance relations. Knowing the total rate and the uncatalyzed rate, the rate constants \(k_1, k_2, k_3\) and \(k_4\) were found to be \((5.4 \pm 0.3) \times 10^{-2}, (1.65 \pm 0.2) \times 10^{-4}, (2.5 \pm 0.3) \times 10^{-3}, (2.5 \pm 0.3) \times 10^{-3}\) dm^3 mol^{-1} s^{-1} respectively by an iterative method. A comparison of the calculated rates and some of the observed rates is given in Table I.

Although the decrease in rate with increasing \([Ce(IV)]\) is due to decrease in free \([H_3PO_2]_m\), in other cases\(^{23}\) which are few, the decrease has been ascribed to dimerization\(^{24}\) or trimerization\(^{25}\) of Ce(IV). We believe that in the presence of a ligand like \(H_3PO_2\), dimerization would be sufficiently minimized. Our results at large \([Ce(IV)]\) show almost constant rate-defying trimerization. It appears from this that trimerization can perhaps occur in aqueous acetic acid medium and not without it.

One more indirect evidence for reactive complexes of Ce(IV) and \(H_3PO_2\) is provided by the linearity of the plots of \([Ce(IV)]\) versus time for each run. Since the stoichiometry is given by Eq.(2) the fraction of the free \([H_3PO_2]_m\) goes on increasing with time in any individual run and thus the decrease in \([Ce(IV)]\) per unit time is almost constant. However, for \([Ce(IV)]/[H_3PO_2]_m > 2\), the plots yield normal curves because there is only one complex (probably 1:1) which is reactive and its concentration goes on decreasing.

Equilibrium (1) does not seem to operate. Since the backward rate constant\(^{26}\) of equilibrium (1) is \(5.0 \times 10^{3}\) dm^3 mol^{-1} s^{-1} at 25° and \([HClO_4] = 4.0\) mol dm^{-3} and the rate constant for the forward reaction is \(4 \times 10^{-3}\) dm^3 mol^{-1} s^{-1} at \([H^+] = 0.5\) mol dm^{-3} and 30°, the equilibrium concentration of Ag(II) would be small. The rate constant for Ag(II)-H_3PO_2 reaction
has been found to be $7.6 \times 10^2 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ at $30^\circ$. Thus if equilibrium (1) were to be significant in this redox reaction, the rate would be independent on $[\text{H}_3\text{PO}_2]$ and the rate constant would be $4 \times 10^{-3} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$. None of these facts is true in the catalysed reaction. There is no inverse effect of $[\text{Ce(II)}]$ on the reaction in the range $0.001$ to $0.05 \text{mol dm}^{-3}$. From all these considerations it appears that Ag(I) catalysis does not operate through Ag(I)/Ag(II) cycle.

An overall activation energy of $(90 \pm 1) \text{kJ mol}^{-1}$ for excess Ce(IV), and an average value of $73 \text{kJ mol}^{-1}$ (with a deviation of not more than $2.1 \text{kJ mol}^{-1}$ in any case) for other ratios of reactants have been obtained. The first value is somewhat comparable to a value of $104 \text{kJ mol}^{-1}$ obtained by Carroll and Thomas\(^8\) or to a value of $98 \text{kJ mol}^{-1}$ obtained by Treindl and Hatala\(^9\) for the uncatalyzed reaction. This is in line with the fact that catalysis by Ag(I) does not operate for $[\text{Ce(IV)}] > [\text{H}_3\text{PO}_2]$. However, one must note that the values obtained by previous workers are composite for all Ce(IV)-complexes.

References
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