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Kinetic and mechanistic aspects of metal ion catalysis in cerium(IV) oxidation

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Contents

Abstract

This review discusses the kinetic aspects of different metal ion catalysis in Ce(IV) oxidation of different types of organic and inorganic substrates in aqueous acid media. The reactions have been categorised with the metal ions acting as the catalysts. The nature of mechanism

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of catalysis in Ce(IV) oxidation depends on the nature of substrate for a particular metal ion catalyst and it also largely depends on the nature of acid medium used. The utility and scope of the catalytic oxidation by Ce(IV) in analytical chemistry are discussed.

Keywords: Cerium(IV); Oxidation; Catalysis; Kinetics

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1. Introduction

In aqueous H_2SO_4 media, Ce(IV) is both thermodynamically and kinetically weaker as an oxidising agent compared to Ce(IV) in aqueous $HClO_4$ media (cf. $E_o = 1.7$ V in 1.0 mol dm^{-3} $HClO_4$; $E_o = 1.4$ V in 1.0 mol dm^{-3} H_2SO_4). However, Ce(IV) in aqueous H_2SO_4 media is highly stable [1] and does not require any special precautions to prevent its photochemical decomposition [2] which occurs spontaneously in aqueous $HClO_4$ media. This is why Ce(IV) in aqueous H_2SO_4 media is very often used in analytical chemistry, specially in cerate oxidimetry [3]. On the other hand, Ce(IV) oxidation of different substances in aqueous H_2SO_4 media is in many cases kinetically highly sluggish and needs some metal ion catalysts [4,5]. Some metal ions (e.g. Ru(III), Ir(III)) even at ultra trace concentration can potentially catalyse the Ce(IV) oxidation reactions in many cases and such reactions can be utilised for catalytic kinetic methods of estimation [4–6]. Thus the use of suitable catalysts in Ce(IV) oxidation reaction in aqueous H_2SO_4 media is of much importance in cerate oxidimetry [4] as well as in catalytic kinetic methods of analysis [4–6]. This is why, understanding of the mechanism of metal ion catalysis in Ce(IV) oxidation reaction is important and several kinetic studies [7] in this direction have been carried out. The mechanistic paths of catalysis have been found to depend largely on the nature of substrate, metal ion acting as the catalyst and reaction medium. Until now, these fascinating aspects have not been reviewed to correlate these findings. The present review aims to contribute in this direction. Here it is worth mentioning that besides the various metal ions, halide ions are also known [8] to catalyse some Ce(IV) oxidation reactions.

2. Ce(IV) species in aqueous H_2SO_4 and $HClO_4$ media

Several equilibrium studies to characterise the different Ce(IV) species in aqueous H_2SO_4 media have been carried out [9a,b]. In this regard, the studies by Hardwick and Robertson [9a] are very important, but later on Bugaenko and Kuan-Lin [9b] have modified the observation made by Hardwick and Robertson who proposed the tri-sulfato species as $Ce(SO_4)_3^{2-}$. From the studies of Bugaenko and Kuan-Lin, it was established that the tri-sulfato species is $HCe(SO_4)_3^-$. According to their studies [9b] in aqueous H_2SO_4 media (up to ca. 2 mol dm^{-3}) the predominant equilibria are:

$$Ce^{4+} + HSO_4^- \overset{Q_1}{\rightleftarrows} Ce(SO_4)^{2+} + H^+ \tag{2.1}$$

$$Ce(SO_4)^{2+} + HSO_4^- \overset{Q_2}{\rightleftarrows} Ce(SO_4)_2 + H^+ \tag{2.2}$$

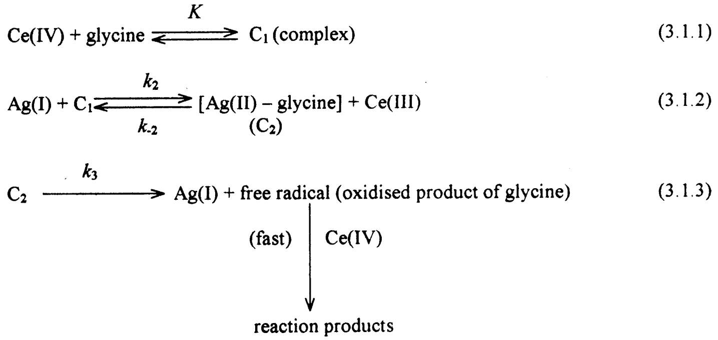
$$Ce(SO_4)_2 + HSO_4^- \overset{Q_3}{\rightleftarrows} HCe(SO_4)_3^- \tag{2.3}$$

At higher concentrations of H_2SO_4, the concentration of the $H_3Ce(SO_4)_4^-$ species gradually increases. The successive equilibrium constants [9a,b] for formation of the species are in the order: $Q_1 > Q_2 \gg Q_3$. Due to such complexation in aqueous H_2SO_4 media, the tendency of Ce(IV) species to undergo hydrolysis is remarkably suppressed, but in aqueous $HClO_4$ media, hydrolysis leads to $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ which further undergo dimerisation [9c].

3. Kinetics and mechanism of different metal ion catalysis in Ce(IV) oxidation

3.1. Ag(I) catalysis

The kinetics of Ag(I) the catalysed oxidation of glycine by Ce(IV) in aqueous $HClO_4$ media has been reported by Singh and co-workers [10]. The reaction shows a first-order dependence with respect to each of the species, i.e. Ce(IV), glycine, $HClO_4$ and Ag(I). The proposed reaction mechanism is (Scheme 1):



Scheme 1.

Applying the steady-state condition to the C_2 complex under the condition, $k_3 \gg k_{-2}$[Ce(III)], the rate is given by: rate $= k_2K$[Ce(IV)][Ag^+][glycine]. Such a reaction mechanism has also been argued [11] for Ag(I) catalysis in the oxidation of glycine by Ce(IV) in aqueous HNO_3 media.

In the Ag(I) catalysed oxidation of isopropanol by Ce(IV) in aqueous H_2SO_4 media, the change in order of the reaction with respect to [alcohol] from unity in the absence of Ag(I) has been explained [12] in terms of formation of a 1:1 complex between Ag(I) and substrate. The proposed reaction mechanism is (Scheme 2):

$$\text{Ag(I)} + \text{S} \overset{K}{\rightleftharpoons} [\text{Ag(I)} - \text{S}]\ (\text{complex})\ ;\ \text{S} = \text{substrate} \tag{3.1.4}$$

$$[\text{Ag(I)} - \text{S}] + \text{Ce(IV)} \longrightarrow \text{Ce (III)} + \text{H}^+ + \text{Ag (I)} + \text{oxidised products of the substrate} \tag{3.1.5}$$

Scheme 2.

The rate equation is:

$$-2.303\frac{\mathrm{d}\log[\text{Ce(IV)}]}{\mathrm{d}t} = k_{\text{obs}} = \frac{kK[\text{Ag}^+][\text{S}]}{\{1 + K[S]\}} \tag{3.1.6}$$

A similar reaction mechanism was proposed [13] in the oxidation of different carboxylic acids by Ce(IV) in aqueous H_2SO_4 media. The mechanistic aspects of Ag(I) catalysis in the oxidation of Hg(I) or Tl(I) by Ce(IV) have been extensively studied [14]. In the presence of a sufficiently large excess of $\{\text{Hg(I)}\}_2$ the rate of the reaction is independent of the concentration of substrate and the rate law is:

$$\frac{-\mathrm{d}[\text{Ce(IV)}]}{\mathrm{d}t} = 2k_1[\text{Ce(IV)}][\text{Ag(I)}]_{\text{initial}} \tag{3.1.7}$$

The proposed reaction mechanism is (Scheme 3):

$$\text{Ce(IV)} + \text{Ag(I)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ce(III)} + \text{Ag (II)} \tag{3.1.8}$$

$$\text{Ag(II)} + \{\text{Hg(I)}\}_2 \xrightarrow{k_2} \text{Ag(I)} + \text{Hg(II)} + \text{Hg(I)} \tag{3.1.9}$$

$$\text{Hg(I)} + \text{Ce(IV)} \xrightarrow{\text{fast}} \text{Ce(III)} + \text{Hg(II)} \tag{3.1.10}$$

Scheme 3.

Assuming the steady-state condition to Ag(II), i.e. $\mathrm{d}[\text{Ag(II)}]/\mathrm{d}t = 0$, we get:

$$\frac{-\mathrm{d}[\text{Ce(IV)}]}{\mathrm{d}t} = \frac{\mathrm{d}[\text{Hg(II)}]}{\mathrm{d}t} = \frac{2k_1[\text{Ce(IV)}][\text{Ag(I)}]_{\text{initial}}}{(k_{-1}/k_2)[\text{Ce(III)}]/[\{\text{Hg(I)}\}_2] + 1} \tag{3.1.11}$$

The value of k_{-1}/k_2 is 0.198 at $[\text{H}^+] = 1.50$ mol dm^{-3}, I = 3.0 mol dm^{-3} at 20°C. Hence in the presence of a large excess of $[\{\text{Hg(I)}\}_2]$, the term including [Ce(III)]/$[\{\text{Hg(I)}\}_2]$ is negligible compared to 1.0. Then it reduces to Eq. (3.1.7). In the case of Ag(I) [14] catalysis in oxidation of Tl(I) by Ce(IV), the same reaction scheme is believed to operate. Here, the value of k_{-1}/k_2 is 35.7, which is much larger than that of k_{-1}/k_2 in the Ce(IV)–Hg(I) system. Hence, the term containing [Ce(III)]/[Tl(I)] cannot be neglected compared to unity. Thus it shows a complicated order with respect to the reactants.

Ag(I) (in the order of 10^{-5} mol dm^{-3}) has been reported [15] to catalyse the oxidation of hypophosphite by Ce(IV) in aqueous H_2SO_4. The detailed mechanistic studies are not reported. However, the rate process is complicated due to the participation of gradually formed phosphite in the redox process. The kinetics of Ag(I) catalysed oxidation of Tl(I) by Ce(IV) in aqueous HNO_3 media has been reported by Sinha and co-workers [16].

3.2. Mn(II) catalysis

In many kinetic studies of oxidation by Ce(IV), Mn(II) has been used as an efficient catalyst. In the Mn(II) catalysed oxidation of isopropyl alcohol by Ce(IV) in aqueous H_2SO_4 under the experimental condition, $[H^+] \gg [Mn(II)] \gg [Ce(IV)]$, the rate of the process [17] increases with the increase of Mn(II) concentration. A Mn(II)/Mn(III) catalytic cycle was proposed to be involved in the oxidation process in which Mn(III) oxidises the alcohol via 1:1 complex formation.

In fact, the equilibrium, $Ce(IV) + Mn(II) \rightleftarrows Ce(III) + Mn(III)$ is rapidly attained [18]. High acid concentration (~ 2.5 mol dm^{-3}) was used to stabilise the Mn(III) species and excess Mn(II) was used so that the important reactive species in the catalysed reaction is Mn(III). In fact, the high acid concentration and high Mn(II) concentration stabilise the Mn(III) species with respect to the disproportionation equilibrium, $2Mn(III) \rightleftarrows Mn(II) + Mn(IV)$. In Ir(III)–Mn(II) mixed catalysed oxidative decarboxylation and deamination of different amino acids by Ce(IV) in aqueous H_2SO_4, Mn(III) has been proposed [19] to be the reactive intermediate in oxidising the amino acids. In the Mn(II) catalysed oxidation of hypophosphite [15], hydrazine [20a,b], Hg(I) [20c] and benzylic acid [21] in aqueous H_2SO_4 by Ce(IV), Mn(III) has been advocated as the reactive species. Both Mn(III) and Mn(IV) have been postulated as the reactive intermediates in many Mn(II) catalysed reaction mechanisms; for example, Tl(I)–Ce(IV) reaction [22a], As(III)–Ce(IV) reaction [22b] and Ce(IV)–oxalate reaction [22c]. In fact, Shaffer proposed [22a] the occurrence of the reactions, $Ce(IV) + Mn(II) \rightleftarrows Ce(III) + Mn(III)$, $Ce(IV) + Mn(III) \rightleftarrows Ce(III) + Mn(IV)$ in explaining the catalytic activity of Mn(II). Here it is interesting to note that Radhakrishnamurti and co-workers have reported [23] Mn(II) retardation in Ce(IV) oxidation of cyclohexanol in acetic acid–water mixtures in the presence of $HClO_4$. This has been attributed to ligand stabilisation of Mn(III) or stabilisation of Mn(IV) (a dismutation product of Mn(III)) through complexation in acetic acid–water system making it ineffective as an oxidant.

In the Mn(II) catalysed oxidation of As(III) in aqueous H_2SO_4, the participation of the Mn(III) species was proposed [24] in the catalytic process under the conditions, $[H^+] \gg [Ce(IV)] \gg [Mn(II)]$. The reaction scheme was proposed as (Scheme 4):

$$\mathrm{Ce(IV) + Mn(II)} \underset{k_b}{\overset{k_a}{\rightleftarrows}} \mathrm{Ce(III) + Mn(III)} \qquad (3.2.1)$$

$$\mathrm{Mn(III) + As(III)} \overset{K}{\rightleftarrows} \mathrm{Mn(III).\,As(III)} \qquad (3.2.2)$$

$$\mathrm{Mn(III).As(III) + H^+} \xrightarrow{k_c} \mathrm{Mn(II) + As(IV)} \qquad (3.2.3)$$

$$\mathrm{Ce(IV) + As(IV)} \xrightarrow{\text{fast}} \mathrm{Ce(III) + As(V)} \qquad (3.2.4)$$

Scheme 4.

This leads to:

$$\text{Rate} = \frac{2k_a k_c K[\text{Ce(IV)}][\text{Mn(II)}][\text{As(III)}][\text{H}^+]}{\{k_b[\text{Ce(III)}] + K[\text{As(III)}](1 - k_c[\text{H}^+])\}} \tag{3.2.5}$$

In the scheme, the disproportionation of Mn(III) has been ignored. Here $H_3Ce(SO_4)_4^-$ has been argued as the kinetically active Ce(IV) species.

3.3. Cu(II) catalysis

The kinetics of Cu(II) catalysed oxidation of mannitol by Ce(IV) in aqueous H_2SO_4 media was reported by Reddy and co-workers [25]. The process is also catalysed by other metal ions like Co(II), Ni(II) and Zn(II) and the catalytic efficiency runs as: Cu(II) > Co(II) > Ni(II) > Zn(II). The order with respect to [mannitol] in the presence of the catalyst metal ions is found to be less than unity (e.g. 0.68 in the presence of Cu(II) and 1.0 in the absence of the catalyst metal ions). The proposed mechanism involves the formation of a 1:1 complex followed by the oxidation by Ce(IV) (Scheme 5).

$$\text{Cu(II)} + C_6H_{12}O_6 \rightleftharpoons \text{complex} \xrightarrow[\text{slow}]{\text{Ce(IV)}} \text{Ce(III)} + \text{oxidised product of mannitol} \tag{3.3.1}$$

Scheme 5.

In the oxidation of different organic carboxylic acids by Ce(IV) in aqueous H_2SO_4, Cu(II) has been found [13] to potentiate the catalytic activity of Ag(I). Here it is important to mention that Ag(I) itself can alone show the catalytic activity, but Cu(II) alone cannot show any catalytic activity in this reaction. The mixed catalyst, Ag(I) + Cu(II), can act synergistically but the rate is independent of [Cu(II)] in the mixed catalyst system. A mechanism involving the rapid oxidation of the radicals produced by Cu(II) has been proposed to explain the results. In fact, Cu(II) is known to trap the radicals efficiently [26,27] and it can oxidise the trapped radicals at a facile step. The Cu(I) thus formed is rapidly oxidised by Ce(IV).

3.4. Cr(III) catalysis

The kinetics of the Cr(III) catalysed oxidation of dimethyl sulfoxide (DMSO) by Ce(IV) in aqueous $HClO_4$ was reported by Raju and co-workers [28]. Here the Cr(III)–Cr(IV) catalytic cycle is believed to operate as follows (Scheme 6):

$$\text{Ce(IV)} + \text{Cr(III)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ce(III)} + \text{Cr(IV)} \tag{3.4.1}$$

$$\text{Cr(IV)} + \text{S} \xrightarrow{k_2} \text{Cr(III)} + \text{S}^{\bullet} \tag{3.4.2}$$

$$\text{Ce(IV)} + \text{S}^{\bullet} + H_2O \longrightarrow \text{Ce(III)} + \text{P} + 2\text{H}^+ \tag{3.4.3}$$

(S = DMSO, P = dimethylsulfone)

Scheme 6.

The above scheme leads to the following rate law:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=\frac{2k_1k_2[\mathrm{Ce(IV)}][\mathrm{Cr(III)}][\mathrm{DMSO}]}{\{k_{-1}[\mathrm{Ce(III)}]+k_2[\mathrm{DMSO}]\}} \tag{3.4.4}$$

Cr(III) is known [29] to efficiently catalyse in the oxidation of As(III) by Ce(IV). A similar reaction mechanism to the case of DMSO was found [30] to operate in the oxidation of As(III) by Ce(IV) in aqueous H_2SO_4. The corresponding rate constants (at 40°C, I = 1.6 mol dm^{-3}) are: $k_1 = 0.59$ dm^3 $mol^{-1}s^{-1}$, $k_{-1}/k_2 = 0.4$. Here, $H_3Ce(SO_4)_4^-$ has been argued as the reactive species.

Cr(III) was reported by Mehrotra and co-workers [31] to catalyse the Ce(IV) oxidation of formic acid. Recently, a detailed kinetic study of the system has been carried out by us [32a]. The proposed mechanism involves the participation of Cr(IV) which binds the substrate to form an inner-sphere complex and then electron transfer occurs within the complex to produce an intermediate, Cr(III) bound to the formate ion radical, which rapidly gets oxidised by Ce(IV). The free radical generated through an inner-sphere electron transfer process is bound to an inert Cr(III) centre and consequently the radical is not readily available in solution to initiate the polymerisation process of acrylonitrile in the bulk. In fact, for the catalysed reaction, polymerisation of acrylonitrile has been found to proceed slowly compared to the uncatalysed reaction, i.e. in the absence of Cr(III). Mn(II) has been found to act antagonistically with Cr(III). It indirectly supports the participation of Cr(IV). A similar reaction mechanism has been suggested for the Cr(III) catalysed oxidation of ethanol [32b] and different diols [32c] by Ce(IV) in aqueous H_2SO_4.

3.5. Os(VIII) catalysis

In the Os(VIII) catalysed oxidation of Tl(I) by Ce(IV) in aqueous H_2SO_4, the rate is directly proportional to the concentration of Os(VIII). The proposed [33] reaction mechanism is (Scheme 7):

$$\mathrm{Ce(SO_4)_2} + \mathrm{Tl(I)} \overset{K}{\rightleftharpoons} \mathrm{TlCe(SO_4)_2^+} \tag{3.5.1}$$

$$\mathrm{TlCe(SO_4)_2^+} + \mathrm{OsO_4} \xrightarrow[\text{slow}]{k} \mathrm{Tl(III)} + \mathrm{Ce(SO_4)_2} + \mathrm{OsO_4^{2-}} \tag{3.5.2}$$

$$2\mathrm{Ce(SO_4)_2} + \mathrm{OsO_4^{2-}} \xrightarrow{\text{fast}} 2\mathrm{Ce(SO_4)_2^-} + \mathrm{OsO_4} \tag{3.5.3}$$

Scheme 7.

This leads to:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=kK[\mathrm{Ce(SO_4)_2}][\mathrm{Tl(I)}][\mathrm{OsO_4}] \tag{3.5.4}$$

In HNO_3 considering the Os(VIII) catalysed oxidation of Tl(I), the same mechanism has been proposed [34] involving $Ce(OH)^{3+}$ as the active oxidant. In the

Os(VIII) catalysed oxidation of As(III) by Ce(IV) in aqueous H_2SO_4, the proposed [35] reaction mechanism is (Scheme 8):

$$\mathrm{Os(VIII)} + \mathrm{As(III)} \xrightleftharpoons{K} \mathrm{Complex\ (C_1)} \qquad (3.5.5)$$

$$\mathrm{C_1} + \mathrm{Ce(IV)} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{Complex\ (C_2)} \qquad (3.5.6)$$

$$\mathrm{C_2} \xrightarrow[\text{slow}]{k} \mathrm{Os(VII)} + \mathrm{Ce(III)} + \mathrm{As(V)} \qquad (3.5.7)$$

$$\mathrm{Os(VIII)} + \mathrm{Ce(IV)} \xrightarrow{\text{fast}} \mathrm{Ce(III)} + \mathrm{Os(VIII)} \qquad (3.5.8)$$

Scheme 8.

This leads to the following rate law for the steady-state of C_2:

$$\frac{-\,\mathrm{d[Ce(IV)]}}{\mathrm{d}t} = \frac{kKk_{-3}}{(k_{-1}+k)}\mathrm{[Os(VIII)][Ce(IV)][As(III)]} \qquad (3.5.9)$$

The Os(VIII) catalysed oxidation of As(III) by Ce(IV) in aqueous H_2SO_4 had been reported earlier by Sandel and co-workers [36]. A detailed kinetic study of this reaction in H_2SO_4 by different workers [37,38] revealed the mechanistic aspects of the reaction. The reaction [37] is first-order in [Os(VIII)] over a wide concentration range and the rate is identical for both Os(IV) and Os(VIII). The Ce(IV) and As(III) dependencies are complex in nature and these depend on the relative ratios of these two species. As(III) reduces Os(VIII) to Os(VI) and Os(IV) by two electron steps. The reduced Os(VI) and Os(IV) are reoxidised to Os(VIII) by Ce(IV) in one electron steps. The process is first-order with respect to [As(III)] at low ratios of [As(III)]/[Ce(IV)] but it tends to be zero-order as the ratio increases. On the other hand, the process is first-order with respect to [Ce(IV)] at low ratios of [Ce(IV)]/[As(III)] but the trend breaks off sharply to a narrow region of zero-order dependence and then it passes through a region of negative dependency to zero dependency as the ratio, i.e. [Ce(IV)]/[As(III)], is increased further. The rates are independent of As(V) or Ce(III) concentrations indicating irreversible reactions. The proposed pathways are (Scheme 9):

$$\mathrm{As(III)} + \mathrm{Os(VIII)} \xrightarrow{k_1} \mathrm{As(V)} + \mathrm{Os(VI)} \qquad (3.5.10)$$

$$\mathrm{Ce(IV)} + \mathrm{Os(VI)} \xrightarrow{k_2} \mathrm{Ce(III)} + \mathrm{Os(VII)} \qquad (3.5.11)$$

$$\mathrm{Ce(IV)} + \mathrm{Os(VII)} \xrightarrow{k_3} \mathrm{Ce(III)} + \mathrm{Os(VIII)} \qquad (3.5.12)$$

$$\mathrm{As(III)} + \mathrm{Os(VI)} \xrightarrow{k_4} \mathrm{As(V)} + \mathrm{Os(IV)} \qquad (3.5.13)$$

$$\mathrm{Ce(IV)} + \mathrm{Os(IV)} \xrightarrow{k_5} \mathrm{Ce(III)} + \mathrm{Os(V)} \qquad (3.5.14)$$

$$\mathrm{Ce(IV)} + \mathrm{Os(V)} \xrightarrow{k_6} \mathrm{Ce(III)} + \mathrm{Os(VI)} \qquad (3.5.15)$$

Scheme 9.

If the steady-state condition is now applied to each of the Os-species then the following rate law is obtained.

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = r = A[\mathrm{Ce(IV)}][\mathrm{As(III)}][\mathrm{Os}]_{\mathrm{T}} \times \frac{k_4[\mathrm{As(III)}] + k_2[\mathrm{Ce(IV)}]}{B[\mathrm{Ce(IV)}]^2 + C[\mathrm{Ce(IV)}][\mathrm{As(III)}] + D[\mathrm{As(III)}]^2} \tag{3.5.16}$$

where, $A = 2k_1k_3k_5k_6$, $B = k_2k_3k_5k_6$, $C = k_1k_5k_6(k_2 + k_9)$ and $D = k_1k_3k_4(k_5 + k_6)$. If $[\mathrm{Ce(IV)}] \gg [\mathrm{As(III)}]$, then Eq. (3.5.16) is reduced to: $r = 2k_1[\mathrm{As(III)}][\mathrm{Os}]_{\mathrm{T}}$, i.e. zero-order dependence on [Ce(IV)] and first-order dependence on [As(III)]; but if $[\mathrm{Ce(IV)}] \ll [\mathrm{As(III)}]$ then Eq. (3.5.16) is reduced to: $r = \{2k_5k_6/(k_5 + k_6)\}[\mathrm{Ce(IV)}][\mathrm{Os}]_{\mathrm{T}}$, i.e. zero-order dependence on [As(III)] and first-order dependence on [Ce(IV)]. The odd numbered oxidation states of osmium, e.g. Os(V) and Os(VII), are relatively unstable in solution. Thus under the reasonable approximations, $k_3 \gg k_2$ and $k_6 \gg k_5$ we obtain, $r = 2k_5[\mathrm{Ce(IV)}][\mathrm{Os}]_{\mathrm{T}}$ when, $[\mathrm{Ce(IV)}] \ll [\mathrm{As(III)}]$.

Now, let us consider the relative importance of the catalytic cycles Os(VIII)/Os(VI) (in the reactions 3.5.10-12) and Os(VI)/Os(IV) (in the reactions 3.5.13-15). For small values of the ratio [Ce(IV)]/[As(III)], the rate determining step is the reaction 3.5.14) and the catalytic cycle will involve the lower oxidation state, i.e. Os(VI)/Os(IV) cycle. As the ratio [Ce(IV)]/[As(III)] is increased, the reaction 3.5.11 starts to compete with the reaction 3.5.13 for the Os(VI) species. At this point, some of the osmium will be forced to enter into the higher oxidation state cycle. When a significant amount of osmium is accumulated to Os(VIII), the rate determining step will start to shift to the reaction 3.5.10 which is slower than the reaction 3.5.14 and consequently the observed rate will decrease. When [Ce(IV)] is made very large, the k_1 path will be the sole rate determining step and the process shows a zero-order dependence on [Ce(IV)].

Recently we have carried out [39] the kinetics and mechanism of the Os(VIII) mediated Ce(IV) oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone ($\mathrm{DMSO_2}$) is aqueous $\mathrm{H_2SO_4}$ under the conditions, $[\mathrm{DMSO}]_{\mathrm{T}} \gg [\mathrm{Ce(IV)}_{\mathrm{T}}] \gg [\mathrm{Os}]_{\mathrm{T}}$ (= added concentration of osmium). The rate of disappearance of [Ce(IV)] shows a first-order dependence on both $[\mathrm{Os}]_{\mathrm{T}}$ and $[\mathrm{DMSO}]_{\mathrm{T}}$ and a zeroth order kinetics with respect to [Ce(IV)]. The rate law is:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = k_{\mathrm{o}} = k[\mathrm{Os}]_{\mathrm{T}}[\mathrm{DMSO}]_{\mathrm{T}} \tag{3.5.17}$$

The values of k and the activation parameters are: $10^2k = 4.9\ \mathrm{dm^3\,mol^{-1}s^{-1}}$ at 40°C, $[\mathrm{H_2SO_4}] = 1.0\ \mathrm{mol\,dm^{-3}}$; $\Delta H^{\neq} = 58 \pm 3\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -88 \pm 5\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The proposed reaction mechanism is (Scheme 10):

$$\mathrm{S} + \mathrm{Os(VIII)} \xrightarrow{k_1} \mathrm{P} + \mathrm{Os(VI)} \tag{3.5.18}$$

$$\mathrm{Ce(IV)} + \mathrm{Os(VI)} \xrightarrow{k_2} \mathrm{Ce(III)} + \mathrm{Os(VII)} \tag{3.5.19}$$

$$\mathrm{Ce(IV)} + \mathrm{Os(VII)} \xrightarrow{k_3} \mathrm{Ce(III)} + \mathrm{Os(VIII)} \tag{3.5.20}$$

$\mathrm{S} = \mathrm{Me_2SO}$, $\mathrm{P} = \mathrm{Me_2SO_2}$

Scheme 10.

Under the steady-state conditions to each of the Os-species, the rate law is:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=\frac{2k_1k_2k_3[\mathrm{Ce(IV)}][\mathrm{S}][\mathrm{Os}]_\mathrm{T}}{\{k_2k_3[\mathrm{Ce(IV)}]+k_1(k_2+k_3)[\mathrm{S}]\}} \tag{3.5.21}$$

Under the conditions, $k_2k_3[\mathrm{Ce(IV)}] \gg k_1(k_2+k_3)[\mathrm{S}]$ and $[\mathrm{S}] \approx [\mathrm{S}]_\mathrm{T}$, Eq. (3.5.21) leads to:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=2k_1[\mathrm{DMSO}]_\mathrm{T}[\mathrm{Os}]_\mathrm{T}=k[\mathrm{DMSO}]_\mathrm{T}[\mathrm{Os}]_\mathrm{T} \tag{3.5.22}$$

The approximation taken is justified by considering the relative values (at 25°C) of the rate constants: $k_1 = 7.3\times10^{-3} \ll k_2 = k_3 = 8.1\times10^{4}$ dm^3 mol^{-1} s^{-1} [37].

3.6. *Ru(III) catalysis*

Sandel and co-workers [36] investigated the dynamics and mechanism of ruthenium catalysed oxidation of As(III) by Ce(IV) in 2.0 mol dm^{-3} H_2SO_4. The rate expression involving the constants A and B (at 25°C) is:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=\frac{A[\mathrm{Ru}][\mathrm{Ce(IV)}]^{2.5}}{1\,+\,B[\mathrm{Ce(IV)}]^{1.5}} \tag{3.6.1}$$

The process shows a first-order dependence on ruthenium concentration but a complex dependency on [Ce(IV)]. The rate process is independent of As(III), As(V) and Ce(III) concentration. The rate process does not depend on the nature of oxidation state of ruthenium originally present.

In the Ru(III) catalysed oxidation of chalcones by Ce(IV) in aqueous H_2SO_4–HOAc, a fractional order both in [chalcone] and [Ru(III)] and unit order in [Ce(IV)] have been explained [40] by considering a rapid pre-equlibrium step leading to the formation of a Ru(III)–substrate complex which is oxidised by Ce(IV) to a Ru(IV)–substrate complex in the rate determining step followed by the rapid redox decomposition of the Ru(IV)–substrate complex, i.e. (Scheme 11).

$$\mathrm{Ru(III)} + \text{substrate} \overset{K}{\rightleftharpoons} \text{Ru(III)–substrate complex, }(\mathrm{C_1}) \tag{3.6.2}$$

$$\mathrm{C_1} + \mathrm{Ce(IV)} \xrightarrow[\text{(slow)}]{k} \text{Ru(IV)–substrate complex, }(\mathrm{C_2}) + \mathrm{Ce\,(III)} \tag{3.6.3}$$

$$\mathrm{C_2} \xrightarrow{\text{fast}} \text{oxidised product of the substrate} + \mathrm{Ru(III)} \tag{3.6.4}$$

Scheme 11.

This leads to:

$$\frac{-\,\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=\frac{kK[\mathrm{substrate}][\mathrm{Ce(IV)}][\mathrm{Ru(III)}]}{1+K[\mathrm{chalcone}]+K[\mathrm{Ru(III)}]} \tag{3.6.5}$$

The proposed rate-law needs critical review. Under the experimental conditions, [Ru(III)] (ca. 10^{-6} to 10^{-7} mol dm^{-3}) $\ll$ [substrate] (ca. 10^{-1} to 10^{-2} mol dm^{-3}), $K[\mathrm{substrate}] \gg K[\mathrm{Ru(III)}]$, the rate Eq. (3.6.5) can hardly explain the observed fractional order in [Ru(III)]. This demands a different reaction mechanism to explain the experimental observations. Such a dubious reaction mechanism has been proposed in the Ru(III) catalysed oxidation of propanol [41], ethyleneglycol [41], mannitol [41] and amines [42] by Ce(IV). Here it is important to note that the proposed reaction mechanism could not explain the observed fractional order in [Ru(III)].

In the Ru(III) catalysed oxidation of substituted cinnamic acids by Ce(IV) in aqueous H_2SO_4–HOAc, the process shows a zeroth order in [Ce(IV)], first-order in [Ru(III)] and a fractional order in [substrate]. The proposed [43] reaction mechanism involves the formation of a Ru(III)–substrate π complex involving the ethylenic π-linkage followed by the rate determining rearrangement of the Ru(III)–substrate π-complex to the σ-complex and its cleavage in a concerted manner giving rise to a Ru(I) species which is rapidly oxidised by Ce(IV) to regenerate the catalyst.

The kinetics of the Ru(III) catalysed oxidation of different primary – (e.g. 2-aminoethanol, 3-aminopropanol), secondary–(e.g., diethanolamine) and tertiary – (e.g. triethanolamine) aminoalcohols by Ce(IV) in aqueous H_2SO_4 have been studied by Upadhyay and co-workers [44]. The reactions exhibit a zeroth order in [Ce(IV)] and a first-order with respect to both the [substrate] and [catalyst]. Here it is proposed that Ce(IV) rapidly and quantitatively oxidises Ru(III) to Ru(VIII) which is the effective oxidant and Ru(VIII)–Ru(VII) cycle was proposed to operate. Kinetic studies of the Ru(III) catalysed oxidation of butanone-2 and pentanone-3 by Ce(IV) in aqueous H_2SO_4 were studied by Singh and co-workers [45]. The reaction rate is independent of [Ce(IV)], but the linear dependence of the reaction rate on [Ru(III)] at its lower concentrations tends towards the zeroth order at its higher concentrations. The process exhibits a first-order dependence on [ketone] throughout the range used. The proposed reaction mechanism involves the formation of an activated complex at the rate determining step between Ru(III) and protonated ketone which rapidly decomposes followed by a fast reaction between Ru(III) – hydride and Ce(IV) (Scheme 12).

$$\mathrm{RC(=O)R'} + \mathrm{H_3O^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RC^+(OH)R'} + \mathrm{H_2O},\ (\mathrm{R} = \mathrm{CH_3}) \tag{3.6.6}$$

$$\mathrm{Ru(III)} + \mathrm{RC^+(OH)R'} \xrightarrow{k_2} [\mathrm{RR'(OH)C{-}Ru(III)}],\ (\text{complex}) \tag{3.6.7}$$

$$\Big\downarrow \text{fast}$$

$$\mathrm{RC(=O)CH_2OH} + 2\mathrm{H^+} + \mathrm{Ru(III){-}H} \tag{3.6.8}$$

$$\mathrm{Ru(III){-}H} + 2\mathrm{Ce(IV)} \xrightarrow{\text{fast}} 2\mathrm{Ce(III)} + \mathrm{Ru(III)} \tag{3.6.9}$$

Scheme 12.

Assuming a steady-state condition for the protonated ketone, the following rate law results.

$$\frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=\frac{2k_1k_2[\mathrm{ketone}][\mathrm{Ru(III)}][\mathrm{H}^+]}{k_{-1}[\mathrm{H_2O}]+k_2[\mathrm{Ru(III)}]} \tag{3.6.10}$$

Very recently, the kinetics of oxidation of formic acid by Ce(IV) in the presence of Ru(III) (ca. 10^{-6} mol dm^{-3}) in aqueous H_2SO_4 was followed [46] at different temperatures (30–50°C). The rate of disappearance of Ce(IV) in the reaction was found to be zero-order with respect to Ce(IV) concentration. At a fixed $[H^+]$, under the condition, $[HCO_2H]_T \gg [Ce(IV)]_T \gg [Ru]_T$, the observed zero-order rate constant (k_o) conforms to:

$$\frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}=k_o=[\mathrm{Ru}]_T[\mathrm{HCO_2H}]_T\{k_b+k_c[\mathrm{HCO_2H}]_T\} \tag{3.6.11}$$

where $[Ru]_T$ and $[HCO_2H]_T$ represent the total concentrations of ruthenium, added as catalyst, and formic acid respectively. Both k_b and k_c are found to have an inverse hydrogen ion dependence. Out of the different possible mono- and bis-complexes. Ru(III)(HCO_2^-) and Ru(III)(HCO_2^-)(HCO_2H) have been found to be kinetically active in the slow oxidative steps (through an inner-sphere mechanism) leading to Ru(III)–H (through hydride transfer from the C–H bond of metal bound formate) and CO_2 followed by the rapid oxidation of Ru(III)–H to Ru(III) by Ce(IV). The activation parameters are: $\Delta H^{\neq}=46\pm3$ kJ mol^{-1}, $\Delta S^{\neq}=-125\pm5$ J K^{-1} (for k_b path) and $\Delta H^{\neq}=47\pm3$ kJ mol^{-1}, $\Delta S^{\neq}=-120\pm5$ J K^{-1} mol^{-1} (for the k_c path).

The kinetics and mechanism of the Ru(III) catalysed oxidation of ethanol by Ce(IV) in aqueous H_2SO_4 were reported [47]. The rate of disappearance of [Ce(IV)] in the title reaction increases sharply with the increase of $[\mathrm{ethanol}]_T$ to a value independent of $[\mathrm{ethanol}]_T$ over a large range (0.2–1.0 mol dm^{-3}) in which the rate law conforms to:

$$\frac{-2.303\,\mathrm{d}\log[\mathrm{Ce(IV)}]}{\mathrm{d}t}=k_{\mathrm{obs}}=(k_c+k_d[\mathrm{H}^+]^{-1})[\mathrm{Ru}]_T \tag{3.6.12}$$

where $[Ru]_T$ gives the total ruthenium concentration added as catalyst. The proposed mechanism involves the formation of a Ru(III)–substrate complex which undergoes oxidation at the rate determining step by Ce(IV) to produce the Ru(IV)–substrate complex followed by rapid redox decomposition giving rise to the catalyst and ethoxide radical which is rapidly oxidised by Ce(IV). The mechanism is consistent with the existence of Ru(III)(C_2H_5OH) species (in the k_c path) and Ru(III)($C_2H_5O^-$) species (in the k_d path) and both are kinetically active. $Ce(SO_4)_2$ has been found kinetically active.

The mechanistic aspects of the Ru(III) catalysed oxidation of Hg(I), hydrazine and diphenylamine by Ce(IV) were discussed by Yatsimirskii [48]. The proposed reaction paths in the oxidation of Hg(I) are (Scheme 13):

$$\mathrm{Ce(IV)} + \mathrm{Ru(III)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ce(IV)} .. \mathrm{Ru(III)}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ce(III)} + \mathrm{Ru(IV)} \tag{3.6.13}$$

$$\mathrm{Ce(IV)} + \mathrm{Ru(IV)} \xrightarrow{k_3} \mathrm{Ce(III)} + \mathrm{Ru(V)}. \tag{3.6.14}$$

$$\mathrm{Ru(V)} + \mathrm{Hg(I)} \xrightarrow{k_4} \mathrm{Ru(IV)} + \mathrm{Hg(II)}. \tag{3.6.15}$$

$$\mathrm{Ru(IV)} + \mathrm{Hg(I)} \xrightarrow{k_5} \mathrm{Ru(III)} + \mathrm{Hg(II)}. \tag{3.6.16}$$

Scheme 13.

Recently, we have carried out [49] the kinetics of the Ru(III) catalysed oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone by Ce(IV) in aqueous H_2SO_4 media at 30–50°C under the conditions, $[\mathrm{DMSO}]_\mathrm{T} \gg [\mathrm{Ce(IV)}]_\mathrm{T} \gg [\mathrm{Ru}]_\mathrm{T}$ (total concentration ruthenium added as catalyst). The pseudo-first-order rate constant obtained from $-\mathrm{d}\ln[\mathrm{Ce(IV)}]/\mathrm{d}t$ shows a first-order dependence on $[\mathrm{Ru}]_\mathrm{T}$. Strikingly, the substrate shows a rate retarding effect. The rate law conforms to:

$$k_\mathrm{obs} = \frac{k_\mathrm{a}[\mathrm{Ru}]_\mathrm{T}}{k_\mathrm{b}[\mathrm{DMSO}]_\mathrm{T} + k_\mathrm{c}} \tag{3.6.17}$$

where k_a, k_b and k_c are the composite rate constants. The following scheme has been proposed to explain the observations (Scheme 14):

$$\mathrm{Ru(III)} + \mathrm{Ce(IV)} \xrightarrow{k_1} \mathrm{Ru(IV)} + \mathrm{Ce(III)} \tag{3.6.18}$$

$$\mathrm{Ru(IV)} + \mathrm{DMSO} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{intermediate (X), (outer-sphere complex)} \tag{3.6.19}$$

$$\mathrm{X} + \mathrm{Ce(IV)} + \mathrm{H_2O} \xrightarrow{k_3} \mathrm{P} + \mathrm{Ce(III)} + \mathrm{Ru(III)} + 2\mathrm{H}^+ \tag{3.6.20}$$

$$\mathrm{Ru(IV)} + \mathrm{Ce(IV)} \xrightarrow{k_4} \mathrm{Ru(V)} + \mathrm{Ce(III)} \tag{3.6.21}$$

$$\mathrm{Ru(V)} + \mathrm{DMSO} + \mathrm{H_2O} \xrightarrow{k_5} \mathrm{P} + \mathrm{Ru(III)} + 2\mathrm{H}^+ \tag{3.6.22}$$

$$(\mathrm{P} = \mathrm{Me_2SO_2})$$

Scheme 14.

The rate retarding effect of DMSO can be explained by considering the simultaneous participation of two competitive catalytic cycles: one involving Ru(III)/Ru(IV) (i.e. Eqs. 3.6.18–20) predominant at higher concentration of the substrate and the other involving Ru(III)/Ru(V) (i.e. Eqs. 3.6.18, 21, 22) predominant at lower concentration of the substrate. The steps (3.6.19 and 3.6.21) mutually compete. The Ru(III)/Ru(V) cycle is known [50] to be more efficient. To explain the negative polymerisation test, it was proposed that in the oxidation of the two-electron donor substrate, i.e. DMSO, the two-electron transfer occurs at a single step.

In the Ru(III) catalysed oxidation of Hg(I) by Ce(IV) in aqueous H_2SO_4, a similar reaction mechanism has been suggested [50].

It is evident that in several cases complexation of Ru(III) with different organic substrates has been considered in pre-equilibrium steps. Now, the question arises regarding the nature of the complex when Ru(III) ($t_{2g}^5e_g^0$) is an inert centre. From the concept of lability, the complexes should be outer-sphere in nature. In most of the cases, the Ru-species have not been characterised. In $H_2SO_4/HSO_4^-/SO_4^{2-}$ media, the sulphate group bound to a Ru(III) centre may participate in a hydrogen bonding interaction [51] with the organic substrates (having –OH, $-CO_2H$ etc. groups) to enhance the K_{os} (outer-sphere association constant) values. The possibility of inner-sphere complex formation cannot be completely ruled out, as it is known [52] that the lability of Ru(III)-centre largely depends on the nature of the already coordinated ligand. In some cases, it is definitely established that Ru(III) forms inner-sphere complexes [53,54] through substitution reaction at fairly high rates. Sometimes, the presence of reducing ligands can also facilitate [55] the substitution process at Ru(III) centre. However, more work is needed in this direction for a better understanding of the proposed reaction mechanism.

3.7. Ir(III) catalysis

The kinetics of the Ir(III) and Ir(III)–Mn(II) catalysed oxidation of different amino acids (e.g. glycine, glutamic acid, serine) by Ce(IV) in aqueous H_2SO_4 media have been reported [19]. In the Ir(III) catalysed reactions, a mechanism involving the formation of an Ir(III)–substrate complex followed by the oxidation of the complex by Ce(IV) at the rate determining step has been proposed. In the mixed catalysis, the Ir(III)–substrate complex reacts with Mn(III) at the rate determining step. Mn(III) gets generated in the reaction, $\mathrm{Ce(IV)} + \mathrm{Mn(II)} \rightleftarrows \mathrm{Ce(III)} + \mathrm{Mn(III)}$. Here it is worth mentioning that Mn(II) and Ir(III) can act synergistically.

Ir(III) has been reported [56] to catalyse the oxidation of diacetone alcohol by Ce(IV) in both aqueous H_2SO_4 and $HClO_4$. The catalysis has been found to be more pronounced in aqueous $HClO_4$. The reactions are of first-order with respect to Ce(IV) and a fractional order with respect to Ir(III) in both the media. The order in [substrate] changes from unity in the uncatalysed reaction to fractional in the catalysed reaction in aqueous H_2SO_4. On the other hand, in aqueous $HClO_4$, the order in [substrate] has been found to be fractional both in the catalysed and uncatalysed reactions. A mechanism involving the formation of an Ir(III)–substrate complex is a rapid pre-equilibrium step followed by its reaction with Ce(IV) in a slow step to produce the Ir(IV)–substrate complex has been proposed. The Ir(IV)–substrate complex rapidly decomposes to generate Ir(III) and the partially oxidised product. The reaction mechanism in aqueous H_2SO_4 is (Scheme 15):

$$\mathrm{Ir(III)} + \mathrm{S} \overset{K}{\rightleftharpoons} \mathrm{Ir(III)}\text{—}\mathrm{S}, \text{ (complex); S = substrate} \qquad (3.7.1)$$

$$\mathrm{Ir(III)}\text{—}\mathrm{S} + \mathrm{Ce(IV)} \xrightarrow{k} \mathrm{Ir(IV)}\text{—}\mathrm{S}, \text{ (complex)} \qquad (3.7.2)$$

$$\mathrm{Ir(IV)}\text{—}\mathrm{S} \xrightarrow{\text{fast}} \mathrm{Ir(III)} + \text{oxidised products of the substrate} \qquad (3.7.3)$$

Scheme 15.

For the Ir(III) catalysed oxidation of dioxane by Ce(IV) in both aqueous H_2SO_4 and $HClO_4$, a similar reaction mechanism has been proposed [57]. Considering the inertness of the Ir(III) centre ($t_{2g}^6e_g^0$) the proposed complexes are considered to be outer-sphere in nature.

The mechanistic aspects of the Ir(III) catalysed oxidation of Hg(I) by Ce(IV) have been discussed by Yatsimirskii [48]. These are (Scheme 16):

$$\mathrm{Ce(IV)} + \mathrm{Ir(III)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ce(IV)} \,..\, \mathrm{Ir(III)}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ce(III)} + \mathrm{Ir(IV)} \qquad (3.7.4)$$

$$\mathrm{Ir(IV)} + \mathrm{Hg(I)} \xrightarrow{k} \mathrm{Ir(III)} + \mathrm{Hg(II)} \qquad (3.7.5)$$

Scheme 16.

A similar reaction mechanism has been proposed [48] for the oxidation of Hg(I) by Mn(III) in the presence of Ir(III). Analogous reaction mechanisms [48] are suggested in the oxidation of different aromatic amines by Ce(IV) and Mn(III) in the presence of Ir(III) acting as a catalyst.

Kinetic studies of the Ir(III) catalysed oxidation of different organic substrates such as formic acid [58], methanol [59], ethanol [60], propan-1-ol [61], propan-2-ol [61] and formaldehyde [62] by Ce(IV) in aqueous H_2SO_4 have been carried out. The rate of disappearance of Ce(IV) shows a first-order dependence on [Ce(IV)] and a fractional order both in $[Ir]_T$ (= total concentration of iridium added as catalyst) and [substrate]. The proposed mechanism involves an association of the oxidant, substrate and catalyst in some pre-equilibrium steps. The oxidation of the substrate occurs through the Ir(III)/Ir(IV) catalytic cycle. In these cases, $Ce(SO_4)^{2+}$ whose concentration is very small has been found kinetically active.

A literature survey on the kinetic studies of Ru(III) or Ir(III) catalysed electron transfer reactions at Ce(IV) centre in aqueous H_2SO_4 clearly indicates that different mechanistic pathways have been proposed for different substrates by different workers; and no clear-cut correlation is obtained. In many cases the observed dependence on the catalyst concentration does not conform to the proposed mechanism. In fact for a better understanding of the mechanistic pathways in the presence of different metal ions as catalyst in Ce(IV) oxidation reaction, more work is needed.

3.8. Pd(II) catalysis

The dynamics of Pd(II) catalysed oxidation of Hg(I) by Ce(IV) in aqueous $HClO_4$ was reported by Raju and co-workers [63]. Here a two step mechanism involving Pd(III)/Pd(II) catalytic cycle was proposed (Scheme 17).

$$\mathrm{Ce(IV) + Pd(II)} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{Ce(III) + Pd(III)} \qquad (3.8.1)$$

$$\mathrm{Pd(III) + Hg(I)} \xrightarrow{k_c} \mathrm{Pd(II) + Hg(II)} \qquad (3.8.2)$$

Scheme 17.

This leads to:

$$\frac{-\,\mathrm{d[Ce(IV)]}}{\mathrm{d}t} = \frac{k_a k_c\mathrm{[Ce(IV)][Pd(II)][Hg(I)]}}{k_b\mathrm{[Ce(III)]} + k_c\mathrm{[Hg(I)]}} \qquad (3.8.3)$$

The rate constants k_a ($= 25.8$ dm^3 mol^{-1} s^{-1}) and k_b/k_c ($= 0.9$) at 25°C, $[HClO_4] = 0.5$ mol dm^{-3} and $I = 0.8$ mol dm^{-3} have been evaluated.

3.9. Hg(II) catalysis

Kinetic studies of the mercuric chloride catalysed oxidation of isopropyl alcohol and acetone by Ce(IV) in aqueous H_2SO_4 media have been reported [64]. The second-order rate constants for the oxidation of isopropanol in the absence of mercuric chloride is independent of the polarity of the medium but the second-order rate constants in the mercuric chloride catalysed path increase with the increase in polarity of the medium. This indicates a polar transition state in the catalysed path (i.e. heterolytic nature of the catalysed reaction) but the uncatalysed path involves a homolytic reaction. The decrease of entropy of activation in the catalysed path from $+54.6$ to -50.4 J K^{-1} mol^{-1} suggests more solvation in the polar transition state in the catalysed path. On the other hand, in the oxidation of acetone, the second-order rate constants of both catalysed and uncatalysed reactions increase with the increase in polarity of the medium. No detailed mechanistic path was proposed by the workers [64].

4. Analytical applications of metal ion catalysis in Ce(IV) oxidation

The knowledge of metal ion catalysis in Ce(IV) oxidation reaction has found some important applications in cerate oxidimetry and the determination of some metal ions at ultra trace concentrations by using the principle of the catalytic kinetic method of analysis. In the estimation of As(III) by cerate oxidimetry, use of Os(VIII) as a catalyst is well documented [4]. By using the principle of the catalytic kinetic method of analysis, both iodide and osmium can be estimated at trace concentrations by using the Ce(IV)–As(III) reaction [65]. The said reaction is also catalysed by ruthenium and Surasiti and co-workers [36] applied the same principle for estimation of submicrogram quantities of ruthenium. Similarly, Ru(III) can also be estimated at ultra-low concentrations by using the Ce(IV)–formic acid reaction [6a], Ce(IV)–ethanol reaction [6b], Ce(IV)–dimethyl sulfoxide (DMSO) reaction [5]. These catalytic kinetic methods of analysis are intended for estimation of metal ions in an exceedingly low concentration range for which the colorimetric method or other methods (except such ultra sensitive methods as neutron activation) cannot be applied. The Ru(III) catalysed Ce(IV)–DMSO reaction was successfully applied for the estimation of DMSO by cerate oxidimetry [5]. Chrome alum catalysed cerate oxidimetry has been applied by Sriramam [29] for estimation of As(III). Chrome alum catalysed cerate oxidimetry has been applied by Sharma and co-workers [31,66] for determination of different types of organic substances. In this regard, the estimation of formic acid by cerate oxidimetry by using bromide as a catalyst is quite important in analytical chemistry [67].

5. Conclusions

Several kinetic studies have been carried out to explore the mechanistic aspects of different metal ion catalysis in the Ce(IV) oxidation of different types of substrates. This review has correlated the different factors to control the mechanistic paths of catalysis in the title oxidation reactions. These may widen the spectrum of cerate oxidimetry in volumetric analysis and organic synthesis. These are also highly promising from the standpoint of the development of catalytic kinetic methods of analysis for trace and ultra trace concentrations of different metal ions.

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