Studies on kinetics and mechanism of iridium(III) catalysed cerium(IV) oxidation of D-mannitol and D-glucose in aqueous acid media

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The kinetics and mechanism of Ce(IV) oxidation of D-mannitol and D-glucose in aqueous H₂SO₄ media in the presence and absence of Ir(III) have been studied and compared under the conditions, [S]₄ >> [Ce(IV)]₄ >> [Ir]₁, where [S]₄ gives the total substrate (D-mannitol or D-glucose) concentration and [Ir]₁ denotes the total concentration of Ir(III) catalyst added. Ir(III) has been found to catalyse the title reactions very efficiently even at trace concentration (ca. 10⁻⁶ to 10⁻⁷ mol dm⁻³). Under the kinetic conditions, both the uncatalysed and catalysed reactions take place simultaneously. The overall process shows a first order dependence on [Ce(IV)] and [S]₄. The catalytic path is first order in [Ir]₁. The catalytic path is suggested to involve the Ir(III)/Ir(IV) catalytic cycle. The process is acid catalysed and inhibited by HSO₄⁻. From the HSO₄⁻ dependence, both Ce(SO₄)₂ and CeSO₄ have been found kinetically active in D-mannitol oxidation while in D-glucose oxidation Ce(SO₄)₂ is the main kinetically active species under comparable conditions. The different kinetic parameters for both the Ir(III) catalysed and uncatalysed paths have been estimated.

Different metal ion catalysts have been employed¹ in Ce(IV) oxidation of different types of both organic and inorganic substrates. Among the different metal ions, Ru(III)² and Ir(III)³ have been found highly efficient and some of these systems have been found⁴ suitable for catalytic kinetic methods of analysis. Such efficient catalysts may also find application in cerate oxidimetry⁴.

The reaction mechanism of Ir(III) catalysis in Ce(IV) oxidation of some substrates has been reported and in different cases different reaction mechanisms have been suggested⁵. Some previous workers have reported⁶ the Ir(III) catalysed decomposition of Ce(IV) in aqueous sulphuric acid media at the elevated temperature through the oxidation of water. All these complicate the understanding of the mechanism of Ir(III) catalysis in Ce(IV) oxidation. In fact, more work is needed in this direction to explore the mechanistic routes in such reactions.

The kinetics and mechanism of Ce(IV) oxidation of the title substrates have been carried out previously by different workers⁸ but no such studies in the presence of Ir(III) to explore the catalytic efficiency of Ir(III) have been reported. Our preliminary observation indicates that Ir(III) even at trace concentrations (ca. 10⁻⁶ to 10⁻⁷ mol dm⁻³) can potentially catalyse the oxidation of the title substrates by Ce(IV) in aqueous sulphuric acid media and the reaction rate becomes measurable by spectrophotometric or titrimetric technique. It is also worth exploring the fact whether the kinetically active Ce(IV) species differ for the uncatalysed and catalysed path. In fact, in different cases for the Ir(III) catalysed paths, different Ce(IV) species have been found to participate in the reactions⁹. From our preliminary studies and analysis of HSO₄⁻ dependence on the uncatalysed path, it appears that more than one Ce(IV) species participate in the reaction. This aspect was not studied in detail by the previous workers. All these have prompted us to explore the kinetic behaviour of the title reactions.

Materials and Methods

The standard Ce(IV) stock solution in aqueous H₂SO₄ media was prepared as discussed earlier¹⁰. The free acid content of the stock solution was determined¹¹ by titration with standard NaOH solution after separation of Ce(IV) as insoluble Ce(III)-oxalate, formed by the addition of an excess of Na₂C₂O₄. Ce(III)-salt solutions were prepared from the corresponding stock solution of Ce(IV) after the treatment with H₂O₂ and the excess of H₂O₂ was decomposed by boiling. Stock solutions of D-glucose (AR, SRL) and D-mannitol (AR, SRL) were freshly prepared and stored in refrigerator. Iridium trichloride hydrate (Johnson-Mathey) was dissolved in 1.0 mol dm⁻³ H₂SO₄ media and kept at about 40°C for several days to attain the equilibrium. The stock solution (ca. 10⁻³ mol dm⁻³) is quite stable and the spectra of the
solution do not change with the treatment of hydrogen peroxide indicating the absence of Ir(IV) in the solution. The concentration of Ir(III) was determined spectrophotometrically using the colour developing agent SnCl2-HBr. For different sets of preparation of catalyst solution, the catalytic activity remained the same. All other chemicals were of analytical grade and doubly distilled water was employed throughout the experiment.

Procedure and kinetic measurements

The quenching technique to follow the rate of disappearance of Ce(IV) by titrimetric process under the kinetic conditions has been discussed in our earlier communications. The pseudo-first order rate constants \( k_{obs} \) were calculated as usual. The \( k_{obs} \) values were reproducible within the experimental error limit (±3-6%). Average values of at least two independent determinations of \( k_{obs} \) were taken for analysis. The reactions were studied up to at least 75% (for slower reactions) and at most up to 90% (for faster reactions) completion of the reaction. A few kinetic runs were carried out after bubbling nitrogen through the reaction mixture and were compared with those obtained under air. However, the results were found to be identical.

Ce(IV) solution in aqueous \( \text{H}_2\text{SO}_4 \) is kinetically and thermodynamically stable and no additional precautions to exclude the diffused light entering the reaction solution were taken. It was reported that Ir(III) catalysed the decomposition of Ce(IV) at its higher concentration (ca. \( 10^{-5} \text{ mol dm}^{-3} \)) in aqueous \( \text{H}_2\text{SO}_4 \) at the elevated temperature (80-90°C). The elevated temperature (80-90°C) through the oxidation of water. To explore the extent of this catalytic decomposition of Ce(IV), some runs were carried out in the absence of substrate, but under otherwise the same experimental conditions. The amount of decomposition in this path was found negligible (max. 4% during the present reaction time). This is why, no correction for this path was taken into consideration.

All the data except those for \( 10^3 \text{ mols dm}^{-3} \) of substrate, \( \text{Ir} \) and catalyst, \( \text{H}_2\text{SO}_4 \) were analysed by the linear least squares method. Error associated with the reported rate constants and activation parameters were estimated as usual.

Product analysis

The qualitative analysis of the oxidised reaction mixture with the excess concentration of the substrate, \( \text{D-glucose or D-mannitol over the concentration of Ce(IV) in the presence and absence of Ir(III) was done. For D-glucose, the presence of arabinose and formic acid was found. It indicated the absence of gluconic acid. By paper chromatography, arabinose was also identified using the authentic sample as the reference one. The chromatographic solvents were ethylacetate-pyridine-water (8:2:1, v/v) and ethylacetate-acetic acid-formic acid-water (18:3:1:4, v/v). Visualising the paper chromatograms was done using a three stages dip of silver nitrate, sodium hydroxide and sodium thiosulphate. Under the kinetic conditions, for mannitol, mannose was detected qualitatively. Thus the stoichiometric equation of the reactions can be written as follows:

\[
\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{Ce(IV)} + \text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_{10}\text{O}_5 + \text{HCO}_2\text{H} + 2\text{Ce(III)} + 2\text{H}^+ \quad \ldots (1)
\]

\[
\text{HOH}_2\text{C(OH)}_2\text{CH}_2\text{OH} + 2\text{Ce(IV)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}^+ + 2\text{Ce(III)} \quad \ldots (2)
\]

Thus, \( \text{C}_6\text{H}_{12}\text{O}_6 \) (mannitol) on oxidation produces aldohexose which on further oxidation produces formic acid and an aldopentose. Similar observations were noted by earlier workers. For both the Ir(III) catalysed and uncatalysed reactions, the same products were obtained.

Results and Discussion

Dependence on \([\text{Ce(IV)}]_f\)

Both in the presence and absence of Ir(III), under the conditions, \([\text{S}]_f \gg [\text{Ce(IV)}]_f \gg [\text{Ir}]_f \) (where, \([\text{S}]_f = [\text{D-mannitol}] \) or \([\text{D-glucose}]_f [\text{Ir}]_f = \text{total concentration of Ir(III) added as catalyst}, \) the rate of disappearance of Ce(IV) shows a first order dependence on \([\text{Ce(IV)}]_f \). The pseudo-first order rate constants \( (k_{obs}) \) have been evaluated from the linear plot of \( \log [\text{Ce(IV)}]_f \) versus time (t) as usual. The observed rate constants \( (k_{obs}) \) are found independent on initial concentration of Ce(IV) in the range (1.5 - 2.5)x10\(^{-3} \text{ mol dm}^{-3} \). The dependence is given by:

\[-d \ln[\text{Ce(IV)}]/dt = k_{obs} \quad \ldots (3)\]

Dependence on \([\text{Ir}]_f\)

At fixed \([\text{S}]_f \) and \([\text{H}_2\text{SO}_4]_f \), the effect of \([\text{Ir}]_f \) on \( k_{obs} \) was followed. The plots of \( k_{obs} \) versus \([\text{Ir}]_f \) are linear (r > 0.99) with positive intercepts measuring the contribution of the relatively slower uncatalysed path (cf. Figs 1, 2). The pseudo-first order rate constants \( (k_{obs}) \) directly measured in the absence of Ir(III) under identical conditions agree with those obtained from the plots of
$k_{obs(T)}$ versus $[\text{Ir}]_T$. The observation is formulated as follows:

$$k_{obs(T)} = k_{obs(u)} + k_{obs(c)} = k_u + k_{cat}[\text{Ir}]_T \quad \ldots \quad (4)$$

The values of $k_{cat}$ and $k_u$ with their activation parameters are given in Table 1.

Dependence on $[S]_T$

From the plot of $k_{obs}$ versus $[S]_T$, it is established that both the uncatalysed and Ir(III) catalysed paths show the first order dependence on $[S]_T$, i.e.

$$k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = k_{cel}[S]_T \quad \ldots \quad (5)$$

![Fig. 1](image1.png)

Fig. 1—Effect of $[\text{Ir(III)}]_T$ on $k_{obs}$ for the Ce(IV) oxidation of $\alpha$-mannitol in aqueous H$_2$SO$_4$ media at different temperatures. $[\text{Ce(IV)}]_T = 2 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 1$ mol dm$^{-3}$, $[\alpha$-mannitol] = 0.02 mol dm$^{-3}$. (A) 30°C, (B) 35°C, (C) 40°C.

![Fig. 2](image2.png)

Fig. 2—Effect of $[\text{Ir(III)}]_T$ on $k_{obs}$ for the Ce(IV) oxidation of $\alpha$-glucose in aqueous H$_2$SO$_4$ media at different temperatures. $[\text{Ce(IV)}]_T = 2 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 1$ mol dm$^{-3}$, $[\alpha$-glucose] = 0.05 mol dm$^{-3}$, (A) 30°C, (B) 35°C, (C) 40°C, (D) 45°C.

Table 1—Kinetic parameters for the Ce(IV) oxidation of $\alpha$-glucose and $\alpha$-mannitol in aqueous H$_2$SO$_4$ media in presence of iridium(III); $[\text{H}_2\text{SO}_4] = 1$ mol dm$^{-3}$, $[\text{Ce(IV)}] = 2 \times 10^{-3}$ mol dm$^{-3}$.

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<th>D-glucose</th>
<th>Temp(°C)</th>
<th>$10^4 k_{obs}/$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
<th>$10^2 k_{cat}/$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
<th>$10^2 k_{act}/$ (s$^{-1}$)</th>
<th>$10^2 k_{cat}/$ (mol dm$^{-3}$s$^{-1}$)</th>
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<td></td>
<td>30</td>
<td>4.56 ± 0.15</td>
<td>(1.89 ± 0.10) (4.54 ± 0.20)</td>
<td>4.7 ± 0.15</td>
<td>1.3 ± 0.08</td>
<td>0.46 ± 0.06</td>
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<td>-111</td>
<td>1.35 ± 0.10</td>
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<td></td>
<td>ΔH$^\circ$ (kJ mol$^{-1}$)</td>
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<td>-90</td>
<td>1.98 ± 0.07</td>
<td>9.3 ± 0.25</td>
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<th>$10^4 k_{cat}/$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
<th>$10^2 k_{act}/$ (s$^{-1}$)</th>
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<td>30</td>
<td>1.8 ± 0.12</td>
<td>0.36 ± 0.06</td>
<td>1.10 ± 0.10</td>
<td>1.36 ± 0.07</td>
<td>1.50 ± 0.06</td>
<td>2.10 ± 0.08</td>
<td>2.36 ± 0.15</td>
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<tr>
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<td>ΔH$^\circ$ (kJ mol$^{-1}$)</td>
<td>-107</td>
<td>-120</td>
<td>-33</td>
<td>-180</td>
<td>-107</td>
<td>-120</td>
<td>-33</td>
<td>-180</td>
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<tr>
<td></td>
<td>ΔS$^\circ$ (JK$^{-1}$mol$^{-1}$)</td>
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(a) $[S]_T = 0.03-0.12$ mol dm$^{-3}$, (b) same as (a) except $[\text{Ir(III)}]_T = 2 \times 10^{-6}$ mol dm$^{-3}$, (c) same as (a) except $[\text{Ir(III)}]_T = 4 \times 10^{-6}$ mol dm$^{-3}$, (d) $[S]_T = 0.05$ mol dm$^{-3}$, (e) same as (d) except $[\text{Ir(III)}]_T = (0-9.0) \times 10^{-6}$ mol dm$^{-3}$, (f) $[S]_T = 0.08$ mol dm$^{-3}$, 1 = $[\text{HClO}_4] + [\text{H}_2\text{SO}_4] = 1.5$ mol dm$^{-3}$, (g) $[S]_T = (0.02-0.06)$ mol dm$^{-3}$, (h) same as (g) except $[\text{Ir(III)}]_T = 1 \times 10^{-6}$ mol dm$^{-3}$, (i) same as (g) except $[\text{Ir(III)}]_T = 3 \times 10^{-6}$ mol dm$^{-3}$, (j) $[S]_T = 0.02$ mol dm$^{-3}$, (k) same as (j) except $[\text{Ir(III)}]_T = (0-8.0) \times 10^{-6}$ mol dm$^{-3}$, (l) $[S]_T = 0.015$ mol dm$^{-3}$, 1 = $[\text{H}_2\text{SO}_4] + [\text{HClO}_4] = 1.5$ mol dm$^{-3}$.
and \[ k_{d(e)} = k_{e}[S] \] ... (6)

The values of \( k_{d(e)} \) and \( k_{e} \) are given in Table 1.

**Dependence on \([\text{HSO}_4^-]\)**

For variations in \([\text{HSO}_4^-]\) (in the range 0.5-1.5 mol dm\(^{-3}\)) at fixed \([H^+]\), \([S]\) and \([\text{Ir}]_{r}\), the composition of the mixture, \([\text{H}_2\text{SO}_4] + [\text{HClO}_4] = [H^+] = 1.75 \text{ mol dm}^{-3}\) (ignoring the dissociation of \([\text{HSO}_4^-]\) was varied\(^{12}\). In such experiments, \([\text{HSO}_4^-]\) shows the overall rate retarding effect. The \([\text{HSO}_4^-]\) dependence (cf. Fig. 3) can be expressed from the experimental fit in the following forms.

\[ k_{d(e)} = m/[\text{HSO}_4^-], \text{ (for d-glucose)} \] ... (7a)

and

\[ k_{d(e)}[\text{HSO}_4^-] = n+p/[\text{HSO}_4^-], \text{ (for d-mannitol)} \] ... (7b)

**Dependence on \([H^+]\)**

To explore the dependence of \( k_{d(e)} \) on \([H^+]\) (in the range 0.25-1.5 mol dm\(^{-3}\)), the composition of the mixture \([\text{H}_2\text{SO}_4] + [\text{NaHSO}_4] = [\text{HSO}_4^-] = 1.75 \text{ mol dm}^{-3}\) was varied assuming \([H^+] = [\text{H}_2\text{SO}_4]. \) It has been found that reactions are catalysed by \([H^+]\) (cf. Table 2). Because of the existence of so many proton dependent equilibria among the reactants, the exact computation of \([H^+]\) and interpretation of \([H^+]\) dependence get very much complicated. Because of this complexity\(^{30,13}\), in the present system, no attempt was made to explain the \([H^+]\) dependence quantitatively from the proposed mechanism. However, the qualitative observation is in agreement with the fact that the Ce(IV) oxidation reaction in aqueous \(\text{H}_2\text{SO}_4\) media gets catalysed by \(H^+\). On protonation, positive charge on the Ce(IV)-sulphato species increases and it facilitates the electron transfer towards the Ce(IV) center. This factor may be one of the contributing factors for the observed acid catalysis\(^{30,14}\).

**Acrylonitrile polymerization test**

Acrylonitrile was added to the reaction mixture under nitrogen atmosphere and the solution became viscous, indicating the generation of free radicals.

**Dependence on the products and other factors**

Under the kinetic conditions in 1.0 mol dm\(^{-3}\) \(\text{H}_2\text{SO}_4\) media, the effects of the organic product and Ce(III) salt up to (3.5 mmol dm\(^{-3}\)) were investigated and no effect was noticed. The \( k_{d(e)} \) values remained unchanged when the reactions were carried out under nitrogen or the presence of light.

**Mechanism of the reaction**

Under the experimental conditions, there was no spectrophotometric and kinetic evidence (strict first order dependence on both the substrate and catalyst) in favour of intermediate complex formation both for the uncatalysed and Ir(III) catalysed reactions. In fact, in aqueous \(\text{H}_2\text{SO}_4\) media, complexation of organic substrate with Ce(IV)-sulphato species is a rare possibility\(^{13,15}\). However, there may be a weak association for the uncatalysed reaction and the following steps given in Scheme 1 are quite reasonable.

**Table 2—Effect of \([H^+]\) on \(k_{d(e)}\) for the Ce(IV) oxidation of d-glucose and d-mannitol in aqueous acid media. \([\text{Ir}]=2\times10^{-2} \text{ mol dm}^{-3} , l=[\text{NaHSO}_4] + [\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3} \)**

<table>
<thead>
<tr>
<th>([H^+]) (mol dm(^{-3}))</th>
<th>(10^2 k_{d(e)} ) (mol dm(^{-3}) s(^{-1}))</th>
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<tbody>
<tr>
<td>0.25</td>
<td>1.9</td>
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<tr>
<td>0.375</td>
<td>2.0</td>
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<tr>
<td>0.5</td>
<td>3.0</td>
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<tr>
<td>0.625</td>
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<td>0.75</td>
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<td>1.25</td>
<td>6.5</td>
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<td>1.5</td>
<td>8.3</td>
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\(\text{d-glucose}=0.12 \text{ mol dm}^{-3}, 40^\circ \text{C} \) \(\text{d-mannitol}=0.03 \text{ mol dm}^{-3}, 35^\circ \text{C}\)
Ce(IV) + S \xleftrightarrow{K_1} \text{complex (C_1)} \quad \ldots \quad (8)

C_1 \xrightarrow{K_1} \text{Ce(III)} + \text{H}^+ + S^* \quad \ldots \quad (9)

S^* + Ce(IV) \xrightarrow{\text{fast}} \text{products} + \text{Ce(III)} + \text{H}^+ \quad \ldots \quad (10)

Scheme 1—Ce(IV) oxidation of D-glucose or D-mannitol in aqueous media

The above scheme is similar to that proposed by Mehrotra et al. Here, the complex (C_1) unimolecularly dissociates in the rate determining step to give Ce(III) and free radical (S^*). Considering the very small value of K_1, Scheme 1 leads to rate law (13).

\frac{d[\text{Ce(IV)}]}{dt} = 2\beta_1 K_1[\text{Ce(IV)}][S]^*_1 \quad \ldots \quad (13)

or, \quad k_{\text{obs}} = \beta_1 K_1[S]^*_1 = k_{\text{obs}}[S]^*_1 \quad \ldots \quad (14)

Similar rate law may also be obtained considering the fact that the substrate is directly oxidised by Ce(IV) in a bimolecular step. In this case, the interaction may occur at the transition state (Scheme 2).

Ce(IV) + S \rightarrow \{ \text{Ce(IV)} \rightarrow S \} \rightarrow \text{Ce(III)} + S^* + \text{H}^+ \quad \ldots \quad (15)

Scheme 2—Direct interaction between the substrate and Ce(IV).

When the K_1 value is very small then it is not possible to discriminate between Schemes 1 and 2. Here, Ce(IV) actually denotes the kinetically active Ce(IV)-species and \( j \) gives the fraction of total Ce(IV) kinetically active. This aspect will be discussed later.

In the case of D-glucose (which predominately exists in cyclic forms), the products are thought to be produced through the intermediate formation of formyl ester. There are two possible sites of radical formation, but the radical formation at the C-1 is probably preferred because of its greater resonance stabilization. The formyl ester is also considered as an intermediate in peridate and lead tetra acetate oxidation of glucose^5,6. In the case of D-mannitol (C_{12}H_{22}O_{11}), the mechanism is similar to that found in the oxidation of monohydrhyth primary alcohols by Ce(IV) in aqueous H_2SO_4 media. Formation of free radical is evident through the acrylonitrile polymerisation test. Our observation for this uncatalysed path agrees with those reported by previous workers^7. But the present investigation leads to different conclusions regarding the identification of kinetically active Ce(IV) species. For the Ir(III) catalysed reactions, Scheme 3 may be outlined.

Ce(IV) + S \xleftrightarrow{K_1} \text{complex (C_1)} \quad \ldots \quad (8)

C_1 + \text{Ir(III)} \xleftrightarrow{K_2} \text{complex (C_2)} \quad \ldots \quad (16)

C_2 \xrightarrow{K_2} \text{Ce(III)} + \text{Ir(IV)} \quad \ldots \quad (17)

C_3 \xrightarrow{\text{fast}} \text{S}^* + \text{H}^+ + \text{Ir(III)} \quad \ldots \quad (18)

S^* + \text{Ce(IV)} \rightarrow \text{product} + \text{Ce(III)} + \text{H}^+ \quad \ldots \quad (19)

Scheme 3—Ir(III) catalysed oxidation of D-mannitol or D-glucose by Ce(IV) in aqueous H_2SO_4 media.

Under the approximation, \([S]_1 = [S]\) and \([\text{Ir}]_1 = [\text{Ir}]_1\). Scheme 3 leads to the rate law:

\[ k_{\text{obs}} = \frac{2\beta_2 K_3 K_4[S][\text{Ir}]_1}{(1 + K_3[S]_1)(1 + K_4[\text{Ir}]_1)} \quad \ldots \quad (20) \]

Equation 20 leads to rate law (21) under the condition, \(1 >> K_3[S]_1, 1 + K_4[\text{Ir}]_1\).

\[ k_{\text{obs}} = 2K_3 K_4[S][\text{Ir}]_1 k_{\text{obs}}[\text{Ir}]_1 = k_{\text{obs}}[\text{Ir}]_1 k_{\text{obs}}[S]_1 \quad \ldots \quad (21) \]

The values of K_1 and K_2 are quite low. In fact, when the higher sulphato species of Ce(IV) are kinetically active, the binding interaction is expected to be quite low. The active Ce(IV)-species are found to be Ce(SO_4)_2^4+ (for D-glucose) and both Ce(SO_4)_2^4+ and Ce(SO_4)_2^6+ (for D-mannitol) (cf. bisulphate dependence and active Ce(IV) species). The absence of both kinetic (i.e. strict first order dependence) and spectrophotometric evidence for the suggested complexes C_1 and C_2 indicates the very low values of K_1 and K_2, leading to weak associations. Here it should
Complexation of Ce(V) and S or Ir(III) and S. The same arguments also prevail for $K_2$. Both the possibilities lead to the same rate law under the condition mentioned above. In such cases, the above rate law can also be obtained by considering Scheme 4. A similar situation has been discussed for the uncatalysed path (cf. Schemes 1 and 2).

\[
\text{Ir(III)} + S \rightleftharpoons \text{Complex (C)} \quad \ldots \quad (22)
\]

\[
\text{C}_2 + \text{Ce(IV)} \to \text{Ir(III)} + \text{Ir(III)} + S \quad \ldots \quad (23)
\]

or, $\text{Ir(III)} + \text{Ir(IV)} \rightarrow \text{Ir(III)} + \text{Ir(IV)} \rightarrow S$ (complex) \\

Scheme 4---Ir(III) catalysed oxidation of D-mannitol or D-glucose by Ce(IV) in aqueous H$_2$SO$_4$ media.

The actual kinetically active Ir(III)-species has not been characterized, but homogeneity of the catalyst solution is evidenced from the fact that different sets of preparation of the catalyst solution show the same catalytic activity. Probably, some sort of sulphato species of Ir(III) is present in the solution. However, it is reasonable to conclude from the standpoint of chemical stability of the Ir(III) centre that it leads to Ir(III)-Ir(IV) catalytic cycle is proposed$^3$ to occur in many cases.

HSO$_4^-$ dependence and kinetically active Ce(IV) species

Both Ir(III) and Ir(IV) species are kinetically inert$^7$ while Ce(IV) centre is relatively more labile$^{15}$. Hence, the relevant equilibria involving Ce(IV) and HSO$_4^-$ are only important. The nature of Ce(IV)-species in aqueous H$_2$SO$_4$ media has been studied by different workers. The important equilibria (considering up to tri-sulphato species) proposed by Hardwick and Robertson$^8$ are:

\[
\text{Ce}^{3+} + \text{HSO}_4^- \rightleftharpoons \text{Ce}^{2+} + \text{H}^+ \quad \ldots \quad (25)
\]

\[
\text{Ce}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{Ce}^{3+} + \text{H}^+ \quad \ldots \quad (26)
\]

\[
\text{Ce}^{3+} + \text{HSO}_4^- \rightleftharpoons \text{Ce}^{2+} + \text{H}^+ \quad \ldots \quad (27)
\]

The equilibrium constants $Q_1, Q_2, Q_3$ are given at 25°C and ionic strength 2 mol dm$^{-3}$. Bugaenko and Kau-Lin$^{15}$ have suggested equilibrium (28) instead of equilibrium 27.

\[
\text{Ce}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{H}^+ \text{Ce}^{(SO_4)_2} \quad \ldots \quad (28)
\]

The value of the equilibrium constant of this process has been found in the range of 5-8 by different workers$^{21}$.

The HSO$_4^-$ dependence at fixed [$H^+$] can be explained by considering the simultaneous participation of both mono and bis-sulphato species of Ce(IV). But the kinetic contribution from Ce(SO$_4$)$_2^{2-}$ is negligible for D-glucose. Thus for the uncatalysed path, the rate expression will have the following general expression by considering the Hardwick-Robertson equilibria.

\[
\text{d}[\text{Ce(IV)}]/\text{d}t = k_3[S][\text{Ce}^{2+}] + k_4[S][\text{Ce}^{2+}] \quad \ldots \quad (29)
\]

The HSO$_4^-$ dependence remains the same in the presence of Ir(III). By considering the relative magnitudes of $Q_1, Q_2$ and $Q_3$, the concentrations of Ce(SO$_4$)$_2^{2-}$ and Ce(SO$_4$)$_2^{3-}$ can be reasonably expressed as follows.

\[
[\text{Ce}^{2+}] = ([\text{Ce}^{2+}]/[\text{H}^+]/[Q_2][\text{HSO}_4^-])^{1/2} \quad \ldots \quad (30)
\]

\[
[\text{Ce}^{3+}] = ([\text{Ce}^{3+}]/[\text{H}^+]/[Q_3][\text{HSO}_4^-]) \quad \ldots \quad (31)
\]

By considering the species Ce(SO$_4$)$_2^{2-}$ and Ce(SO$_4$)$_2^{3-}$ kinetically active, the HSO$_4^-$ dependence can be explained by considering equation (32):

\[
f = f_1 + f_2 = [\text{H}^+]^2/[Q_2][\text{HSO}_4^-] + [\text{H}^+]/[Q_3][\text{HSO}_4^-] \quad \ldots \quad (32)
\]

Using relation (32) in Eq. 26, it reduces to Eq. (33).

\[
k_{\text{obs}} = ([k_3[H]^+]/[Q_2][\text{HSO}_4^-])
+ ([k_4[H]^+]/[Q_3][\text{S}]) \quad \ldots \quad (33)
\]

or $k_{\text{obs}}[\text{HSO}_4^-] = [k_3[H]^+]/[Q_2][\text{S}] + [k_4[H]^+]/[Q_3][\text{S}] \quad \ldots \quad (34)$

(taking $k_3 = (k_3[H]^+)/[Q_2][\text{S}]$, and $k_4 = (k_4[H]^+)/[Q_3][\text{S}]$, at fixed acid concentration)

The plot of $k_{\text{obs}}[\text{HSO}_4^-]$ versus 1/[HSO$_4^-$] (in the case of D-mannitol cf. Fig. 3) indicates that both Ce(SO$_4$)$_2^{2-}$ (i.e. $k_2$ path) and Ce(SO$_4$)$_2^{3-}$ (i.e. $k_6$ path) are kinetically active, while for D-glucose only Ce(SO$_4$)$_2^{2-}$ (i.e. $k_6$ path) is the main species kinetically active. Thus for D-glucose, the plot of $k_{\text{obs}}$ versus 1/[HSO$_4^-$] is linear with zero intercept.

Ce(SO$_4$)$_2^{2-}$ has been found kinetically active in many cases$^{6,21}$. Both Ce(SO$_4$)$_2^{2-}$ and Ce(SO$_4$)$_2^{3-}$ have
been found to participate simultaneously in the oxidation of malic acid\textsuperscript{16} as in the present case of D-
mannitol oxidation. Ce(SO\textsubscript{4})\textsubscript{2} as the sole kinetically
active species as in the present case of D-glucose oxidation has been reported earlier in many cases\textsuperscript{20b,22}.

Origin of acid catalysis
The Ce(IV) sulphato complexes may undergo
protonation as follows:

\[
\text{Ce(SO}_4\text{)}^2^+ + H^+ \rightleftharpoons \text{HCE(SO}_4\text{)}^2^+ \quad \ldots (35)
\]

\[
\text{Ce(SO}_4\text{)}_2^+ + H^+ \rightleftharpoons \text{HCE(SO}_4\text{)}_2^+ \quad \ldots (36)
\]

\[
\text{HCE(SO}_4\text{)}_2^+ + H^+ \rightleftharpoons \text{H}_2\text{CE(SO}_4\text{)}_2^2^+ \quad \ldots (37)
\]

The increase in acid concentration would thus
enhance the concentration of protonated form of
Ce(IV) species. With the increase in positive charge
on the Ce(IV)-species, the electron transfer towards
the Ce(IV)-center would take place more readily. This
explains the origin of the acid catalysis\textsuperscript{14}. Here it
should be mentioned that the bisulphate dependence
discussed above reveals only the nature of sulphato
species (i.e., number of sulphato groups present at the
active Ce(IV) center) without considering the degree
of their protonation. The observed acid catalysis is not
due to the acid catalysed maturatation of the aldohexoses as the maturatation process is much faster\textsuperscript{25,26} than the present redox reaction under the
experimental conditions. In fact, the maturatation
equilibrium is almost immediately attained\textsuperscript{25} and the
rate of glucose oxidation is not affected by the process
of maturatation of glucose. Thus the observed rate
of oxidation of D-glucose is the sum total of the rates
contributed by each of the \( \alpha \)- and \( \beta \)-anomers in
addition to the possible contribution from the free
aldehydic form.

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