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Kinetics and mechanism of the Ir(III)-catalyzed oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium

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Abstract—For the first time, the Ir(III) catalysis of the iodate oxidation of xylose and maltose in aqueous alkaline medium has been investigated. The reactions exhibit first-order kinetics with respect to lower $[IO_3^-]$ and $[OH^-]$ and show zero-order kinetics at their higher concentrations. Unity order at low concentrations of maltose becomes zero order at its higher concentrations, whereas zero-order kinetics with respect to [xylose] was observed throughout its variation. The reaction rate is found to be directly proportional to [Ir(III)] in the oxidation of both reducing sugars. Negligible effect of $[Cl^-]$ and nil effect of ionic strength (μ) on the rate of oxidation have also been noted. The species, $[IrCl_3(H_2O)_2OH]^-$ was ascertained as the reactive species of Ir(III) chloride for both the redox systems. Various activation parameters have been calculated. Formic acid and arabinonic acid for maltose and formic acid and threonic acid for xylose were identified as the main oxidation products of the reactions. Mechanisms consistent with the observed kinetic data and spectral evidence have been proposed for the oxidation of xylose and maltose.

Keywords: Mechanism; Xylose; Maltose; Potassium iodate; Alkaline medium; Ir(III) Catalysis

1. Introduction

The study of carbohydrates is one of the most exciting fields of organic chemistry. Vast literature is available on the kinetics of oxidation of carbohydrates by various organic and inorganic oxidants. The oxidation of aldoses by chlorine, bromine and iodine have been reported in alkaline media.[1] The aldonic acids as primary products of oxidation of aldoses by bromine have been extensively studied by Isbell and co-workers,[2] who pointed out that β-aldoses (C-1 equatorial) are oxidized much faster than α-aldoses (C-1 axial). The catalyzed and uncatalyzed oxidation of sugars have been studied in detail by using *N*-halo compounds.[3–11] Inorganic oxidants such as Cu(II), ammonical Ag(I) and Nessler's reagent have been used in the uncatalyzed oxidation of sugars in aqueous alkaline medium.[12–14] The mechanisms for the oxidations of some aldoses by Cr(VI), V(V), Ce(IV), Mn(III), Ir(IV), Au(III) and periodic acid have been investigated in acidic media.[15] Reports regarding the use of periodate in the uncatalyzed oxidation of carbohydrates and polymeric substrate and Ru(III)- and ruthenate ion-catalyzed oxidation of reducing sugars in alkaline medium are also available.[16–18] The uncatalyzed oxidation of oxalic acid, acetophenone and benzaldehydes and Ru(III)-catalyzed oxidation of α-hydroxy acids by iodate in acidic medium have been reported.[19–22] In the reported Ru(III)- and Os(VIII)-catalyzed oxidation of styrene and stillbene in acidic medium, IO_3^- has also been used as an oxidant.[23] But as of this date no report is available, in which iodate as an oxidant and Ir(III) chloride as homogeneous catalyst have been used in the oxidation of monosaccharides and disaccharides in alkaline medium. In view of the biological importance of reducing sugars, and also in view of the fact that no investigation on the kinetic oxidation of reducing sugars with iodate as an oxidant and Ir(III) chloride as homogeneous catalyst in alkaline medium has so far been made, the present study has been undertaken. In this study our main aim was to ascertain the following:

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(1) IO_3^- as an oxidant in alkaline medium behaves in the same way as it behaved in the reported Ru(III)-catalyzed oxidation of indigo carmine by iodate in aqueous sulfuric acid solution.[24]

(2) The role of reducing sugar molecule in the presence of Ir(III) chloride as catalyst and IO_3^- as an oxidant in alkaline medium is similar to the reported role of reducing sugar in the presence of Ir(III) chloride and *N*-bromoacetamide (NBA) in acidic medium.[6]

(3) Ir(III) Chloride in alkaline medium participates in the reaction under investigation in the same way, as it is reported for Ir(III)-catalyzed oxidation of reducing sugars by NBA in acidic medium.[6]

(4) There is any possibility of the formation of a complex between the reactive species of Ir(III) chloride and the reactive species of potassium iodate in alkaline medium in the same form as it is reported in the Ir(III) chloride-catalyzed oxidation of reducing sugars by NBA in acidic medium.[6]

(5) The formation of an activated complex results by the interaction of two oppositely charged species in the same way as it is reported for Ir(III) catalyzed oxidation of reducing sugars by NBA in acidic medium.[6]

2. Experimental

2.1. General procedures

A solution of Ir(III) chloride (Johnson–Mathey & Co. Ltd) was prepared in HCl of known strength (10.00×10^{-2} mol/L) and its concentration was maintained at 6.69×10^{-3} mol/L. A standard stock solution of KIO_3 (E. Merck) was prepared by dissolving a known weight of KIO_3 in double-distilled water, and its concentration was ascertained iodometrically. Standard solutions of xylose and maltose (A.R. grade) were freshly prepared. NaOH and KCl (E. Merck) were employed to maintain the required alkalinity and ionic strength, respectively. All the reactions were studied at constant temperature 40 °C (±0.1 °C). The reaction was initiated by adding the requisite volume of pre-equilibrated sugar solution to the reaction mixture, and the progress of the reaction was monitored by iodometrically estimating the amount of unreacted iodate at regular time intervals. The unreacted iodate in presence of excess potassium iodide and perchloric acid is converted into iodine, and the liberated iodine is titrated against a standard solution of sodium thiosulfate using starch solution as an indicator.

2.2. Stoichiometry and product analysis

A set of solutions of varying $[IO_3^-]$:[reducing sugar] ratios were equilibrated at room temperature for 72 h under the conditions of $[IO_3^-] \gg$ [sugar]. Estimation of residual $[IO_3^-]$ in different sets showed that 1 mole of sugar consumed 2 and 4 mol of IO_3^- for xylose and maltose, respectively. Accordingly, the following stoichiometric equations were formulated:

$$\underset{\text{D-xylose}}{C_5H_{10}O_5} + 2IO_3^- \xrightarrow{Ir(III)/OH^-} \underset{\text{Threonic acid}}{C_4H_8O_5} + \underset{\text{Formic acid}}{HCOOH} + 2IO_2^-$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + 4IO_3^- \xrightarrow{Ir(III)/OH^-} \underset{\text{Arabinonic acid}}{2C_5H_{10}O_6} + \underset{\text{Formic acid}}{2HCOOH} + 4IO_2^-$$

Formic acid and arabinonic acid in the case of maltose and formic acid and threonic acid in the case of xylose were identified as the main oxidation products by the help of equivalence and kinetic studies and also by TLC and conventional spot test methods.

3. Results

The oxidation of xylose and maltose were investigated at different initial concentrations of the reactants. The time course of the reaction in the oxidation of both reducing sugars is shown in Figure 1. In the case of xylose, the initial rate of the reaction, that is, $(-dc/dt)$ in each kinetic run, was calculated from the slope of the tangent of the plot of unconsumed $[IO_3^-]$ versus time at fixed $[IO_3^-]$, except in $[IO_3^-]$ variation when a tangent has been drawn at a fixed time. In the case of maltose, the initial rate of reaction was calculated by the slope of the straight line obtained by the plot of unconsumed $[IO_3^-]$ versus time (Fig. 1). For the determination of the order of reaction with respect to each reactant, the help of Ostwald's isolation method in conjunction with van't Hoff's differential method has been taken. Considering IO_3^-, reducing sugar, hydroxyl ions and Ir(III) chloride as the main reactants, the general form of rate equation for the reaction can be written as

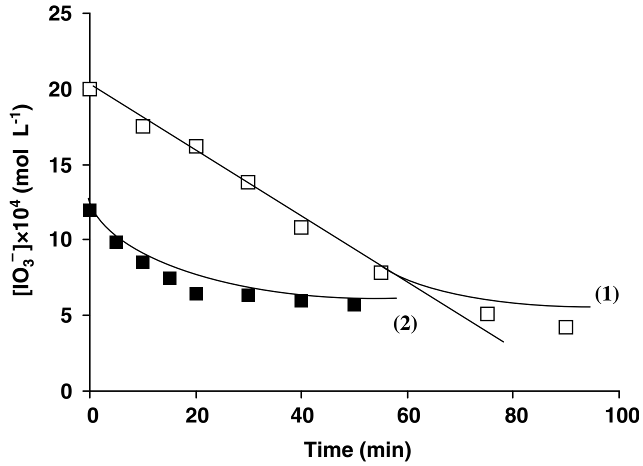


Figure 1. Plots between remaining $[IO_3^-]$ and time at 40 °C: (1) $[IO_3^-] = 2.00\times10^{-3}$ mol/L, $[OH^-] = 20.00\times10^{-2}$ mol/L, $[Ir(III)] = 13.38\times10^{-6}$ mol/L, $[maltose] = 2.00\times10^{-2}$ mol/L, $[\mu] = 0.25$ mol/L. (2) $[IO_3^-] = 1.20\times10^{-3}$ mol/L, $[OH^-] = 20.00\times10^{-2}$ mol/L, $[Ir(III)] = 26.76\times10^{-6}$ mol/L, $[xylose] = 2.00\times10^{-2}$ mol/L, $[\mu] = 0.25$ mol/L.

Table 1. Effect of variations in $[IO_3^-]$ and ionic strength (μ) of the medium on the rate of oxidation of xylose and maltose at 40 °C

$[IO_3^-]\times10^3$ (mol/L)	μ (mol/L)	$k_1\times10^4$ (s^{-1})	
		Xylose	Maltose
0.40	0.25	5.95	2.08
0.80	0.25	6.25	1.95
1.00	0.25	6.00	2.00
1.20	0.25	6.67	1.98
1.60	0.25	6.25	1.93
2.00	0.25	6.36	1.97
2.40	0.25	6.25	1.89
2.80	0.25	5.95	1.51
3.20	0.25	—	1.32
3.60	0.25	4.44	—
4.00	0.25	4.44	1.04
1.00	0.25	5.00	2.22
1.00	0.50	4.75	2.24
1.00	0.75	5.00	2.22
1.00	1.00	5.00	2.24
1.00	1.25	4.69	2.16

Solution conditions: $[OH^-] = 20.00\times10^{-2}$ mol/L, $[Sugar] = 2.00\times10^{-2}$ mol/L, $[Ir(III)] = 26.76\times10^{-6}$ mol/L (xylose) and 13.38×10^{-6} mol/L (maltose).

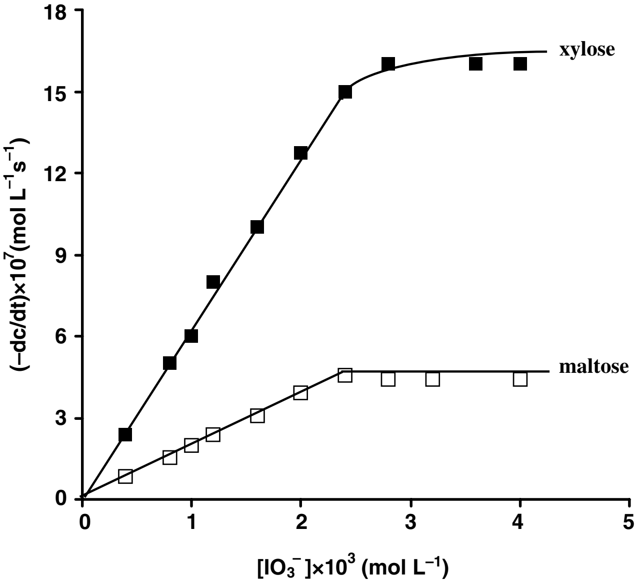


Figure 2. Plots between ($-$dc/dt) and $[IO_3^-]$ at 40 °C: $[OH^-] = 20.00\times10^{-2}$ mol/L, $[Ir(III)] = 26.76\times10^{-6}$ mol/L (xylose) and 13.38×10^{-6} mol/L (maltose), $[Sugar] = 2.00\times10^{-2}$ mol/L, $[\mu] = 0.25$ mol/L.

$$\text{rate} = k[IO_3^-]^\alpha[\text{sugar}]^\beta[Ir(III)]^\gamma[OH^-]^\delta \tag{1}$$

For the determination of the experimental rate law, first of all a series of experiments with varying initial concentration of IO_3^- were performed at constant concentrations of all other reactants and at constant temperature 40 °C. In the light of Ostwald's isolation method, the concentrations of reducing sugar and OH^- ions were fixed in large excess with respect to IO_3^- throughout its variation. Since the concentrations of those in excess will not change very much during the course of reaction and Ir(III) being a catalyst is reproduced in the reaction, the rate law (Eq. 1) under this condition becomes

$$\text{rate} = k_1[IO_3^-]^\alpha \tag{2}$$

where k_1, the apparent rate constant, $= k[\text{sugar}]^\beta[Ir(III)]^\gamma[OH^-]^\delta$.

Kinetic results obtained with the variation of IO_3^- from 0.4×10^{-3} to 4.0×10^{-3} mol/L are presented in Table 1 and also in Figure 2. It is clear from Figure 2 that in the oxidation of both xylose and maltose, there is direct proportionality between the rate and $[IO_3^-]$ throughout its variation except at higher concentrations, where the rate is unaffected by the $[IO_3^-]$. This shows that the order of reaction with respect to $[IO_3^-]$ is unity up to its 2.40×10^{-3} mol/L, and thereafter it becomes zero order. Almost constant values of the pseudo first-order rate constant (k_1) up to its 2.40×10^{-3} mol/L also support the above experimental findings, where unity order with respect to IO_3^- has been concluded (Table 1). Since throughout the study of variations of all other reactants concentrations, the concentration of IO_3^- was fixed in its lower range; hence, for the purpose of calculation of pseudo-first-order rate constant, k_1, the order with respect to $[IO_3^-]$ has been taken as unity. The pseudo first-order rate constant, k_1, was calculated as

$$k_1 = \frac{(-dc/dt)}{[IO_3^-]} \tag{3}$$

After establishing the first-order kinetics with respect to $[IO_3^-]$ in its lower range, nearly ten-fold variations in the concentrations of xylose and maltose were made under pseudo first-order conditions and on the basis of observed kinetic data, zero-order kinetics in [xylose] throughout its variation and first-order kinetics in [maltose] in its lower range were observed (Figs. 3 and 4). It is also observed that the reaction rate becomes independent of maltose at its higher concentrations (Fig. 4). Since in an unusual way, unity order in lower maltose concentration was observed; hence, to verify the kinetic results, experiments for the variations of [maltose] have been performed under three different conditions at 40 °C. The results thus obtained are presented in Figure 4. It is apparent from Figure 4 that there is first-order kinetics at low [maltose], which becomes zero order at higher [maltose]. Unity order in [Ir(III)] up to nearly 10-fold variation was observed in the oxidation of both the reducing sugars (Fig. 5). At low concentrations the pseudo first-order rate constant (k_1) is found to be directly proportional to [OH^-], and at higher concentrations it becomes almost independent of [OH^-] in the oxidation of both xylose and maltose (Fig. 6). When variation in ionic strength of the medium was made, it was observed that there is almost no change in pseudo-first-order rate constant, k_1, values with the change in ionic strength of the medium (Table 1). Since there was no effect of [Cl^-] on the rate of oxidation, the ionic strength of the medium was fixed by the addition of KCl to the reaction mixture. Observed k_1 values at 30, 35, 40 and 45 °C were utilized to calculate E_a, $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and the Arrhenius frequency factor (A) in the oxidation of aforesaid reducing sugars (Table 2). On the basis of observed first-order kinetics in lower concentrations of IO_3^- and OH^-, zero order in [xylose], first order in lower concentrations of maltose and first order in [Ir(III)], the following experimental rate laws in the form of Eqs. 4 and 5 can be proposed for the oxidation of xylose and maltose, respectively.

$$-\frac{d[IO_3^-]}{dt} = k'[OH^-][IO_3^-][Ir(III)] \tag{4}$$

and

$$-\frac{d[IO_3^-]}{dt} = k''[OH^-][IO_3^-][Ir(III)][S] \tag{5}$$

where 'S' stands for maltose in Eq. 5 and k' and k'' are the composite rate constants for xylose and maltose respectively.

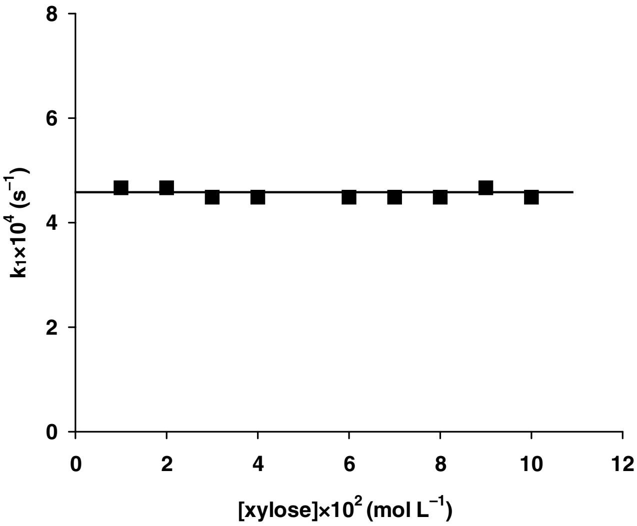


Figure 3. Plot between k_1 and [xylose] at 40 °C: [IO_3^-] = 1.00 × 10^{-3} mol/L, [OH^-] = 20.00 × 10^{-2} mol/L, [Ir(III)] = 26.76 × 10^{-6} mol/L.

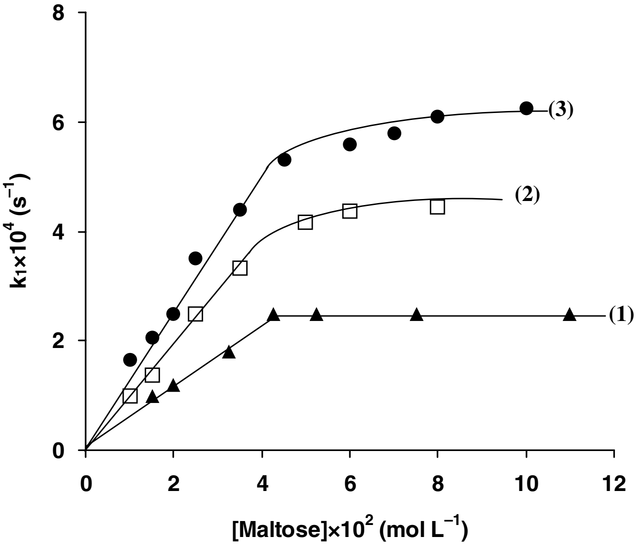


Figure 4. Plots between k_1 and [maltose] at 40 °C: (1) [IO_3^-] = 0.80 × 10^{-3} mol/L, [OH^-] = 15.00 × 10^{-2} mol/L, [Ir(III)] = 20.07 × 10^{-6} mol/L. (2) [IO_3^-] = 1.00 × 10^{-3} mol/L, [OH^-] = 10.00 × 10^{-2} mol/L, [Ir(III)] = 13.38 × 10^{-6} mol/L. (3) [IO_3^-] = 1.00 × 10^{-3} mol/L, [OH^-] = 20.00 × 10^{-2} mol/L, [Ir(III)] = 13.38 × 10^{-6} mol/L.

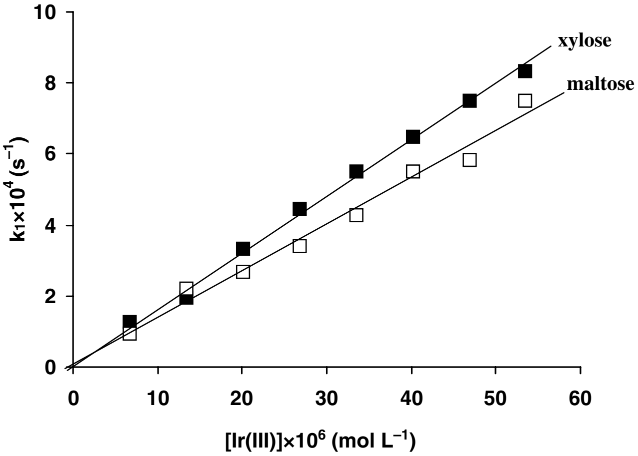


Figure 5. Plots between k_1 and [$IrCl_3$] at 40 °C: [IO_3^-] = 1.00 × 10^{-3} mol/L, [OH^-] = 20.00 × 10^{-2} mol/L, [Sugar] = 2.00 × 10^{-2} mol/L.

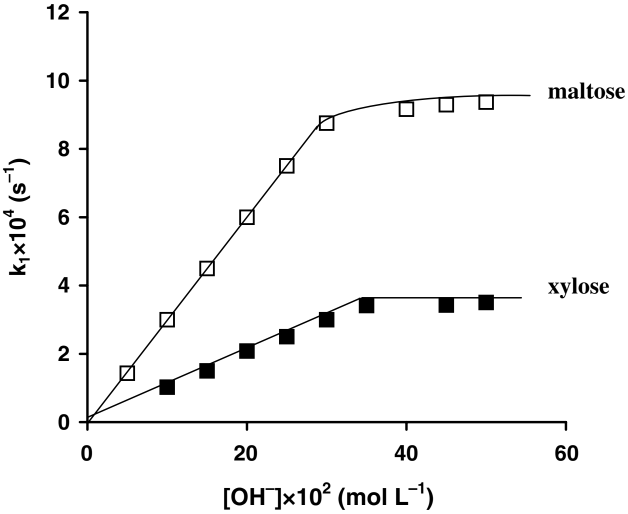


Figure 6. Plots between k_1 and $[OH^-]$ at 40 °C: $[IO_3^-] = 1.00 \times 10^{-3}$ mol/L, $[\text{Sugar}] = 2.00 \times 10^{-2}$ mol/L, $[\text{Ir(III)}] = 26.76 \times 10^{-6}$ mol/L (xylose) and 13.38×10^{-6} mol/L (maltose), $[\mu] = 0.55$ M.

Table 2. The values of composite rate constant and activation parameters for the oxidation of xylose and maltose at 40 °C

Activation parameters	Xylose	Maltose
E_a (kJ mol^{-1})	61.57	58.77
k' (mol^{-2} L^2 s^{-1})	1.12×10^2	—
k'' (mol^{-3} L^3 s^{-1})	—	0.39×10^4
$\Delta S^\#$ (J K^{-1} mol^{-1})	−17.37	22.26
$\Delta H^\#$ (J K^{-1} mol^{-1})	58.98	56.18
$\Delta G^\#$ (J K^{-1} mol^{-1})	53.55	46.69
A (mol^{-2} L^2 s^{-1})	1.87×10^{12}	—
A (mol^{-3} L^3 s^{-1})	—	2.22×10^{14}

4. Discussion

4.1. Reactive species of Ir(III) chloride in alkaline medium

A spectrophotometric study of the kinetics of the hydration of $IrCl_6^{3-}$ and of the addition of a Cl^- to $[Ir(OH_2)Cl_5]^{2-}$ in 1.0–2.5 M $HClO_4$ (or HCl) at 50 °C is reported,[25] where evaluation of the rate constants and the equilibrium constant K for the reversible reaction

$$IrCl_6^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ir(H_2O)Cl_5]^{2-} + Cl^-$$

have been made. Visible and ultraviolet absorption spectra of the new Ir(III) complexes $Ir(H_2O)_2Cl_4^-$ and $Ir(H_2O)_3Cl_3$, together with the spectra of $IrCl_6^{3-}$ and $Ir(OH_2)Cl_5^{2-}$ in 2.5 F $HClO_4$–1.2 F $NaClO_4$ are also reported[26] and found in reasonable agreement with the results reported by Poulsen and Garner[25] in water and by Jørgensen.[27] A few recent reports are available in the literature, in which kinetic studies have been made for the oxidation of reducing sugars by acidic solution of N-bromosuccinimide[28] (NBS) and NBA[6] in presence of Ir(III) as the homogeneous catalyst. In each case, the existence of the following equilibrium:

$$[IrCl_6]^{3-} + H_2O \rightleftharpoons [IrCl_5(H_2O)]^{2-} + Cl^-$$

has been assumed, and on the basis of the effect of $[Cl^-]$ on the rate of reaction, $IrCl_6^{3-}$ is taken as the reactive species of Ir(III) chloride in acidic medium. Very recently a study concerning the separation of rhodium and iridium and chloridation and chlorination of Ir(III) and Ir(IV) is reported.[29] In this paper authors have made efforts to study the effect of HCl concentration and temperature on Ir(III) speciation at equilibrium. According to them, at room temperature and at 70 °C, Ir(III) chloride in 0.1 M HCl concentration will remain as $[IrCl_3(H_2O)_3]$, whereas in 8 M HCl solution, it will remain as $[IrCl_5(H_2O)]^{2-}$ and $[IrCl_6]^{3-}$, respectively. Between concentrations of 0.1 and 8 M HCl, $[IrCl_3(H_2O)_3]$, $[IrCl_4(H_2O)_2]^-$ and $[IrCl_5(H_2O)]^{2-}$, are reported to be the predominant species. In the present investigation, since the solution of the catalyst, Ir(III) chloride, has been prepared in 0.1 M HCl, and in view of the observed kinetic data and the reported literature, it is reasonable to assume that the starting species of Ir(III) chloride is $[IrCl_3(H_2O)_3]$. Furthermore, since the study for the catalyzed oxidation of reducing sugars has been made in alkaline medium, a decision about the reactive species of Ir(III) chloride can be made only after taking into account the effect of $[OH^-]$ on the rate of oxidation. On the basis of (1) the observed kinetic data relating to first-order kinetics at low concentrations of OH^- in the oxidation of both xylose and maltose and (2) an increase in absorbance from 1.68 to 2.08 and 2.44 of Ir(III) chloride solution and Ir(III) chloride solution with two different concentrations of OH^- (Fig. 7: (2), (3) and (4)), it can be concluded that the following equilibrium is established:

$$[IrCl_3(H_2O)_3] + OH^- \rightleftharpoons [IrCl_3{\cdot}OH(H_2O)_2]^- + H_2O$$

Out of two species, $[IrCl_3(H_2O)_3]$ and $[IrCl_3{\cdot}OH(H_2O)_2]^-$, the species $[IrCl_3{\cdot}OH(H_2O)_2]^-$ can be assumed as the reactive species of Ir(III) chloride in the oxidation of xylose and maltose, because with the reactive species $[IrCl_3{\cdot}OH(H_2O)_2]^-$, and taking into consideration the existence of above equilibrium in the reaction, a rate law can be derived which will show that there is a positive effect of $[OH^-]$ on the rate of oxidation.

4.2. Reactive species of potassium iodate in alkaline medium

It is reported that KIO_3 has been used as an oxidant in the oxidation of acetophenones,[20] ferrocyanide,[30] thiocynate[31] and 1,3-dihydroxybenzene[32] in acidic medium. In each case IO_3^- has been regarded as the reactive

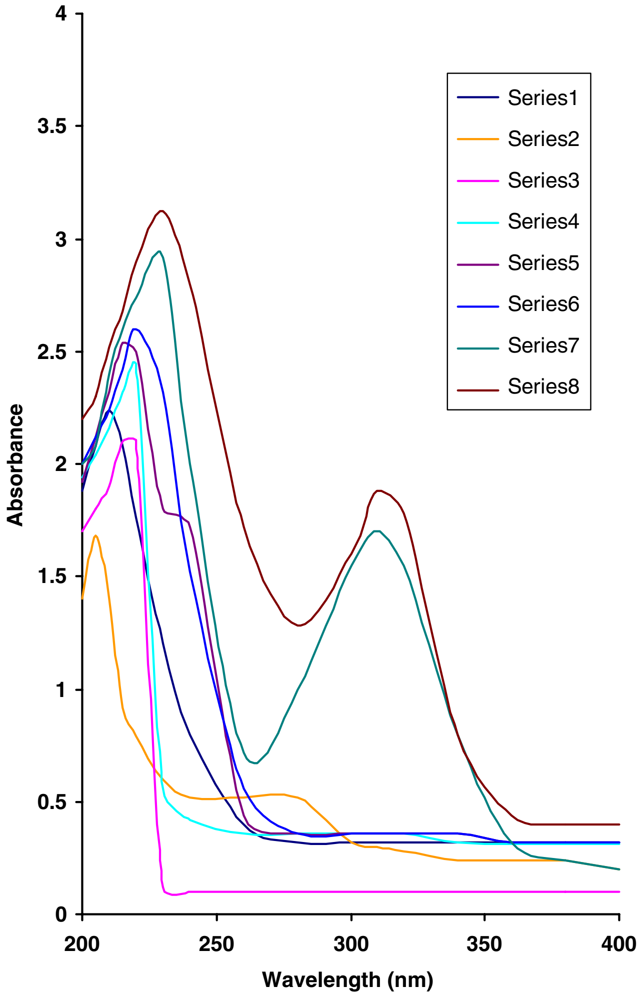


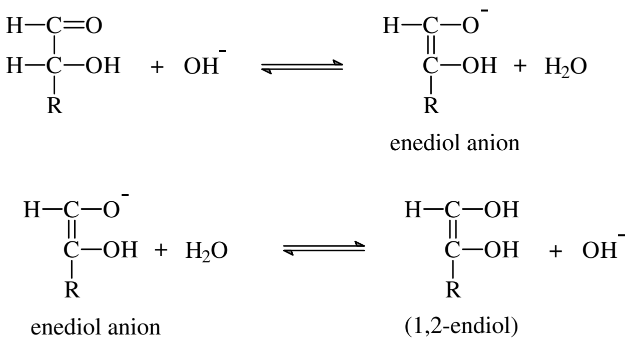
Figure 7. Spectra: (1) $[IO_3^-] = 1.00 \times 10^{-3}$ mol/L. (2) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L. (3) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L, $[OH^-] = 20.00 \times 10^{-2}$ mol/L. (4) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L, $[OH^-] = 50.00 \times 10^{-2}$ mol/L. (5) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L, $[OH^-] = 20.00 \times 10^{-2}$ mol/L, $[IO_3^-] = 1.00 \times 10^{-3}$ mol/L. (6) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L, $[OH^-] = 20.00 \times 10^{-2}$ mol/L, $[IO_3^-] = 2.00 \times 10^{-3}$ mol/L. (7) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L, $[OH^-] = 20.00 \times 10^{-2}$ mol/L, $[IO_3^-] = 1.00 \times 10^{-3}$ mol/L, $[maltose] = 2.00 \times 10^{-2}$ mol/L. (8) $[Ir(III)] = 2.68 \times 10^{-5}$ mol/L, $[OH^-] = 20.00 \times 10^{-2}$ mol/L, $[IO_3^-] = 1.00 \times 10^{-3}$ mol/L, $[maltose] = 10.00 \times 10^{-2}$ mol/L.

species of KIO_3 in acidic medium. Kinetic studies for Os(VIII)-[23] and Ru(III)-catalyzed[23,24] oxidation of organic compounds by an acidic solution of iodate are also reported. In these cases either HIO_3 or IO_3^- has also been concluded to be the reactive species of KIO_3 in acidic medium. Until now, no report is available in the literature where KIO_3 has been used as an oxidant in either the catalyzed or uncatalyzed oxidation of organic compounds in alkaline medium. However, a few reports are available where $NaIO_4$ has been used as an oxidant in Ru(III)-[17] and ruthenate ion-catalyzed[18] oxidation of reducing sugars in alkaline medium. On the basis of equivalence and kinetic studies for both the redox processes, IO_4^- is reported to be finally converted into IO_3^-, which very well supports the existence of IO_3^- in alkaline medium. In view of the reported kinetic data and spectral evidence, it can very easily be concluded that the species IO_3^- is the reactive species of KIO_3 in the oxidation of xylose and maltose in alkaline medium.

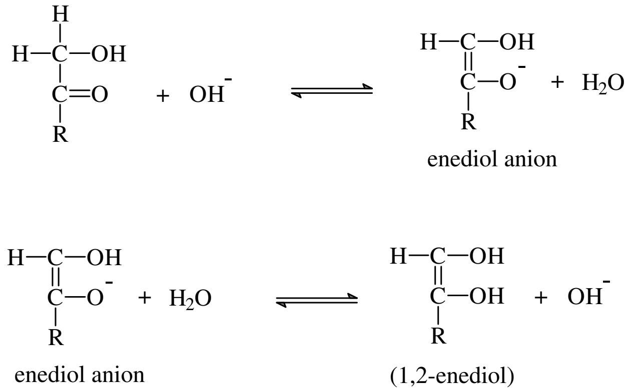
4.3. Reactive form of sugar in alkaline medium

It is reported[33] that in the presence of alkali reducing sugars undergo a tautomeric change resulting in the formation of an enediol anion and an enediol. The base-catalyzed formation of the enediol can be shown as follows:

(a) *Aldehydo sugars*



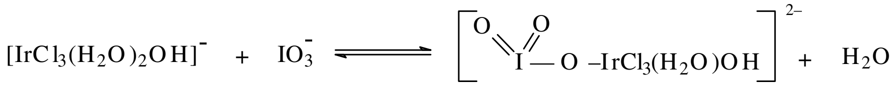
(b) *Keto sugars*

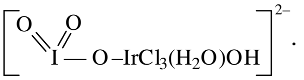


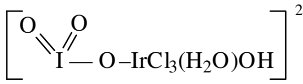
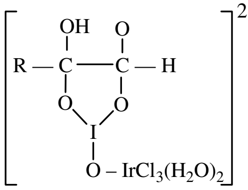
The formation of the enediol anion and the enediol in the presence of alkali is also supported by the work of Isbell and co-workers.[34] In the present study the observed order with respect to $[OH^-]$ for the Ir(III)-catalyzed oxidation of reducing sugars has led us to assume that it is the enediol form of sugar which is actually taking part in the reactions under investigation.

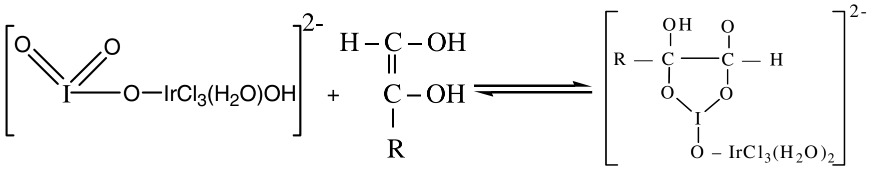
4.4. Spectral evidence for the formation of complexes during the course of reaction

After making a decision about the reactive species of both Ir(III) chloride and potassium iodate, and also about the reactive form of reducing sugars, efforts have been made to ascertain the possibility of the formation of a complex or complexes during the course of reaction. It is reported that transition metal ions such as Ru(III)[2] and Pd(II)[3] form complexes with the reducing sugar molecule in acidic medium. It is also reported[3,4] that the complexes thus formed have tendencies to react with reactive species of oxidant NBA and also with Hg(II), whose function in the reaction was as a Br^- ion scavenger and as co-catalyst. In the oxidation of xylose by an alkaline solution of potassium iodate in presence of Ir(III) as homogeneous catalyst, it has been observed that order with respect to xylose concentration is zero throughout its 10-fold variation. This shows that the enediol form of xylose will not take part in the reaction before the rate-determining step, although in fast steps, it will combine with the most reactive complex to form the reaction products along with regeneration of the catalyst. It is thus clear that the possibility of the formation of a complex in oxidation of xylose occurs only between reactive species of Ir(III) chloride and reactive species of potassium iodate in alkaline medium. In order to probe the possible formation of a complex between $[IrCl_3(H_2O)_2OH]^-$ and IO_3^-, spectra for the solution of Ir(III) chloride and OH^- and for the solutions of Ir(III) chloride and OH^- with two different concentrations of IO_3^- have been collected (Fig. 7: (3), (5) and (6)). From the spectra, it is clear that with the addition of potassium iodate solution there is an increase in absorbance from 2.08 to 2.54 and 2.62, with a slight shift in λ_{max} value towards longer wavelength, that is, from 216 to 217 and 220 nm. This increase in absorbance with the increase in $[IO_3^-]$ can be considered as an indication of increased formation of the complex between a reactive species of Ir(III) chloride and a reactive species of potassium iodate in alkaline medium according to the following equilibrium:



The shift in λ_{max} value towards longer wavelength is due to the combination of a chromophore, IO_3^-, and an auxochrome, OH^-, to give rise to another chromophore, .

Contrary to the observed zero effect of [xylose] on the rate of oxidation, first-order kinetics at low [maltose] and zero-order kinetics at high [maltose] have been observed in Ir(III)-catalyzed oxidation of maltose by an alkaline solution of potassium iodate. By considering the first-order kinetics in respect to the maltose concentration, an effort was made to probe the possibilities of the formation of a complex or complexes between $[IrCl_3(H_2O)_2OH]^-$ and IO_3^- and between the complex, if any, formed due to interaction of reactive species of the catalyst and reactive species of oxidant, and the reactive form of reducing sugar molecule in the catalyzed oxidation of maltose. Conclusions for the formation of complexes in the reaction under investigation have been drawn on the basis of spectra collected for Ir(III), OH^- and IO_3^- solutions and Ir(III), OH^-, IO_3^- and maltose solutions. From the observed spectra it is apparent that when iodate solutions of concentrations 1×10^{-3} and 2×10^{-3} M were added to the solution of Ir(III) chloride and OH^-, an increase in absorbance from 2.08 to 2.54 and 2.62 was obtained (Fig. 7: (3), (5) and (6)). This spectral information led us to conclude that the above equilibrium exists in solution, indicating an increasing formation of the complex, . When maltose solutions of two different concentrations were added to the solution of Ir(III), OH^- and IO_3^-, again an increase in absorbance was noted (Fig. 7: (5), (7) and (8)). This shows that the complex formed (λ_{max} 217 nm) subsequently combines with the reactive form of maltose to give a most reactive activated complex of the type  according to the following equilibrium:



4.5. Reaction mechanisms for the oxidation of xylose and maltose

On the basis of (1) the discussion made above for the reactive species of Ir(III) chloride, potassium iodate, and also for the reactive form of reducing sugars, (2) spectral information collected for the formation of a complex or complexes during the course of reaction and (3) kinetic orders observed with respect to $[IO_3^-]$, [Ir(III)], $[OH^-]$, [xylose] and [maltose], the reactions shown in Schemes 1 and 2 can be proposed for the oxidation of xylose and maltose, respectively.

On the basis of the above reaction scheme, the rate in terms of decrease in concentration of IO_3^- can be expressed as

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = 2k_3[C_3], \tag{6}$$

where 2 indicates that 1 mol of xylose is oxidized by 2 mol of KIO_3.

On applying the law of chemical equilibrium to steps (i) and (ii), Eqs. 7 and 8, respectively, are obtained:

$$C_2 = K_1[C_1][OH^-] \tag{7}$$

and

$$C_3 = K_2[C_2][IO_3^-] \tag{8}$$

Eqs. 7 and 8 will give Eq. 9

$$C_3 = K_1K_2[C_1][OH^-][IO_3^-] \tag{9}$$

On substituting the value of C_3 from Eq. 9 to Eq. 6, we get Eq. 10

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = 2k_3K_1K_2[C_1][OH^-][IO_3^-] \tag{10}$$

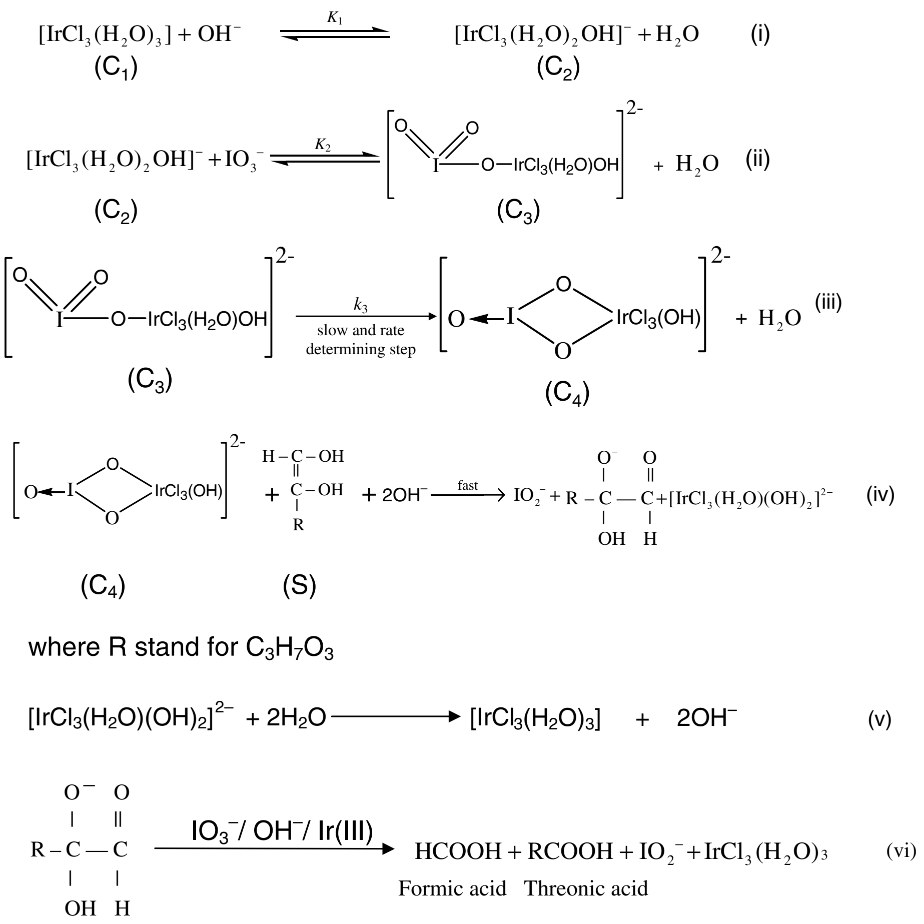
According to Scheme 1, the total concentration of Ir(III), that is, $[\text{Ir(III)}]_T$ at any time in the reaction can be shown as Eq. 11

$$[\text{Ir(III)}]_T = [C_1] + [C_2] + [C_3] \tag{11}$$

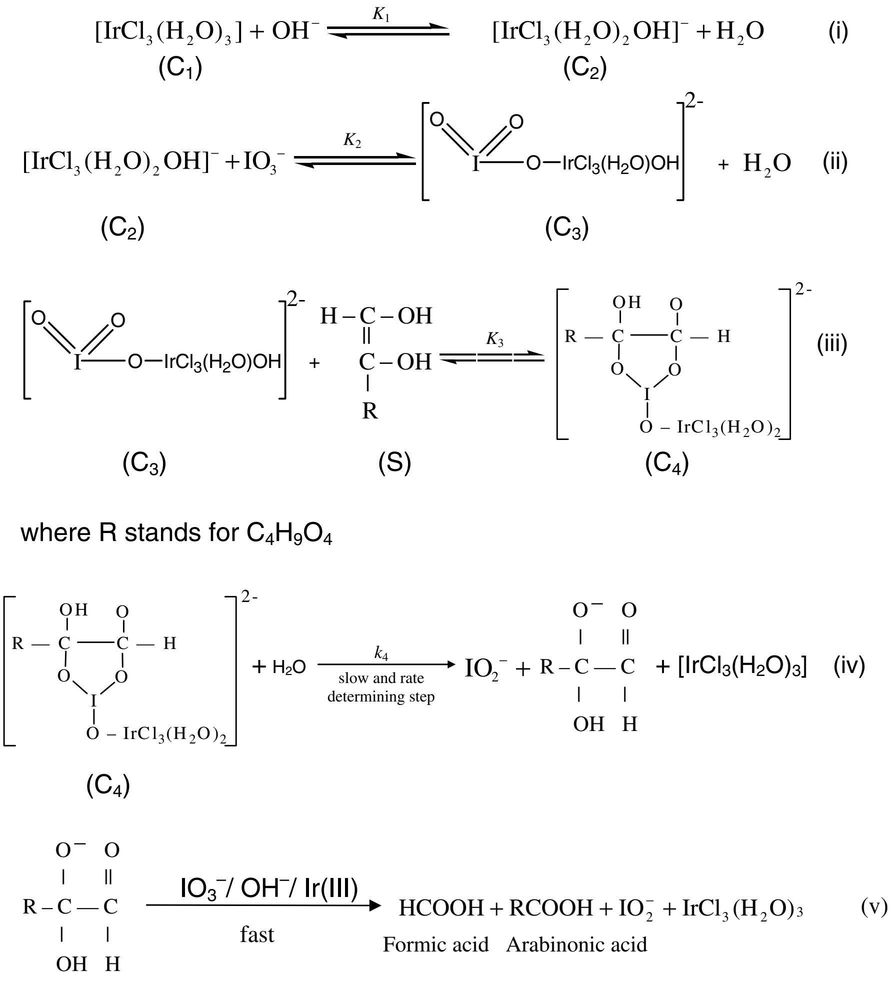
Eq. 12 based on Eqs. 7, 9 and 11 is as follows

$$[C_1] = \frac{[\text{Ir(III)}]_T}{1 + K_1[OH^-] + K_1K_2[OH^-][IO_3^-]} \tag{12}$$

On substituting the value of $[C_1]$ from Eq. 12 to Eq. 10, we get Eq. 13



Scheme 1.



Scheme 2.

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{2k_3K_1K_2[OH^-][IO_3^-][Ir(III)]_T}{1 + K_1[OH^-] + K_1K_2[OH^-][IO_3^-]} \quad (13)$$

The rate law 13 derived on the basis of proposed Scheme 1 is in close agreement with the kinetic information obtained experimentally about the effect of $[IO_3^-]$, $[Ir(III)]_T$, $[OH^-]$ and [S] on the rate of oxidation of xylose.

Eq. 13 can also be written as

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{2k_3K_1K_2[OH^-][IO_3^-][Ir(III)]_T}{1 + K_1[OH^-]\{1 + K_2[IO_3^-]\}} \quad (14)$$

According to Eq. 8

$$K_2[IO_3^-] = \frac{[C_3]}{[C_2]} \quad (15)$$

Since at low concentration of IO_3^-, $[C_3] \ll [C_2]$, hence according to Eq. 15 the inequality $K_2[IO_3^-] \ll 1$ can be assumed as a valid one. Under this condition, Eq. 14 will become Eq. 16

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{2k_3K_1K_2[OH^-][IO_3^-][Ir(III)]_T}{1 + K_1[OH^-]} \quad (16)$$

If it is assumed that $K_2[IO_3^-] \gg 1$ at high concentrations of IO_3^-, then under this condition, 1 will be negligible in comparison to $K_2[IO_3^-]$ and Eq. 14 will be reduced to Eq. 17

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{2k_3K_1K_2[OH^-][IO_3^-][Ir(III)]_T}{1 + K_1K_2[OH^-][IO_3^-]} \quad (17)$$

According to Eq. 7

$$K_1[OH^-] = \frac{[C_2]}{[C_1]} \quad (18)$$

Equilibrium reaction (i) shows that, at low concentrations of hydroxyl ion, $[C_2]$ will be less than $[C_1]$, and hence the inequality $K_1[OH^-] \ll 1$ can be assumed as valid one which will lead Eq. 16 to take the form of Eq. 19.

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = 2k_3K_1K_2[OH^-][IO_3^-][Ir(III)]_T$$

or

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = k'[\mathrm{OH}^-][\mathrm{IO_3}^-][\mathrm{Ir(III)}]_\mathrm{T} \tag{19}$$

where $k' = 2k_3K_1K_2$.

Eq. 19 is the rate law, valid for low concentrations of OH^- and $\mathrm{IO_3}^-$ and for all concentrations of Ir(III) lying between 6.69×10^{-6} M and 53.52×10^{-6} M and is well in agreement with experimental findings.

At high concentrations of $\mathrm{IO_3}^-$ and OH^-, $K_1K_2[\mathrm{IO_3}^-][\mathrm{OH}^-]$ will be very much greater than 1, and under this condition, Eq. 17 will finally be converted into Eq. 20

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = 2k_3[\mathrm{Ir(III)}]_\mathrm{T} \tag{20}$$

Eq. 20 is valid only for higher concentrations of $\mathrm{IO_3}^-$ and OH^-. Observed zero-order kinetics with respect to each $[\mathrm{IO_3}^-]$ and $[\mathrm{OH}^-]$ at their higher concentrations are well in accordance with the rate law 20.

Using Eq. 19, and making use of the kinetic data obtained for low $[\mathrm{IO_3}^-]$ and $[\mathrm{OH}^-]$ at 40 °C and under uniform conditions, the values of a composite rate constant (k') have been calculated and are presented in Table 3. Almost the same values of k' for the variations of $[\mathrm{IO_3}^-]$ and $[\mathrm{OH}^-]$ in their lower range, clearly prove the validity of the rate law 19 and in turn the rate law 13 and hence the proposed mechanism.

On the basis of above reaction Scheme 2 and stoichiometric data, the rate in terms of disappearance of $[\mathrm{IO_3}^-]$ can be written as Eq. 21

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = 4k_4[\mathrm{C_4}] \tag{21}$$

where 4 indicates that 1 mol of maltose is oxidized by 4 mol of $\mathrm{KIO_3}$.

On applying the law of chemical equilibrium to steps (i), (ii) and (iii), we get Eqs. 22–24, respectively.

$$C_2 = K_1[\mathrm{C_1}][\mathrm{OH}^-] \tag{22}$$

$$C_3 = K_1K_2[\mathrm{C_1}][\mathrm{OH}^-][\mathrm{IO_3}^-] \tag{23}$$

and

$$C_4 = K_1K_2K_3[\mathrm{C_1}][\mathrm{OH}^-][\mathrm{IO_3}^-][\mathrm{S}] \tag{24}$$

On putting the value of C_4 from Eq. 24 into Eq. 21, we have Eq. 25

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = 4k_4K_1K_2K_3[\mathrm{C_1}][\mathrm{OH}^-][\mathrm{IO_3}^-][\mathrm{S}] \tag{25}$$

According to mechanism, at any moment in the reaction the total concentration of Ir(III), that is, $[\mathrm{Ir(III)}]_\mathrm{T}$ can be expressed as Eq. 26

$$[\mathrm{Ir(III)}]_\mathrm{T} = [\mathrm{C_1}] + [\mathrm{C_2}] + [\mathrm{C_3}] + [\mathrm{C_4}] \tag{26}$$

Table 3. The calculated values of composite rate constants for the variations of $[\mathrm{IO_3}^-]$ and $[\mathrm{OH}^-]$ in the Ir(III)-catalyzed oxidation of xylose and maltose at 40 °C

$[\mathrm{IO_3}^-] \times 10^3$ (mol/L)	$[\mathrm{OH}^-] \times 10^2$ (mol/L)	Composite rate constant	
		$k' \times 10^2$ ($\mathrm{mol^{-2}\,L^2\,s^{-1}}$) Xylose	$k'' \times 10^4$ ($\mathrm{mol^{-3}\,L^3\,s^{-1}}$) Maltose
0.4	20.00	1.11	0.39
0.8	20.00	1.16	0.36
1.0	20.00	1.12	0.37
1.2	20.00	1.20	0.37
1.6	20.00	1.17	0.36
2.0	20.00	1.19	0.37
2.4	20.00	1.17	0.35
1.00	5.00	1.07	—
1.00	10.00	1.12	0.38
1.00	15.00	1.12	0.37
1.00	20.00	1.12	0.39
1.00	25.00	1.12	0.37
1.00	30.00	1.09	0.37
1.00	35.00	—	0.36

Solution conditions: [Sugar] = 2.00×10^{-2} mol/L, [Ir(III)] = 26.76×10^{-6} mol/L (xylose) and 13.38×10^{-6} mol/L (maltose), $[\mu] = 0.25$ mol/L (for $[\mathrm{IO_3}^-]$ variation) and 0.55 mol/L (for $[\mathrm{OH}^-]$ variation).

With the help of Eqs. 22–24 and 26, we can write Eq. 27

$$[\mathrm{C_1}] = \frac{[\mathrm{Ir(III)}]_\mathrm{T}}{1 + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{OH}^-][\mathrm{IO_3}^-] + K_1K_2K_3[\mathrm{IO_3}^-][\mathrm{OH}^-][\mathrm{S}]} \tag{27}$$

On substituting the value of $[\mathrm{C_1}]$ from Eq. 27 to Eq. 25, we get Eq. 28

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = \frac{4k_4K_1K_2K_3[\mathrm{OH}^-][\mathrm{IO_3}^-][\mathrm{S}][\mathrm{Ir(III)}]_\mathrm{T}}{1 + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{OH}^-][\mathrm{IO_3}^-] + K_1K_2K_3[\mathrm{OH}^-][\mathrm{IO_3}^-][\mathrm{S}]} \tag{28}$$

Eq. 28 can also be written as Eq. 29

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = \frac{4k_4K_1K_2K_3[\mathrm{OH}^-][\mathrm{IO_3}^-][\mathrm{S}][\mathrm{Ir(III)}]_\mathrm{T}}{1 + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{OH}^-][\mathrm{IO_3}^-]\{1 + K_3[\mathrm{S}]\}} \tag{29}$$

At low concentrations of S, the inequality $K_3[\mathrm{S}] \ll 1$ can be assumed as valid and under this condition Eq. 29 will be reduced to Eq. 30

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{IO_3}^-]}{\mathrm{d}t} = \frac{4k_4K_1K_2K_3[\mathrm{IO_3}^-][\mathrm{OH}^-][\mathrm{S}][\mathrm{Ir(III)}]_\mathrm{T}}{1 + K_1[\mathrm{OH}^-]\{1 + K_2[\mathrm{IO_3}^-]\}} \tag{30}$$

At high concentrations of S, Eq. 29 will be reduced to Eq. 31 because in this range, the existence of the inequality $K_3[\mathrm{S}] \gg 1$ will make 1 negligible in comparison to $K_3[\mathrm{S}]$.

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{4k_4K_1K_2K_3[IO_3^-][OH^-][S][Ir(III)]_T}{1 + K_1[OH^-]\{1 + K_2K_3[IO_3^-][S]\}} \quad (31)$$

Further, when at low concentrations of IO_3^-, $K_2[IO_3^-] \ll 1$ then $K_2[IO_3^-]$ in comparison to 1 can be neglected in Eq. 30, which under this condition will be reduced to Eq. 32.

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{4k_4K_1K_2K_3[IO_3^-][OH^-][S][Ir(III)]_T}{1 + K_1[OH^-]} \quad (32)$$

At high concentrations of IO_3^- and S, the inequality $K_2K_3[IO_3^-][S] \gg 1$ will reduce Eq. 31 to Eq. 33.

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = \frac{4k_4K_1K_2K_3[IO_3^-][OH^-][S][Ir(III)]_T}{1 + K_1K_2K_3[IO_3^-][S][OH^-]} \quad (33)$$

From Eqs. 32 and 33, it is clear that at low concentrations of OH^-, Eq. 32 with inequality $K_1[OH^-] \gg 1$, and at high concentrations of OH^-, Eq. 33 with inequality $K_1K_2K_3[IO_3^-][S][OH^-] \gg 1$, will be reduced to Eqs. 34 and 35, respectively.

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = 4k_4K_1K_2K_3[IO_3^-][OH^-][S][Ir(III)]_T \quad (34)$$

and

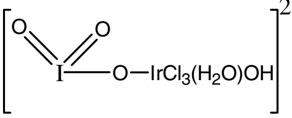
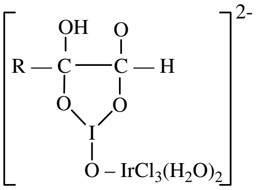
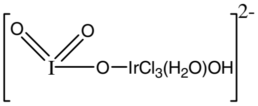
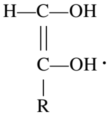
$$\text{rate} = -\frac{d[IO_3^-]}{dt} = 4k_4[Ir(III)]_T \quad (35)$$

The rate law 34 can also be written as

$$\text{rate} = -\frac{d[IO_3^-]}{dt} = k''[IO_3^-][OH^-][Ir(III)]_T[S] \quad (36)$$

where $k'' = 4k_4K_1K_2K_3$.

When the validity of the rate law 34 or 36 was tested by the kinetic data observed at low concentrations of substrate under uniform experimental conditions for the variations of OH^- and IO_3^-, it was found that the values of k'' remain almost the same for both the variations in their lower range (Table 3). This proves the validity of rate law 34 and in turn rate law 29, and hence the proposed mechanism.

In the present study of the Ir(III)-catalyzed oxidation of reducing sugars, Schemes 1 and 2 have been proposed for xylose and maltose, respectively. In Scheme 1, the most unstable activated complex,  , is formed by the interaction of two similarly charged species, that is, $[IrCl_3(H_2O)_2\text{-}OH]^-$ and IO_3^-, as a result of which the transition state will be a more highly charged species. Due to this more solvent molecules will be required than for the separate ions. This would lead to a decrease in entropy. The observed negative entropy of activation supports the formation of aforesaid activated complex by the interaction of two similarly charged species in step (ii) of Scheme 1. For the oxidation of maltose, a separate reaction path (Scheme 2) has been proposed, where the most reactive activated complex,  has been shown to be formed by the interaction of a charged species  and a neutral molecule . In this case, the transition state will have the same charge, but it will be dispersed over a greater volume, as a result of which the transition state will be less polar than the reactants. This would lead to an increase in entropy. The observed positive entropy of activation in the Ir(III)-catalyzed oxidation of maltose is certainly evidence for step (iii) of Scheme 2. In step (iii) the complex in the transition state has the same charge dispersed over greater volume than the charged species while interacting with the neutral species in the reactant state. Since the order of the frequency factor in the oxidation of xylose and maltose is not the same, it is reasonable to assume that the proposed reaction mechanisms as shown in Schemes 1 and 2 are well in accordance with the observed kinetic data.

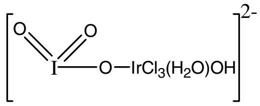
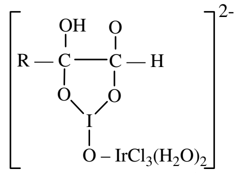
4.6. Comparative studies

The results of the present study of the Ir(III)-catalyzed oxidation of xylose and maltose by potassium iodate in alkaline medium were compared with the results reported for Ru(III)-catalyzed[24] oxidation of indigo carmine by iodate in acidic medium and the Ir(III)-catalyzed[6] oxidation of reducing sugars by NBA in acidic medium. When the present study in respect of the role of iodate was compared with the Ru(III)-catalyzed[24] oxidation of indigo carmine, it is found that the species IO_3^- is the reactive species of potassium iodate in acidic as well as in alkaline medium. As far as the kinetic order with respect to IO_3^- is concerned, it is first-order throughout the variation of $[IO_3^-]$ in the reported Ru(III)-catalyzed[24] oxidation and first to zero order in the present study of the Ir(III)-catalyzed oxidation of reducing sugars. When the present study has been made for the effect of [sugar] on the rate of oxidation, it is found that in the case of xylose the rate is independent of [xylose] and in the case of maltose, it is first order at low concentrations of maltose and becomes zero order at its higher concentrations. The reported[6] zero-order kinetics in [sugar] for Ir(III)-catalyzed oxidation seems to be similar with the present study as far as order with respect to xylose is concerned, but dissimilar as far as the order with respect to maltose is concerned. Since the present study has been performed in alkaline medium, the reducing sugar molecule participates in the reaction in the enediol form, whereas in the reported[6] Ir(III)-catalyzed oxidation, it participates in the reaction as such. On the basis of the observed kinetic data and spectral information, it is concluded that $[IrCl_3(H_2O)_2OH]^-$ is the reactive species of Ir(III) chloride in the present study of the oxidation of reducing sugars in aqueous alkaline medium, whereas in the reported[6] Ir(III)-catalyzed oxidation of reducing sugars, the reactive species of Ir(III) chloride was found to be $[IrCl_6]^{3-}$. The proposed reaction Schemes 1 and 2 in the present study clearly show that there is formation of a complex between the reactive species of Ir(III) chloride and reactive species of potassium iodate in alkaline medium, which is well supported by the observed kinetic data and also by the spectral evidence collected. This finding in the present paper is clearly in line with the result reported[6] for Ir(III)-catalyzed oxidation, where the formation of a complex occurs between the reactive species of Ir(III) chloride and the reactive species of NBA in acidic medium. In the present paper, on the basis of the observed entropy of activation, it is supported that in the case of xylose, the formation of the most unstable activated complex takes place by the interaction of two similarly charged species and in the case of maltose, it takes place by the interaction of a charged species and a natural molecule. This result is contrary to the result reported[6] for Ir(III)-catalyzed oxidation, where on the basis of positive entropy of activation, it is proposed that the rate-determining step involves the interaction between two oppositely charged species.

5. Conclusions

The following conclusions were drawn from the observed kinetic data and from the spectral information collected for the Ir(III)-catalyzed oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium.

(1) IO_3^- and $[IrCl_3(H_2O)_2OH]^-$ have been assumed as the reactive species of potassium iodate and Ir(III) chloride in alkaline medium, respectively.

(2) The complex,  and the complex,  have been proposed as the most unstable activated complex in the oxidation of xylose and maltose, respectively.

(3) Step (ii) of Scheme 1, in which the interaction between two similarly charged species results in the formation of an activated complex, is supported by observed negative entropy of activation. Step (iii) of Scheme 2, in which the interaction between a charged species and a natural molecule results in the formation of an activated complex, is supported by the observed positive entropy of activation.

(4) First-order kinetics observed at low concentrations of maltose distinguishes Scheme 2 from Scheme 1 where zero-order kinetics with respect to [xylose] throughout its variation has been observed.

(5) The rate of oxidation of either xylose or maltose is unaffected by the ionic strength of the medium.

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