First and novel oxidation of D-fructose by potassium iodate using [IrCl₃(H₂O)₂OH]⁻ complex as a homogeneous catalyst in alkaline medium

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ABSTRACT

The kinetics of Ir(III)-catalyzed oxidation of D-fructose by potassium iodate was studied in an aqueous alkaline medium at 40 °C. The experimental result shows a first order dependence on iodate and [OH⁻] at their low concentrations, but tending towards zeroth order at their higher concentrations. Zero order kinetics with respect to [D-fructose] was observed throughout its variation. The linear dependence of the reaction rate at lower [Ir(III)] chloride tends towards zero order at its higher concentrations. Variation in [Cl⁻] and ionic strength of the medium did not bring about any significant change on the rate of reaction. The decrease in the rate of reaction with increase in the dielectric constant of the medium was observed in the oxidation of D-fructose. Kinetic and equivalence studies together with product analysis, observed effect of dielectric constant of the medium on the rate of reaction, activation parameters and multiple regression analysis furnished a basis for the formation of a common reaction mechanism for the iridium(III)-catalyzed oxidation of D-fructose by iodate in the alkaline medium.

1. Introduction

Different oxidizing agents have been used for different metal ion catalysts like chromium(III) [1], ruthenium(III) [2–4], iridium(III) [5,6], and palladium(II) [7,8] in the oxidation of organic compounds. Among the various metal ions, iridium(III) and ruthenium(III) are highly efficient. Recently the use of transition metal ions either alone or as binary mixtures as catalysts have received much interest in many redox reactions. Their oxidizing and catalytic activities are due to the existence of variable oxidation states, as a consequence of partly filled d or f orbital. Their ability to form both σ and π bonds with other moieties or ligands is one of the chief factors for importing catalytic properties to transition metal ions as well as their complexes. Reaction mechanism of various elementary reactions must be investigated to analyze the effect on selectivity [9]. Therefore, the basic study of catalytic reaction will prove the scientific basis for improving catalyst selectivity and making highly efficient catalyst.

Carbohydrates are biologically important substances whose microbiological and physiological activities depend largely on their redox behavior. The catalyzed and uncatalyzed oxidation of sugars has been studied in detail by using N-halo compounds [10–12]. Oxidation of monosaccharides by different oxidizing agents is of special importance due to their biological relevance [13–16]. Lack of studies on the oxidation of D-fructose by iodate in the presence of Ir(III) in the alkaline medium has encouraged us to investigate the kinetic behavior of the title reaction in order to continue our study on the role of metal ions in oxidation reactions by iodate. Preliminary experimental results indicate that the reactions of D-fructose (Fru) with iodate in the alkaline medium without a catalyst were sluggish, but the reaction becomes facile in the presence of a small amount of Ir(III) catalyst. Therefore, in order to explore the mechanism of D-fructose-iodate reactions in an alkaline medium and also to study the catalytic actions of Ir(III), Ir(III) has been selected as a catalyst in the present work. The main objectives of the present study are to: (i) elucidate a plausible mechanism, (ii) deduce an appropriate rate law, (iii) identify the oxidation products, (iv) ascertain the various reactive species, (v) find the catalytic efficiency of Ir(III), (vi) determine the complex formation and (vii) the role of fructose molecule in the presence of Ir(III) chloride as catalyst and IO_3^- as oxidant in an alkaline medium.

2. Experimental

2.1. Material

A stock solution of Ir(III) chloride (Johnson Metthey) was prepared by dissolving the sample in hydrochloric acid of known

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strength. An allowance for the amount of hydrochloric acid present in the catalyst solution was made while the reaction mixture for kinetic studies was prepared. Sodium perchlorate, potassium iodate, sodium hydroxide, D-fructose (E. Merck) were used as supplied without further purification by preparing their solutions in doubly distilled water. Sodium perchlorate was used to maintain the ionic strength of the medium. All other reagents were of AR grade and doubly distilled water was used throughout the work. The reaction vessels were coated from outside with black paint to avoid any photochemical reaction.

2.2. Kinetic procedure

A thermostatic water bath was used to maintain the desired temperature within ±0.1 °C. The calculated amount of the reactants, i.e., potassium iodate, NaOH, Ir(III) chloride and water, except D-fructose were taken in a reaction vessel which was kept in a thermostatic water bath. After allowing sufficient time to attain the temperature of the experiment, a requisite amount of D-fructose solution, also thermostated at the same temperature was rapidly pipetted out and run into the reaction vessel. The total volume of the reaction mixture was 100 ml in each case. 5 ml aliquots of the reaction mixture was pipetted out at different time intervals and quenched with 4% potassium iodide containing 5 ml of known strength of perchloric acid solution. The progress of reaction was iodometrically monitored by measuring the unconsumed amount of potassium iodate. The rate of reaction ($-dc/dt$) was determined by the slope of the tangent drawn at a fixed [IO$_3^-$] in each kinetic run. In each case, the order of reaction was measured with the help of log–log plot of $-dc/dt$ versus concentration of the reactants.

2.3. Stoichiometry and product analysis

The reaction mixture containing D-fructose, Ir(III) chloride and NaOH with excess of potassium iodate were kept for 72 h at 40 °C. The total amount of iodate consumed by one mole of D-fructose for its complete oxidation was determined. Iodometric determination of the unconsumed iodate showed that two moles of the oxidant were consumed per mole of D-fructose forming sodium salts of formic acid and arabinonic acid. Accordingly, the following stoichiometric equation could be formulated:

$$C_6H_{12}O_6 + 2IO_3^- \xrightarrow{Ir(III)/OH^-} \underset{\text{Formate ion}}{HCOO^-} + \underset{\text{Arabinonate ion}}{C_5H_9O_6^-} + 2HIO_2$$

Sodium salts of formic acid and arabinonic acid were identified as the oxidation product in the oxidation of D-fructose. The major product was identified as the sodium salt of formic acid by TLC and by spot test [17].

3. Kinetics results and discussion

The kinetics of Ir(III)-catalyzed oxidation of fructose by potassium iodate was investigated at several initial concentrations of the reactants in an alkaline medium at 40 °C. The rate of the reaction ($-dc/dt$) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of the oxidant. The first order rate constant (k_1) was calculated from

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

At lower concentrations of iodate, the rate of reaction followed first order kinetics and shifted to zero order at its higher concentration (Table 1, Fig. 1). The rate of the reaction for different concentra-

Table 1
Effect of variation of [KIO$_3$], Fructose and [Ir(III)] on the rate of Ir(III)-catalyzed oxidation of D-fructose by iodate in alkaline medium at 40 °C

[KIO$_3$] × 10^4 M	[D-Fru] × 10^2 M	[Ir(III)] × 10^5 M	$(-dc/dt)$ × 10^8 M s^{-1}	k_1 × 10^5 (s^{-1})
4.0	2.0	6.70	10.11	36.10
5.0	2.0	6.70	11.66	27.76
6.0	2.0	6.70	14.58	28.58
8.0	2.0	6.70	23.80	36.61
10	2.0	6.70	26.19	30.81
25	2.0	6.70	30.00	12.76
40	2.0	6.70	34.72	9.18
50	2.0	6.70	38.52	8.30
10.0	1.0	2.68	16.66	16.66
10.0	1.5	2.68	15.68	15.68
10.0	2.0	2.68	15.68	15.68
10.0	3.0	2.68	16.66	16.66
10.0	4.0	2.68	16.66	16.66
10.0	5.0	2.68	15.68	15.68
10.0	6.0	2.68	16.66	16.66
10.0	7.0	2.68	16.66	16.66
10.0	8.0	2.68	16.66	16.66
10.0	10.0	2.68	15.68	15.68
10.0	2.0	0.67	4.10	4.10
10.0	2.0	1.34	7.98	7.98
10.0	2.0	2.01	12.82	12.82
10.0	2.0	2.68	16.66	16.66
10.0	2.0	5.36	20.00	20.00
10.0	2.0	6.70	26.19	26.19
10.0	2.0	8.04	30.55	30.55
10.0	2.0	9.38	33.33	33.33

Conditions: [NaOH] = 0.20 M, [KCl] = 1.80 × 10^{-3} M.

tions of fructose was found to be the same, revealing that the order of reaction with respect to fructose was zero (Table 1). The plot of rate constant k_1 versus [Ir(III)] was linear passing through the origin, suggesting first order dependence of the rate of reaction on the [Ir(III)]. It also shows that the reaction will not proceed with measurable velocity in the absence of Ir(III) (Table 1, Fig. 2). Kinetics of catalyzed oxidation of fructose indicates that on increasing [NaOH], the rate of reaction increases at low concentrations and shifts to zero order at its higher concentrations of NaOH (Table 2, Fig. 3). This shows a positive effect of [OH$^-$] on the rate of oxidation of fructose. Variations of ionic strength of the medium and [Cl$^-$] did not bring about any significant change in k_1 values under the constant experimental conditions (Table 3). The rate of reaction increased with a decrease in the dielectric constant of the medium (by increasing the % of ethanol by volume) (Table 3). Ethanol was not oxidized by potassium iodate under the experimental conditions.
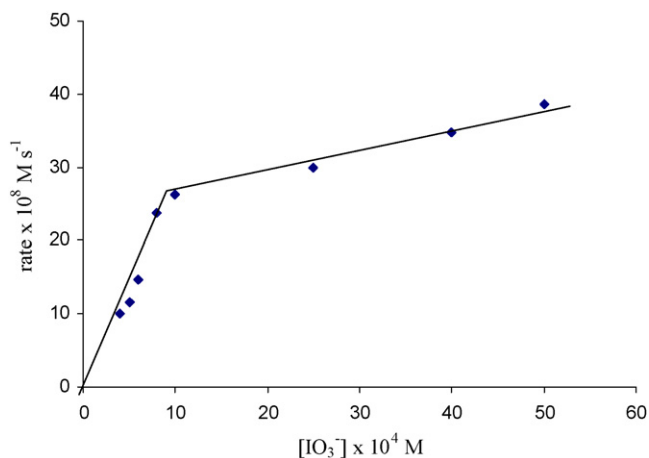

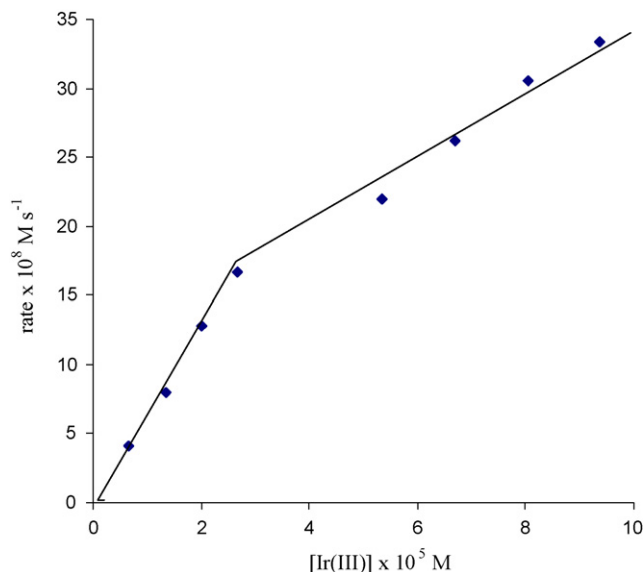**Fig. 1.** Plot between rate of reaction and [IO$_3^-$] under the condition of Table 1.

Fig. 2. Plot between rate constant k_1 and [Ir(III)] under the conditions of Table 1.

Table 2
Comparison of observed rates in the variation of [OH$^-$] with the calculated rates[a] for the Ir(III)-catalyzed oxidation of D-fructose by iodate in alkaline medium

[NaOH] $\times 10^2$ M	Rate $\times 10^8$ M s^{-1}		
	Observed	Calculated[b]	Predicted[c]
05.00	5.55	5.26	6.00
08.00	8.33	7.96	8.28
10.00	10.25	9.59	9.64
12.00	13.88	11.12	10.92
20.00	16.66	16.32	15.48
22.22	18.0	17055	16.53
25.00	19.6	18.98	18.03
30.00	22.22	21.29	20.43

[a] *Conditions*: [IO$_3^-$] = 10.00 × 10^{-4} M, [IrCl$_3$] = 2.68 × 10^{-5} M, [D-fructose] = 2.00 × 10^{-2} M, [NaOH] = 0.20 M, [KCl] = 1.80 × 10^{-3}, T = 40 °C.
[b] Calculated on the basis of rate law (12).
[c] Calculated with the help of multiple regression analysis.

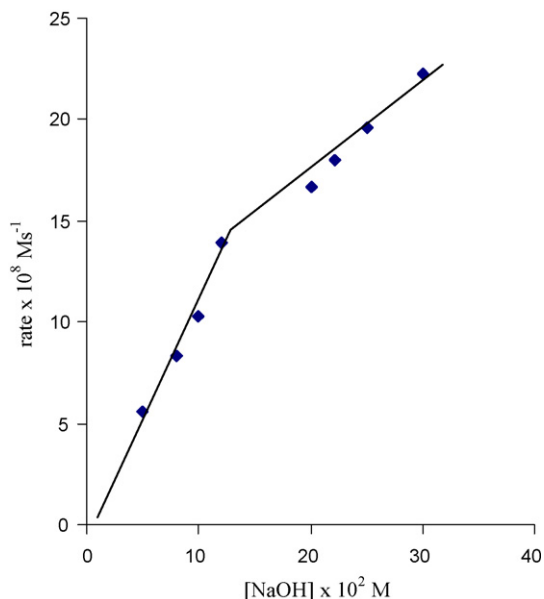**Fig. 3.** Plot between rate of reaction and [NaOH] under the condition of Table 1.

Table 3
Effect of variation of [KCl], ionic strength and dielectric constant of the medium on the rate of Ir(III)-catalyzed oxidation of D-fructose by iodate in alkaline medium at 40 °C

KCl $\times 10^3$ M	$\mu \times 10^2$ M	% Ethanol	$k_1 \times 10^5$ s^{-1}
1.8	25.00	–	15.68
2.8	25.00	–	15.15
3.8	25.00	–	15.27
4.8	25.00	–	15.15
5.8	25.00	–	15.27
6.8	25.00	–	15.68
9.8	25.00	–	15.15
1.80	25.00	5	16.66
1.80	25.00	10	18.75
1.80	25.00	15	24.24
1.80	25.00	20	33.33
1.80	25.00	30	41.65
1.80	25.00	40	53.87
1.80	25.00	50	76.51
1.80	4.04	–	15.15
1.80	7.6	–	15.20
1.80	11.16	–	15.20
1.80	14.72	–	15.12
1.80	18.28	–	15.20
1.80	28.96	–	15.15
1.80	36.08	–	15.18

Conditions: [IO$_3^-$] = 10.00 × 10^{-4} M, [IrCl$_3$] = 2.68 × 10^{-5} M, [D-fructose] = 2.00 × 10^{-2} M [NaOH] = 0.20 M.

The reaction was performed at different temperatures (308–323 K) (Table 4). The activation energy E_a was calculated from the linear Arrhenius plot of log k_1 versus $1/T$. With the help of the rate constant k_r, the other activation parameters such as enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), Gibbs free energy of activation ($\Delta G^{\#}$) and Arrhenius factor (A) were calculated (Table 4). The following form of rate law was used to calculate the activation parameters in the Ir(III) chloride catalyzed oxidation of fructose by potassium iodate in an alkaline medium.

$$-\frac{d[IO_3^-]}{dt} = k_r[IO_3^-][Ir(III)][OH^-]$$

3.1. Test for free radical

The addition of the reaction mixture to aqueous acryl amide monomer solutions in dark did not initiate polymerization, indicating the absence of formation of free radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions.

Table 4
Values of rate constant at different temperatures and activation parameters of Ir(III)-catalyzed oxidation of D-fructose by iodate in alkaline medium

Temp. (K)	$k_1 \times 10^5$ (s^{-1})
308	14.91
313	21.42
318	33.33
323	40.47
Activation parameters	
E_a (kcal)	14.08
$k_r \times 10^2$ (mol^{-2} L^2 s^{-1})	3.70
$\Delta S^{\#}$ (eu)	22.29
$\Delta H^{\#}$ (kcal)	13.45
$\Delta G^{\#}$ (kcal)	6.48
$A \times 10^2$ (mol^{-2} L^2 s^{-1})	3.80

Conditions: [IO$_3^-$] = 10.00 × 10^{-4} M, [IrCl$_3$] = 5.36 × 10^{-5} M, [D-fructose] = 2.00 × 10^{-2} M [NaOH] = 0.20 M, [KCl] = 1.80 × 10^{-3} M, μ = 25.00 × 10^{-2} M.

3.2. Reactive species of iodates

IO_3^- has been used as an oxidant in the oxidation of acetophenone [18], ferrocyanide [19], 1,3-dihydroxybenzene [20] and thiocyanate [21] in an acidic medium. In each case, IO_3^- has been taken as the reactive species of sodium iodate or potassium iodate in the acidic medium. Kinetic studies for Os(VIII) [22] and Ru(III) [23] catalyzed oxidation of organic compounds by an acidic solution of iodate were also reported. Oxidation of organic or inorganic compounds have been studied by sodium or potassium iodate in the presence of iridium and ruthenium in an alkaline medium [24,25]. It has already been reported by several workers that IO_3^- is the reactive species of potassium or sodium iodate in the acidic medium. On the basis of observed kinetic data and spectral evidence, IO_3^- has been assumed as the reactive species of potassium iodate in an alkaline medium. Kinetic data collected for Ir(III)-catalyzed oxidation of D-fructose by potassium iodate clearly showed that IO_3^- is the reactive species of potassium iodate in the alkaline medium.
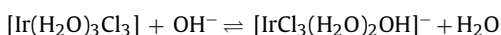
3.3. Reactive species of iridium(III) chloride in the alkaline medium

A spectrophotometric study of the kinetics of hydration of $IrCl_6^{3-}$ and addition of the Cl^- to $[Ir(H_2O)Cl_5]^{2-}$ in 1.0–2.5 M $HClO_4$ (or HCl) at 50 °C was reported [26], where the rate constants and the equilibrium constant (K) for the reversible reaction were given.

$$IrCl_6^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ir(H_2O)Cl_5]^{2-} + Cl^-$$
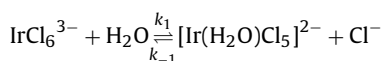
Visible and ultraviolet absorption spectra of the new Ir(III) complexes $[Ir(H_2O)_2Cl_4]^-$ and $[Ir(H_2O)_3Cl_3]$, together with the spectra of $[Ir(Cl_6)]^{3-}$ and $[Ir(H_2O)Cl_5]^{2-}$ in 2.5F $HClO_4$–1.2F $NaClO_4$, were also reported [27] and found in reasonable agreement with those reported by Poulsen and Garner [26] and by Jorgensen [28]. When Ir(III) chloride dissolved in 0.1 M HCl solution, $IrCl_6^{3-}$ and $[Ir(H_2O)Cl_5]^{2-}$ species were formed. On the basis of the effect of $[Cl^-]$ on the rate of the reaction and also assuming the existence of the above equilibrium in the reaction, $IrCl_6^{3-}$ is taken as the reactive species of Ir(III) chloride in the acidic medium.

This paper presents a brief account of the results of the study of the effect of HCl concentration and temperature on Ir(III) species at equilibrium. At room temperature and at 70 °C, Ir(III) chloride in 0.1 M HCl remains as $[IrCl_3(H_2O)_3]$, whereas in 8 M HCl it remains as $[IrCl_5(H_2O)]^{2-}$ and $[IrCl_6]^{3-}$ respectively. $[IrCl_3(H_2O)_3]$, $[IrCl_4(H_2O)_2]^-$ and $[IrCl_5(H_2O)]^{2-}$ are reported to be predominant species in the concentration range of 0.1–8 M HCl. In view of the observed kinetic data and the reported literature, it may be reasonably assumed that the reactive species of Ir(III) chloride is $[IrCl_3(H_2O)_3]$. The Ir(III)-catalyzed oxidation of D-fructose has been studied in an alkaline medium by varying the NaOH concentration to understand its effect on the reactive species of Ir(III) chloride. On the basis of observed kinetic data related to first order kinetics at low concentrations of NaOH in the oxidation of D-fructose and an increase in absorbance from 1.68 to 2.08 and 2.44 of Ir(III) chloride solution with two different concentrations of NaOH, it may be concluded that the following equilibrium is established:

$$[Ir(H_2O)_3Cl_3] + OH^- \rightleftharpoons [IrCl_3(H_2O)_2OH]^- + H_2O$$

Out of these two species $[Ir(H_2O)_3Cl_3]$ and $[IrCl_3(H_2O)_2OH]^-$, the species $[IrCl_3(H_2O)_2OH]^-$ [24] can be safely assumed to be the reactive species of iridium(III) chloride.

4. Reaction path proposed for Ir(III)-catalyzed oxidation of D-fructose

On the basis of observed orders with respect to different reactants taking part in the reaction and on the basis of spectral information collected for various complexes formed in the reaction, Scheme 1 can be proposed for the aforesaid reaction in the following way.

### 4.1. Reactive form of sugar in alkaline medium

It is reported [29] that in the presence of alkali, the reducing sugars undergo a tautomeric change resulting in the formation of an enediol and an enediol anion.

The formation of the enediol anion in alkaline medium is also supported by the work of Isbell and co-workers [30]. In the present investigation, the observed rate of reaction with respect to $[OH^-]$ for the Ir(III)-catalyzed oxidation of D-fructose has led us to conclude that the enediol form of sugar is actually taking part in the reactions under investigation.

It is reported that Pd(II) [31,32] and Ru(III) [33] form complexes with the reducing sugar. It has been observed that the order with respect to [D-fructose] is zero throughout its tenfold variation. This indicates that the enediol form of fructose does not take part in the reaction before the rate-limiting step but in fast steps it combines with the most reactive complex to form the reaction products. Thus, it is clear that the formation of a complex in the oxidation of fructose occurs between reactive species of Ir(III), i.e., $[IrCl_3(H_2O)_2OH]^-$ and reactive species of iodate, i.e., IO_3^- in an alkaline medium. In order to verify the existence of the aforementioned complex, spectra for the solution of Ir(III) chloride and OH^- with two different concentrations of IO_3^- have been studied. From the spectra, it is clear that there is an increase in absorbance from 2.08 to 2.54 and 2.62 with the addition of potassium iodate solution with a slight shift in λ_{max} value towards longer wavelength, i.e., from 216 to 217 and 220 nm. This increase in absorbance with the increase in $[IO_3^-]$ may be con-
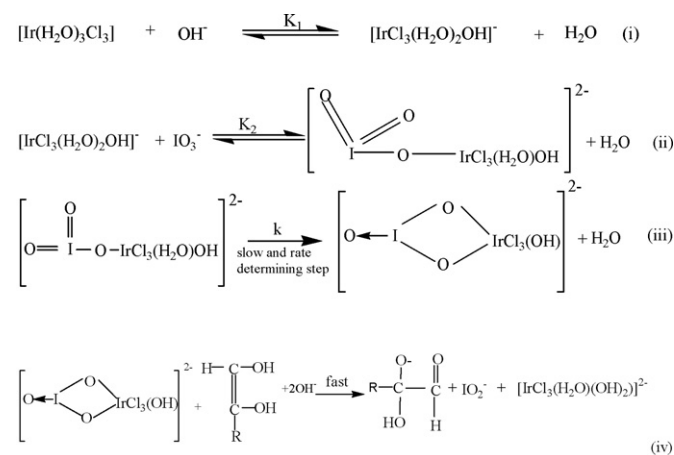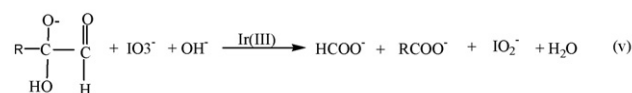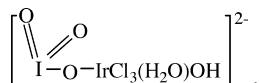

Scheme 1.

sidered as an indication of the formation of a complex between the reactive species of Ir(III) chloride and the reactive species of iodate in an alkaline medium expressed by the Eq. (ii) in Scheme 1.The shift in λ_{max} value towards longer wavelength may be ascribed to the combination of a chromophore, IO_3^-, and an auxochrome, OH^-, which results in the formation of another chromophore

$$\left[\begin{array}{c} O \\ \| \nearrow O \\ I-O-IrCl_3(H_2O)OH \end{array} \right]^{2-}.$$

4.2. Suggested mechanism

On the basis of observed kinetic results and taking [IrCl$_3$ (H$_2$O)$_2$OH]$^-$ and IO_3^- as the most active species of iridium chloride and potassium iodate respectively, the reaction steps in Scheme 1 are being proposed for the oxidation of fructose by iodate ion in the presence of iridium(III) chloride.

Taking all the steps in Scheme 1 for the oxidation of fructose and stoichiometry of the reaction, the following rate law Eq. (1) may be written in terms of loss of concentration of iodate ion

$$\text{Rate} = \frac{2kK_1K_2[OH^-][IO_3^-]_T[Ir(III)]_T}{1 + K_1[OH^-] + K_1K_2[OH^-][IO_3^-] + K_1K_2[OH^-][Ir(III)]_f} \quad (1)$$

Eq. (1) is valid for all the concentrations of IO_3^-, OH^- and Ir(III).

Since, at any time t, in the reaction (Scheme 1), C_3 will always be less than C_1, the right hand side of Eq. (1) will be less than 1 and as a result the inequality K_1K_2 $[OH^-][IO_3^-] \ll 1$ can be assumed to be a valid one. Since $[Ir(III)]_T$ is in the order of 10^{-5}, the inequality K_1K_2 $[OH^-]$ $[Ir(III)]_T \ll 1$ can also be taken as valid one. Now with these inequalities and with first order in low $[IO_3^-]$ at which the experiments were performed for the study of the effect of $[OH^-]$ and [fructose] on the rate of reaction and first order in $[Ir(III)]_T$ (except at very high concentration of Ir(III)), it is reasonable to assume that $1 + K_1[OH^-] \gg K_1K_2[OH^-]$ $[Ir(III)]_T + K_1K_2[OH^-][IO_3^-]$ and under this condition Eq. (1) will be reduced to Eq. (2)

$$\text{Rate} = -\frac{d[IO_3^-]}{dt} = \frac{2kK_1K_2[OH^-][IO_3^-]_T[Ir(III)]_T}{1 + K_1[OH^-]} \quad (2)$$

Eq. (2) is the rate law valid for low concentrations of IO_3^- and Ir(III) and for all the concentrations of OH^-.

Eq. (2) can also be written as

$$\frac{1}{\text{Rate}} = \frac{1}{2kK_1K_2[OH^-][IO_3^-]_T[Ir(III)]_T} + \frac{1}{2kK_2[IO_3^-]_T[Ir(III)]_T} \quad (3)$$

where Rate = $-d[IO_3^-]/dt$.

According to Eq. (3), the plot between 1/rate and 1/[OH$^-$] will be a straight line having an intercept on y-axis. A straight line was obtained with an intercept on 1/rate axis when 1/rate was plotted against 1/[OH$^-$] (Fig. 4). This proves the validity of the rate law (2) and hence the validity of proposed reaction scheme (Scheme 1). The values of K_1 and kK_2 calculated from the slope and intercept of the straight line for the oxidation of D-fructose were 2.13 and 10.19. Utilizing values of these constants, i.e., K_1 and kK_2 the reaction rates for the variation of [OH$^-$] in the Ir(III)-catalyzed oxidation of fructose have been calculated with the help of rate law (2) and found to be very close to the rates observed experimentally (Table 2). The close resemblance between the calculated and the observed rates further proves the validity of the rate law (2) and hence the proposed reaction scheme (Scheme 1).

4.3. Multiple regression analysis

With the help of multivariate regression analysis a relationship between observed pseudo first order rate constant (k_1) and concen-
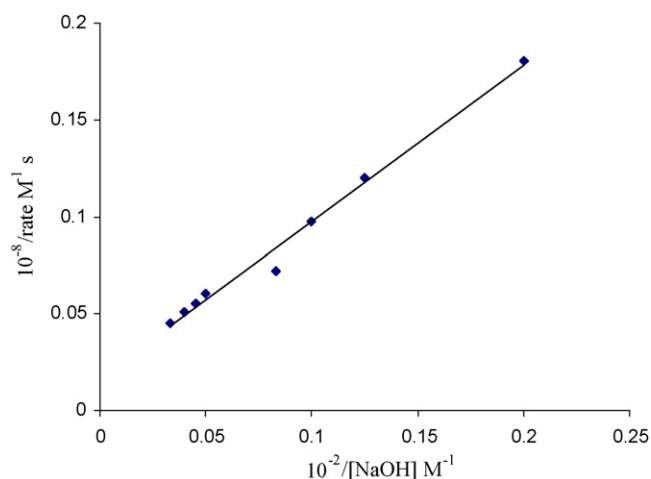

Fig. 4. Plot between 1/rate and 1/[OH$^-$] under the condition of Table 1.

trations of all the reactants of the reaction except IO_3^- was found to be:

$$k_1 = k[OH^-]^{0.68}[Ir(III)]^{0.65} \quad (4)$$

where $k = 4.53 \times 10^{-1}$.

With the help of Eq. (4), the reaction rate predicted for the variation of hydroxyl ion concentrations in the oxidation of fructose was found to be very close to the calculated and the observed rates (Table 2). The close similarity among the three rates, i.e., the observed, calculated and predicted clearly proves the validity of the rate law (2) and hence the proposed reaction mechanism.

For the oxidation of fructose, a reaction path was proposed where the most reactive activated complex was formed by the interaction of a similarly charged species [IrCl$_3$(H$_2$O)$_2$OH]$^-$ and IO_3^-. In this case the transition state will have the same charge, but with a dispersion over a larger volume. This results in the transition state that is less polar than the reactants which leads to an increase in its entropy. The observed positive entropy of activation for the oxidation of fructose by iodate in the presence of homogeneous catalyst Ir(III) chloride certainly is evidence for step (ii) of Scheme 1. In step (iii) the complex in the transition state has the same charge dispersed over larger volume than the charged species. The proposed mechanism is also supported by the moderate values of energy of activation and other parameters.

4.4. Effect of dielectric constant and calculation of the size of the activated complex

The change in dielectric constant (D) of the medium has been made by addition of ethanol to the reaction mixture. It was found that no reaction of the solvent occurs with the oxidant under experimental conditions. It is clear from Table 3, that, $-dc/dt$ and k_1 (rate constant) values increase with the decrease in D of the medium. The decrease in first order rate constant with the increase in D of the medium is also evident from plot of log k_1 versus $1/D$ (Fig. 5). The plot of log k_1 versus $1/D$ was linear with a negative slope supporting the involvement of similar charges in the rate-limiting step in the proposed mechanism. The value of the size of the activated complex, d_{AB}, has been found to be 3.57 Å.

4.5. Comparative studies

An attempt has been made to compare our experimental findings with the results reported earlier for Ir(III) chloride catalyzed
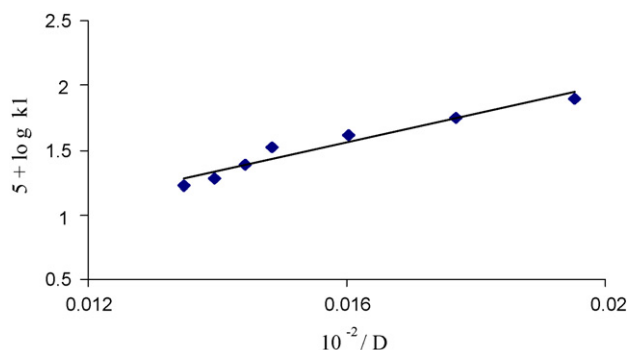
Fig. 5. Plot between $\log k_1$ and $1/D$ under the condition of Table 3.

oxidation of reducing sugars by iodate [24] in an alkaline medium and N-bromoacetamide [34] in an acidic medium. Ru(III) chloride oxidations of indigo carmine [23] in an acidic medium and reducing sugar [25] by iodate in an alkaline medium have been compared with our experimental findings. The studies were focused upon how an oxidant, i.e., iodate, in an alkaline medium affect (1) the oxidation of sugar, (2) the catalytic activity of iridium and (3) the mode of participation of other reactants in the formation of most unstable activated complex. When the results of the present study were compared with respect to iodate in iridium catalyzed oxidation of reducing sugar [24], it was found that the species $IO_3{}^-$ is the reactive species of potassium iodate in both the cases. As far as the kinetic order with respect to sugar is concerned, it is first to zero order [24] in the oxidation of maltose and zero order in the present study of the iridium catalyzed oxidation of fructose. The outcome of the present study shows similarities to Ir(III)-catalyzed oxidation of reducing sugars [34], being first to zero order with respect to oxidant as well as catalyst and zero order with respect to reducing sugars. Since the present study has been performed in an alkaline medium, the reducing sugar molecule participates in the reaction in the enediol form, whereas in the reported Ir(III)-catalyzed oxidation [34], it participates in the reaction as such. As far as order of reaction with respect to oxidant [25] is concerned, it is first order at its low concentrations, which deviates towards zero order at its higher concentrations. Zero order kinetics with respect to fructose was found in the present case and was also reported in Ru(III)-catalyzed oxidation of D-glucose and D-fructose [25]. Observed first to zero order kinetics in [Ir(III)] in the present study shows dissimilarity to the reported Ru(III)-catalyzed oxidation reaction [25]. Comparisons of the results of the present study with respect to the role of iodate to the Ru(III)-catalyzed oxidation of indigo carmine, reflect 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 oxidation and first to zero order in the present study of the Ir(III)-catalyzed oxidation of fructose. Based on the observed kinetic data and spectral information, it may be concluded that $[IrCl_3(H_2O)_2OH]^-$ is the reactive species in the oxidation of fructose in an alkaline medium, whereas in the reported Ir(III)-catalyzed oxidation of reducing sugars [34], the reactive species of Ir(III) chloride was found to be $[IrCl_6]^{3-}$.

5. Conclusion

Oxidation of fructose by iodate in an alkaline medium is very sluggish, but it becomes facile in the presence of Ir(III) catalyst. $IO_3{}^-$ and $[IrCl_3(H_2O)_2OH]^-$ have been assumed as the reactive species of potassium iodate and Ir(III) chloride in the alkaline medium, respectively. On the basis of the observed positive effect of $[OH^-]$

on the rate of oxidation reaction, it is concluded that the enediol form of fructose participates in the fast step of the reaction scheme proposed for the iridium-catalyzed oxidation of fructose. Positive entropy of activation is supported by the formation of the most unstable activated complex, which forms by the interaction of two similarly charged species. The rate of reaction of fructose is unaffected by the ionic strength of the medium. Oxidation products have been identified and activation parameters have also been evaluated. The observed results have been explained by a plausible mechanism and the related rate law has been deduced. It can be concluded that Ir(III) acts as an efficient catalyst in the oxidation of fructose by iodate in alkaline medium.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.07.021.

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