Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry
2017, 6 (6): 1158-1170
(International Peer Reviewed Journal)

Kinetics and Mechanism of Ir(III)-Catalyzed Oxidation of D-Galactose by Potassium Iodate in Aqueous Alkaline Medium

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Accepted on 17th November 2017, Published online on 27th November 2017

ABSTRACT

The kinetics of Ir (III)-catalyzed oxidation of galactose by potassium iodate in alkaline medium have been made at 40^0C. *The reaction exhibits first-order kinetics with respect to Ir (III).Unity order at low concentrations of galactose,* OH^- *and* IO_3^-*becomes zero order at their higher concentrations throughout their variations. Negligible effects of* Cl^- *and ionic strength of the medium on the rate of oxidation have been noted. The reaction was studied at four different temperatures and observed values of rate constants were utilized to calculate various activation parameters. A most probable reaction mechanism consistent with the observed kinetic data and spectral evidence has been proposed for the oxidation of galactose.*

Keywords: Mechanism, D-Galactose, Potassium iodate, Alkaline medium, Ir(III) Catalysis.

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 has 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 coworkers [2] who pointed out that β -aldoses (C-1 equatorial) are oxidized much faster than α -aldoses (C-1 axial).The transition metal catalyzed reactions are important for the chemical industry from both practical and economic point of view. Transition metal ions are found to be good catalysts and their complexes are also able to catalyze a wide variety of reactions like hydrogenation, oxidation and polymerization. The applications of transition metal catalysts such as Ru(III)[3, 4], Rh(III)[5, 6],Cu(II)[7] and Pd(II) [8], [9] in kinetic studies of redox reactions involving organic substrates are reported in literature. It was found that these catalysts work efficiently in both acidic and alkaline media. The use of Ir(III) chloride as a non-toxic and homogeneous catalyst has been reported[10]. Kinetic studies on Ir(III)-catalyzed oxidation of sulphanilic acid by diperiodatocuprate(III) [11] and arginine and lysine by hexacyano ferrate(III) [12] in alkaline medium have also been carried out. Kinetic studies regarding catalyzed oxidations of reducing sugars by various oxidants, viz N-bromoacetamide (NBA), N-bromosuccinimide (NBS)[13,14] and sodium metaperiodate in acidic and alkaline medium using transition metal ions, viz Os(VIII) [15], Pd(II)[16,17], Ru(VIII) [18], ruthenate ion [19], Ir(III) [20], Rh(III) [21] as homogeneous catalysts are also available in literature. Although iodate has been reported to be used as an oxidant in several uncatalyzed [22] reactions, there are very few reports where iodate has been used as an oxidant in catalyzed [23, 24] reactions. It is reported [25] that carbohydrates are biologically important substances whose microbiological and physiological activities depend largely on their redox behavior. In view of the above-mentioned facts and no information available for Ir(III)- catalyzed oxidation of galactose by iodate in alkaline medium, the present study has been undertaken.

MATERIALS AND METHODS

Chemicals and solutions: The solution of iridium (III) chloride (Johnson–Mathey & Co. Ltd) was prepared by dissolving 1g of sample in 0.1 M HCl and strength of Ir(III) chloride ($IrCl_3.3\ H_2O$) was found to be 3.35×10^{-3}M. 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 solution of D-galactose (A.R. grade) was freshly prepared daily. All other standardized solutions were prepared with double distilled water. The standard solution of sodium hydroxide (Qualigens chemicals) was used to maintain the required alkalinity. Ionic strength was maintained by adding calculated amount of KCl solution to the reaction mixture. All other reagents were of AR grade and doubly distilled water was used throughout the work. The reaction mixture containing appropriate amount of all reactants i.e. NaOH, Ir (III)-chloride, KIO_3 and water except substrate (galactose) was taken in a reaction vessel and placed in a thermostatic bath at constant temperature 40°C with an accuracy of ±0.1°C. A freshly prepared solution of galactose was also kept in the same thermostatic bath at same temperature. When both the solutions have acquired the temperature of bath measured amount of galactose solution was pipette out and mixed in conical containing reaction mixture. As soon as the galactose solution was mixed with the reaction mixture the reaction gets initiated. To know the actual progress of the reaction, 5mL of reaction mixture was taken out and poured in a conical flask containing 5mL of KI (4%) solution and 5mL of $HClO_4$ solution and titrated iodometrically against standard hypo solution using starch as indicator.

Measuring the unconsumed KIO_3 by 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 $[IO_3^-]$ >> [sugar]. Estimation of residual $[IO_3^-]$ in different sets showed that

1 mole of sugar consumed 2 moles of IO_3^-. Accordingly, the following stoichiometric equation was formulated:

$$\underset{\text{D-galactose}}{C_6H_{12}O_6 + 2IO_3^- + 2NaOH} \longrightarrow \underset{\text{Sodium salts of Galactonic acid and formic acid}}{C_6H_{12}O_7Na + HCOONa + 2IO_2^- + 2H_2O}$$

RESULTS AND DISCUSSION

In order to propose a probable reaction mechanism for Ir(III) catalyzed oxidation of galactose by potassium iodate in alkaline medium, it is necessary to study the effect of variation in concentration of different reactants on the rate of reaction. The kinetics of oxidation of galactose was investigated at several initial reactant concentrations. 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

$$k_1 = (-dc/dt) / [IO_3^-]$$

The effect of [iodate] was studied by varying the [iodate] in the reaction medium $0.5\text{x } 10^{-3} – 4\text{x } 10^{-3}$M at constant concentrations of all other reactants. First-order dependence of the reaction at lower [iodate] which tends to zero-order at its higher concentrations (Fig.1).

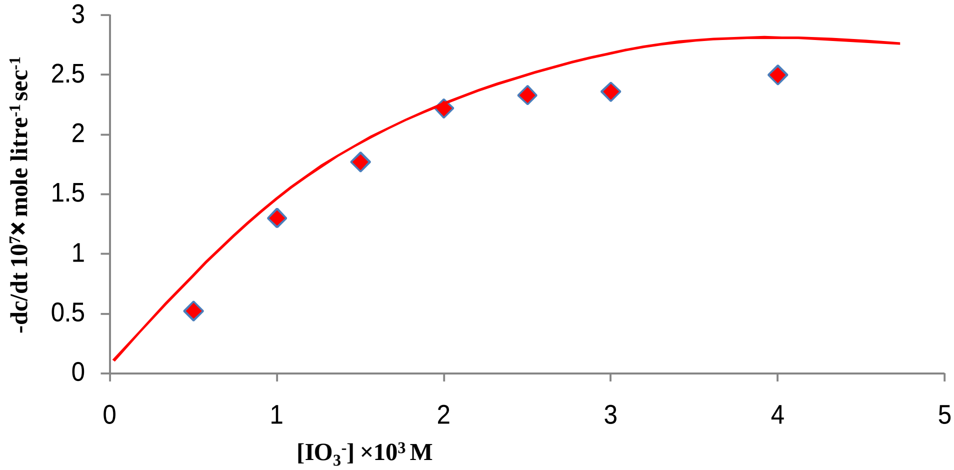


Fig 1. Plot between –dc/dtand [IO_3^-] at 40 ^{0}C
[Ir(III)] = 3.35x10^{-5}, [D-galactose] = 5× 10^{-2} M, [OH^-] = 10.00× 10^{-2} M, μ = 0.60 M

First order kinetics was observed with respect to the catalyst i.e. Ir(III) is shown by increasing k_1 values in direct proportionality with Ir(III)-chloride concentration (Fig 2).

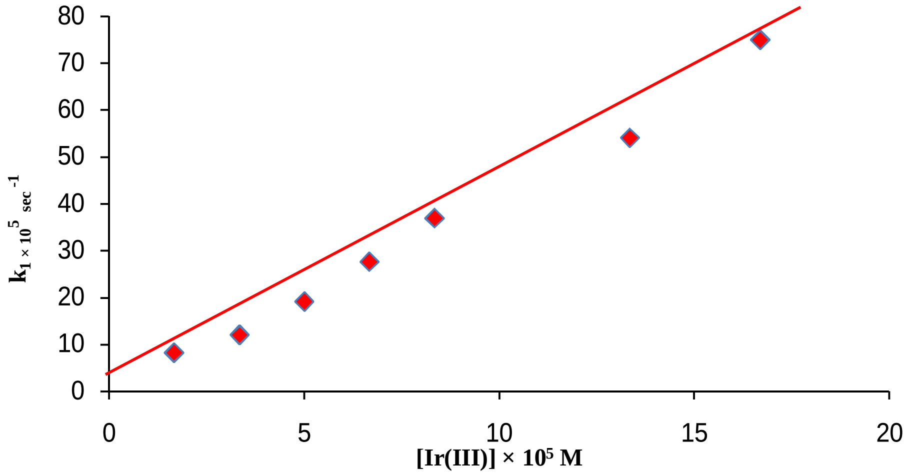


Fig 2. Plot between k_1 and [Ir(III)] at 40 ^{0}C
[IO_3^-] = 1.00 ×10^{-3} M, [D-galactose] = 5× 10^{-2} M, [OH^-] = 10.00× 10^{-2} M, μ = 0.60 M

To find out the dependence of rate on [galactose], kinetic runs are performed by varying the concentration of galactose in the range of 1.0 x 10^{-2} – 10.0 x 10^{-2} M keeping the concentrations of all other reactants constant at constant temperature. The first-order dependence of the reactions at lower [galactose] which tends to zero-order at its higher concentrations was noted (Fig 3).

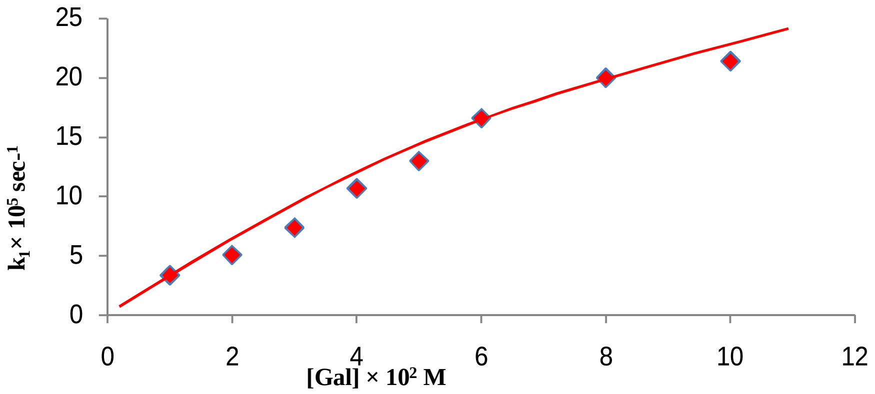


Fig 3. Plot between k_1 and [Gal at 40 ^{0}C
$[IO_3^-] = 1.00 \times 10^{-3}$ M, [Ir(III)] = 3.35x10^{-5} M, $[OH^-] = 10.00\times 10^{-2}$ M, μ = 0.60 M

A series of experiments were carried out at varying OH^- concentrations and results thus obtained show that the linear dependence of the reaction rate at lower $[OH^-]$ tends towards zero-order at its higher concentrations (Fig 4).

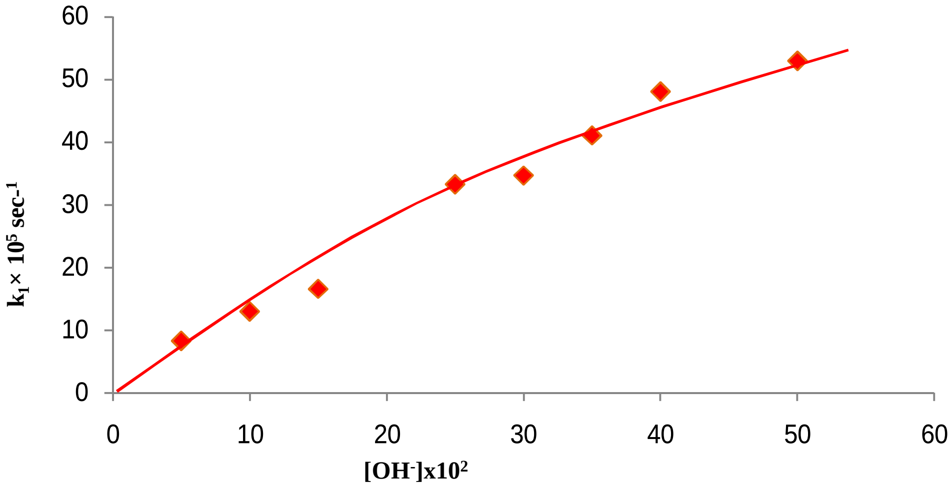


Fig.4. Plot between k_1 and $[OH^-]$ at 40 ^{0}C
$[IO_3^-] = 1.00 \times 10^{-3}$ M, [Ir(III)] = 3.35x10^{-5} M, [Gal.] = 5.00×10^{-2} M, μ = 0.60 M

Nil effect of ionic strength and dielectric constant of the medium were denoted. The reaction was studied at four different temperatures viz. 35^{0}C, 40 ^{0}C, 45^{0}C & 50^{0}C and observed k_1 values were utilized to calculate various activation parameters i.e., $\Delta G^\#$, $\Delta S^\#$, $\Delta H^\#$& A, presented in Table 1.

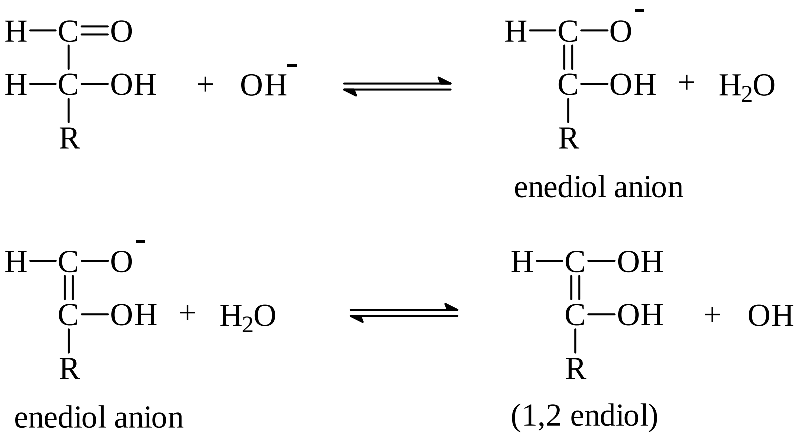
Table 1: Activation parameters for Ir (III)-catalyzed oxidation of D-galactose by KIO_3 at 40^{0}C

Reducing Sugar	E_a (KJmol^{-1})	k_r (M^{-3} s^{-1})	$\Delta S^\#$ (J/Kmol)	$\Delta H^\#$ (KJmol^{-1})	$\Delta G^\#$ (KJmol^{-1})	A (M^{-3} s^{-1})
D-galactose	17.50	7.76×10^2	36.21	16.87	59.54	1.07×10^{15}

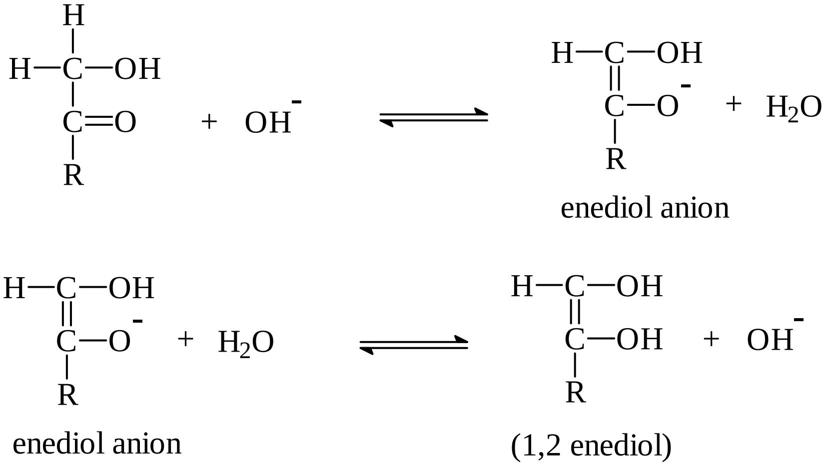
Reactive species of potassium iodate in alkaline medium: It is reported that KIO_3 has been used as an oxidant in the oxidation of acetophenones [26], ferrocyanide[27], thiocynate and 1,3-dihydroxybenzenein acidic medium. In each case IO_3^- has been regarded as the reactive.IO_3^-, which very well supports 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 galactose in alkaline medium.

Reactive species of sugar in alkaline medium: It is reported [28] 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) Aldehyde 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 [29].

In the present study the observed fractional positive 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 reaction under investigation.

Reactive species of Ir (III) chloride in alkaline medium: In the present study of the oxidation of D-galactose by KIO_3, Ir(III)-chloride has been used as homogeneous catalyst. 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[24], 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 galactose 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 of OH^- in the oxidation of galactose 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^- , it can be concluded that the following equilibrium is established:

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

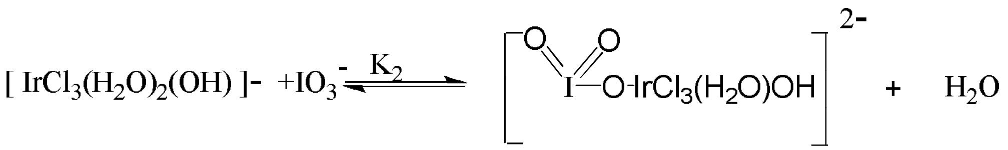
Out of two species, $[IrCl_3(H_2O)_3]$ and $[IrCl_3OH(H_2O)_2]^-$, the species $[IrCl_3OH(H_2O)_2]^-$ can be assumed as the reactive species of Ir(III) chloride in the oxidation of galactose, because with the reactive species $[IrCl_3OH(H_2O)_2]^-$ and taking into consideration the existence of above equilibrium in the reaction, a rate law can be derived.

Spectrophotometricevidence for the formation of complexes during the course of reaction: It is reported [21] that $[IrCl_3 (H_2O)_2OH]^-$ is the reactive species of Ir(III) chloride and IO_3^- is the reactive species of KIO_3 in alkaline medium. Experiments were performed to verify the formation of complex between reactive species of Ir(III) chloride i.e. $[IrCl_3(H_2O)_2OH]^-$ and reactive species of potassium iodate i.e. IO_3^- in the oxidation of galactose. The spectra of solution containing Ir(III) chloride alone, solution of Ir(III)-chloride with two different concentrations of OH^-, solution of Ir(III)-chloride, OH^-& KIO_3 and solution of Ir(III)chloride, OH^-, KIO_3 and reducing sugar have been taken (Fig 5). From Fig 5 it is clear that when sodium hydroxide solution of two different concentration is added to the solution of Ir(III) chloride, an increase in absorbance from 1.68 to 2.08 with a shift in λ_{max} towards longer wavelength was observed. On the basis of this, an inference about the existence of the following equilibrium in reaction can be drawn.

$$[IrCl_3(H_2O)_3] + OH^- \xrightleftharpoons{K_1} [\, IrCl_3(H_2O)_2(OH)\,]^- + H_2O \qquad (\,i)$$

On the addition of OH^- solution to the solution of Ir(III) chloride, the equilibrium (i) will shift towards right hand side and as result, there will be more and more formation of reactive species $[IrCl_3(H_2O)_2OH]^-$. Positive effect of OH^- concentration on the rate of reaction also supports, the existence of above equilibrium (i) in the reaction under investigation.

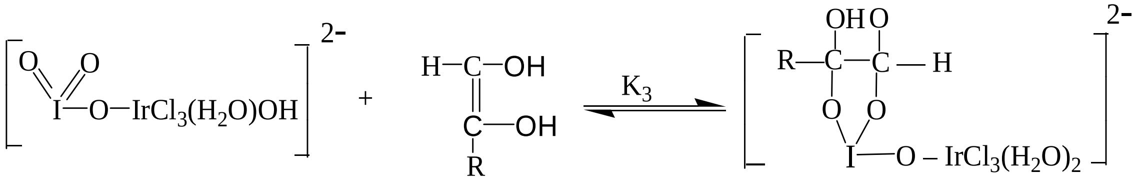
Further in order to verify the existence of a complex between $[IrCl_3(H_2O)_2OH]^-$ and IO_3^- in the oxidation of galactose, when the solutions of IO_3^- of two different concentration was added to the solution of Ir(III) chloride and OH^-, it was observed that with addition of IO_3^- solution, there is an increase in absorbance from 2.08 to 2.40 and with a shift in λ_{max} towards longer wavelength. The increase in absorbance with the addition of potassium iodate solution can be attributed due to formation of a new complex between $[IrCl_3 (H_2O)_2 OH]^-$ and IO_3^-according to the following equilibrium.



(ii)

The absorbance at longer wavelength is due the combination of chromophore IO_3^- and auxochrome OH^- to give rise to another chromophore. The shift in wavelength from 218 nm to 224 contention support that there is a formation of a new complex $[IrCl_3 (H_2O)(OH) IO_3]^{2-}$ which is entirely different from the complex $[IrCl_3 (H_2O)_2 OH]^-$.

Further when spectra for solutions containing Ir(III)- chloride, OH^-& IO_3^- and Ir(III)- chloride, OH- & IO_3^- with three different concentration of galactose were recorded (Fig 5). It is found that there is an increase in absorbance from 2.57 to 2.63 and 2.76, this increase in absorbance is due to more & more formation of complex C_4 according to the following equilibrium.



Where Rstands for $C_4H_9O_4$

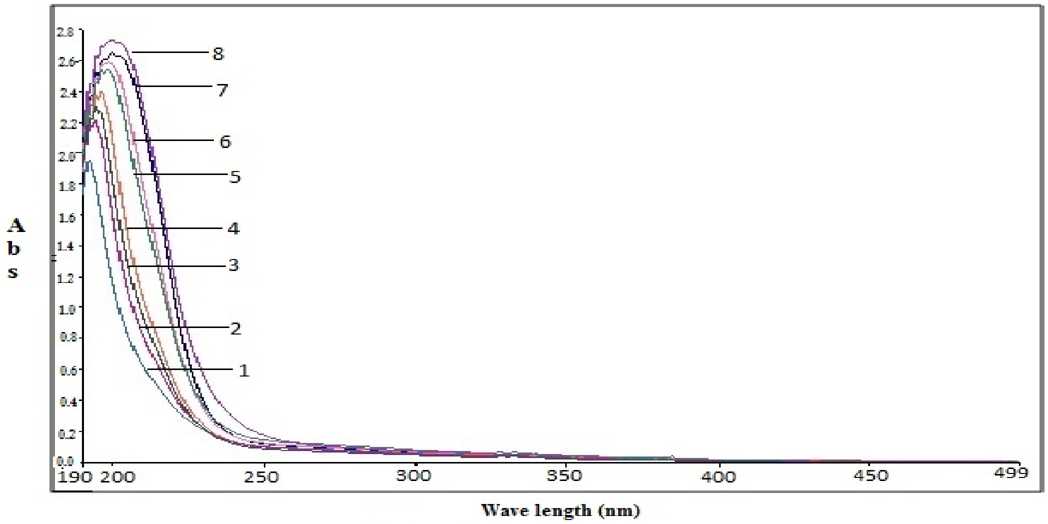
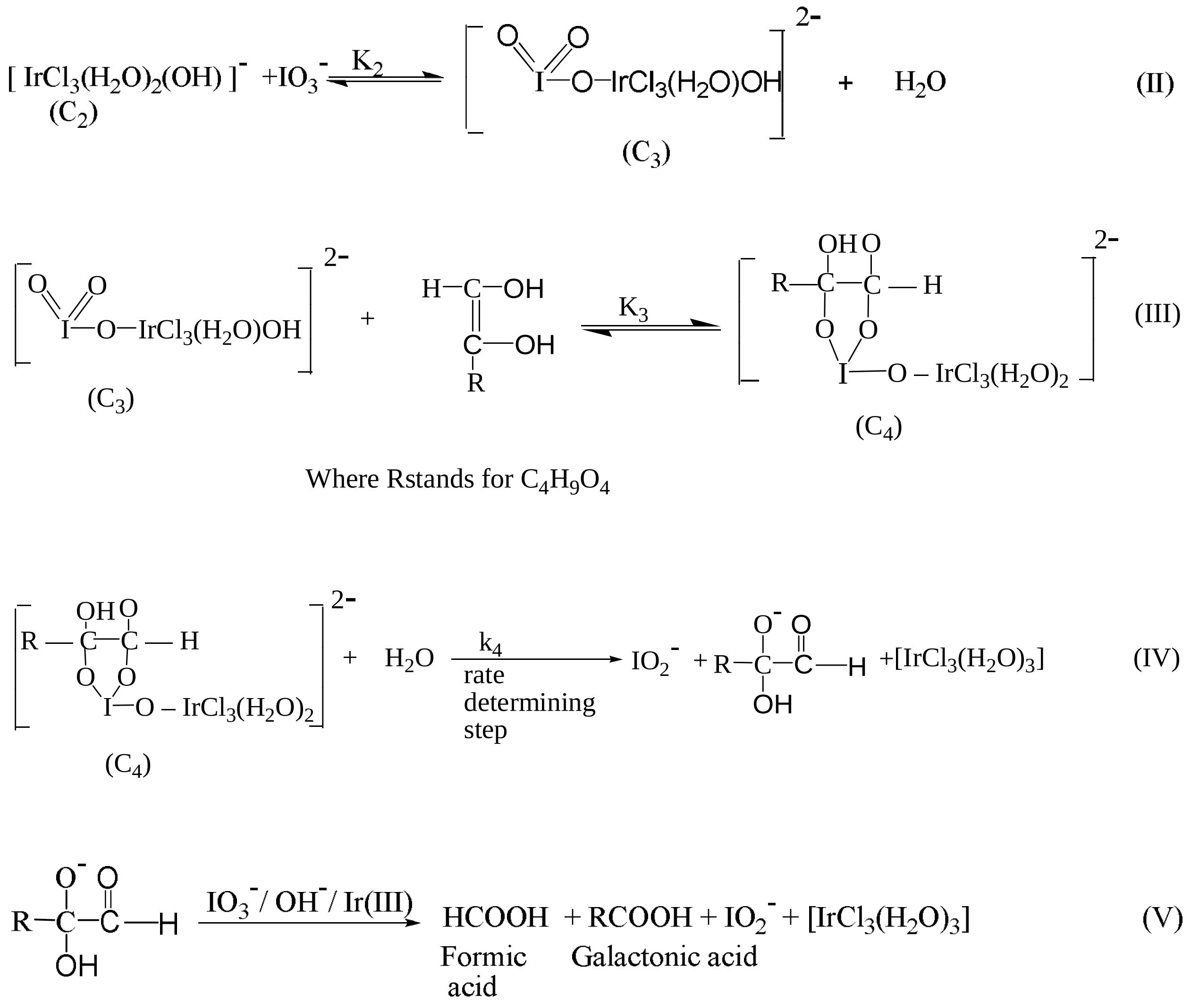


Fig.5. Spectra of various solutions containing Ir(III), OH^-, $IO_3^-$and Galactose at room temperature (1) [Ir(III)] = 2×10^{-6} M, (2) [Ir(III)] = 2×10^{-6} M, [OH^-] = 10.00×10^{-3} M, (3) [Ir(III)] = 2×10^{-6} M, [OH^-] = 20.00×10^{-3} M, (4) [Ir(III)] = 2×10^{-6} M, [OH^-] = 10.00×10^{-3} M, [IO_3^-] = 1.00×10^{-5} M, (5) [Ir(III)] = 2×10^{-6} M, [OH^-] = 10.00×10^{-3} M, [IO_3^-] = 2.00×10^{-5} M, (6) [Ir(III)] = 2×10^{-6} M, [OH^-] = 10.00×10^{-3} M, [IO_3^-] = 2.00×10^{-5} M, [Galactose] = 2.00×10^{-2} M (7) [Ir(III)] = 2×10^{-6} M, [OH^-] = 10.00×10^{-3} M, [IO_3^-] = 2.00×10^{-5} M, [Galactose] = 4.00×10^{-2} M, (8) [Ir(III)] = 2×10^{-6} M, [OH^-] = 10.00×10^{-3} M, [IO_3^-] = 2.00×10^{-5} M [Galactose] = 8.00×10^{-2} M.

Reaction mechanism and derivation of rate law: On the basis of observed kinetic data, spectroscopic evidence and activation parameters, a most probable mechanism for Ir(III)-catalyzed oxidation of D-galactose by iodate in alkaline medium has been proposed.

$$\underset{(C_1)}{[IrCl_3(H_2O)_3]} + OH^- \overset{K_1}{\rightleftharpoons} \underset{(C_2)}{[IrCl_3(H_2O)_2(OH)]^-} + H_2O \qquad (I)$$



Where Rstands for $C_4H_9O_4$

Scheme-1

On the basis of above reaction Scheme -1 and stoichiometric data, the rate in terms of disappearance of IO_3^- can be written as equation (1)

$$\text{rate} = \frac{-d[IO_3^-]}{dt} = 2\,k_4\,[C_4] \qquad (1)$$

On applying the law of chemical equilibrium to step (I) and (II) and (III) we get equations (2) and (3) and (4) respectively,

$$[C_2] = K_1\,[C_1]\,[OH^-] \qquad (2)$$

$$[C_3] = K_1K_2\,[C_1]\,[OH^-]\,[IO_3^-] \qquad (3)$$

$$[C_4] = K_3K_2K_1\,[C_1]\,[OH^-]\,[IO_3^-]\,[S] \qquad (4)$$

The total concentration of Ir(III) i.e. $[\mathrm{Ir(III)}]_T$present in the reaction at any moment can be expressed as-

$$[\mathrm{Ir(III)}]_T = [C_1]\,[C_2]\,[C_3]\,[C_4] \qquad (5)$$

$$[C_1] = \frac{[\mathrm{Ir(III)}]_T}{1 + K_1\,[\mathrm{OH}^-] + K_1K_2\,[\mathrm{OH}^-]\,[\mathrm{IO}_3^-] + K_1K_2K_3\,[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]\,[S]} \qquad (6)$$

With the help of equations (1), (4) and (6), we can write the expression for the rate of reaction as-

$$\text{rate} = -\frac{d[\mathrm{IO}_3^-]}{dt} = \frac{2\,k_4K_3K_2K_1[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]\,[S]\,[\mathrm{Ir(III)}]_T}{1 + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{OH}^-]\,[\mathrm{IO}_3^-] + K_1K_2K_3\,[\mathrm{OH}^-]\,\mathrm{IO}_3^-]\,[S]} \qquad (7)$$

The rate law (7) derived on the basis of proposed Scheme-1is in close agreement with the kinetic information obtained experimentally about the effect of $[\mathrm{IO}_3]^-[\mathrm{Ir(III)}]_T$, $[\mathrm{OH}]^-$ and [S] on the rate of oxidation of galactose.

Equation (7) can also be written as

$$\text{rate} = -\frac{d[\mathrm{IO}_3^-]}{dt} = \frac{2\,k_4K_3K_2K_1[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]\,[S]\,[\mathrm{Ir(III)}]_T}{1+K_1[\mathrm{OH}^-]+K_1K_2\,[\mathrm{IO}_3^-]\,[\mathrm{OH}^-]\{1+K_3\,[S]\,\}} \qquad (8)$$

At low concentration of S, the inequality $K_3[S] << 1$ can be assumed as valid one and under this condition equation (8) will be reduced to equation (9).

$$\text{rate} = -\frac{d[\mathrm{IO}_3^-]}{dt} = \frac{2\,k_4K_3K_2K_1\,[\mathrm{OH}^-]\,[S]\,[\mathrm{IO}_3^-]\,[\mathrm{Ir(III)}]_T}{1 + K_1\,[\mathrm{OH}^-] + K_1K_2\,[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]} \qquad (9)$$

At high concentration of S, the inequality $K_3\,[S] >> 1$ can be assumed as valid one and under this condition equation (8) will be reduced to equation (10).

$$\text{rate} = -\frac{d[\mathrm{IO}_3^-]}{dt} = \frac{2k_4K_3K_2K_1\,[\mathrm{OH}^-]\,[S]\,[\mathrm{IO}_3^-]\,[\mathrm{Ir(III)}]_T}{1 + K_1\,[\mathrm{OH}\text{-}] + K_1K_2K_3\,[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]\,[S]} \qquad (10)$$

At low concentration of $[\mathrm{OH}^-]$, the inequality $K_3\,[\mathrm{OH}^-] << 1$ can be assumed as valid one and under this condition equation (10) will be reduced to equation (11).

$$\text{rate} = \frac{-d[\mathrm{IO}_3^-]}{dt} = \frac{2\,k_4K_3K_2K_1\,[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]\,[S]\,[\mathrm{Ir(III)}]_T}{1 + K_1K_2K_3\,[\mathrm{OH}^-]\,[\mathrm{IO}_3^-]\,[S]} \qquad (11)$$

Equation (11) clearly shows the observed unity order in $[\mathrm{Ir(III)}_T]$ and $[\mathrm{IO}_3^-]$,$[\mathrm{OH}^-]$ [S] first order at low concentration becomes zero order at their higher concentrations.

On reversing equation (11), we have equation (12)

$$\frac{[\mathrm{Ir(III)}]_T}{\text{rate}} = \frac{1}{2\,k_4K_3K_2K_1\,[\mathrm{OH}^-]\,[S]\,[\mathrm{IO}_3^-]} + \frac{1}{2k_4} \qquad (12)$$

According to equation (12), if a plot is made between $[\mathrm{Ir(III)}]_T$ /rate and $1/[\mathrm{IO}_3^-]$or 1/[S] for the oxidation of D-galactose, a straight line having positive intercept on *y*-axis will be obtained. When plots were made between $[\mathrm{Ir(III)}]_T$ /rate and $1/[\mathrm{IO}_3^-]$ and between $[\mathrm{Ir(III)}]_T$ /rate and 1/[S] straight lines having positive intercepts on *y*-axis were obtained (Figs. 6 and 7). This not only proves the validity of rate law (11) but also gives support to the proposed reaction scheme. From the slopes and intercepts of the straight lines, the values of k_4 and$K_1K_2K_3$have been calculated and found as $1.25\text{x}10^2\ M^{-1}\ S^{-1}$, $9.38\text{x}10^4\ M^{-2}$, $9\ M^{-1}\ S^{-1}$ and $1.01\text{x}10^5$ respectively for the oxidation of galactose. Utilizing these values of rate constants, the reaction rates for the variations of $[\mathrm{IO}_3^-]$, [Ir(III)] and [D-galactose] have been calculated according to the rate law

(11) and found to be in close agreement with the observed rates (Table 2). This further confirms the validity of rate law (11) and hence the proposed mechanism.

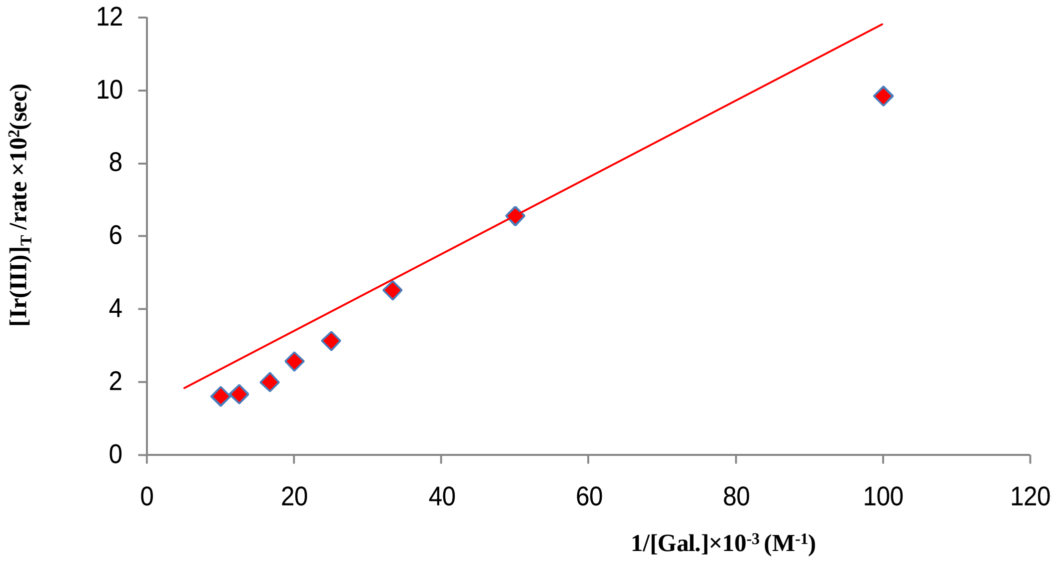


Fig.6. Plot between $[Ir(III)]_T$/rate and 1/[Gal.]
$[Ir(III)] = 3.35 \times 10^{-5}$ M, $[IO_3^-] = 1.00\times 10^{-3}$ M, $[OH^-] = 10 \times 10^{-2}$ M, $\mu = 0.60$ M.

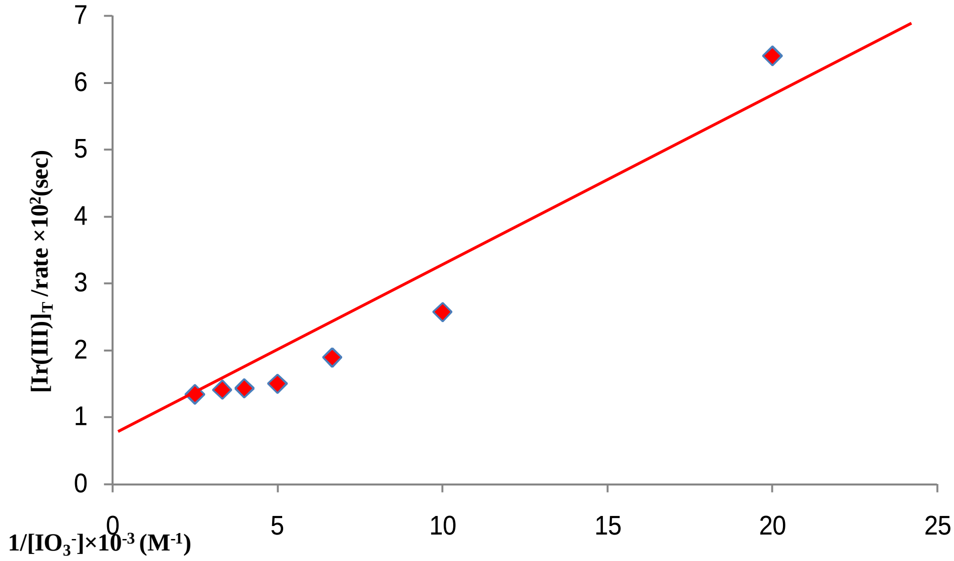


Fig.7. Plot between $[Ir(III)]_T$/rate and 1/$[IO_3^-]$
$[Ir(III)] = 3.35 \times 10^{-5}$ M, $[OH^-] = 10.00\times 10^{-2}$ M, [D-galactose] = 5×10^{-2} M, $\mu = 0.60$ M

Table 2. Experimental and Calculated values of the rate for the variations of [IO_3^-], and [Gal.] in the Ir(III)-catalyzed oxidation of Galactose by KIO_3 at 40^0C

[IO_3^-]x10^3(M)	[Gal.] x10^2(M)	dc/dt x 10^7(M sec^{-1})Experimental rate	Rate Calculated on the basis of rate law
0.50	5.00	0.52	0.77
1.00	5.00	1.30	1.30
1.50	5.00	1.77	1.72
2.00	5.00	2.22	2.01
2.50	5.00	2.33	2.25
3.00	5.00	2.36	2.43
4.00	5.00	2.50	2.72
1.00	1.00	0.31	0.33
1.00	2.00	0.51	0.61
1.00	3.00	0.74	0.81
1.00	4.00	1.07	1.05
1.00	5.00	1.30	1.22
1.00	6.00	1.66	1.38
1.00	8.00	2.00	1.63
1.00	10.00	2.08	1.84

CONCLUSIONS

The following conclusions can be derived from the observed kinetic data and spectral information collected for the Ir(III) catalyzed oxidation of D-galactose by potassium iodate in alkaline medium:

1. The reactive species of KIO_3 is considered as [IO_3^-].
2. [$IrCl_3(H_2O)_2OH^-$] is considered to be the active species of Ir(III) chloride among the various species of Ir(III) chloride in alkaline medium.
3. The formation of a reactive complex, $C_{3,}$ between reactive species of Ir(III) chloride and IO_3^- in alkaline medium is well supported by observed kinetic and spectral data.
4. Oxidation of D-galactose by iodate in alkaline medium is very sluggish, but it becomes facile in the presence of Ir(III) catalyst so It can be concluded that Ir(III) acts as an efficient catalyst in the oxidation of D-galactose by iodate in alkaline medium.
5. In step (III) of reaction scheme 1, an interaction between a charged species, C_3 and a neutral molecule, enediol resulting in the formation of most reactive activated complex is well supported by the observed positive entropy of activation and spectroscopic data.
6. Interaction between a charged species and a molecule confirms nil effect of ionic strength.
7. The positive value of $\Delta S^{\#}$ suggests that the intermediate complex is less ordered than the reactants. A high positive value of $\Delta G^{\#}$ indicates that the transition state is highly solvate.

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