

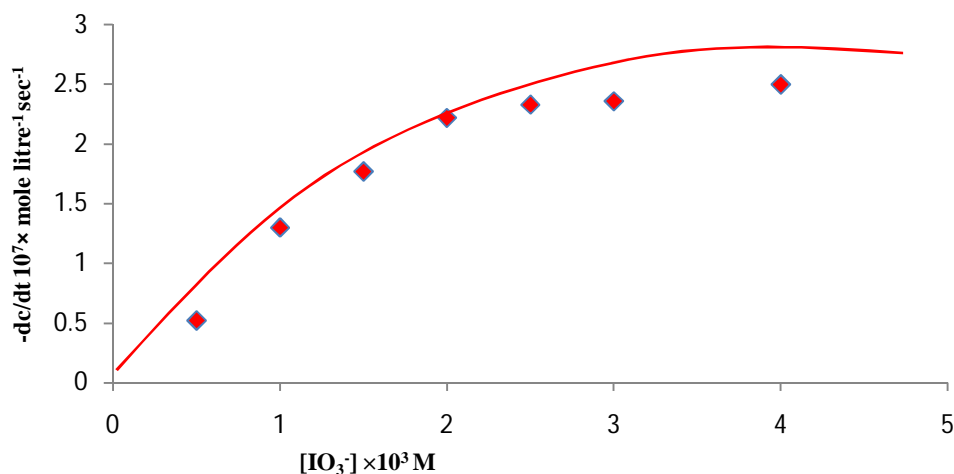
**Kinetics and Mechanism of Ir(III)-Catalyzed Oxidation of D-Galactose by Potassium Iodate in Aqueous Alkaline Medium****Brijesh Kumar Prajapati, Jaya Srivastava, Ranju Pradhan, Shailesh Kumar Singh, Ashok Kumar Singh and Shahla Rahmani\***\*Department of Chemistry, University of Allahabad, Uttar Pradesh, 211002, **INDIA**Email: [shahlaau@gmail.com](mailto:shahlaau@gmail.com), [ashokeks@rediffmail.com](mailto:ashokeks@rediffmail.com)Accepted on 17<sup>th</sup> November 2017, Published online on 27<sup>th</sup> November 2017**ABSTRACT**

The kinetics of Ir (III)-catalyzed oxidation of galactose by potassium iodate in alkaline medium have been made at 40°C. The reaction exhibits first-order kinetics with respect to Ir (III). Unity order at low concentrations of galactose, OH<sup>-</sup> and IO<sub>3</sub><sup>-</sup> becomes zero order at their higher concentrations throughout their variations. Negligible effects of Cl<sup>-</sup> 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**

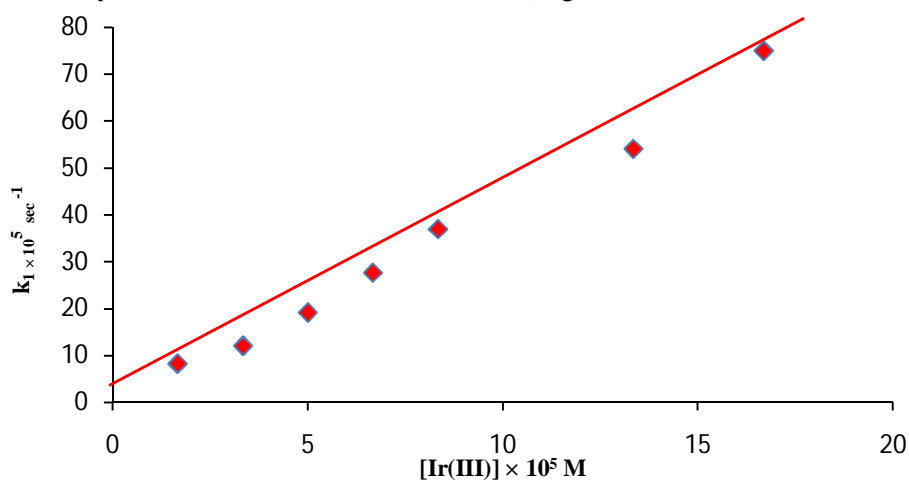
The study of carbohydrates is one of the most exciting fields of organic chemistry. Vast literature is available on the kinetics of oxidation of carbohydrates by various organic and inorganic oxidants. The oxidation of aldoses by chlorine, bromine, and iodine has been reported in alkaline media [1]. 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  $\beta$ -aldoses (C-1 equatorial) are oxidized much faster than  $\alpha$ -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





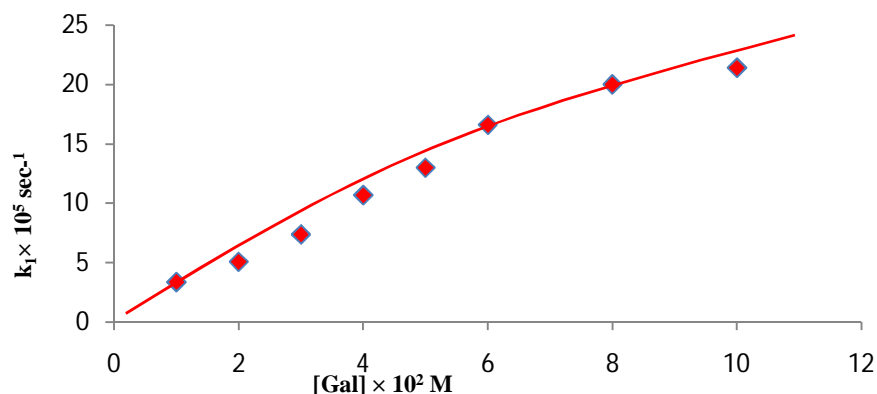
**Fig 1.** Plot between  $-dc/dt$  and  $[IO_3^-]$  at  $40^\circ C$   
 $[Ir(III)] = 3.35 \times 10^{-5}$ ,  $[D\text{-galactose}] = 5 \times 10^{-2}$  M,  $[OH^-] = 10.00 \times 10^{-2}$  M,  $\mu = 0.60$  M

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).



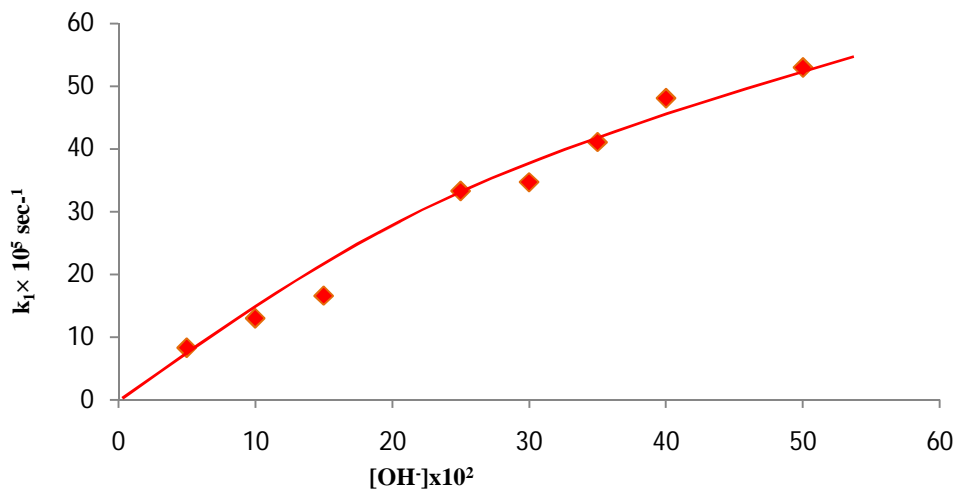
**Fig 2.** Plot between  $k_1$  and  $[Ir(III)]$  at  $40^\circ C$   
 $[IO_3^-] = 1.00 \times 10^{-3}$  M,  $[D\text{-galactose}] = 5 \times 10^{-2}$  M,  $[OH^-] = 10.00 \times 10^{-2}$  M,  $\mu = 0.60$  M

To find out the dependence of rate on [galactose], kinetic runs are performed by varying the concentration of galactose in the range of  $1.0 \times 10^{-2}$  –  $10.0 \times 10^{-2}$  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  $[\text{Gal}]$  at  $40^\circ\text{C}$   
 $[\text{IO}_3^-] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Ir(III)}] = 3.35 \times 10^{-5} \text{ M}$ ,  $[\text{OH}^-] = 10.00 \times 10^{-2} \text{ M}$ ,  $\mu = 0.60 \text{ M}$

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



**Fig.4.** Plot between  $k_1$  and  $[\text{OH}^-]$  at  $40^\circ\text{C}$   
 $[\text{IO}_3^-] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Ir(III)}] = 3.35 \times 10^{-5} \text{ M}$ ,  $[\text{Gal.}] = 5.00 \times 10^{-2} \text{ M}$ ,  $\mu = 0.60 \text{ M}$

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

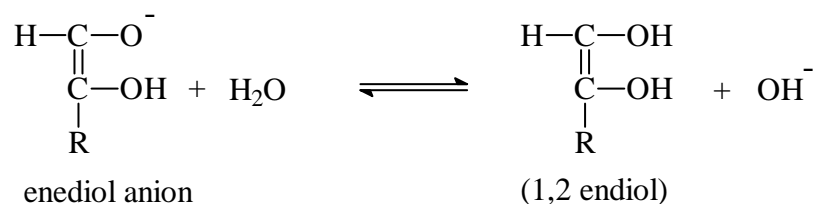
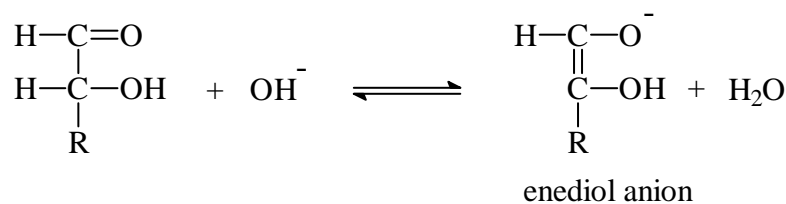
**Table 1:** Activation parameters for Ir (III)-catalyzed oxidation of D-galactose by  $\text{KIO}_3$  at  $40^\circ\text{C}$

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

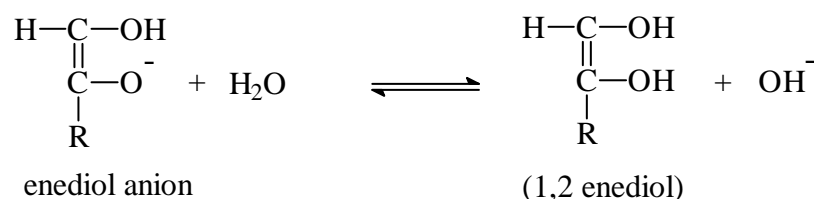
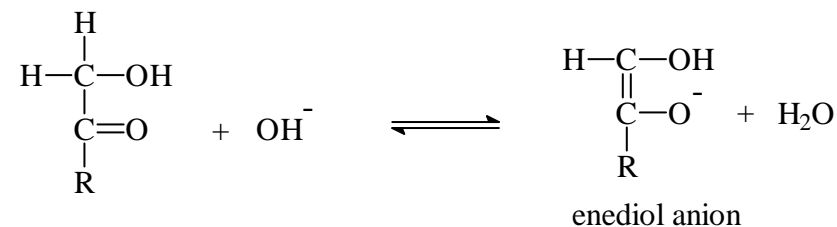
**Reactive species of potassium iodate in alkaline medium:** It is reported that  $\text{KIO}_3$  has been used as an oxidant in the oxidation of acetophenones [26], ferrocyanide[27], thiocyanate and 1,3-dihydroxybenzene in acidic medium. In each case  $\text{IO}_3^-$  has been regarded as the reactive species, which very well supports the existence of  $\text{IO}_3^-$  in alkaline medium. In view of the reported kinetic data and spectral evidence, it can very easily be concluded that the species  $\text{IO}_3^-$  is the reactive species of  $\text{KIO}_3$  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

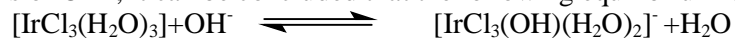


The formation of the enediol anion and the enediol in the presence of alkali is also supported by the work of Isbell and co-workers [29].

In the present study the observed fractional positive order with respect to  $[\text{OH}^-]$  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.

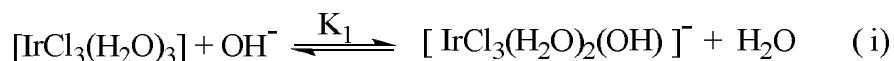
**Reactive species of Ir (III) chloride in alkaline medium:** In the present study of the oxidation of D-galactose by  $\text{KIO}_3$ , Ir(III)-chloride has been used as homogeneous catalyst. In the present investigation,

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  $[\text{IrCl}_3(\text{H}_2\text{O})_3]$ . 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  $[\text{OH}^-]$  on the rate of oxidation. On the basis of (1) the observed kinetic data relating to first-order kinetics of  $\text{OH}^-$  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  $\text{OH}^-$ , it can be concluded that the following equilibrium is established:



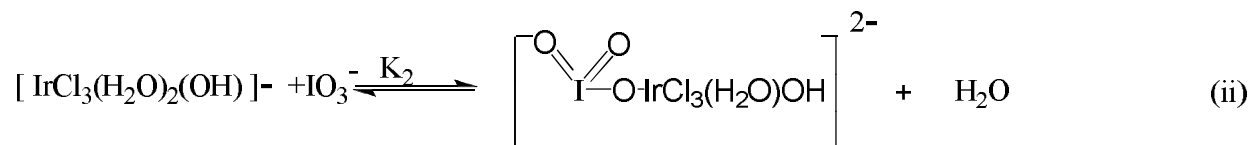
Out of two species,  $[\text{IrCl}_3(\text{H}_2\text{O})_3]$  and  $[\text{IrCl}_3\text{OH}(\text{H}_2\text{O})_2]^-$ , the species  $[\text{IrCl}_3\text{OH}(\text{H}_2\text{O})_2]^-$  can be assumed as the reactive species of Ir(III) chloride in the oxidation of galactose, because with the reactive species  $[\text{IrCl}_3\text{OH}(\text{H}_2\text{O})_2]^-$  and taking into consideration the existence of above equilibrium in the reaction, a rate law can be derived.

**Spectrophotometric evidence for the formation of complexes during the course of reaction:** It is reported [21] that  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$  is the reactive species of Ir(III) chloride and  $\text{IO}_3^-$  is the reactive species of  $\text{KIO}_3$  in alkaline medium. Experiments were performed to verify the formation of complex between reactive species of Ir(III) chloride i.e.  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$  and reactive species of potassium iodate i.e.  $\text{IO}_3^-$  in the oxidation of galactose. The spectra of solution containing Ir(III) chloride alone, solution of Ir(III)-chloride with two different concentrations of  $\text{OH}^-$ , solution of Ir(III)-chloride,  $\text{OH}^-$  &  $\text{KIO}_3$  and solution of Ir(III)chloride,  $\text{OH}^-$ ,  $\text{KIO}_3$  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  $\lambda_{\text{max}}$  towards longer wavelength was observed. On the basis of this, an inference about the existence of the following equilibrium in reaction can be drawn.



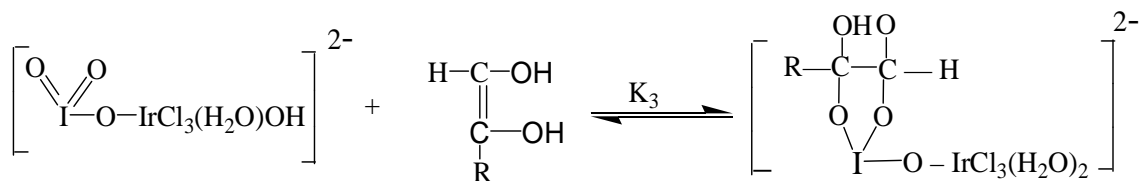
On the addition of  $\text{OH}^-$  solution to the solution of Ir(III) chloride, the equilibrium (i) will shift towards right hand side and as result, there will be more and more formation of reactive species  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$ . Positive effect of  $\text{OH}^-$  concentration 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  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$  and  $\text{IO}_3^-$  in the oxidation of galactose, when the solutions of  $\text{IO}_3^-$  of two different concentration was added to the solution of Ir(III) chloride and  $\text{OH}^-$ , it was observed that with addition of  $\text{IO}_3^-$  solution, there is an increase in absorbance from 2.08 to 2.40 and with a shift in  $\lambda_{\text{max}}$  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  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$  and  $\text{IO}_3^-$  according to the following equilibrium.

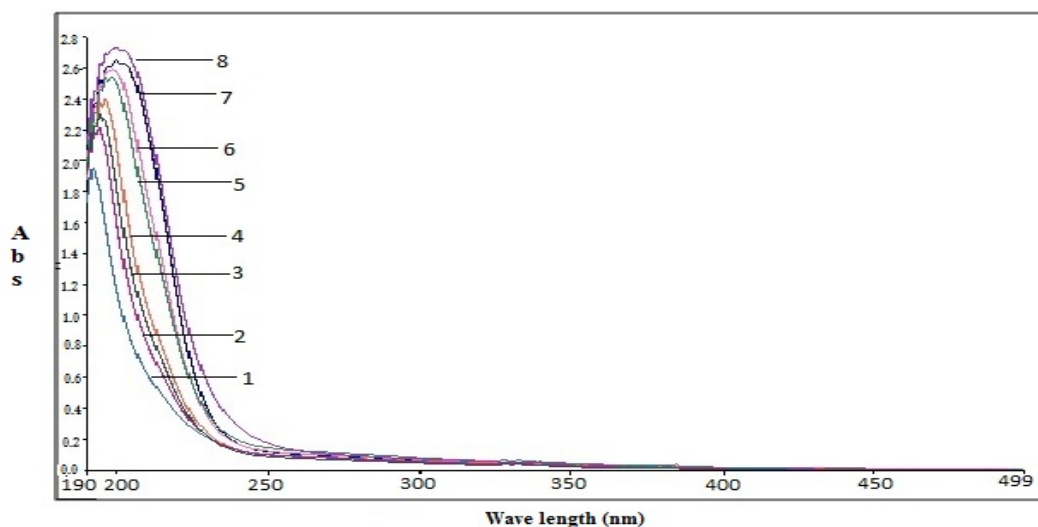


The absorbance at longer wavelength is due the combination of chromophore  $\text{IO}_3^-$  and auxochrome  $\text{OH}^-$  to give rise to another chromophore. The shift in wavelength from 218 nm to 224 nm support that there is a formation of a new complex  $[\text{IrCl}_3(\text{H}_2\text{O})(\text{OH})\text{IO}_3]^{2-}$  which is entirely different from the complex  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$ .

Further when spectra for solutions containing Ir(III)- chloride, OH<sup>-</sup> & IO<sub>3</sub><sup>-</sup> and Ir(III)- chloride, OH<sup>-</sup> & IO<sub>3</sub><sup>-</sup> 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<sub>4</sub> according to the following equilibrium.

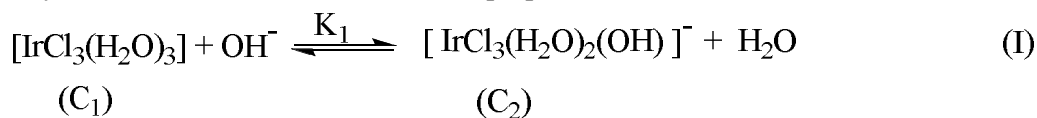


Where R stands for C<sub>4</sub>H<sub>9</sub>O<sub>4</sub>



**Fig.5.** Spectra of various solutions containing Ir(III), OH<sup>-</sup>, IO<sub>3</sub><sup>-</sup> and Galactose at room temperature  
 (1) [Ir(III)] = 2×10<sup>-6</sup> M, (2) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 10.00×10<sup>-3</sup> M, (3) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 20.00×10<sup>-3</sup> M, (4) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 10.00×10<sup>-3</sup> M, [IO<sub>3</sub><sup>-</sup>] = 1.00×10<sup>-5</sup> M, (5) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 10.00×10<sup>-3</sup> M, [IO<sub>3</sub><sup>-</sup>] = 2.00×10<sup>-5</sup> M, (6) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 10.00×10<sup>-3</sup> M, [IO<sub>3</sub><sup>-</sup>] = 2.00×10<sup>-5</sup> M, [Galactose] = 2.00×10<sup>-2</sup> M (7) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 10.00×10<sup>-3</sup> M, [IO<sub>3</sub><sup>-</sup>] = 2.00×10<sup>-5</sup> M, [Galactose] = 4.00×10<sup>-2</sup> M, (8) [Ir(III)] = 2×10<sup>-6</sup> M, [OH<sup>-</sup>] = 10.00×10<sup>-3</sup> M, [IO<sub>3</sub><sup>-</sup>] = 2.00×10<sup>-5</sup> M, [Galactose] = 8.00×10<sup>-2</sup> 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.







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

$$[\text{Ir(III)}]_{\text{T}} = [\text{C}_1] [\text{C}_2] [\text{C}_3] [\text{C}_4] \quad (5)$$

$$[\text{C}_1] = \frac{[\text{Ir(III)}]_{\text{T}}}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-] [\text{IO}_3^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{IO}_3^-] [\text{S}]} \quad (6)$$

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

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2 k_4 K_3 K_2 K_1 [\text{OH}^-] [\text{IO}_3^-] [\text{S}] [\text{Ir(III)}]_{\text{T}}}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-] [\text{IO}_3^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{IO}_3^-] [\text{S}]} \quad (7)$$

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

Equation (7) can also be written as

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2 k_4 K_3 K_2 K_1 [\text{OH}^-] [\text{IO}_3^-] [\text{S}] [\text{Ir(III)}]_{\text{T}}}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{IO}_3^-] [\text{OH}^-] \{1 + K_3 [\text{S}]\}} \quad (8)$$

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

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2 k_4 K_3 K_2 K_1 [\text{OH}^-] [\text{S}] [\text{IO}_3^-] [\text{Ir(III)}]_{\text{T}}}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-] [\text{IO}_3^-]} \quad (9)$$

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

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2 k_4 K_3 K_2 K_1 [\text{OH}^-] [\text{S}] [\text{IO}_3^-] [\text{Ir(III)}]_{\text{T}}}{1 + K_1 [\text{OH}^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{IO}_3^-] [\text{S}]} \quad (10)$$

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

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2 k_4 K_3 K_2 K_1 [\text{OH}^-] [\text{IO}_3^-] [\text{S}] [\text{Ir(III)}]_{\text{T}}}{1 + K_1 K_2 K_3 [\text{OH}^-] [\text{IO}_3^-] [\text{S}]} \quad (11)$$

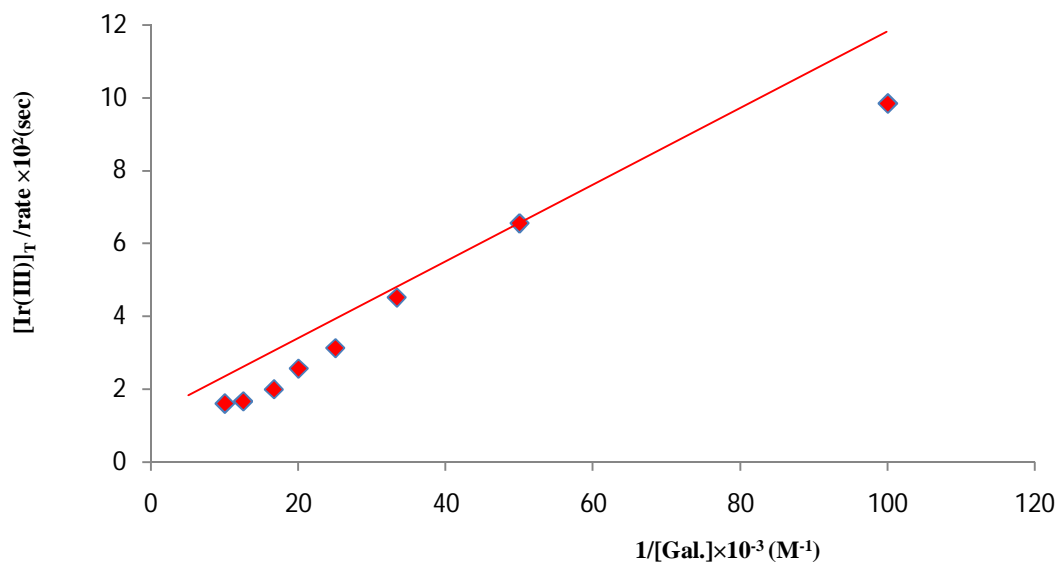
Equation (11) clearly shows the observed unity order in  $[\text{Ir(III)}]_{\text{T}}$  and  $[\text{IO}_3^-]$ ,  $[\text{OH}^-]$   $[\text{S}]$  first order at low concentration becomes zero order at their higher concentrations.

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

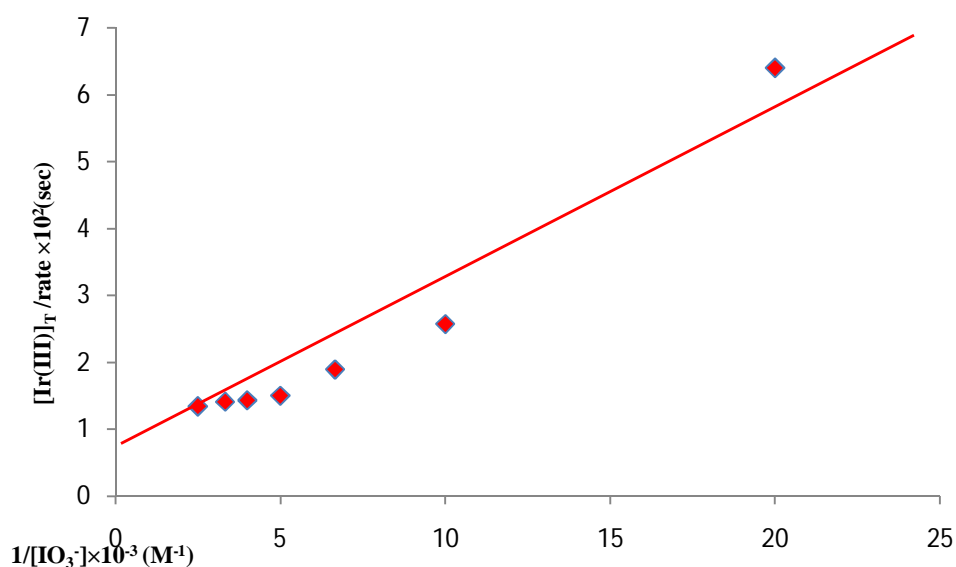
$$\frac{[\text{Ir(III)}]_{\text{T}}}{\text{rate}} = \frac{1}{2 k_4 K_3 K_2 K_1 [\text{OH}^-] [\text{S}] [\text{IO}_3^-]} + \frac{1}{2 k_4} \quad (12)$$

According to equation (12), if a plot is made between  $[\text{Ir(III)}]_{\text{T}}/\text{rate}$  and  $1/[\text{IO}_3^-]$  or  $1/[\text{S}]$  for the oxidation of D-galactose, a straight line having positive intercept on y-axis will be obtained. When plots were made between  $[\text{Ir(III)}]_{\text{T}}/\text{rate}$  and  $1/[\text{IO}_3^-]$  and between  $[\text{Ir(III)}]_{\text{T}}/\text{rate}$  and  $1/[\text{S}]$  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  $K_1 K_2 K_3$  have been calculated and found as  $1.25 \times 10^2 \text{ M}^{-1} \text{ S}^{-1}$ ,  $9.38 \times 10^4 \text{ M}^{-2}$ ,  $9 \text{ M}^{-1} \text{ S}^{-1}$  and  $1.01 \times 10^5$  respectively for the oxidation of galactose. Utilizing these values of rate constants, the reaction rates for the variations of  $[\text{IO}_3^-]$ ,  $[\text{Ir(III)}]$  and  $[\text{D-galactose}]$  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  $[\text{Ir(III)}]_{\text{T}}/\text{rate}$  and  $1/[\text{Gal.}]$   
 $[\text{Ir(III)}] = 3.35 \times 10^{-5} \text{ M}$ ,  $[\text{IO}_3^-] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{OH}^-] = 10 \times 10^{-2} \text{ M}$ ,  $\mu = 0.60 \text{ M}$ .



**Fig.7.** Plot between  $[\text{Ir(III)}]_{\text{T}}/\text{rate}$  and  $1/[\text{IO}_3^-]$   
 $[\text{Ir(III)}] = 3.35 \times 10^{-5} \text{ M}$ ,  $[\text{OH}^-] = 10.00 \times 10^{-2} \text{ M}$ ,  $[\text{D-galactose}] = 5 \times 10^{-2} \text{ M}$ ,  $\mu = 0.60 \text{ M}$

**Table 2.** Experimental and Calculated values of the rate for the variations of  $[\text{IO}_3^-]$ , and  $[\text{Gal.}]$  in the Ir(III)-catalyzed oxidation of Galactose by  $\text{KIO}_3$  at  $40^\circ\text{C}$ 

$[\text{IO}_3^-] \times 10^3 (\text{M})$	$[\text{Gal.}] \times 10^2 (\text{M})$	$\text{dc/dt} \times 10^7 (\text{M sec}^{-1})$ 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  $\text{KIO}_3$  is considered as  $[\text{IO}_3^-]$ .
2.  $[\text{IrCl}_3(\text{H}_2\text{O})_2\text{OH}^-]$  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,  $\text{C}_3$ , between reactive species of Ir(III) chloride and  $\text{IO}_3^-$  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,  $\text{C}_3$  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  $\Delta S^\ddagger$  suggests that the intermediate complex is less ordered than the reactants. A high positive value of  $\Delta G^\ddagger$  indicates that the transition state is highly solvate.

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