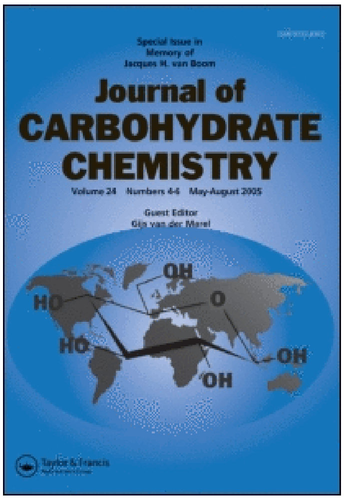

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Surya Prakash Singh[a]; Ashok Kumar Singh[a]; Ajaya Kumar Singh[b]
[a] Department of Chemistry, University Of Allahabad, Allahabad, India [b] Department of Chemistry, Government V.Y.T.PG. Autonomous College Durg, Chhattisgarh, India

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Kinetics of Ir (III)-catalyzed Oxidation of D-glucose by Potassium Iodate in Aqueous Alkaline Medium

Surya Prakash Singh,[1] Ashok Kumar Singh,[1]
and Ajaya Kumar Singh[2]

[1]Department of Chemistry, University Of Allahabad, Allahabad, India
[2]Department of Chemistry, Government V.Y.T.PG. Autonomous College Durg, Chhattisgarh-491001, India

The kinetics of Ir (III) chloride-catalyzed oxidation of D-glucose by iodate in aqueous alkaline medium was investigated at 45°C. The reaction follows first-order kinetics with respect to potassium iodate in its low concentration range but tends to zero order at its higher concentration. Zero-order kinetics with respect to [D-glucose] was observed. In the lower concentration range of Ir (III) chloride, the reaction follows first kinetics, while the order shifts from first to zero at its higher concentration range. The reaction follows first-order kinetics with respect to $[OH^-]$ at its low concentration but tends towards zero order at higher concentration. Variation in $[Cl^-]$ and ionic strength of the medium did not bring about any significant change in the rate of reaction. The first-order rate constant increased with a decrease in the dielectric constant of the medium. The values of rate constants observed at four different temperatures were utilized to calculate the activation parameters. Sodium salt of formic acid and arabinonic acid have been identified as the main oxidation products of the reaction. A plausible mechanism from the results of kinetic studies, reaction stoichiometry, and product analysis has been proposed.

Keywords Kinetics; Oxidation; Ir (III) chloride; D-glucose; Potassium iodate

INTRODUCTION

Glucose is one of the very important carbohydrates in biology. The study of carbohydrates is one of the most exciting fields of organic chemistry. Vast

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Address correspondence to Ajaya Kumar Singh, Department of Chemistry, Govt. V.Y.T.PG. Autonomous College Durg (CG). E-mail ajayaksingh_au@yahoo.co.in

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 catalyzed and uncatalyzed oxidation of sugars has been studied in detail by using N-halo compounds.[3–5] Different metal ion catalysts like chromium (III),[6] ruthenium (III),[7–9] Ir (III) chloride,[10,11] and Pd (II)[12,13] have been used in the oxidation by different oxidizing agents. Among the different metal ions, ruthenium (III) and iridium (III) are highly efficient. Lack of studies on the oxidation of glucose by iodate in the presence of Ir (III) chloride in the alkaline medium has encouraged us to investigate the kinetic behavior of the title reaction in order to continue our study on metal ion in oxidation reactions by iodate. This study will enable understanding the complicated biochemical reaction in living bodies and will also help to understand the catalytic activities of Ir (III) chloride along with oxidative capacity of iodate in alkaline solution. Preliminary experimental results indicate that the reactions of D-glucose with iodate in alkaline medium without a catalyst were too sluggish to be measured, but the reactions become facile in the presence of a micro-quantity of Ir (III) chloride catalyst. Therefore, in order to explore the mechanism of D-glucose-iodate reactions in alkaline medium and also to study the catalytic action of Ir (III) chloride, Ir (III) chloride as a catalyst was selected in the present work. In the present communication, we report for the first time the results of the detailed investigation on the kinetic and mechanistic aspects of Ir (III) chloride-catalyzed oxidation of D-glucose by potassium iodate in alkaline medium at 45°C. Objectives of the present study are (a) to elucidate a plausible mechanism, (b) to deduce an appropriate rate law, (c) to identify the oxidation products, (d) to ascertain the various reactive species, (e) to find the catalytic efficiency of Ir (III) chloride, and (f) to determine the complex formation.

EXPERIMENTAL

Material

Sodium perchlorate, potassium iodate, sodium hydroxide, and D-glucose (E. Merck) were used as supplied without further purification by preparing their solutions in doubly distilled water. A stock solution of Ir (III) chloride (Johnson Metthey) was prepared by dissolving the sample in hydrochloric acid of known strength. Sodium perchlorate was used to maintain the ionic strength of the medium. All other reagents were of AnalaR 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.

Kinetic Procedure

A thermostated 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-glucose was 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-glucose solution, also thermostated at the same temperature, was rapidly pipetted out and run into the reaction vessel. Measuring the unconsumed amount of potassium iodate iodometrically monitored the progress of reaction. The rate of reaction (–dc/dt) was determined by the slope of the tangent drawn at a fixed [IO_3^-] in each kinetic run. The order of reaction in each reactant was measured with the help of log-log plot of (–dc/dt) versus concentration of the reactants.

Stoichiometry and Product Analysis

The reaction mixture containing the D-glucose, Ir (III) chloride, and NaOH with excess of potassium iodate was kept for 72 h at 35°C. The total amount of iodate consumed by 1 mole of D-glucose for its complete oxidation was determined. Iodometric determination of the unconsumed iodate showed that 2 mole of the oxidant were consumed per mole D-glucose forming sodium salt of formic acid and arabinonic acid. Accordingly, the following stoichiometric equation could be formulated:

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

Sodium salt of formic acid and arabinonic acid were identified as the oxidation product in the oxidation of D-glucose. The sodium salt of formic acid was analyzed by NUCON gas chromatography using porapak-Q 101 columns and programmed oven temperature having an FID detector. The major product was identified as sodium salt of formic acid in the Ir (III) chloride-catalyzed oxidation of D-glucose by comparison of retention time with the retention time of standard solutions. Sodium formate was also confirmed by spot test,[14] help of equivalence and kinetic studies, and TLC methods.

RESULTS AND DISCUSSION

Kinetics Study

The kinetics of Ir (III) chloride-catalyzed oxidation of D-glucose by potassium iodate was investigated at several initial concentrations of the reactants in alkaline medium at 45°C. The rate (i.e. –d*c*/d*t*) of the reaction in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of oxidant, potassium iodate. In the variation of oxidant (IO_3^-), tangent has been drawn at a fixed time. The first-order rate constant (k_1) was calculated as:

$$k_1 = (-\mathrm{d}c/\mathrm{d}t)/[IO_3^-]$$

The first-order dependence of reaction on IO_3^- at its lower concentrations tends to zero order at its higher concentrations. This is also obvious from the plot of (–d*c*/d*t*) versus [IO_3^-] (Table 1, Fig. 1), indicating first-order kinetics at lower concentrations and tending toward zero-order kinetics in its higher concentrations. The rates of the reaction (–d*c*/d*t*), were calculated at different concentrations of D-glucose. This was found to be the same for [D-glucose], showing zero-order kinetics with respect to [D-glucose] (Table 1). Since order of reaction with respect to D-glucose is zero, in each kinetic run, the rate of reaction (–d*c*/d*t*) will always be equal to the standard zero-order rate constant. The plot of rate constant k_1 versus [Ir (III) chloride] was linear passing through the origin, suggesting first-order dependence of the rate of reaction on the [Ir (III) chloride]. At the same time, it also shows that the reaction does not proceed with measurable velocity in the absence of [Ir (III) chloride] (Table 1, Fig. 2). Kinetics of catalyzed oxidation of D-glucose indicates that on increasing [NaOH], the value of (–d*c*/d*t*) increases at low concentrations and shifts to zero order at its higher concentrations of NaOH, which is also evident from the plot

Table 1: Effect of variation of (KIO_3), glucose, and (Ir (III)) on the rate of Ir (III)-catalyzed oxidation of D-glucose by iodate in alkaline medium at 45°C

$[KIO_3]$ x 10^4 M	[D-Glu] x 10^2 M	[Ir (III)] x 10^5 M	(–dc/dt) x 10^8 M sec^{-1}	k_1 x 10^5 (sec^{-1})
4.0	2.0	2.68	5.09	16.41
8.0	2.0	2.68	10.71	14.28
10.0	2.0	2.68	13.09	13.63
15.0	2.0	2.68	15.14	10.81
40.0	2.0	2.68	20.83	5.34
50.0	2.0	2.68	23.10	5.20
60.0	2.0	2.68	24.20	5.01
10.0	1.0	2.68	13.85	13.85
10.0	2.0	2.68	13.33	13.33
10.0	3.0	2.68	13.85	13.85
10.0	4.0	2.68	13.33	13.33
10.0	6.0	2.68	13.33	13.33
10.0	7.0	2.68	13.85	13.85
10.0	2.0	0.67	3.35	3.35
10.0	2.0	1.34	6.18	6.18
10.0	2.0	2.68	13.13	13.13
10.0	2.0	4.02	19.25	19.25
10.0	2.0	6.7	24.62	24.62
10.0	2.0	8.04	26.12	26.12
10.0	2.0	9.38	26.92	26.92

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

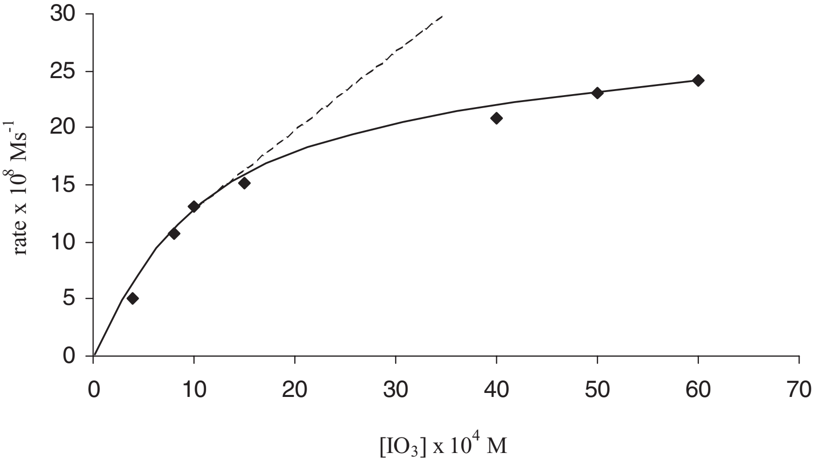


Figure 1: Dependence of reaction rate on (IO_3^-) from data and conditions given in Table 1.

of (–d*c*/d*t*) versus [NaOH] (Table 2, Fig. 3). This shows a positive effect of $[OH^-]$ on the rate of oxidation of D-glucose. Variation 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 dielectric constant of the medium (by increasing the percentage of ethanol by volume) (Table 2). Control experiments performed showed that ethanol was not oxidized by potassium iodate under the experimental conditions. The reaction was studied at different temperatures ranging from 308 to 323 K. (Table 4). From the linear Arrhenius plots of log k_1 versus $1/T$, the

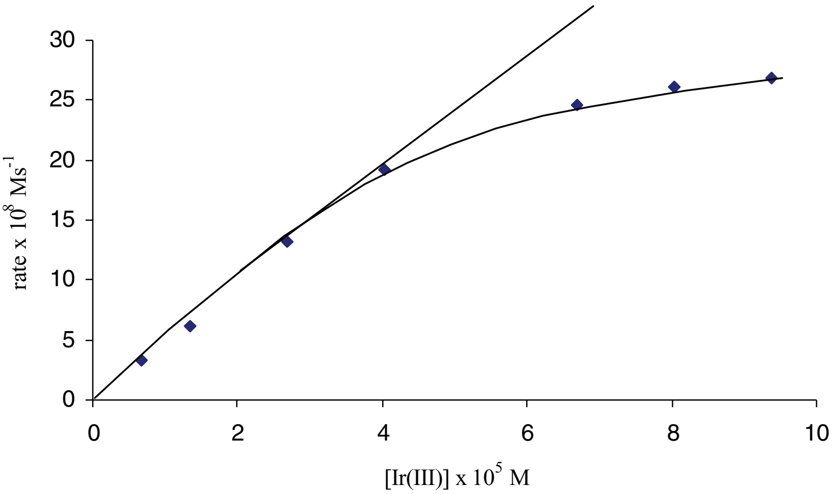


Figure 2: Dependence of rate constant (*k*) on (Ir (III)) from data and conditions given in Table 1.

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

	Rate x 10^8 M sec^{-1}		
[NaOH] x 10^2 M	**Observed**	**Calculated**[b]	**Predicted**[c]
05.00	5.12	5.67	6.15
06.66	7.29	7.12	7.17
08.00	8.33	8.16	7.97
10.00	10.00	9.55	9.00
12.00	12.12	10.78	9.95
15.00	13.33	12.36	11.24
20.00	14.85	14.48	13.16
22.22	15.15	15.27	13.87
25.00	15.32	16.16	14.87

[a] Conditions: (IO_3^-)= 10.00 × 10^{-4} M, ($IrCl_3$) = 2.68 × 10^{-5} M, (D-glucose) = 2.00 × 10^{-2} M, (NaOH) = 0.20 M, (KCl) = 1.80 × 10^{-3} M, T = 45°C.

[b] Calculated on the basis of rate law (2).

[c] Calculated with the help of multiple regression analysis.

activation energy *Ea* was calculated. With the help of the rate constant k_r, values of 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, valid for the conditions under which temperature dependence has been measured, was used to calculate the activation parameters in the Ir (III) chloride-catalyzed oxidation of D-glucose by potassium iodate in alkaline medium:

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

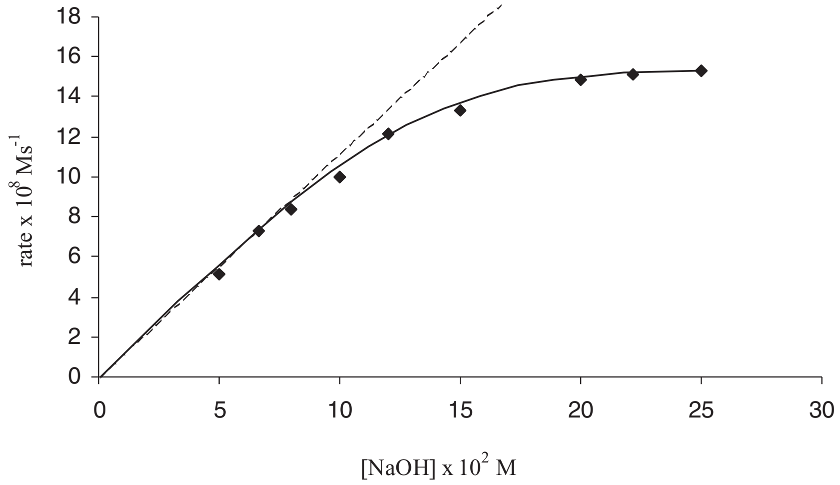


Figure 3: Dependence of reaction rate on (NaOH) from data and conditions given in Table 1.

Table 3: Effect of variation of (KCl), ionic strength, and dielectric constant of the medium on the rate of Ir (III) chloride-catalyzed oxidation of D-glucose by iodate in alkaline medium at 45°C

KCl x 10^3 M	μ **x 10^2** M	**% Ethanol**	**k_1 x 10^5 sec^{-1}**
1.8	25.00	—	9.72
2.8	25.00	—	10.00
3.8	25.00	—	9.72
4.8	25.00	—	9.70
5.8	25.00	—	9.78
6.8	25.00	—	10.00
9.8	25.00	—	9.52
1.80	25.00	5	15.85
1.80	25.00	10	18.18
1.80	25.00	15	25.00
1.80	25.00	20	34.27
1.80	4.04	—	26.00
1.80	7.6	—	26.19
1.80	11.16	—	25.92
1.80	14.72	—	25.00
1.80	18.28	—	26.26
1.80	28.96	—	26.19
1.80	36.08	—	26.26

Conditions: $(IO_3^-) = 10.00 \times 10^{-4}$ M, $(IrCl_3) = 2.68 \times 10^{-5}$ M, (D-glucose) $= 2.00 \times 10^{-2}$ M, (NaOH) $= 0.20$ M.

Test for Free Radical

The addition of the reaction mixtures to aqueous acryl amide monomer solutions, in the dark, did not initiate polymerization, indicating the absence of

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

Temp.(K)	**k_1 x 10^5 (sec^{-1})**
308	05.83
313	09.09
318	13.33
323	16.66
E_a(kJ)	53.00
$k_r \times 10^2$	5.40
(mol^{-2} sec^{-1})	74.22
$\Delta S^{\#}$	
(J)	50.33
$\Delta H^{\#}$	
(kJ)	26.54
$\Delta G^{\#}$	5.48
(kJ)	
$A \times 10^2$	
(mol^{-2} sec^{-1})	

Conditions: $(IO_3^-) = 10.00 \times 10^{-4}$ M, $(IrCl_3) = 2.68 \times 10^{-5}$ M, (D-glucose) $= 2.00 \times 10^{-2}$ M, (NaOH) $= 0.20$ M, (KCl) $= 1.80 \times 10^{-3}$ M.

formation of free radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions.

Reactive Species of Iodates

There is only one report[15] available in the literature that oxidation of organic or inorganic compounds by sodium or potassium iodate in the presence of iridium has been studied in alkaline medium and IO_3^- has been assumed as the reactive species of potassium iodate in alkaline medium. Kinetic data collected for Ir (III) chloride-catalyzed oxidation of D-glucose by potassium iodate clearly show that IO_3^- is the reactive species of potassium iodate in alkaline medium.

Reactive Species of Iridium (III) Chloride in Alkaline Medium

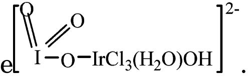
$[IrCl_3(H_2O)_3]$, $[IrCl_4(H_2O)_2]^-$, and $[IrCl_5(H_2O)]^{2-}$ are reported to be predominant species in concentration range of 0.1 M to 8 M HCl. In view of the observed kinetic data and the reported literature, it is reasonable to assume that the reactive species of Ir (III) chloride is $[IrCl_3\,(H_2O)_3]$. Since the study for the Ir (III) chloride-catalyzed oxidation of D-glucose has been made in alkaline medium, a decision can be made about reactive species of Ir (III) chloride after taking into account the effect of NaOH concentration. On the basis of observed kinetic data related to first-order kinetics at low concentrations of NaOH in the oxidation of D-glucose 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 can be concluded that the following equilibrium is established:

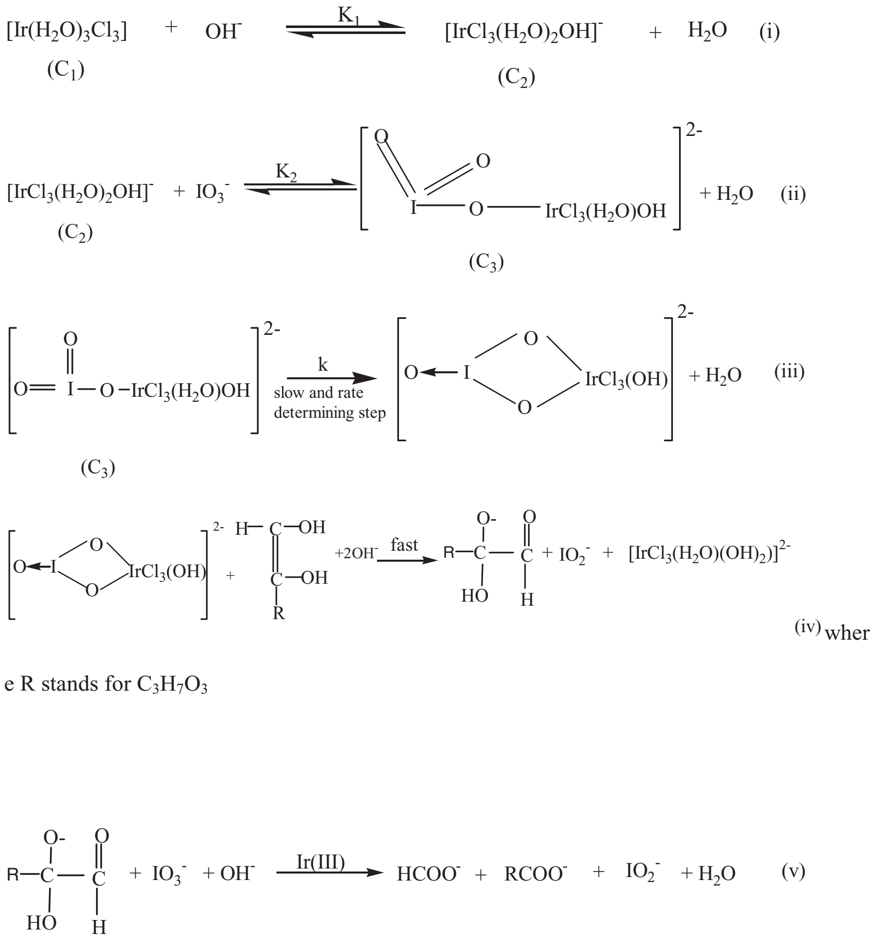
$$\left[Ir\left(H_2O\right)_3 Cl_3\right] + OH^- \rightleftharpoons \left[IrCl_3\left(H_2O\right)_2 OH\right]^- + H_2O$$

Out of these two species (i.e., $[IrCl_3(H_2O)_3]$ and $[IrCl_3(H_2O)_2OH]^-$), the species $[IrCl_3(H_2O)_2OH]^-$ can be safely assumed the reactive species of iridium (III) chloride in the present investigation.

Reactive Form of Sugar in Alkaline Medium

It is reported[16] that in the presence of alkali, reducing sugars undergo a tautomeric change resulting in the formation of an enediol and an enediol anion. The formation of the enediol and an enediol anion in alkaline medium is also supported by the work of Isbell and coworkers.[17] The observed reaction rate with respect to $[OH^-]$ for the Ir (III) chloride-catalyzed oxidation of D-glucose has led us to assume that enediol form of sugar which is actually taking part in the reactions under investigation.

The possibility of the formation of a complex in oxidation of D-glucose occurs between reactive species of Ir (III) chloride (i.e., $[IrCl_3\,(H_2O)_2OH]^-$) and reactive species of iodate (i.e., IO_3^-) in alkaline medium. In order to verify the existence of an above complex, spectra for the solution of Ir (III) chloride and OH^- with two different concentrations of IO_3^- have been collected. 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 toward longer wavelength (i.e., from 216 to 217 and 220 nm). This increase in absorbance with the increase in $[IO_3^-]$ can be considered as an indication of formation of complex between the reactive species of Ir (III) chloride and reactive species of iodate in alkaline medium (Sch. 1). The shift in λ_{max} value toward longer wavelength is due to the fact that the combination of a chromophore, IO_3^-, and an auxochrome, OH^-, gives rise to another chromophore  .



where R stands for $C_3H_7O_3$

Reaction Scheme 1. Plausible mechanism for the stepwise Ir (III)-catalyzed oxidation of D-glucose.

Suggested Mechanism

On the basis of observed kinetic results and taking $[IrCl_3(H_2O)_2OH]^-$ and IO_3^- as the most active species of Ir (III) chloride and potassium iodate, respectively, the following reaction steps (Sch. 1) have been proposed in the oxidation of glucose by iodate ion in the presence of Ir (III) chloride.

On the basis of all the steps in Scheme 1 for the oxidation of D-glucose and stoichiometry of the reaction, the rate of the reaction in terms of loss of concentration of iodate ions can be written as equation (1):

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

Equation (1) is the rate law that is valid for all the concentrations of IO_3^- and OH^- and Ir (III) chloride on the rate oxidation of glucose.

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

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

Equation (2) is the rate law valid for low concentration of $[IO_3^-]$ and Ir (III) chloride and for all the concentrations of $[OH^-]$. Equation (2) can also be written as:

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

where $\text{Rate} = -\frac{d[IO_3^-]}{dt}$

According to equation (3), if a plot is made between $\frac{1}{\text{rate}}$ and $1/[OH^-]$, a straight line having an intercept on y-axis will be obtained. When a plot was made between 1/Rate and $1/[OH^-]$, a straight line having intercept on 1/Rate axis was obtained (Fig. 4). This proves the validity of the rate law (2) and hence the proposed reaction Scheme 1. From the slope and intercept of the straight line, the values of K_1 and kK_2 have been calculated and found to be 4.66 and 5.60, respectively. Utilizing K_1 and kK_2 values, the reaction rates for

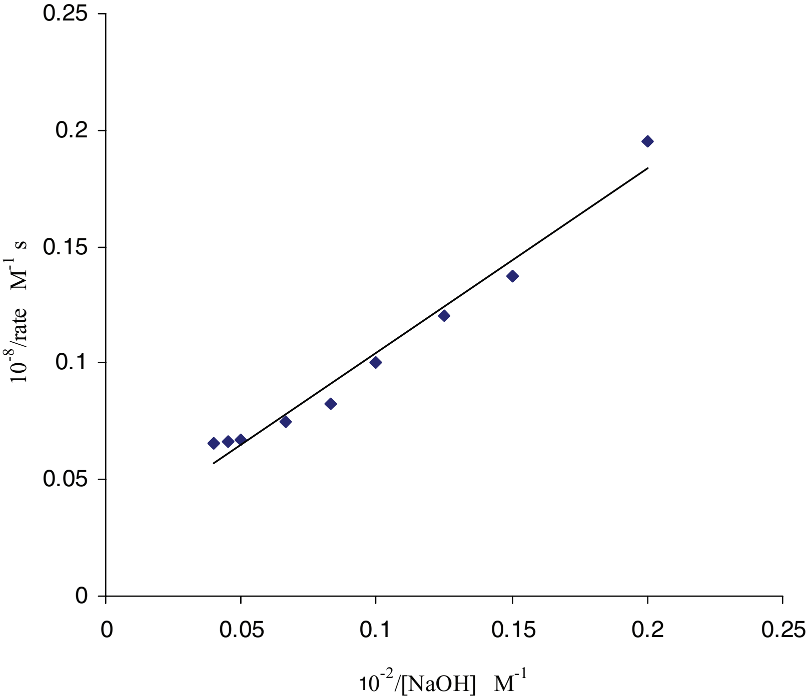


Figure 4. Dependence of 1/Rate on 1/(OH)$^{-}$ from data and conditions given in Table 1.

the variation of [OH^{-}]in the Ir (III) chloride-catalyzed oxidation of D-glucose have been calculated by 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 1.

Multiple Regression Analysis

With the help of multivariate regression analysis, a relationship in the case of D-glucose between observed pseudo first-order rate constant, k_1, and concentrations of all the reactants of the reaction except [IO$_3^-$] was found as :

$$k_1 = k[\mathrm{OH}^-]^{0.55}[\mathrm{Ir(III)}]^{0.50} \tag{4}$$

where $k = 6.07 \times 10^{-2}$

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

For the oxidation of D-glucose, a reaction path has been proposed where the most reactive activated complex has been formed by the interaction of a similarly charged species $[IrCl_3(H_2O)_2OH]^-$ and IO_3^-. In this case the transition state will have the same charge, but it will be dispersed over a larger 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 oxidation of glucose by iodate in the presence of Ir (III) chloride is certainly evidence for step (ii) of Scheme 1. In step (ii) the complex in the transition state has the same charge dispersed over a larger volume than the charged species. The proposed mechanism is also supported by the moderate values of energy of activation and other parameters.

Effect of Dielectric Constant and Calculation of the Size of the Activated Complex

In order to find out the effect of dielectric constant of the medium on the reaction rate, the reaction has been studied with different dielectric constant (D) of the medium at constant concentration of all other reactants at constant temperature. It is clear from the Table 3 that $-dc/dt$ and k (rate constant) values are increased with the decrease in dielectric constant of the medium. The dependence of the rate constant on the dielectric constant of the medium is given by the following equation:

$$\log k_1 = \log k_0 - \frac{Z_A Z_B e^2 \tilde{N}}{2.303\,(4\pi \in_0)\, d_{AB} RT} \times \frac{1}{D}$$

The decrease in first-order rate constant with the increase in dielectric constant of the medium is also evident form plots of log k_1 versus $1/D$ (Fig. 5). The plot of log k_1 versus $1/D$ was linear, having a negative slope. This clearly supports the involvement of similar charges in the rate-limiting step in the proposed mechanism. The value of d_{AB} has been evaluated with the help of the slope of the straight line and found to be $1.60A^0$.

Comparative Studies

An effort has also been made to compare our experimental findings with the results earlier reported for oxidation of reducing sugars by N-bromoacetamide[18] in the presence of Ir (III) chloride and also Ru (III) chloride oxidation of indigo carmine[19] by iodate in acidic medium. The present paper shows similarity with Ir (III) chloride-catalyzed oxidation of reducing sugars being first to zero order with respect to oxidant and catalyst and zero order with respect to reducing sugars. 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 Ir (III) chloride-catalyzed

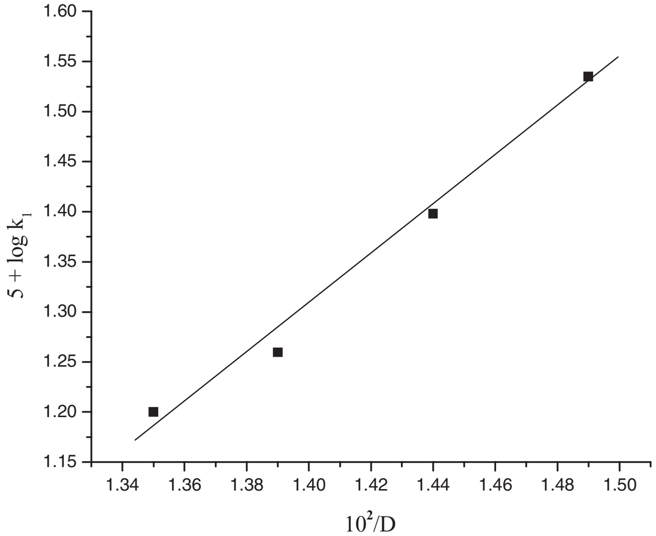


Figure 5. Dependence of log k_1 on 1/D from data and conditions given in Table 2.

oxidation, it participates in the reaction as such. When the present study with respect to the role of iodate was compared with the Ru (III)-catalyzed oxidation of indigo carmine, it was found that the species IO_3^- was 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 reducing sugars. 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 glucose in alkaline medium, whereas in the reported[20] Ir (III) chloride-catalyzed oxidation of reducing sugars, the reactive species of Ir (III) chloride was found to be $[IrCl_6]^{3-}$.

CONCLUSION

Oxidation of glucose by iodate in alkaline medium is very sluggish, but it becomes facile in the presence of Ir (III) chloride catalyst. 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. The rate of reaction of glucose is unaffected by the ionic strength of the medium. Oxidation products have been identified. Activation parameters were 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) chloride acts as an efficient catalyst for the oxidation of D-glucose by iodate in alkaline medium.

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