



iJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 5 Issue: XII Month of publication: December 2017

DOI:

www.ijraset.com

Call: ☎ 08813907089

E-mail ID: ijraset@gmail.com

Iridium (III) Catalyzed Oxidation of D-Sorbitol By Sodium N-Chloro-P-Toluenesulfonamide in Perchloric Acid Medium: Mechanistic Approach and Kinetic Modelling

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Abstract: The present papers deals with the kinetics and mechanism of homogeneously Ir(III) chloride catalysed oxidation of D-sorbitol by chloramine-T [CAT] in perchloric acid medium in the temperature range of 30 to 45 °C. The reaction is carried out in the presence of mercuric acetate as a scavenger for chloride ion. The experimental results show first order kinetics with respect to the oxidant [CAT] and catalyst [Ir(III)] while zero order with respect to substrate, i.e., D-Sorbitol was observed. The reaction shows negligible effect of $[\text{Hg}(\text{OAc})_2]$, $[\text{H}^+]$ and ionic strength of the medium. Chloride ion positively influence the rate of reaction. A transient complex, formed between Ir(III) and chloramine-T in a slow and rate determining step, reacts with the D-sorbitol to give the product in a series of fast steps, which lead to regeneration of the catalyst. The reaction between chloramine-T and D-Sorbitol in acid medium shows 2:1 stoichiometry. To calculate activation parameters, the reactions have been studied at four different temperatures between 30 to 45 °C. A mechanism involving the complex formation between catalyst and oxidant has been proposed. D-Gluconic acid has been identified chromatographically and spectroscopic ally as the final product of oxidation of D-Sorbitol. Based on the kinetic data, reaction stoichiometry and product analysis, a reaction mechanism has been proposed and rate law has been derived.

Key Words: Kinetics, mechanism, Ir(III) catalysis, D-sorbitol, chloramine-T, acidic medium.

I. INTRODUCTION

The sodium salts of arylhalosulfonamides generally known as organic haloamines have attracted the attention of chemists, as versatile redox titrants [1]. The miscellaneous chemical behaviour of organic haloamines is accredited in general to their ability to act as halonium cations, hypohalites, N-anions which act both as bases and nucleophiles and nitrenoids in limiting cases [2]. As a result, these compounds react with a wide range of functional groups to cause numerous kinds of molecular changes. Aromatic N-haloamines act as mild oxidants in both acid and alkaline solutions due to the presence of strongly polarized N-linked halogen in +1 state [3,4]. A prominent member of this group Sodium N-chloro-p-toluenesulfonamide or Chloramine-T (CAT; $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa}\cdot 3\text{H}_2\text{O}$) is used as halogenating and oxidizing agent [4-6]. CAT is a byproduct in the manufacture of saccharin [7]. Depending upon the pH of the medium, it forms various oxidizing species and thus shows a variety of kinetic results [8,9]. Several researchers have studied the oxidizing behavior of CAT [10-13] and numerous studies focus on the mechanistic aspects of the redox reactions in acidic media. In most of the studies one of the species, RNHCl ($\text{R} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$), HOCl , or H_2OCl^+ , has been considered as the reactive species [14]. It can behave as both electrophile and nucleophile depending on the reaction conditions. A polyhydric alcohol or polyalcohol is a hydrogenated form of carbohydrate, whose carbonyl group (aldehyde or ketone, reducing sugar) has been reduced to primary and secondary hydroxyl group. D-Sorbitol, a polyhydric alcohol with about half the sweetness of sucrose. D-Sorbitol occurs naturally and is also produced synthetically from glucose. It was formerly used as a diuretic and may still be used as a laxative and in irrigating solutions for some surgical procedures. It is also used in many manufacturing processes, as a pharmaceutical aid, and in several research applications. Commonly the study oxidation of polyhydric alcohols has great importance in sugar chemistry. Various investigation on oxidation involving polyhydric alcohols and various oxidants i.e., cerium(VI) [15-17], potassium bromate [18], N-Bromosuccinimide [19] in the presence/absence of catalyst in acidic medium have been reported by various workers. However, there are only few reports available in the literature for the oxidation of D-Sorbitol [20].

Various transition metal catalysts have been used in the N-haloamine oxidation of organic substrates [21]. Recently, the use of transition metal ions, such as osmium, ruthenium and iridium either alone or as binary mixtures, as catalyst in various redox processes has drawn considerable attention [22]. Iridium(III) chloride is an important platinum group metal ion and has been extensively used as homogeneous catalyst in a number of redox reactions [23]. Several studies have reported the use of Ir(III) chloride as a non-toxic and homogeneous catalyst [24-27]. Preliminary experimental results indicate that the reaction of D-Sorbitol with CAT in the acidic medium without a catalyst were very sluggish but the reaction becomes facile in the presence of Ir(III) catalyst.

In the present study, we examine the kinetic and mechanistic aspect of the Ir(III) catalyzed oxidation of D-Sorbitol by CAT in acidic medium with the following objectives: (i) to ascertain the reactive species of catalyst and oxidant, (ii) find the oxidative capacity of oxidant (CAT) (iii) find the catalytic efficiency of Ir(III), (iv) identify the oxidation products, (v) to elucidate the plausible reaction mechanism, (vi) to deduce rate law consistent with kinetic results and (vii) to calculate the activation parameters.

II. EXPERIMENTAL

A. Materials

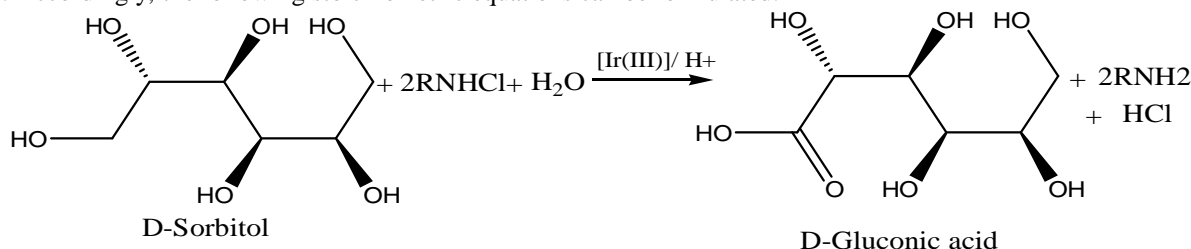
A stock standard solution of chloramine-T (S.D. Fine Chem. Ltd) was prepared by dissolving its known weight in doubly distilled water and its concentration was estimated iodometrically. In order to avoid photochemical deterioration, the solution of chloramine-T was preserved in black coated flask. The standard solution of D-Sorbitol (E.Merck) was freshly prepared. Iridium(III) chloride (Johnson Matthey) solution was prepared in HCl of known strength (0.018 N). Other reagents used were, A.R. grade and their solutions were also prepared in doubly distilled water. The reaction vessels were also black coated from outside to avoid photochemical effects.

B. Kinetic measurements or Procedure

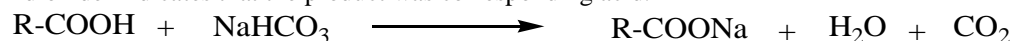
The kinetic runs were carried out at 35 ± 0.1 °C. The reaction was initiated by mixing the already thermo stated solution of D-Sorbitol to the thermally equilibrated reaction mixture containing required volume of solution of Chloramine-T, H^+ , Ir(III) and all other reagents. Aliquots (5ml) of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5ml of 4% KI solution and 5ml of dilute sulphuric acid. The liberated iodine equivalent to unconsumed oxidant was estimated with standard sodium thiosulphate solution using starch as an indicator. The initial rates were obtained from the slope of concentration vs. time graph in the initial stages of the reactions by plane mirror method.

C. Stoichiometry and product analysis

In order to ascertain the stoichiometry of the reaction, different sets of experiments with varying $[RNHCl]:[D-Sorbitol]$ ratios were performed at 35 °C for 48 h and constant concentrations of all other reactants under the conditions $[RNHCl] \gg [D-Sorbitol]$. Iodometric estimation of unconsumed $[RNHCl]$ in different sets shows that 2 moles of $RNHCl$ were consumed to oxidize 1 mole of D-sorbitol. Accordingly, the following stoichiometric equations can be formulated:



D-Gluconic acid, the main product in the oxidation of D-Sorbitol was identified by the help of chromatography (TLC) and conventional (spot test) method. The acidic group (-COOH) was confirmed by adding sodium bicarbonate into the solution. Evolution of carbon dioxide indicates that the product was corresponding acid.



The nature of D-Gluconic acid further confirmed by its IR spectrum (fig. 1). The symmetric stretching vibration of ν_{OH} observes at 3345 cm^{-1} , out of plane bending (OH) observe at 920 cm^{-1} in the IR spectrum indicates the presence of CH_2OH group in studied molecule.

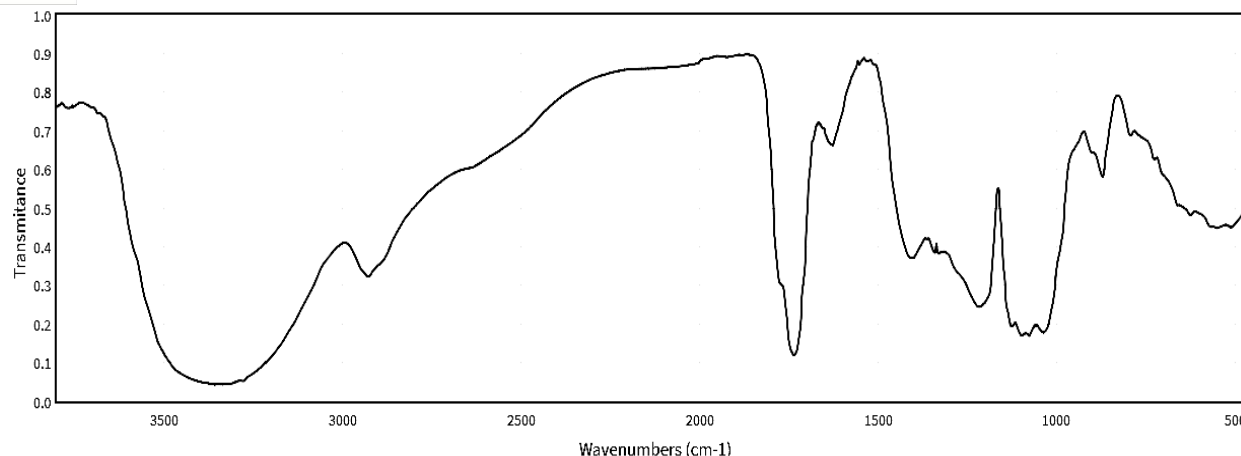


Fig. 1. IR-Spectra of the main product D-gluconic acid

The C-O stretching vibration observed at 1237 cm^{-1} and C=O stretching at 1725 cm^{-1} . The C-O-H in plane bending appears at 1165 cm^{-1} confirms the presence of – OH group to the carbon frame .The C-C stretching vibration appears at 1020 cm^{-1} .The C-H stretching vibration of ν (C-H) appears at 2943 cm^{-1} .

III. RESULT AND DISCUSSION

Kinetics of Ir(III) catalyzed oxidation of D-Sorbitol by chloramine-T in acidic medium was investigated at 35°C . The kinetic results were collected at several initial concentrations (Table1). The order of reaction with respect to each reactant was determined by varying the concentration of oxidant, D-Sorbitol, Ir(III) chloride (Table 1), H^+ ions, $[\text{Cl}^-]$ and mercuric acetate one by one in different sets keeping concentration of all other reactants constant at constant temperature 35°C . In each kinetic runs, the initial rate (i.e., $-\text{dc}/\text{dt}$) of the reaction was determined from the slope of the tangent drawn at a fixed concentration of chloramine-T except for the chloramine-T variation in which the slope of the tangent was drawn at fixed time. The first order reaction rate constant (k_1) for the variation of all the reagents were calculated:

$$k_1 = \frac{-\text{dc}/\text{dt}}{[\text{RNHCl}]^*}$$

Where $[\text{RNHCl}]^*$ denotes the $[\text{RNHCl}]$ at which $(-\text{dc}/\text{dt})$ was determined.

Table 1. Effect of variation of oxidant, D-sorbitol, Ir(III) at 35°C

[Oxidant] x 10^3 M (Chloramine-T)	[Substrate]x 10^2 M (D- sorbitol)	[Ir(III)] x 10^5 M	$(-\text{dc}/\text{dt})\times 10^7\text{ ML}^{-1}\text{s}^{-1}$
0.83	2.00	8.02	3.45
1.00	2.00	8.02	4.07
1.25	2.00	8.02	4.95
1.67	2.00	8.02	6.65
2.50	2.00	8.02	10.12
5.00	2.00	8.02	20.28
1.00	0.33	8.02	3.72
1.00	0.40	8.02	4.47
1.00	0.50	8.02	3.95
1.00	0.66	8.02	3.56
1.00	1.00	8.02	4.28
1.00	2.00	8.02	4.07

1.00	2.00	2.67	1.35
1.00	2.00	4.01	2.05
1.00	2.00	5.34	2.66
1.00	2.00	6.67	3.42
1.00	2.00	8.02	4.07
1.00	2.00	9.35	5.06

Solution conditions: $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$, $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$.

A plot of $(-dc/dt)$ versus $[\text{Chloramine-T}]$ was linear with the slope value (0.97) near unity, which further confirms first order dependence of reaction on chloramine-T (Fig. 2). The first order kinetics w.r.t. $[\text{Chloramine-T}]$ was also confirmed by 'least-square method' (Fig. 3). A plot of $(-dc/dt)$ versus $[\text{Ir(III)}]$ gives a slope which is close to the average value of first order rate constant at 35 °C (Fig. 4). Insignificant effect on the rate was observed on increasing the concentration of the substrate, indicating zero order in substrate *i.e.* D-Sorbitol (Table1).

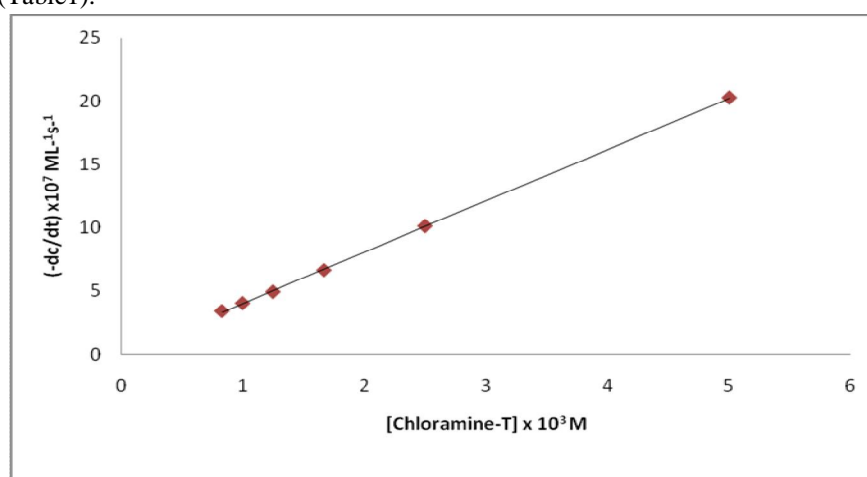


Fig. 2. Plot between $(-dc/dt)$ and $[\text{Chloramine-T}]$ for the oxidation of D-sorbitol at 35 °C. $[\text{Ir (III)}] = 8.02 \times 10^{-5} \text{ M}$, $[\text{D-sorbitol}] = 2.00 \times 10^{-2}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$, $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$.

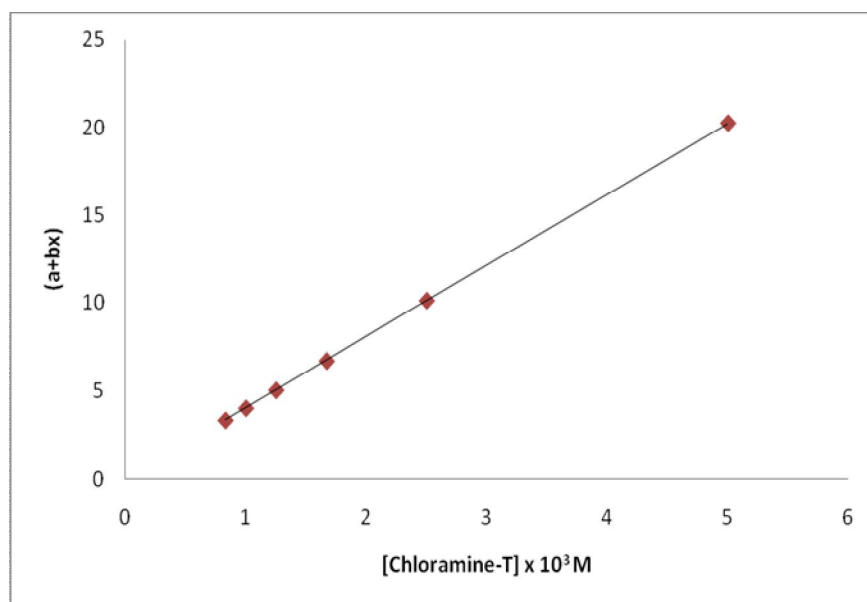


Fig. 3. Plot between $(a + bx)$ and $[\text{Chloramine-T}]$ for the oxidation of D-sorbitol at 35 °C. $[\text{Ir (III)}] = 8.02 \times 10^{-5} \text{ M}$, $[\text{D-sorbitol}] = 2.00 \times 10^{-2}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$, $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$.

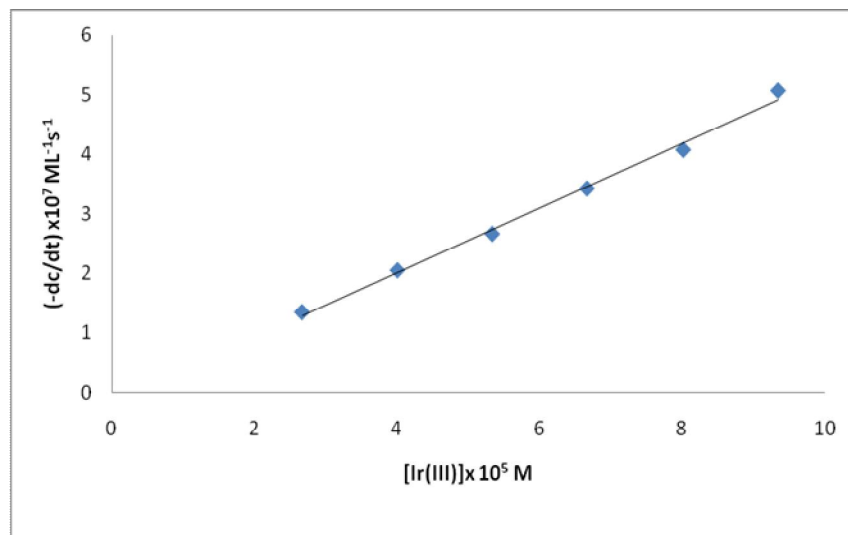


Fig. 4. Plot between $(-dc/dt)$ and $[Ir(III)]$ for the oxidation of D-sorbitol at $35^{\circ}C$. $[D\text{-sorbitol}] = 2.00 \times 10^{-2} M$, $[Chloramine-T] = 1.00 \times 10^{-3}$, $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-3} M$, $[KCl] = 1.00 \times 10^{-3} M$.

Variation of $[KCl]$ concentration shows positive effect on reaction rate (Fig. 5) (Table 2). Negligible effect of mercuric acetate eliminate the probability of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without $[CAT]$. Hence, the function of mercuric acetate is to act as scavenger for any chloride ion formed in the reaction [28]. It helps to eliminate the parallel oxidation by Cl_2 which would have been formed as a result of interaction between Cl^- and $RNHCl$ ion. Experimental data indicate negligible effect of ionic strength of the medium on the rate (affected by addition of $NaClO_4$). In acidic solution of chloramine-T quick formation of $RNHCl$ has been reported [29]. The reaction is unaffected by H^+ concentration (Table 2)

Table 2. Effect of variation of $HClO_4$, KCl and $NaClO_4$ at $35^{\circ}C$

$[HClO_4] \times 10^3 M$	$[KCl] \times 10^3 M$	$NaClO_4 \times 10^3 M$	$(-dc/dt) \times 10^7 ML^{-1} s^{-1}$
0.83	1.00	1.00	3.42
1.00	1.00	1.00	4.07
1.25	1.00	1.00	2.96
1.67	1.00	1.00	3.98
2.50	1.00	1.00	3.72
5.00	1.00	1.00	3.50
1.00	0.83	1.00	3.64
1.00	1.00	1.00	4.07
1.00	1.25	1.00	4.45
1.00	1.67	1.00	4.92
1.00	2.50	1.00	5.35
1.00	5.00	1.00	5.96
1.00	1.00	0.83	4.24
1.00	1.00	1.00	4.07
1.00	1.00	1.25	3.56
1.00	1.00	1.67	3.25
1.00	1.00	2.50	3.92
1.00	1.00	5.00	3.36

Solution conditions: $[Ir(III)] = 8.02 \times 10^{-5} M$, $[Chloramine-T] = 1.00 \times 10^{-3} M$, $[D\text{-sorbitol}] = 2.00 \times 10^{-2}$, $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$.

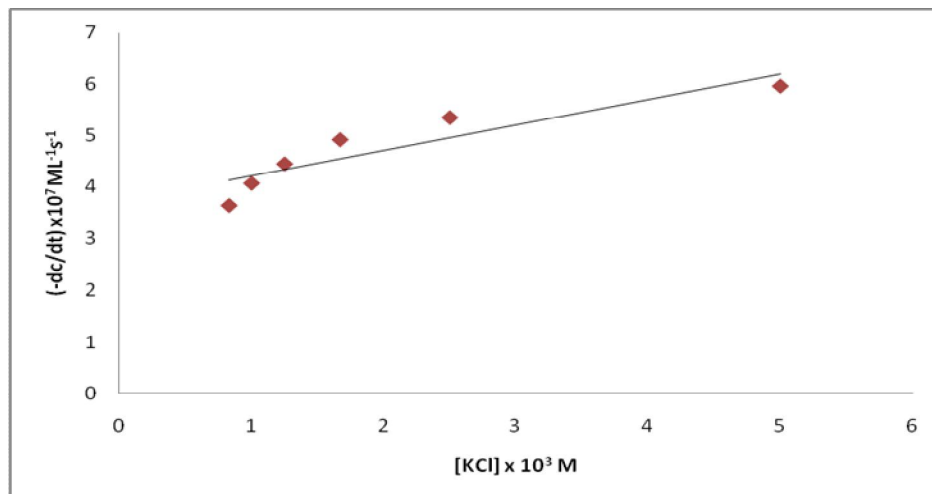


Fig. 5. Plot between $(-dc/dt)$ and $[KCl]$ for the oxidation of D- sorbitol at 35 °C. $[Ir(III)] = 8.02 \times 10^{-5} M$, $[D-sorbitol] = 2.00 \times 10^{-2} M$, $[Chloramine-T] = 1.00 \times 10^{-3}$, $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-3} M$.

The kinetic measurements were also taken in the temperature range of 30-45 °C and the specific rate constants were obtained at 30 °C, 35 °C, 40 °C and 45 °C. These specific rate constants were used to draw a plot of $\log k$ versus $1/T$ (Fig. 6) which was linear. The various activation parameters were calculated from the slope of curves obtained from the Fig. 6. The value of energy of Activation (E_a), Arrhenius factor (A), entropy of activation (ΔS^\ddagger), free energy of activation (ΔG^\ddagger) and enthalpy of activation (ΔH^\ddagger) were calculated from rate measurement and these values have been provided in Table-3. Moderate ΔH^\ddagger and ΔS^\ddagger values are favorable for electron transfer reaction. The value of ΔH^\ddagger was due to energy of solution changes in transition state. The high positive value of ΔG^\ddagger represents highly solvated transition state. The negative value of ΔS^\ddagger indicates that the intermediate complex is more ordered than the reactants so the formation of activated complex occurs with reduction in the degree of freedom [30]. The observed modest enthalpy of activation and higher rate constant for the slow step shows that oxidation presumably occurs by means of an inner sphere mechanism [31].

Table 3. Activation parameters for the oxidation of D-sorbitol

Parameters	Temperature(°C)	D-sorbitol
$K_1 \times 10^4 s^{-1}$	30	3.15
$K_1 \times 10^4 s^{-1}$	35	4.07
$K_1 \times 10^4 s^{-1}$	40	6.27
$K_1 \times 10^4 s^{-1}$	45	8.12
Log A	--	7.88
E_a (kJ mol ⁻¹)	35	42.90
ΔG^\ddagger (kJ mol ⁻¹)	35	70.51
ΔH^\ddagger (kJ mol ⁻¹)	35	40.33
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	35	-98.05

Solution conditions: $[Ir(III)] = 8.02 \times 10^{-5} M$, $[Chloramine-T] = 1.00 \times 10^{-3} M$, $[D-Sorbitol] = 2.00 \times 10^{-2}$, $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-3} M$, $[KCl] = 1.00 \times 10^{-3} M$.

This conclusion is supported by earlier observations. The activation parameters evaluated for the catalyzed reaction explain the catalytic effect on the reaction. Kinetic observations show that the reaction under investigation is complex reaction, which usually takes place in more than one step.

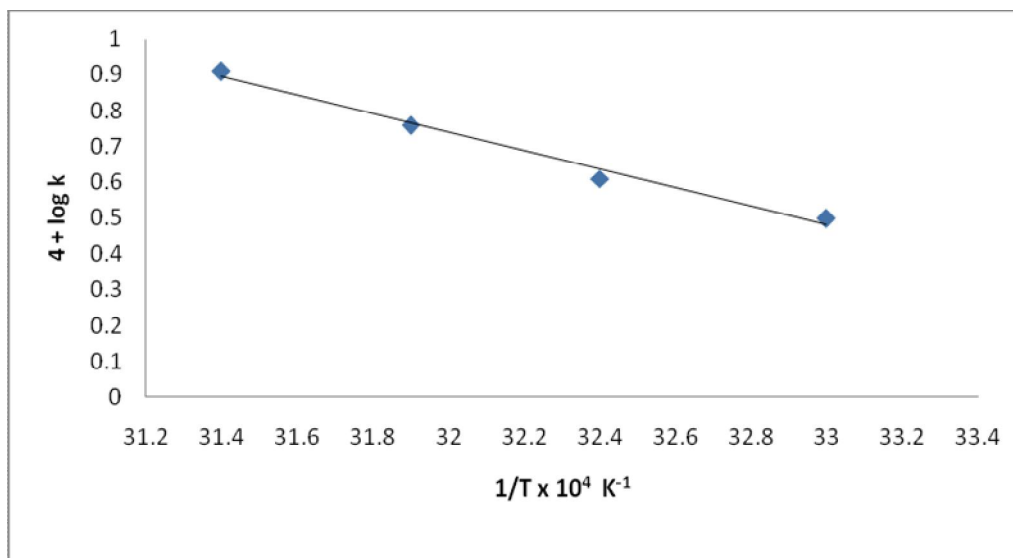
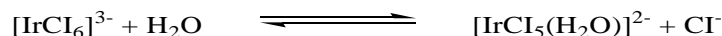


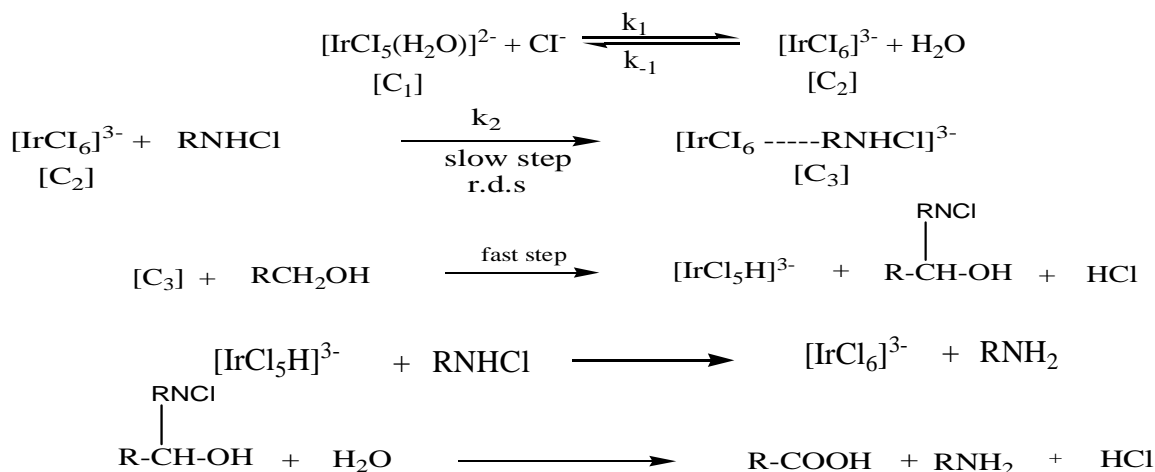
Fig. 6. Arrhenius plot for the oxidation of D-sorbitol. $[\text{Ir (III)}] = 8.02 \times 10^{-5} \text{ M}$, $[\text{Chloramine-T}] = 1.00 \times 10^{-3} \text{ M}$, $[\text{D-sorbitol}] = 2.00 \times 10^{-2}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$, $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$.

A. Mechanism and derivation of rate law

The acidic solution of Iridium chloride exists as $[\text{IrCl}_6]^{3-}$. It has also been reported that $[\text{IrCl}_6]^{3-}$ is involved in equilibrium as follows [32] :



Thus either $[\text{IrCl}_6]^{3-}$ or $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ may act as catalytic species [33]. If $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ is taken as catalytic species the rate law would require negative effect of chloride ion contrary to the positive effect of chloride ion on the oxidation rate observed by us. Hence the only choice is $[\text{IrCl}_6]^{3-}$ which when assumed as reactive species of Iridium trichloride in acidic medium, explains the positive effect of chloride ion. The kinetic results reported in table 1, 2, 3 along with the above discussion lead us to suggest the following reaction scheme:



Where,

$\text{R} = \text{CH}_2\text{OH}(\text{CHOH})_n$, for D-Sorbitol ($n = 4$)

$[\text{P}] = \text{Product i.e. D-Gluconic acid}$

Now, Considering the above reaction steps and applying the steady-state treatment with reasonable approximation, the rate law may be written as

$$\text{Rate} = \frac{-d[\text{RNHCl}]}{dt} = k_2 [C_2] [\text{RNHCl}] \quad (i)$$

$$[\text{Ir(III)}]_T = [C_1] + [C_2] \quad (ii)$$

$$\frac{d[C_1]}{dt} = k_{-1} [C_2] - k_1 [C_1][Cl^-] \quad (iii)$$

$$[C_1] = \frac{k_{-1} [C_2]}{k_1 [Cl^-]} \quad (iv)$$

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

(where $K_1 = k_{-1}/k_1$)

Putting the value of $[C_1]$ in equation (ii), we get :

$$\begin{aligned} [Ir(III)]_T &= [C_1] + [C_2] \\ [Ir(III)]_T &= \frac{[C_2]}{K_1 [Cl^-]} + [C_2] \\ &= \left[\frac{[C_2] + K_1 [Cl^-][C_2]}{K_1 [Cl^-]} \right] \\ &= [C_2] \left[\frac{1 + K_1 [Cl^-]}{K_1 [Cl^-]} \right] \end{aligned}$$

This gives ,
$$[C_2] = \frac{[Ir(III)]_T K_1 [Cl^-]}{1 + K_1 [Cl^-]}$$

Putting the value of C_2 in equation (i), we get,

$$Rate = \frac{K_1 k_2 [Ir(III)]_T [Cl^-] [RNHCl]}{1 + K_1 [Cl^-]}$$

The above equation is final rate law which well explains the experimental first-order kinetics with respect to [chloramine-T] and [Ir(III)] on the rate of oxidation and also order with respect to $[Cl^-]$ is fractional positive.

IV. COMPARATIVE STUDIES

The results of present study of Ir(III) catalyzed oxidation of D-sorbitol by chloramine-T in acidic medium can be compared with the results for the Ru(III) catalyzed oxidation of polyhydric alcohols (D-mannitol and D-sorbitol) by $KBrO_3$ in alkaline medium [20]. The present study being similar in order with respect to oxidant and catalyst but shows significant change as far as order with respect to Cl^- ion is concerned. The observed positive effect of $[Cl^-]$ on the rate of oxidation in present study is contrary to the reported negative effect of $[Cl^-]$ in the oxidation of polyhydric alcohols (D-mannitol and D-sorbitol) using Ru(III) chloride as a catalyst [20]. The most reactive species of Ir(III) chloride is $[IrCl_6]^{3-}$ in acidic medium in present study while $[RuCl_2(H_2O)_3(OH)]$ reported as most reactive species of Ru(III) chloride in alkaline medium [20]. The stoichiometric analysis of present study shows 2 mole of oxidant $[RNHCl]$ consumes 1 mole of substrate i.e. D-sorbitol, On the other hand in Ru(III) catalyzed reaction one mole of oxidant $[KBrO_3]$ consumes one mole of substrate i.e. polyhydric alcohols [20]. On the basis of facts mentioned above, it can be inferred that the present study differs in some respects from the study reported for Ru(III) chloride catalyzed oxidation.

V. CONCLUSION

The following conclusions can be derived in the present study of Ir(III) catalyzed oxidation of D-sorbitol by chloramine-T in acidic medium. (a) Among the various species of Ir(III) in acidic medium, $[IrCl_6]^{3-}$ is considered as the reactive species while (b) $RNHCl$ is the reactive species of Chloramine-T in acidic medium. (c) In the absence of catalyst oxidation of D-sorbitol by Chloramine-T is very sluggish, but it becomes facile in the presence of Ir(III) catalyst. (d) The stoichiometry of the reaction was found to be 2:1 and

the oxidation products of were identified (e) Activation parameters were computed from the Arrhenius plot. (f) 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 act as an efficient catalyst for the oxidation of D-sorbitol by Chloramine-T in acidic medium.

VI. ACKNOWLEDGEMENT

The first author thankfully acknowledges the CSIR, New Delhi, India for providing financial assistance in the form of Research Fellowship.

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