

Kinetic, Mechanistic and Thermodynamic Investigations on Iridium (III) catalyzed Oxidation of D-Mannitol by N-chloro-p-toluenesulfonamide in Perchloric Acid Medium

Jyoti Pandey¹ Abhishek Verma², Reena Patel², Sheila Srivastava^{3,*}

Assistant Professor, Department of Applied Chemistry, BBAU, Lucknow, UP, India¹

Ph.D. Student, Department of Applied Chemistry, BBAU, Lucknow, UP, India²

Associate Professor, Department of Chemistry, Feroze Gandhi College, Raebareli, UP, India³

ABSTRACT: The present papers deals with the kinetics and mechanism of homogeneously Ir(III) chloride catalyzed oxidation of D-mannitol 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-Mannitol was observed. The reaction shows negligible effect of [Hg(OAc)₂], [H⁺] and ionic strength of the medium. Chloride ion positively influence the rate of reaction. The reaction between chloramine-T and D-Mannitol 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. Mannonic acid has been identified chromatographically and spectroscopically as the final product of oxidation of D-Mannitol. Based on the kinetic data, reaction stoichiometry and product analysis, a reaction mechanism has been proposed and rate law has been derived.

KEYWORDS: Kinetics, mechanism, Ir(III) catalysis, D-Mannitol, 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; p-CH₃C₆H₄SO₂NCINa.3H₂O) 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 (R = CH₃C₆H₄SO₂), HOCl, or H₂OCl⁺, has been considered as the reactive species [14]. It can behave as both electrophile and nucleophile depending on the reaction conditions.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

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. Mannitol is found in abundance in nature, particularly in exudates from trees, and in marine algae and fresh mushrooms. It is an isomer of sorbitol and is typically produced today by the hydrogenation of specialty glucose syrups. Mannitol is commercially available in variety of powder and granular forms. 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], potassium bromate [16], N-Bromosuccinimide [17] 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-mannitol [18-20].

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-mannitol 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-mannitol 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

2.1. 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-mannitol (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.

2.2. Kinetic measurements or Procedure

The kinetic runs were carried out at 35 ± 0.1 °C. The reaction was initiated by mixing the already thermostated solution of D-mannitol 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.

2.3 Stoichiometry and product analysis

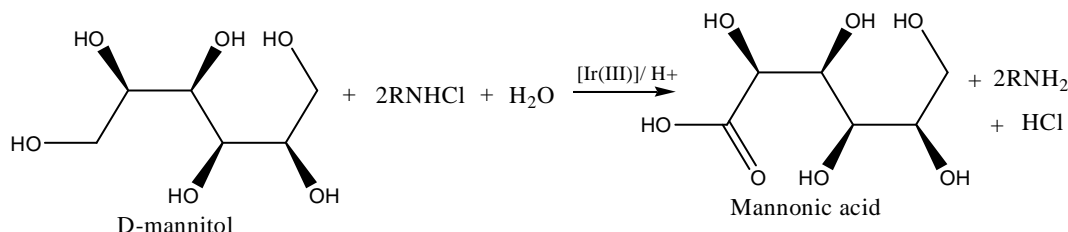
In order to ascertain the stoichiometry of the reaction, different sets of experiments with varying $[RNHCl]:[D\text{-mannitol}]$ ratios were performed at 35 °C for 48 h and constant concentrations of all other reactants under the conditions $[RNHCl] \gg [D\text{-mannitol}]$. Iodometric estimation of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

International Journal of Innovative Research in Science, Engineering and Technology

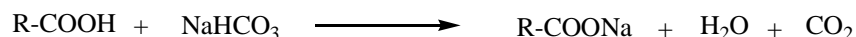
(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017



Mannonic acid, the main product in the oxidation of D-mannitol 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 mannonic acid further confirmed by its IR spectrum (figure 1). The symmetric stretching vibration of ν OH observes at (A) 3323 cm⁻¹, out of plane bending (OH) observe at (F) 914 cm⁻¹ in the IR spectrum indicates the presence of CH₂OH group in studied molecule.

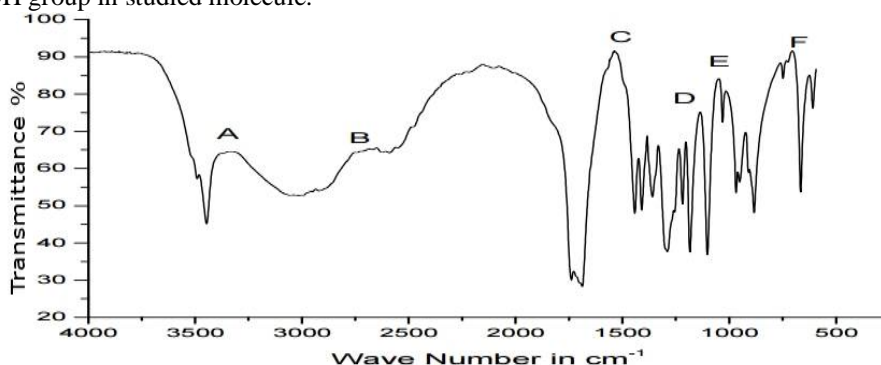


Figure 1. IR-Spectra of the main product Mannonic acid

The C-O stretching vibration observed at (D) 1249 cm⁻¹ and C=O stretching at (C) 1715 cm⁻¹. The C-O-H in plane bending appears at (E) 1156cm⁻¹ confirms the presence of - OH group to the carbon frame .The C-C stretching vibration appears at (E) 1012cm⁻¹.The C-H stretching vibration of ν (C-H) appears at (B) 2936cm⁻¹. The bending vibration observes at 770.97 cm⁻¹.

III. RESULT AND DISCUSSION

Kinetics of Ir(III) catalyzed oxidation of D-mannitol 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-mannitol, Ir(III) chloride (Table 1), H⁺ ions, [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., -dc/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 (k₁) for the variation of all the reagents were calculated:

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

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

Table 1. Effect of variation of oxidant, D-mannitol, Ir(III) at 35⁰C

[Oxidant] x 10 ³ M (Chloramine-T)	[Substrate]x 10 ² M (D-mannitol)	[Ir(III)] x 10 ⁵ M	(-dc/dt)x10 ⁷ ML ⁻¹ s ⁻¹	k ₁ x 10 ⁴ S ⁻¹
0.83	2.00	8.02	2.96	3.36
1.00	2.00	8.02	3.62	4.46
1.25	2.00	8.02	4.52	5.31
1.67	2.00	8.02	5.96	7.64
2.50	2.00	8.02	8.95	9.94
5.00	2.00	8.02	17.92	19.26
1.00	0.33	8.02	2.62	3.01
1.00	0.40	8.02	3.32	4.00
1.00	0.50	8.02	2.94	3.50
1.00	0.66	8.02	2.60	2.92
1.00	1.00	8.02	3.28	3.81
1.00	2.00	8.02	3.62	4.52
1.00	2.00	2.67	1.20	1.33
1.00	2.00	4.01	1.82	2.09
1.00	2.00	5.34	2.42	2.84
1.00	2.00	6.67	2.98	3.63
1.00	2.00	8.02	3.62	4.46
1.00	2.00	9.35	4.18	5.35

Solution conditions: [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

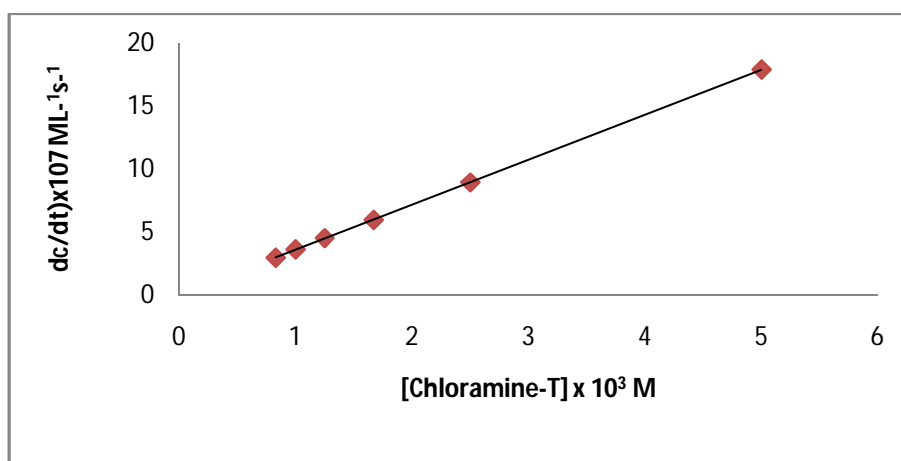


Figure 2. Plot between (-dc/dt) and [Chloramine-T] for the oxidation of D-mannitol at 35⁰C.
[Ir (III)] = 8.02 x 10⁻⁵ M, [D-mannitol] = 2.00 x 10⁻², [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M
[KCl] = 1.00 x 10⁻³ M

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

A plot of $(-dc/dt)$ versus [Chloramine-T] was linear with the slope value (0.93) near unity, which further confirms first order dependence of reaction on chloramine-T (figure 2). The first order kinetics w.r.t. [Chloramine-T] was also confirmed by 'least-square method' (figure 3).

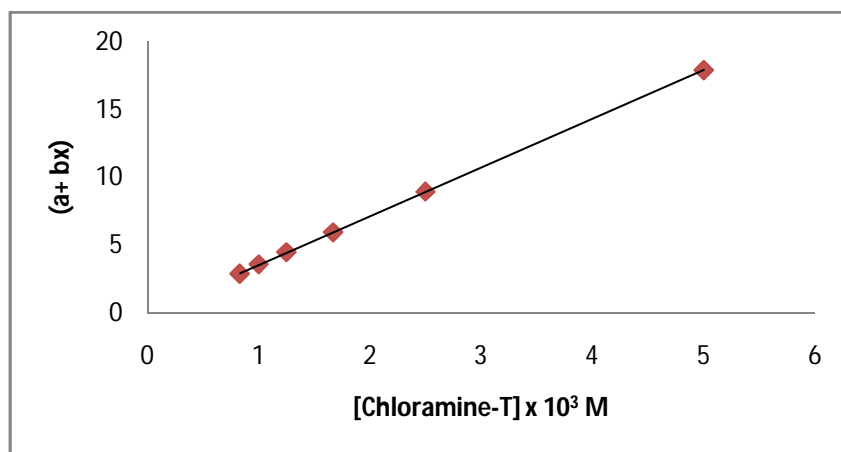


Figure 3. Plot between $(a + bx)$ and [Chloramine-T] for the oxidation of D-mannitol at 35 °C. [Ir (III)] = 8.02×10^{-5} M, [D-mannitol] = 2.00×10^{-2} , [Hg(OAc)₂] = 1.25×10^{-3} M, [HClO₄] = 1.00×10^{-3} M, [KCl] = 1.00×10^{-3} M.

A plot of $(-dc/dt)$ versus [Ir(III)] gives a slope which is close to the average value of first order rate constant at 35°C (figure 4).

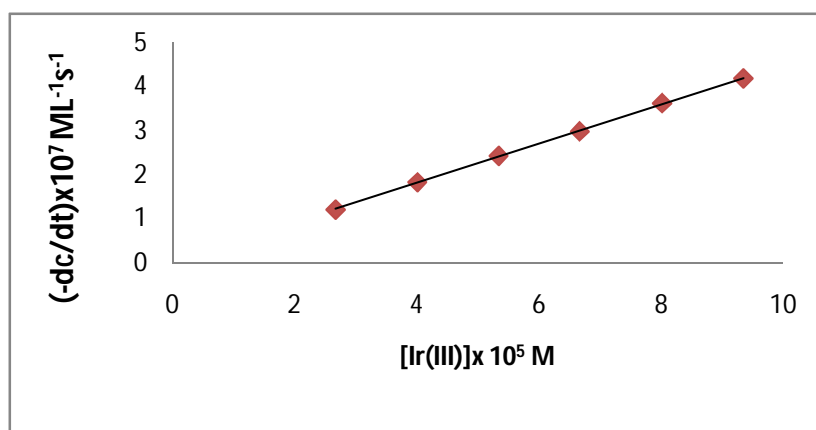


Figure 4. Plot between $(-dc/dt)$ and [Ir(III)] for the oxidation of D-mannitol at 35 °C. [D-mannitol] = 2.00×10^{-2} M, [Chloramine-T] = 1.00×10^{-3} , [Hg(OAc)₂] = 1.25×10^{-3} M, [HClO₄] = 1.00×10^{-3} M, [KCl] = 1.00×10^{-3} M.

Insignificant effect on the rate was observed on increasing the concentration of the substrate, indicating zero order in substrate *i.e.* D-mannitol (Table 1). Variation of [KCl] concentration shows positive effect on reaction rate (figure 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 Cl₂ which would have been formed as a result of interaction between Cl⁻ and RNHCl ion. Experimental data indicate negligible

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

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).

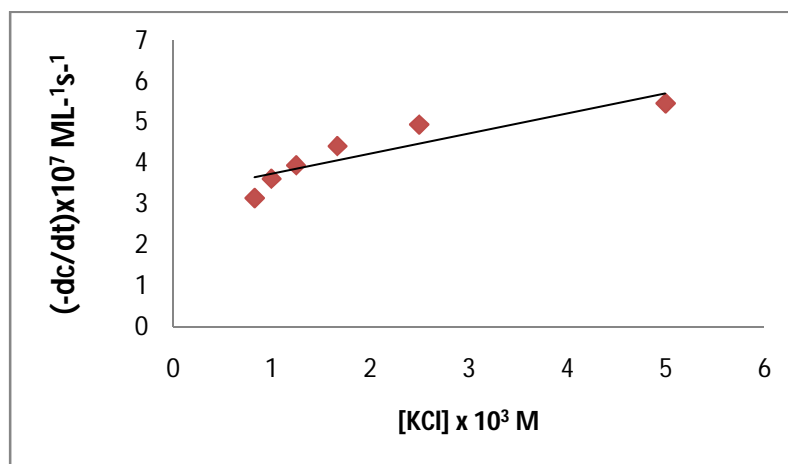


Figure 5. Plot between $(-dc/dt)$ and $[\text{KCl}]$ for the oxidation of D-mannitol at 35°C . $[\text{Ir (III)}] = 8.02 \times 10^{-5} \text{ M}$, $[\text{D-mannitol}] = 2.00 \times 10^{-2} \text{ M}$, $[\text{Chloramine-T}] = 1.00 \times 10^{-3}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{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

Table 2. Effect of variation of HClO_4 , KCl and NaClO_4 at 35°

$[\text{HClO}_4] \times 10^3 \text{ M}$	$[\text{KCl}] \times 10^3 \text{ M}$	$\text{NaClO}_4 \times 10^3 \text{ M}$	$(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ s}^{-1}$	$k_1 \times 10^4 \text{ S}^{-1}$
0.83	1.00	1.00	3.18	3.78
1.00	1.00	1.00	3.62	4.52
1.25	1.00	1.00	2.96	3.44
1.67	1.00	1.00	3.42	4.17
2.50	1.00	1.00	3.70	4.68
5.00	1.00	1.00	3.30	3.83
1.00	0.83	1.00	3.15	3.70
1.00	1.00	1.00	3.62	4.46
1.00	1.25	1.00	3.95	4.70
1.00	1.67	1.00	4.42	5.39
1.00	2.50	1.00	4.94	6.25
1.00	5.00	1.00	5.46	7.09
1.00	1.00	0.83	3.82	4.60
1.00	1.00	1.00	3.62	4.46
1.00	1.00	1.25	2.85	3.27
1.00	1.00	1.67	3.45	4.20
1.00	1.00	2.50	3.80	4.52
1.00	1.00	5.00	3.35	3.89

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

The kinetic measurements were also taken in the temperature range of 30 – 45°C and the specific rate constants were obtained at 30° , 35° , 40° and 45°C . These specific rate constants were used to draw a plot of $\log k$ versus $1/T$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

(figure 6) which was linear. The various activation parameters were calculated from the slope of curves obtained from the Figure 6.

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

Parameters	Temperature($^{\circ}$ C)	D-mannitol
$K_1 \times 10^4 \text{ s}^{-1}$	30	2.52
$K_1 \times 10^4 \text{ s}^{-1}$	35	3.62
$K_1 \times 10^4 \text{ s}^{-1}$	40	4.98
$K_1 \times 10^4 \text{ s}^{-1}$	45	7.22
Log A	--	9.13
E_a (kJ mol $^{-1}$)	35	50.56
ΔG^* (kJ mol $^{-1}$)	35	70.58
ΔH^* (kJ mol $^{-1}$)	35	47.99
ΔS^* (JK $^{-1}$ mol $^{-1}$)	35	-74.08

Solution conditions: [Ir (III)] = 8.02×10^{-5} M, [Chloramine-T] = 1.00×10^{-3} M, [D-mannitol] = 2.00×10^{-2} , [Hg(OAc) $_2$] = 1.25×10^{-3} M, [HClO $_4$] = 1.00×10^{-3} M, [KCl] = 1.00×10^{-3} M.

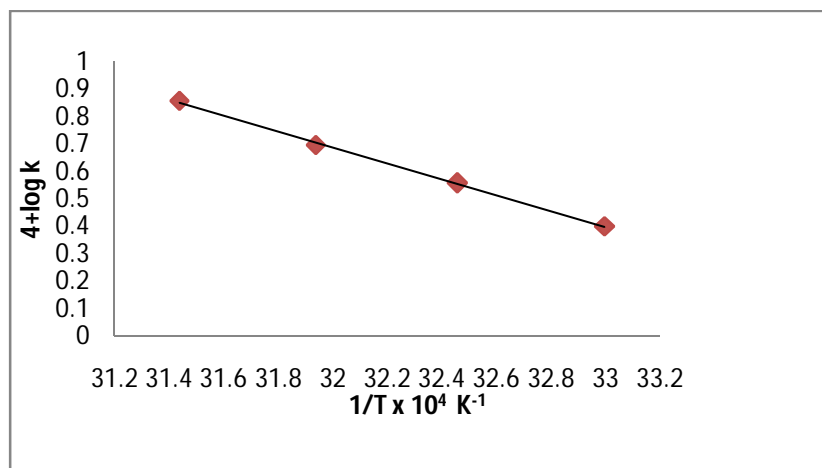


Figure 6. Arrhenius plot for the oxidation of D-mannitol . [Ir (III)] = 8.02×10^{-5} M [Chloramine-T] = 1.00×10^{-3} M, [D-mannitol] = 2.00×10^{-2} , [Hg(OAc) $_2$] = 1.25×10^{-3} M, [HClO $_4$] = 1.00×10^{-3} M, [KCl] = 1.00×10^{-3} M.

The value of energy of Activation (E_a), Arrhenius factor (A), entropy of activation (ΔS^*), free energy of activation (ΔG^*) and enthalpy of activation (ΔH^*) were calculated from rate measurement and these values have been provided in Table-3. Moderate ΔH^* and ΔS^* values are favorable for electron transfer reaction. The value of ΔH^* was due to energy of solution changes in transition state. The high positive value of ΔG^* represents highly solvated transition state. The negative value of ΔS^* 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

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

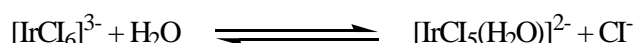
Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

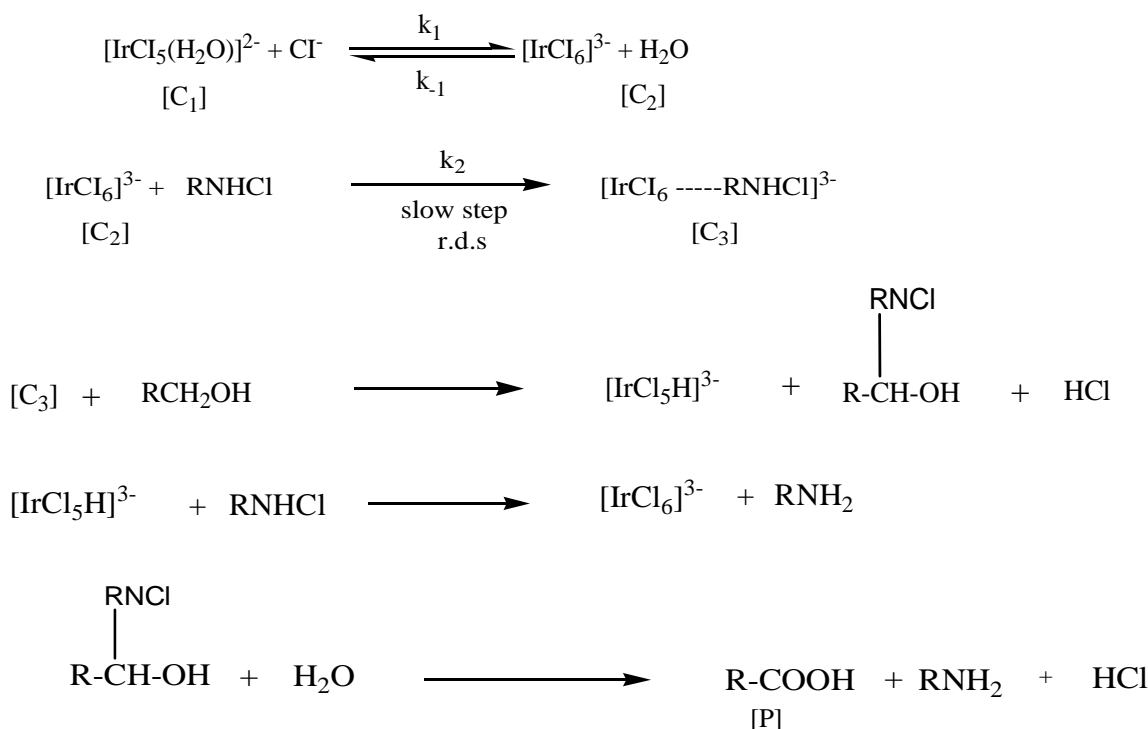
sphere mechanism [31]. This conclusion is supported by earlier observations. The activation parameters evaluated for the catalyzed reaction explain the catalytic effect on the reaction. Kinetic observations show that the reaction under investigation is complex reaction, which usually takes place in more than one step.

3.1. 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-mannitol ($n = 4$)

[P] = Product i.e. Mannonic acid

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

$$\text{Rate} = \frac{-d[\text{RNHCl}]}{dt} = k_2[\text{C}_2][\text{RNHCl}] \quad (i)$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

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

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

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

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

(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-mannitol 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

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

$[\text{IrCl}_6]^{3-}$ in acidic medium in present study while $[\text{RuCl}_2(\text{H}_2\text{O})_3(\text{OH})]$ reported as most reactive species of Ru(III) chloride in alkaline medium [20]. The stoichiometric analysis of present study shows 2 mole of oxidant $[\text{RNHCl}]$ consumes 1 mole of substrate i.e. mannitol, On the other hand in Ru(III) catalyzed reaction one mole of oxidant $[\text{KBrO}_3]$ 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-mannitol by chloramine-T in acidic medium. (a) Among the various species of Ir(III) in acidic medium, $[\text{IrCl}_6]^{3-}$ 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-mannitol 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 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-mannitol by Chloramine-T in acidic medium.

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

REFERENCES

- [1] Puttaswamy, J.P. Shubha, R.V. and Jagadeesh, "Ruthenium(III)-catalyzed oxidative cleavage of p-aminoazobenzene by chloramine-B in alkaline medium and uncatalyzed reaction in acid medium: Spectrophotometric kinetic and mechanistic study", Trans. Met. Chem., vol. 32, p.991 (2007).
- [2] Jennings, V.J., "Analytical Applications of Chloramine-T", Critical Rev. Anal-Chem., vol.3, no.4, p.407(1974)
- [3] Kolvari, A. Choghamarani, A.G. Salehi, P. Shirini, F. and Zolfigol, M A., "Applications of N- halo reagents in organic synthesis", J. Iran. Chem. Soc., vol.4, number 2, pp.126 (2007).
- [4] Umamoto, T. Fukami, S. Tomizava, G. Harasava, K. Kavada, K. and Tomita, K., "Formal electrophilic reactions of fluorine presumably involve alternative Mechanisms", J. Am. Chem. Soc., vol.112, p.8563 (1990).
- [5] Ramananda, M. G. and Ananda, S., "Kinetics and mechanism of oxidation of o-toluidine by sodium -N-chloro benzene sulphonamide in acid medium", Asian J. Chem., vol. 11, no. 4, p.1348 (1999).
- [6] Singh, A. K. Negi, R. Jain, B. Katre, Y. Singh, S.P. and Sharma V. K., "Kinetics and Mechanism of Ru(III)-Catalyzed Oxidation of Paracetamol by Chloramine-T in Aqueous Acidic Medium", Catal. Lett., vol. 132, p. 285 (2009).
- [7] Campbell, M.M. and Johnson, G., "Chloramine-T and related N-halogeno-N-metallo reagents" Chem. Rev., vol. 8, p.65 (1978).
- [8] Singh, A.K. Negi, R. Katre, Y. and Singh, S.P. " Mechanistic study of novel oxidation of paracetamol by chloramine-T using micro-amount of chloro-complex of Ir(III) as a homogeneous catalyst in acidic medium", J. Mol. Catal A: Chem., vol. 302, p.36 (2009).
- [9] Puttaswamy, Jagadeesh, R.V. and Vaz, N., "Ru(III)-catalyzed oxidation of some N-heterocycles by chloramine-T in hydrochloric acid medium: a kinetic and mechanistic study", J. Mol. Catal A., vol.229, p.211 (2009).
- [10] Filler, R., "Oxidations and Dehydrogenations with N-Bromosuccinimide and related N- Haloimides", Che. Rev., vol. 63, p.21 (1963).
- [11] Wadhwani, M. and Jain, S., "Kinetic study of oxidation of some monosaccharides by Chloramine-T induced by visible light source", Res. J. Chem. Sci., vol. 4, no.7, p.61 (2014).
- [12] Veena, M.S. Prashanth, M.K. Kumar, K.Y. Muarlidhara, H.B. and Nayaka, Y.A., "Kinetics and mechanistic study of oxidation of amoxicillin by chloramine-T in acid medium", J. Chil. Chem. Soc., vol. 60 no. 3, p.3063 (2015).
- [13] Wadhwani, M. and Jain, S., "Ultraviolet Light Induced Oxidation of Malonic Acid by Chloramine-T in an Aqueous Acidic Medium: A Kinetic Study", Ind. J. Adv. Chem. Sci., vol.40, no.1, p. 36 (2016).
- [14] Singh, A.K. Negi, R. Jain, B. Katre, Y. Singh, S.P. and Sharma V.K., "Pd (II) catalyzed oxidative degradation of paracetamol by chloramine-T in acidic and alkaline media", Ind. Eng. Chem. Res., vol.50, p.8407 (2011).
- [15] Rajeswari, V. Hosahalli, Anita P. SavanurSharanappat, Nandibeworr and Shivamrti A., "Ru(III) mediated oxidation of D-Mannitol by cerium (IV) in aqueous Sulphuric acid medium: a kinetic & mechanistic approach" wiley inter science, vol. 10J, p.1002 (2010).
- [16] Srivastava, S. Srivastava, P., "Kinetics and mechanism of Oxidation of D- Mannitol by Potassium bromate in aqueous acidic medium", Pelg. res. Lib., vol. 1, no.1, p.13 (2010).
- [17] Singh, B. Singh, D. Singh, S. and Kumar, A., "Kinetics and Mechanism of Ru(III) catalysis in the oxidation of Erythritol and Dulcitol by NBS", Trans. Met. chem., vol.16, p. 610 (1991).

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

- [18] Agarwal, A. Sharma, G. Khandelwal, C.L. and Sharma P.D., "Kinetics and Mechanism of Oxidation of Mannitol by Sulphato-cerium(IV) Species in Aqueous Acid Medium", *Inorg. React. Mech.*, vol. 4, no.3, p.233(2002).
- [19] Aparna, R. and Das, A.K., "Studies on kinetics and mechanism of iridium(III) catalysed cerium(IV) oxidation of D-mannitol and D-glucose in aqueous acid media", *Indian J. chem.*, vol.41(A), p. 2468 (2002).
- [20] Srivastava, S. and Singh, A.L., "Mechanistic studies of oxidation of D-sorbitol and D-mannitol by an alkaline solution of potassium bromate in the presence of chloro complex of Ru(III) as homogeneous catalyst", *Oxid. Communi.*, vo. 36, no.1, p., 41(2013).
- [21] Puttaswamy, Vaz, N., Ruthenium(III) and osmium(VIII)-catalyzed oxidation of 2-thiouracil by bromamine-B in acid and alkaline media: a kinetic and mechanistic study. *Trans. Met. Chem.*, vol. 28, p.409 (2003).
- [22] Hiremath, C.V. Kiran, T.S. and Nandibewoor, S.T., "Os(VIII)/Ru(III) catalysed oxidation of aspirin drug by a new oxidant, diperiodatoargentate(III) in aqueous alkaline medium: A comparative kinetic study", *J. Mol. Catal. A. Chem.*, vol.248, p.163 (2006).
- [23] Uma, V. Sethuram, B. and Rao, T.N., "Kinetics of oxidation of isopropanol by IO_4^- catalyzed by metal ion", *React. Kinet. Catal. Lett.*, vol. 18, p.283(1981).
- [24] Song, W. Zhao, R. Jiang, Q., "Catalyzed oxidation of Tetrahydrofurfuryl alcohol by Cerium(iv) in aqueous sulphuric acid medium.", *Acta. Phys. Chim. Sin.*, vol. 21,no.08, p.929(2005).
- [25] Singh, A.K. Rahmani, S, Singh B. Singh, R.K. and Singh M., " Mechanism of Ir(III)-catalysed and Hg(II)-co-catalysed oxidation of reducing sugars by N-bromoacetamide in acidic medium", *J. Phys.Org. Chem*, vol.17, no.3, p. 249 (2004).
- [26] Bai, W. Zhai, Y. Liu, H. Lu, H. Song, W., "Kinetics and mechanism of iridium(III) catalyzed oxidation of ethylene glycol by cerium(IV) in sulfuric acid media" *Ind. J. Chem.*,vo. 47A, p.1194 (2008).
- [27] Singh, A.K. Sachdev, N. Srivastava, A. Jain, B. and Khtre, Y., "Oxidation of d-glucose by N-bromophthalimide in the presence of chlorocomplex of iridium (III): a kinetic and mechanistic study" *Res. Chem. Intermed.*, vol. 38,p. 507 (2012).
- [28] Venkatasubramanian, N. and Thiagarajan, V., "The mechanism of oxidation of alcohols by bromine" *Tetra. Lett.* vol.9, p.1711 (1968).
- [29] Grover, N. Kambo, N. and Upadhyay, S.K., " Kinetics and mechanism of palladium(II) catalysed oxidation of some alpha-aminoacids by chloramine-T in perchloric acid", *Ind. J. Chem.*, vol. 41(A), p.2482 (2012).
- [30] Lewis, E. S., *Investigation of Rates and Mechanism of Reactions in Techniques of Chemistry*, A Weissberger, 3rd ed., Wiley, New York, p. 421.(1974).
- [31] Onkar, A. S., Naik, P. N., Gunagi, S.D., Nandibewoor, S.T. and Chimatadar, A.S., "Kinetics and mechanism of oxidation of tyrosine by vanadium(V) in aqueous hydrochloric and ethanoic acid medium", *Ind. J. Chem.*, vol.51A, p.1574(2012).
- [32] Gopalakrishnan, G. Pai, B.R. and Venkatasubramanian, N., "Oxidation of alcohols by N-Bromosuccinimide-A curious dependence on initial concentration of the oxidant", *Ind. J. Chem*, vol.19B, p.293 (1998).
- [33] Chang, J.C. and Garner, G.S. "Kinetics of aquation of Aquopentachloroiridate(III) and Chloride anation of Diaquotetrachloroiridate(III) anions", *Inorg. Chem.*vol., 4, no.2, p.209(1965).