

Research note

Kinetic, Mechanistic, and Thermodynamic Investigations of Iridium (III) Catalyzed Oxidation of D-Mannitol by N-Chloro-P-Toluenesulfonamide in Perchloric Acid Medium

J. Pandey¹, A. Verma¹, R. Patel¹, Sh. Srivastava^{2*}

¹ Department of Applied Chemistry, BBAU, Lucknow-226025, U.P., India

² Chemical laboratories, Feroze Gandhi College, Raebareli-229001, U.P., India

ARTICLE INFO

Article history:

Received: 2016-05-24

Accepted: 2016-11-10

Keywords:

Kinetics

Mechanism

Ir(III) Catalysis

D-Mannitol

Chloramine-T

Acidic Medium

ABSTRACT

The present paper 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 influences 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 derived.

1. Introduction

The sodium salts of arylhalosulfonamides, generally known as organic haloamines, have attracted the attention of many 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 the group of Sodium N-chloro-p-toluenesulfonamide or

*Corresponding author: she_ila72@yahoo.com

Chloramine-T (CAT; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa}\cdot 3\text{H}_2\text{O}$) is used as a halogenating and oxidizing agent [4-6]. CAT is a byproduct in the manufacture of saccharin [7]. Depending upon the pH of the medium, various oxidizing species are formed, thus showing a variety of kinetic results [8,9]. Several researchers have studied the oxidizing behavior of CAT [10-13], and numerous studies have focused 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 groups. 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 special 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 investigations into 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 a 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 is very sluggish; however, the reaction becomes facile in the presence of Ir(III) catalyst.

In the present study, we examine the kinetic and mechanistic aspects of 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) fine the oxidative capacity of oxidant (CAT), (iii) find the catalytic efficiency of Ir(III), (iv) identify the oxidation products, (v) elucidate the plausible reaction mechanism, (vi) deduce rate law consistent with kinetic results, and (vii) calculate the activation parameters.

2. 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 a 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 of 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.

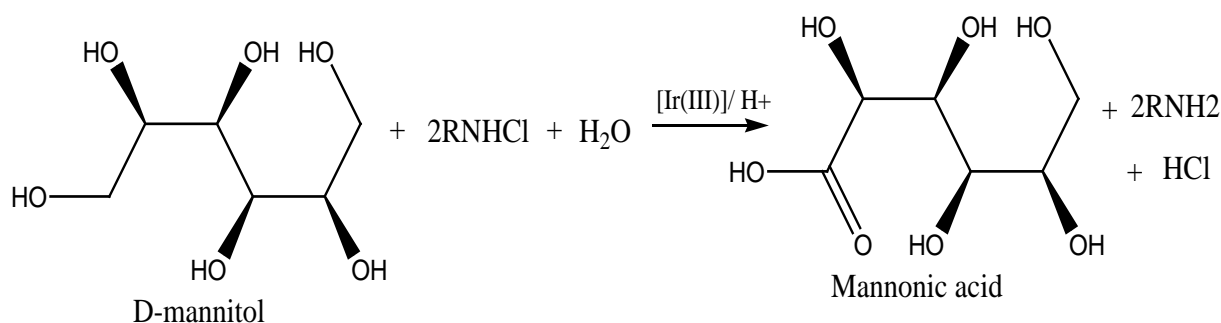
2.2. Kinetic measurements or procedure

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 (5 ml) of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5 ml of 4 % KI solution and 5 ml of dilute sulphuric acid. The liberated iodine equivalent to unconsumed oxidant was

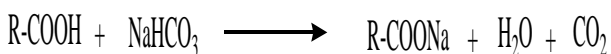
estimated with standard sodium thiosulphate solution using starch as an indicator. The initial rates were obtained from the slope of concentration vs. time graph in the initial stages of the reactions by plane mirror method.

2.3. Stoichiometry and product analysis

In order to ascertain the stoichiometry of the reaction, different sets of experiments with varying [RNHCl]:[D-mannitol] ratios were performed at 35 °C for 48 h and constant concentrations of all other reactants under the conditions $[RNHCl] \gg [D-mannitol]$. 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:



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 to the solution. Evolution of carbon dioxide shows the product to be the corresponding acid.



The nature of mannonic acid is further confirmed by its IR spectrum (figure 1). The symmetric stretching vibration of ν OH

observed at (A) 3323 cm^{-1} and out of plane bending (OH) at (F) 914 cm^{-1} in the IR spectrum indicate the presence of CH_2OH group in the studied molecule.

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

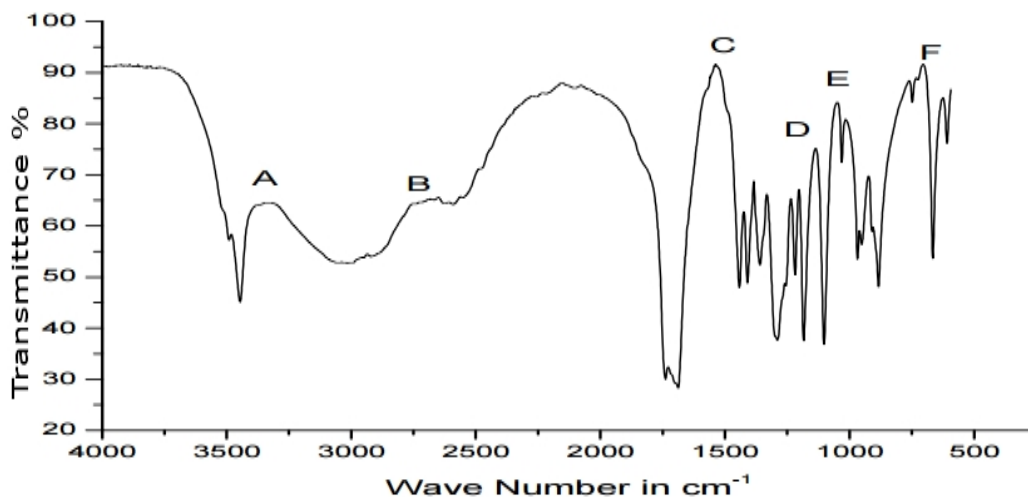


Figure 1. IR-Spectra of the main product Mannonic acid.

3. 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 (Table 1). The order of reaction with respect to each reactant was determined by varying the concentrations of oxidant, D-mannitol, Ir(III) chloride (Table 1), H⁺ ions, [Cl⁻], and mercuric acetate, one by one, in different sets keeping concentrations of all other reactants constant at constant temperature 35 °C. In each of 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 where the slope of the tangent was drawn at a fixed time. The first-order reaction rate constant (k₁) for the variations of all the reagents was calculated:

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

where [RNHCl]* denotes the [RNHCl] at which (-dc/dt) was determined.

A plot of (-dc/dt) versus [Chloramine-T] was linear with the slope value (0.93) close to unity, which further confirms the 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). A plot of (-dc/dt) versus [Ir(III)] gives a slope which is close to the average value of the first-order rate constant at 35 °C (figure 4). Insignificant effect on the rate was observed in 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 eliminates 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 a 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 ions. Experimental data indicate the negligible effect of ionic strength of the medium on the rate (affected by addition of NaClO₄). In acidic solution of chloramine-T, quick formation of RNHCl has been reported [29]. The reaction is unaffected by H⁺ concentration (Table 2).

Kinetic, Mechanistic, and Thermodynamic Investigations of Iridium (III) Catalyzed Oxidation of D-Mannitol by N-Chloro-P-Toluenesulfonamide in Perchloric Acid Medium

Table 1

Effects of variations of oxidant, D-mannitol, Ir(III) at 35 °C.

[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.

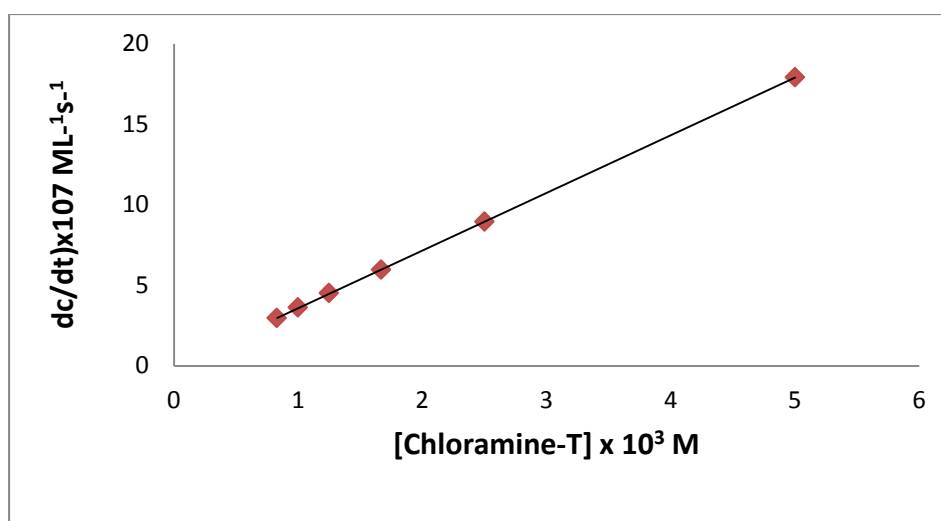


Figure 2. Plot between (-dc/dt) and [Chloramine-T] for the oxidation of D-mannitol at 35 °C. [Ir (III)] = 8.02 x 10⁻⁵ M, [D-mannitol] = 2.00 x 10⁻², [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

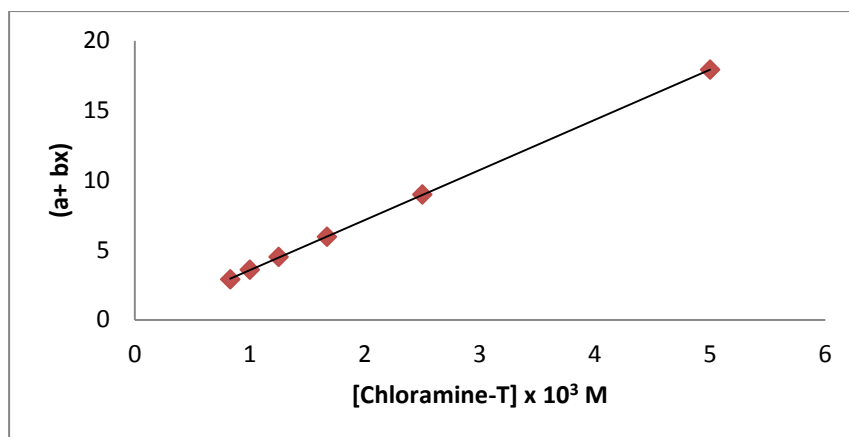


Figure 3. Plot between $(a + bx)$ and $[\text{Chloramine-T}]$ for the oxidation of D-mannitol at 35°C . $[\text{Ir (III)}] = 8.02 \times 10^{-5} \text{ M}$, $[\text{D-mannitol}] = 2.00 \times 10^{-2}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.00 \times 10^{-3}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

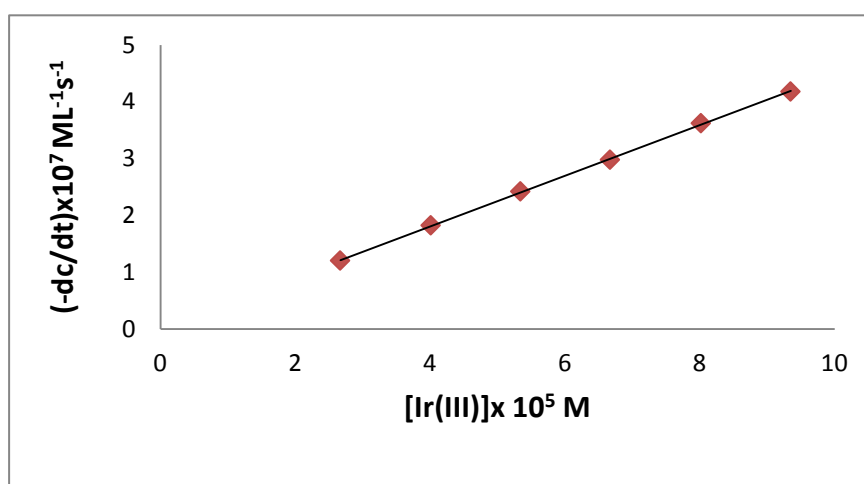


Figure 4. Plot between $(-dc/dt)$ and $[\text{Ir(III)}]$ for the oxidation of D-mannitol at 35°C . $[\text{D-mannitol}] = 2.00 \times 10^{-2} \text{ M}$, $[\text{Chloramine-T}] = 1.00 \times 10^{-3}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$, $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$.

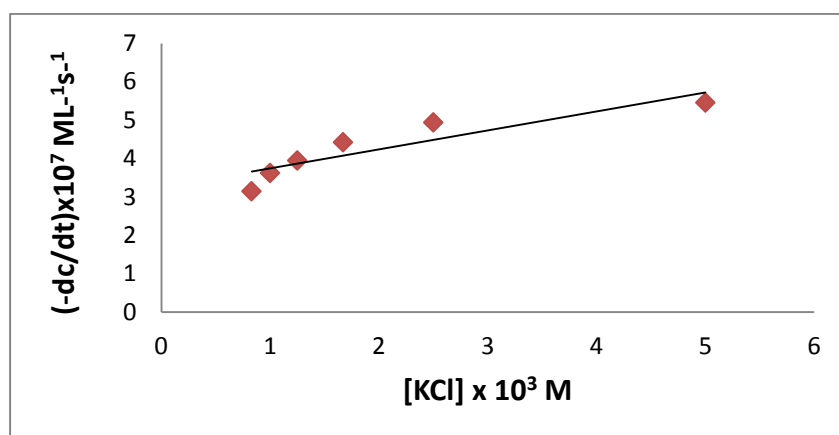


Figure 5. Plot between $(-dc/dt)$ and $[\text{KCl}]$ for the oxidation of D-mannitol at 35°C . $[\text{Ir (III)}] = 8.02 \times 10^{-5} \text{ M}$, $[\text{D-mannitol}] = 2.00 \times 10^{-2} \text{ M}$, $[\text{Chloramine-T}] = 1.00 \times 10^{-3}$, $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{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

Table 2

Effects of variations of HClO₄, KCl, and NaClO₄ at 35 °C.

[HClO ₄] x 10 ³ M	[KCl] x 10 ³ M	NaClO ₄ x 10 ³ M	(-dc/dt) x 10 ⁷ ML ⁻¹ s ⁻¹	k ₁ x 10 ⁴ 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

The kinetic measurements were also carried out at 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 (figure 6) which was linear. The various activation parameters were calculated from the slope of curves obtained from Figure 6. The values 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 are 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 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, which usually takes place in more than one step.

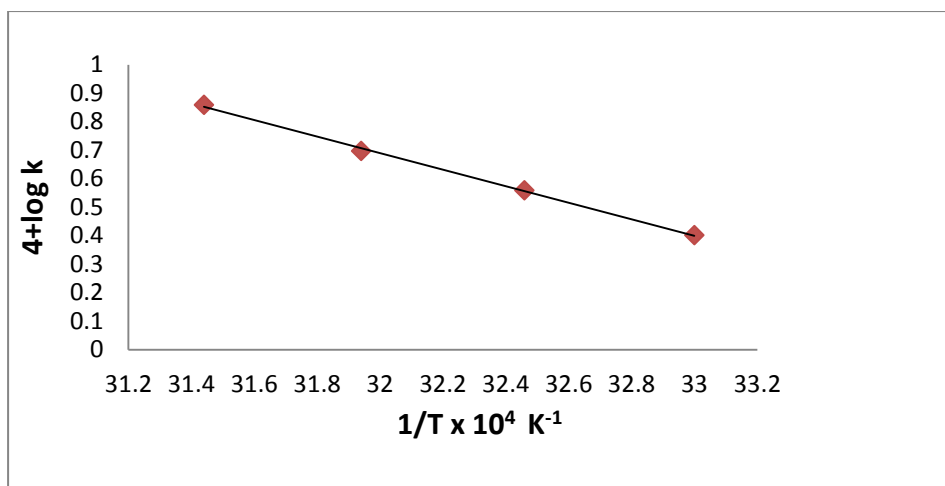


Figure 6. Arrhenius plot for the oxidation of D-mannitol . [Ir (III)] = 8.02 x 10⁻⁵ M , [Chloramine-T] = 1.00 x 10⁻³ M, [D-mannitol] = 2.00 x 10⁻² , [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

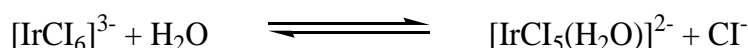
Table 3

Activation parameters for the oxidation of D-mannitol.

Parameters	Temperature(°C)	D-mannitol
K ₁ x 10 ⁴ s ⁻¹	30	2.52
K ₁ x 10 ⁴ s ⁻¹	35	3.62
K ₁ x10 ⁴ s ⁻¹	40	4.98
K ₁ x 10 ⁴ s ⁻¹	45	7.22
Log A	--	9.13
Ea (kJ mol ⁻¹)	35	50.56
ΔG* (kJ mol ⁻¹)	35	73.38
ΔH * (kJ mol ⁻¹)	35	67.94
ΔS* (JK ⁻¹ mol ⁻¹)	35	-17.64

3.1. Mechanism and derivation of rate law

The acidic solution of Iridium chloride exists as [IrCl₆]³⁻. It has also been reported that

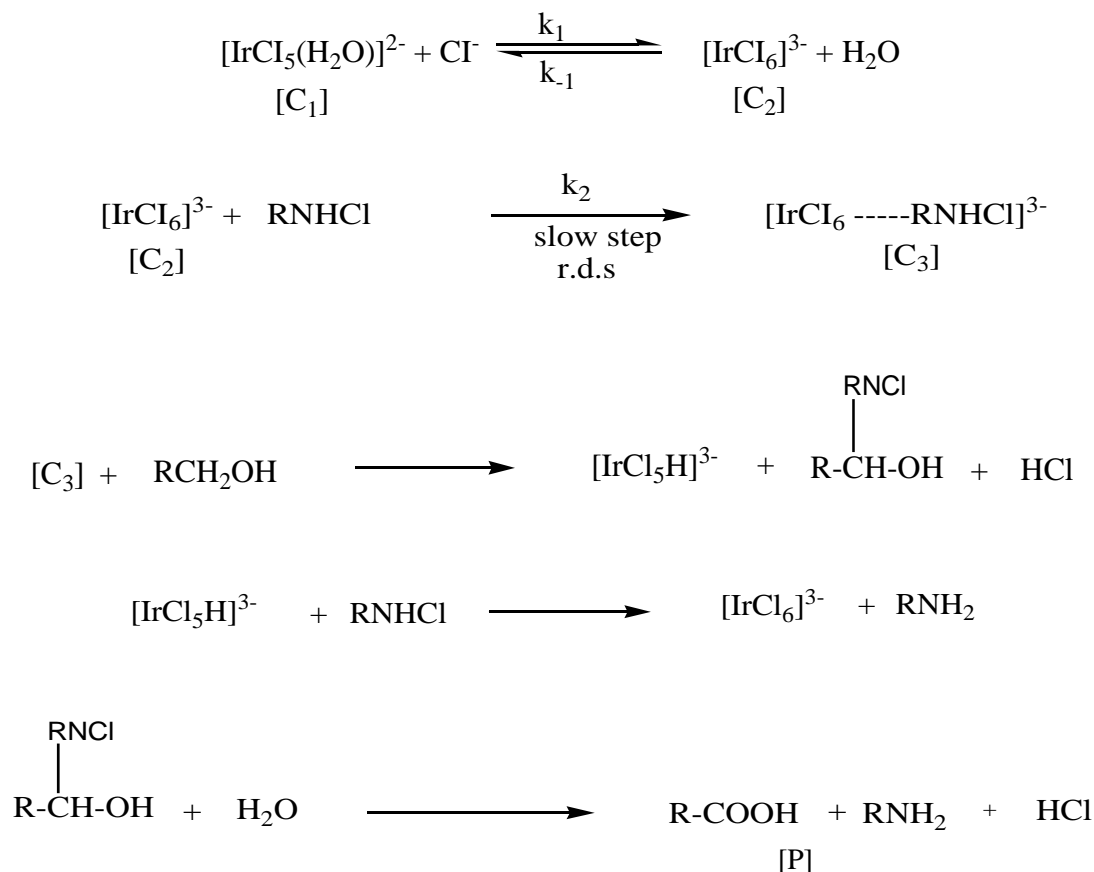


Thus, either [IrCl₆]³⁻ or [IrCl₅H₂O]²⁻ may act as catalytic species [33]. If [IrCl₅H₂O]²⁻ is taken as catalytic species, the rate law would require negative effect of chloride ion contrary to the positive effect of chloride ion on the oxidation rate observed by us. Hence, the only choice is [IrCl₆]³⁻ which, when

[IrCl₆]³⁻ is involved in equilibrium as follows [32]:

assumed as reactive species of Iridium trichloride in acidic medium, explains the positive effect of chloride ion. The kinetic results reported in tables 1, 2, 3 along with the above discussion lead us to suggest the following reaction scheme:

Kinetic, Mechanistic, and Thermodynamic Investigations of Iridium (III) Catalyzed Oxidation of D-Mannitol by N-Chloro-P-Toluenesulfonamide in Perchloric Acid Medium



where

R = CH₂OH(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 follows:

$$\text{Rate} = \frac{-d[\text{RNHCl}]}{dt} = k_2[C_2][\text{RNHCl}] \quad (1)$$

$$[\text{Ir(III)}]_T = [C_1] + [C_2] \quad (2)$$

$$\frac{d[C_1]}{dt} = k_{-1}[C_2] - k_1[C_1][\text{Cl}^-] \quad (3)$$

$$[C_1] = \frac{k_{-1}[C_2]}{k_1[\text{Cl}^-]} \quad (4)$$

$$[C_1] = \frac{[C_2]}{K_1[\text{Cl}^-]} \quad (5)$$

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

Putting the value of [C₁] into equation (2),
we get:

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

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

This gives:

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

Putting the value of C_2 into equation (1), we get:

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

The above equation is the 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 the order of reaction with respect to $[Cl^-]$ is fractionally positive.

4. Comparative studies

The results of the present study of Ir(III) catalyzed oxidation of D-mannitol by chloramine-T in acidic medium can be compared with those of the Ru(III) catalyzed oxidation of polyhydric alcohols (D-mannitol and D-sorbitol) by $KBrO_3$ in alkaline medium [20]. The present study, with similar orders with respect to oxidant and catalyst, shows a 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 the present study is contrary to the reported negative effect of $[Cl^-]$ on 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 the present study, while $[RuCl_2(H_2O)_3(OH)]$ is reported as the most reactive species of Ru(III) chloride in alkaline medium [20]. The stoichiometric analysis of the present study shows that 2 moles of oxidant $[RNHCl]$

consume 1 mole of substrate, i.e., mannitol. 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 the 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.

5. Conclusions

The following conclusions can be derived from 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, $[IrCl_6]^{3-}$ was 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, it became 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 were explained by a plausible mechanism, and the related rate law was deduced. It can be concluded that Ir(III) chloride acts as an efficient catalyst for the oxidation of D-mannitol by Chloramine-T in acidic medium.

Acknowledgements

The first author thankfully acknowledges the University Grants Commission, 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.*, **32**, 991 (2007).
- [2] Jennings, V. J., "Analytical applications of chloramine-T", *Critical Rev. Anal. Chem.*, **3** (4), 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.*, **4** (2), 126 (2007).
- [4] Umemoto, T., Fukami, S., Tomizava, G., Harasava, K., Kavada, K. and Tomita, K., "Formal electrophillic reactions of fluorine presumably involve alternative Mechanisms", *J. Am. Chem. Soc.*, **112**, 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.*, **11** (4), 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.*, **132**, 285 (2009).
- [7] Campbell, M. M. and Johnson, G., "Chloramine-T and related N-halogeno-N-metallo reagents", *Chem. Rev.*, **8**, 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.*, **302**, 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.*, **229**, 211 (2009).
- [10] Filler, R., "Oxidations and dehydrogenations with N-bromosuccinimide and related N-haloimides", *Che. Rev.*, **63**, 21 (1963).
- [11] Wadhvani, M. and Jain, S., "Kinetic study of oxidation of some monosaccharides by chloramine-T induced by visible light source", *Res. J. Chem. Sci.*, **4** (7), 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.*, **60** (3), 3063 (2015).
- [13] Wadhvani, 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.*, **40** (1), 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.*, **50**, 8407 (2011).
- [15] Rajeswari, V., Hosahalli, A. P., Savanur Sharanappat, N. 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*, **10** (J), 1002 (2010).
- [16] Srivastava, S. and Srivastava, P., "Kinetics and mechanism of oxidation of D-Mannitol by potassium bromate in aqueous acidic medium", *Pelg. Res. Lib.*, **1** (1), 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.*, **16**, 610 (1991).
- [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.*, **4** (3), 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.*, **41** (A), 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.*, **36** (1), 41 (2013).
- [21] Puttaswamy and 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.*, **28**, 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.*, **248**, 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.*, **18**, 283 (1981).
- [24] Song, W., Zhao, R. and Jiang, Q., "Catalyzed oxidation of tetrahydrofurfuryl alcohol by cerium(IV) in aqueous sulphuric acid medium.", *Acta. Phys. Chim. Sin.*, **21** (8), 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.*, **17** (3), 249 (2004).
- [26] Bai, W., Zhai, Y., Liu, H., Lu, H. and Song, W., "Kinetics and mechanism of iridium(III) catalyzed oxidation of ethylene glycol by cerium(IV) in sulfuric acid media", *Ind. J. Chem.*, **47** (A), 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.*, **38**, 507 (2012).
- [28] Venkatasubramanian, N. and Thiagarajan, V., "The mechanism of oxidation of alcohols by bromine", *Tetra. Lett.* **9**, 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.*, **41** (A), 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.*, **51** (A), 1574 (2012).
- [32] Gopalakrishanan, 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.*, **19** (B), 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.*, **4** (2), 209 (1965).