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Kinetic investigation of Ru (III) catalysed oxidation of lactose by chloramine-T in acidic medium

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Abstract

The kinetic investigation in Ru (III) catalysed oxidation of lactose by chloramine T in acidic medium has been done in the temperature range 30^0- 50^0 C. The reaction is carried out in the presence of mercuric acetate as a scavenger for Cl^- ion. The reaction has a first order dependence on chloramine T as well as on Ru(III) and Zero order of the reaction with respect to substrate. Positive effect of $[Cl^-]$ was observed in the oxidation of lactose. An increase in the rate of reaction with the decrease in $Hg(OAc)_2$ was observed for the redox system. The rate of oxidation is unaffected by the change in the ionic strength (μ) of the medium. The oxidation product of the reaction was identified as Lactobionic acid, was analysed through spot and spectroscopic studies respectively. On the basis of kinetic results and product analysis a probable mechanism were suggested.

Keywords: kinetics, oxidation, chloramine T, Ru (III), catalysis, lactose

1. Introduction

Transition metal ions are found to be good catalysts and their complexes are also able to catalyze a wide variety of reactions like hydrogenation, oxidation and polymerisation [1-5]. The applications of transition metal catalysts such as Ir (III), Ru (III), Rh (III), Cu (II) and Pd (II) in kinetic studies of redox reactions involving organic substrates are reported in literature [6-14]. It was found that these catalysts work efficiently in both acidic and alkaline media. The use of Ru (III) chloride as a non toxic and homogenous catalyst has been reported.

Carbohydrates are the most abundant class of organic compounds in living organisms. Lactose is a disaccharide of galactose and glucose, often found in milk. It is important due to their wide occurrence and multihydroxy functionality that allows coordination and chelating to many metal ions. Thus the oxidation of carbohydrate is a basic source of life [15-17]. Lactobionic acid as a oxidation product of the redox reaction having reducing sugar as reductant are reported to have industrial and biological significance.

A prominent member of the class of N haloaryl sulphonamides is sodium N- chloro p- toluenesulfonamide or chloramine T ($p\text{-}CH_3C_6H_4SO_2NClNa.\ 3H_2O$ or CAT) which is by product in the manufacture of saccharine. Generally, CAT undergoes a two electron change in its reaction forming the reduction products, p-toluene sulphonamide or PTS ($p\text{-}CH_3C_6H_4SO_2NH_2$) and sodium chloride [18-20]. Since compounds such as hypochlorite and CAT can act as sources of chlorine, they are used in the disinfection of drinking water. As a result, CAT can find its way into the animal stomach, including that of the human. Therefore, there was a need for understanding the oxidation mechanism of the sugar in acidic medium so that the study could throw some light on the fate of the sugar in the biological systems in vivo. A literature search showed no reports on the mechanism of oxidation of Lactose by CAT in acid solutions. Hence, it was thought worthwhile to iodometrically investigate the kinetics and mechanism of oxidation of Lactose by CAT in acidic solutions.

2. Materials and methods

2.1 Materials and Reagents

Appropriate amount of Lactose, was prepared by dissolving a known amount in double distilled water. An aqueous solution of Chloramine-T (E. Merck) was prepared, standardized periodically by the iodometric titration, and stored in brown bottles to prevent its photochemical deterioration. The catalyst, ruthenium (III) chloride (Sigma) solution was prepared in HCl. All the other reagents were of analytical grade, and their solutions were prepared by dissolving the requisite amounts in triple distilled water. HCl and $NaClO_4$ were employed to maintain the pH and ionic strength respectively.

2.1.1 Kinetic measurements

Required amounts of solutions of Lactose, $NaClO_4$ and acid were taken and requisite volume of water was added to keep the total volume constant for all runs and thermo stated at 35 ±0.1^0 C for thermal equilibrium. An equilibrated solution of CAT of required amount was added to the mixture and shaken appropriately. The reaction progress was studied iodometrically by the estimation of unreacted CAT in a measured aliquot (5 ml) of the reaction mixture with time up to about two half-lives. The first order rate contant ca;lculated from the plots of log [CAT] against time.

2.1.2 Stoichiometry and product analysis

The stoichiometry of the reaction was determined by eqalibrating varying ratios of [CAT] to sugars at 35^0 C for 48 hrs under kinetic condition. Estimation of unconsumed CAT revealed that, one mole of substrate consumes two mole of oxidant. The oxidation of lactose leads to the formation of

lactobionic acid respectively. The stiochiometric determination indicated the following overall reaction.
Identification of end product formed in the above reaction i.e. corresponding acid was carried

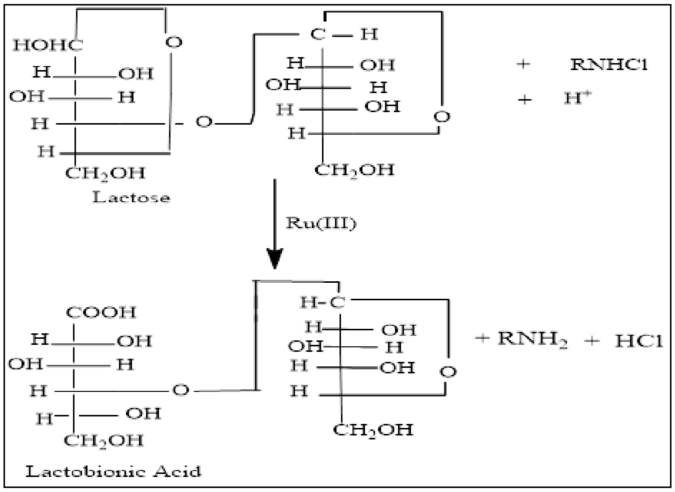


Fig 1

We take neutralized 5 ml of acid with excess of ammonia in a boiling test tube. Then boiled the solution to remove excess of ammonia, cooled and added few drops of neutral $FeCl_3$ solution. A reddish brown colour ppt. is obtained, which confirms presence of carboxylic acid.

3. Results and Discussion

Ruthenium (III) catalysed oxidation of D (+) Lactose was investigated at several initial reactant concentrations (Table 1). First order kinetics was observed in case of oxidant, i.e. CAT which was also confirmed by a plot of (-dc/dt) versus [CAT] (Fig.1). Zero order dependence on substrate was established by varying the amount of D(+) Lactose at fixed concentration of all other component.

Ru(III) catalysed oxidation of lactose was studied at several initial concentrations of the reactants(Table 1). The graphically obtained values of (-dc/dt)/[Ru(III)] clearly indicate the first order dependence on Ru (III)(Fig. 2). It shows a straight line which is close the average value of first order rate constant of Ru(III).

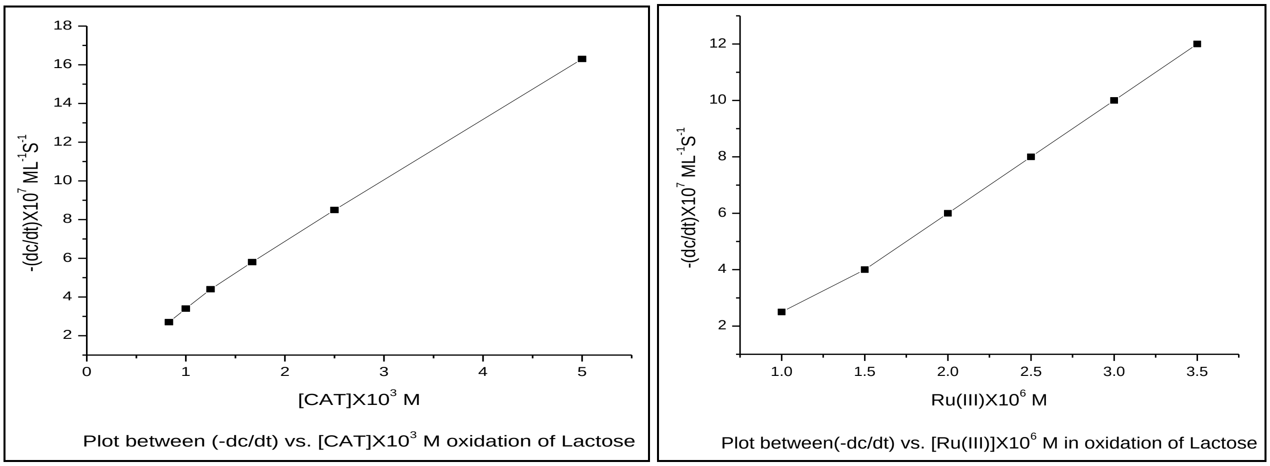
Kinetic results show negligible effect of ionic strength of the medium (affected by addition of $NaClO_4$) and addition of $Hg(OAc)_2$. The negligible effect of mercuric acetate excludes the possibility of its involvement either as catalyst or as an oxidant. Hence its function is to act as a scavenger for chloride ion formed in the reaction. Positive effect of chloride ions on reaction rate was obvious from kinetic data in (Table 2). Effect of hydrogen ion variation, which means rate of reaction, is not affected by increase or decrease of $[H^+]$ concentrations.

The rate measurements were taken at different temperatures 30^0-50^0C and specific rate constant were used to draw a plot of log K vs 1/T, which was linear (Fig. 3). The values of energy of activation (ΔE*), Arrhenius factor (A), entropy of activation (ΔS*) and free energy of activation (ΔG*) were calculated and these values have been recorded (Table 4).

In acidic solution of CAT quick formation of RNHCl has been reported. First order dependence on chloramine T suggests that RNHCl is itself involved in slow step as an oxidant.

Table 1: Effect of variation of [CAT], Ru (III) and Lactose on the reaction rate at 35^0C

$[CAT]X10^3$ $moldm^{-3}$	$Ru(lll)X10^6 Moldm^{-3}S^{-1}$	$[LCT]X10^3$ M	$(-dc/dt) X 10^7$	$K_1 X 10^4 S^{-1}$
0.83	1.0	2.5	2.70	3.25
1.00	1.0	2.5	3.40	3.40
1.25	1.0	2.5	4.40	3.52
1.67	1.0	2.5	5.70	3.41
2.5	1.0	2.5	8.50	3.40
5.0	1.0	2.5	16.3	3.26
2.5	1.0	2.5	3.2	3.20
2.5	1.5	2.5	4.8	3.20
2.5	2.0	2.5	6.5	3.25
2.5	2.5	2.5	8.0	3.20
2.5	3.0	2.5	10.0	3.34
2.5	3.5	2.5	11.7	3.34
2.5	1.0	1.67	3.5	-
2.5	1.0	2.00	3.3	-
2.5	1.0	2.50	3.4	-
2.5	1.0	3.40	3.6	-
2.5	1.0	5.00	3.5	-
2.5	1.0	10.0	3.5	-



Plot between (-dc/dt) vs. [CAT]X10^3 M oxidation of Lactose

Plot between(-dc/dt) vs. [Ru(III)]X10^6 M in oxidation of Lactose

Fig 2

Table 2: Effect of variation of $HClO_4$, KCl, $Hg(OAc)_2$ and $NaClO_4$ on the reaction rate at 35^0C

$[HClO_4]X10^3$Mol	$[KCl]X10^3$ Mol	$[Hg(OAc)_2]X10^3$ Mol	$[NaClO_4]$ X 10^3 Mol	(-dc/dt)X10^7 $ML^{-1}S^{-1}$
0.83	2.5	2.5	2.5	3.5
1.0	2.5	2.5	2.5	3.8
1.25	2.5	2.5	2.5	4.0
1.67	2.5	2.5	2.5	4.2
2.5	2.5	2.5	2.5	4.3
5.0	2.5	2.5	2.5	4.5
2.5	0.83	2.5	2.5	3.4
2.5	1.0	2.5	2.5	3.6
2.5	1.25	2.5	2.5	3.7
2.5	1.67	2.5	2.5	3.8
2.5	2.5	2.5	2.5	3.8
2.5	5.0	2.5	2.5	3.9
2.5	2.5	0.83	2.5	3.2
2.5	2.5	1.0	2.5	3.4
2.5	2.5	1.25	2.5	3.7
2.5	2.5	1.67	2.5	3.6
2.5	2.5	2.5	2.5	3.5
2.5	2.5	5.0	2.5	3.5
2.5	2.5	2.5	0.83	3.6
2.5	2.5	2.5	1.0	3.7
2.5	2.5	2.5	1.25	3.6
2.5	2.5	2.5	1.67	3.8
2.5	2.5	2.5	2.5	3.5
2.5	2.5	2.5	5.0	3.6

3.1. Effect of temperature on the rate

The oxidation reactions were studied at different temperatures in the range 30^0-50^0C while the concentrations of CAT and substrate were kept constant. The observed rate constant increased with increase in temperature as the data in **Table 3** shown. The Arrhenius parameters were calculated from the logarithmic plot of the observed rate constant against the reciprocal of the temperature in Kelvin (**Fig. 3**). This was obtained from the slope of linear plot. Other thermodynamic parameters were also evaluated and summarised in **Table 4**. The entropy of activation was found to be negative, suggesting the compactness of the transition state as compared to the ground state.

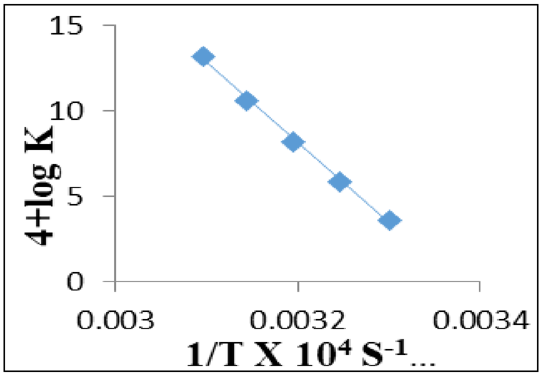


Fig 3: a plot of log K vs 1/T

Table 3: Effect of the temperature on the Reaction Rate

T^0 C	-(dc/dt)
30^0C	3.6
35^0C	5.8
40^0C	8.2
45^0C	10.6
50^0C	13.2

Table 4: Values of Activation Parameter

Substrate	Ea($KJmol^{-1}$)	log A	ΔH*($KJmol^{-1}$)	ΔS*($JKmol^{-1}$)	ΔG*($KJmol^{-1}$)
Lactose	52.26	9.60	49.70	-17.08	45.40

Discussion and Mechanism

$$\mathrm{RNClNa^+} \longrightarrow \mathrm{RNCl^-} + \mathrm{Na^+} \quad\text{————}\quad (\mathrm{I})$$

$$\mathrm{RNCl^-} \xrightarrow{\text{Fast}} \mathrm{RNHCl} \quad\text{————}\quad (\mathrm{II})$$

$$\mathrm{RNHCl} + \underset{[Y]}{[\mathrm{RuCl_5(H_2O)}]^{2-}} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{[X]}{[\mathrm{RuCl_5(H_2O)RNHCl}]^{2-}} \quad\text{————}\quad (\mathrm{III})$$

$$\underset{[X]}{[\mathrm{RuCl_5(H_2O)RNHCl}]^{2-}} + \underset{\substack{\text{Lactose}\\ [S]}}{\mathrm{C_{12}H_{22}O_{11}}} \underset{\text{Slow}}{\overset{K_2}{\rightleftharpoons}} \underset{[X']}{\mathrm{C_{12}H_{21}O_{12}\,Cl^-}} + \mathrm{RNH_2} + [\mathrm{RuCl_5H_2O}]^{2-} \text{——} (\mathrm{IV})$$

$$\mathrm{C_{12}H_{21}O_{12}Cl^-} + \mathrm{H_2O} \xrightarrow[-H^+]{Na^+} \underset{\text{Formic acid}}{\mathrm{HCOOH}} + \underset{\text{Arabinonic acid}}{\mathrm{C_5H_{10}O_6}} + \underset{\text{lyxonic acid}}{\mathrm{C_5H_{10}O_6}} + \mathrm{NaCl} \quad\text{——}\quad (\mathrm{V})$$

$$[P]$$

Where R= $CH_3C_4H_6SO_2NCl$ Na i.e. [CAT]
Step (4) is slow and rate determine step rate of reaction. The rate of reaction is terms of consumption of concentration of [RNHCl] ions may be written as equation (1).

$$\frac{-d[\mathrm{RNCl^-}]}{dt} = K_2[X][S] \quad\text{————}\quad (1)$$

Concentration of the complex i.e. [X] may be determined by applying steady state treatment to [X]
Hence,

$$\frac{d[X]}{dt} = K_1[\mathrm{RNHCl}][Y] - K_{-1}[X] - K_2[X][S] = 0$$

$$[X] = \frac{K_1[\mathrm{RNHCl}][Y]}{\{K_{-1}+K_2[S]\}} \quad\text{————}\quad (2)$$

$$\frac{-d[\mathrm{RNCl^-}]}{dt} = \frac{K_2K_1[\mathrm{RNHCl}][Y][S]}{\{K_{-1}+K_2[S]\}} \quad\text{————}\quad (3)$$

The total concentration of Ru(III) chloride, i.e. $[Ru(III)]_T$ may be written by equation (4)

$$[\mathrm{Ru(III)}]_T = [Y] + [X] \quad\text{————}\quad (4)$$

Putting value from equation (2) to equation (4), we get

$$[\mathrm{Ru(III)}]_T = [Y] + \frac{K_1[\mathrm{RNHCl}][Y]}{\{K_{-1}+K_2[S]\}}$$

$$[\mathrm{Ru(III)}]_T = [Y]\left\{\frac{K_{-1}+K_2[S]+K_1[\mathrm{RNHCl}]}{K_{-1}+K_2[S]}\right\}$$

$$[Y] = [\mathrm{Ru(III)}]_T\left\{\frac{K_{-1}+K_2[S]}{K_{-1}+K_2[S]+K_1[\mathrm{RNHCl}]}\right\} \quad\text{————}\quad (5)$$

On comparing ion equation (3) to (5)

$$\frac{d[\mathrm{RNCl^-}]}{dt} = \frac{K_2K_1[\mathrm{RNHCl}]\,[\mathrm{Ru(III)}]_T\ K_{-1}+K_2[S]}{K_{-1}+K_2[S]\{K_{-1}+K_1[\mathrm{RNHCl}]+K_2[S]\}}$$

$$\frac{d[\mathrm{RNCl^-}]}{dt} = \frac{K_1[\mathrm{RNHCl}][\mathrm{Ru(III)}]_T[S]}{K_{-1}+K_1[\mathrm{RNHCl}]+K_2[S]} \quad\text{————}\quad (6)$$

On assuming, $K_2[S] >> K_{-1} + K_1$ [RNHCl] and on neglecting the second term in the denominator of equation (6), we get

$$\frac{d[\mathrm{RNCl^-}]}{dt} = \frac{K_2K_1[\mathrm{RNHCl}][\mathrm{Ru(III)}]_T[S]}{K_2[S]}$$

$$= K_1[\mathrm{RNHCl}]\ [\mathrm{Ru(III)}]_T \quad\text{..................}\quad (7)$$

The above equation confirms all the orders which are observed with respect to different species.

Conclusion

The results obtained for the oxidation of lactose by CAT in acidic medium is summarised as follows

- The present study shows that in Ru(III) catalysed oxidation of lactose by chloramines T in acidic medium, RNHCl may be reactive species of CAT and $[RuCl_5(H_2O)]^{2-}$may be assumed that reactive species of Ru(III) chloride in acidic medium. The formation of reactive complex, X, between reactive species of Ru(III) chloride and reducing sugar molecule in acidic medium is well supported by the observed kinetics. The rate determining step of the proposed reaction involves the interaction between reactive complex, X and RNH_2 resulting
- In the formation of most activated complex, X'. This is supported by the observed negative entropy of activation.

References

1. Singh AK, Srivastava J, Srivastava S, Rahmani S. Kinetics of oxidation of Glucose and cellobiose by acidic solution of NBA using Transition Metal Complex species, $[RuCl_3(H_2O)_2OH]^-$, as catalyst. Chinese Journal of Chemistry. 2008; 26(6):1057-1067.
2. Warner MC, Backwall JE. Kinetics and Mechanism of Ru (III) catalysed oxidation of reducing sugars by Chloramine T in alkaline medium. Acc. Chem. Res., 2013; 46:2545-2555.
3. Neelumbo kamboo, Santosh K. Uppadhya, Transition Metal Chemistry, 2000; 25:461-464.
4. Filler R. Oxidation and dehydrogenation with NBS and related N. haloamides, Chem. Rev., 1963; 63:21-43.
5. Odebunmi EO, Owalude SO. Kinetics of oxidation of sugars by chromium (VI) in per chloric acid medium. J of Chem. Society of Nigeria. 2005; 30(2):187-191.
6. Singh AK, Srivastava S, Srivastava J, Srivastava R, Srivastava P, Mol J. Cata. A Chem, 2007; 278:72-80.
7. Hoshali RV, Byadagi KS, Nandibewoor S, Chimatadar SA. Kinetic Catalysis, 2012; 53:65-70.
8. Srivastava S, Lakshmi Chaudhary, Kulina Singh. Ru (III) catalysed mechanistic investigation of Oxidation of cyclopentanol by $NaIO_4$ in acidic medium: a Kinetic approach. Int. J Res. In phy. Chem. 2012; 2(2):6-10.
9. Srivastava S, Sangeeta Srivastava, Arti Jaiswal. Kinetics and mechanism of Rh (III) catalysed oxidation of glycerol by acidified sodium periodate. J of Saudi. Chem. Soc. 2008; 12(3):321-328.
10. Srivastava S, sangeeta Srivastava, Shalini Srivastava, Parul, Arti Jaiswal, Kinetics. Mechanism of Rh (III) catalysed oxidation of Mannitol by acidified Sodium periodate. Bulletin of Catalysis Society of India, 2007; 6:140-146.
11. Singh AK, Srivastava R, Srivastava S, Srivastava J, Rahmani S, Singh B, *et al*. J mol. Catal. A: Chem., 2009; 310:64-70.
12. Singh AK, Singh RK, Srivastava R, Srivastava S, Srivastava J, Rahmani S. Trans. Metal Chem., 2010; 35:349-355.
13. Rashmi Tripathi, Santosh K. Uppadhaya, Journal of Indian chemical Society. 2007; 84(8):777-780.
14. Srivastava S, Pushpanjali Singh, Pd (II) catalysis in oxidation of D- Fructose by chloramineT in acidic medium: A kinetic study, Bulletin of the Catalysis Society of India, 2008; 7:12-19.
15. Meena Wadhwani, Shubha Jain, Rekha Nagwanshi, Sandhya Bageria. Kinetics of lactose with photochemical generated radicals. J chem. Chem., Eng., 2013; 7:187-192.
16. Ashok kumar singh, Rashmi, Shala Rahmani, Priyanka Singh. Kinetics of iodate oxidation of lactose in presence of $[IrCl_3(H_2O)_2OH]^-$ as homogenous catalyst. Ind. J Chem., 2013; 52A:854-862.
17. Kiranmai VS, Kulochana, Kishore cholkan, waseem M. Kayani, Gilles K. Kouassi, R.V. Jagadeesh, netkal M. Made Gowda, Oxidative conversion of lactose by CAT in sulphuric acid medium: a kinetic and mechanistic study. American J of Organic chemistry. 2012; 2(1):18-24.
18. Rangappa KS. Oxidation of monosaccarides by N-metallo haloaryl sulphonamide. J Ind. Chem. Soc., 2004, 81.
19. Rangappa KS, Raghavendra MP, Mahadevappa DS, Gowda DC. Kinetics and mechanism of oxidation of erythro-series pentoses and hexoses by N- chloro p-toluene sulphonamide. Carbohydrate Research. 1998; 2:57-67.
20. Singh B, Aniruddh Singh, Singh AK, Chayya Singh, Ashish, Kumud lata, Kinetics and mechanism of Ru(III) catalysed Oxidation of amino alcohols by CAT. Int. J of pure and applied Chem., 2011; 6:23-29.