Kinetic Studies on the Mechanism of Oxidation of Adonitol with Ru (III) by Acidic Chloramine T

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Abstract

The kinetics of oxidation of adonitol by chloramine T has been investigated at 40°C in different acid concentrations. At low acid concentration (0.08–0.50M), simultaneous catalysis by H^+ *and* Cl^- *ions is noted. The rate shows a first-order dependence on Chloramine T and Ru (III), but is independent of adonitol. The influence of mercuric acetate was found to be insignificant. The rate remains same with the variation in the ionic strength of the medium indicating the involvement of non ionic species in rate determining step. There were no free radicals during the course of reaction. The reaction product was identified by FTIR and UV spectroscopic techniques. Kinetic runs were performed at different temperatures and thermodynamic parameters were computed. A mechanism consistent with observed parameters is proposed and rate law is derived. The probable active species of catalyst and oxidant have been identified in acid media.*

Keywords: *Kinetics, Mechanistic, Ru (III), catalysis, D-Adonitol, chloramine T*

Introduction

Sugar alcohols are obtained through hydrogenation of mono- and disaccharides. The most common sugar alcohols[1] derived from monosaccharides are sorbitol[2], mannitol[3], xylitol[4] and erythritol[5]. Most of these sugar alcohols are chemically converted from corresponding sugars using a metal catalyst such as raney-nickel. Adonitol is a naturally occurring sugar alcohol with five carbon atoms ($C_5H_{12}O_5$)**.** It is acyclic, polyhydric alcohol[6-7] formed by the reduction of ribose[8]. These are used in chewing gum, ice creams & nutritional tablets[9].

Among various transition metals[10], the use of Pt group metal ions[11] especially Ru (III)[12-13], Os (III)[14], Ir (III)[15], Rh (III)[16] and Pd (II)[17] as catalyst due to their strong catalytic properties is reported. Literature reveals that Ru (III) complexes are frequently used as catalyst for the oxidation of various organic compounds like sugars, alcohols, ketones etc., in acidic and alkaline medium[18-20]. It is an efficient catalyst in many redox reactions[21-22] involving different complexities due to the formation of intermediate complexes, free radicals and multiple oxidation states [23]. Many organic substrates were oxidized by these sulfonamides and the kinetic and mechanistic aspects of these reactions are well documented[24-27]. A prominent member of this group Chloramine-T (CAT) is a well known analytical reagent and used as halogenating and oxidizing agent [28-30] in acidic and basic media.

A review of the literature provides information about quantitative determination, biodegradation and mechanism of action of adonitol. Oxidation of adonitol by mild oxidants has not been reported. The purpose of the present study was to apply redox reaction, to develop simple, accurate, sensitive and reproducible method for analysis of adonitol. In the present communication we are reporting kinetic and mechanistic aspects of adonitol oxidation by chloramine-T in perchloric acid medium at 40^0 C.

Experimental

All the reagents were of analytical grade, and double distilled water was used throughout the work. A solution of the compound was prepared in double distilled water. A stock solution of CAT (BDH, AR) was prepared in double distilled water and standardized by the iodometric method, and preserved in brown bottles. A solution of Ru (III) chloride (E. Merck) was prepared by dissolving a known weight of $RuCl_3$ in HCl of known strength and stored in a black coated bottle to prevent photochemical oxidation. KCl, $HClO_4$ and $Hg(OAc)_2$ of known strength are also used without further purification. All other reaction vessels were also coated black from outside to avoid any photochemical degradation.

Kinetics

The oxidation of adonitol by CAT in presence of Ru (III) catalyst was monitored iodometrically. A thermostatic water bath was used to maintain the desired temperature within ± 0.10 C. The appropriate volume of amount of CAT, $HClO_4$, Ru(III) chloride, KCl, $Hg(OAc)_2$ and water ,were mixed in black coated conical flask and thermo stated at 40^0 C for thermal equilibrium. After allowing sufficient time to attain the temperature of the experiment, requisite volume of adonitol solution, also thermo stated at the same temperature was rapidly pipette out and poured into the reaction vessel. The total volume of the reaction mixture was 50 ml each time. 5 ml aliquots of the reaction mixture was pipette out at different intervals of time and quenched with 4% acidified KI solution. The progress of the reaction was monitored by iodometric estimation of unreacted oxidant.

Stoichiometry and product analysis

The kinetic runs performed by keeping excess of adonitol over CAT in $HClO_4$ at 40^0 C confirm the following stoichiometry as one mole of adonitol consumed two moles of CAT. Thus overall reaction may be represented as

$$RCH_2OH + 2CH_3C_6H_4SO_2NNaCl + H_2O \longrightarrow RCOOH + 2CH_3C_6H_4SO_2NH_2 + 2NaCl$$

Where R= $CH_2OH(CHOH)_4$

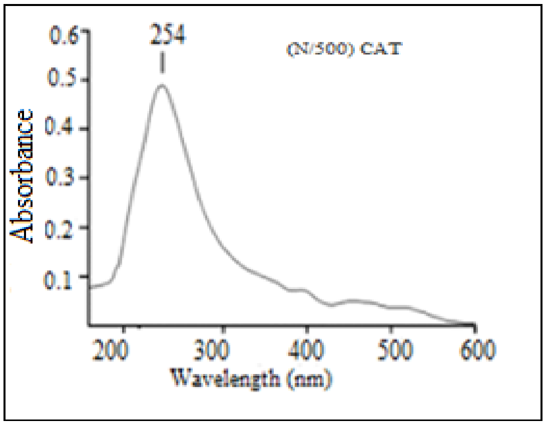
The product analysis by conventional method shows the formation of an adonoic acid after the reaction. The reaction mixture was kept for 48 hours under kinetic conditions and then added PCl_5 to it. The reaction mixture was reflux until the clear solution obtained. Then cool and add 4-5 ml of concentrated ammonia solution in the reaction mixture and heat it on water bath for 4-5 minutes, then cool and filter the solid precipitate. The precipitate was washed with cold water and recrystallized in hot water (Melting point for amide derivative of adonoic acid i.e adonamide was found to be 110^0C.

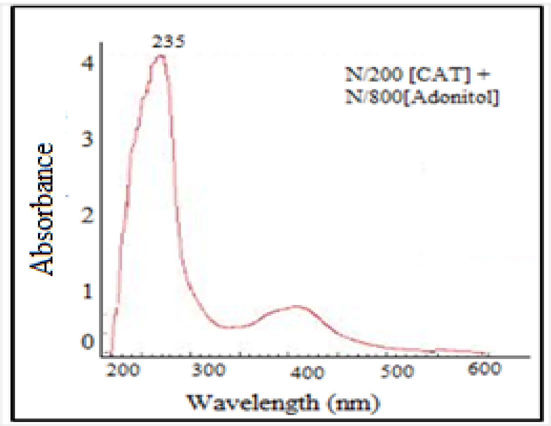
$$RCOOH + PCl_5 \longrightarrow RCOCl_3 + POCl_3 + HCl$$

$$RCOCl + NH_4OH \longrightarrow RCONH_2 + HCl + H_2O$$

Spectral Measurements

The absorption spectra of solutions of different concentrations of Ru (III) ion and CAT were recorded in the visible region ranges in 200-600 nm. Formation of adonoic acid is oxidation product in the presence of acidic medium in the reaction mixture. The absorbance bands of these solutions were observed at 235nm (fig. b) as compared to the observed peak at 254 nm for individual CAT (fig. a).





This was further confirmed by FT-IR spectrum, which shows a sharp peak at 1715 cm^{-1} and 1212 cm^{-1} for C=O and C-O stretching vibrations of the carbonyl group of free carboxylic acid. The high intensity band for –C-H stretching vibration was observed at 2940 cm^{-1}. The –OH stretching vibration for free carboxylic acid was observed in the range of 2500-3300 cm^{-1} and centered around 3000 cm^{-1}.The stretching vibration for Hydrogen bonded -OH group was observed at 3160 cm^{-1}.(fig. c) The observed band at 1415 cm^{-1} for $–CH_2$ bending vibration. The band at 1097 cm^{-1} was appeared due to C-O stretching vibration of hydroxyl group. The $–CH_2$ rocking vibration was observed at 780 cm^{-1}.

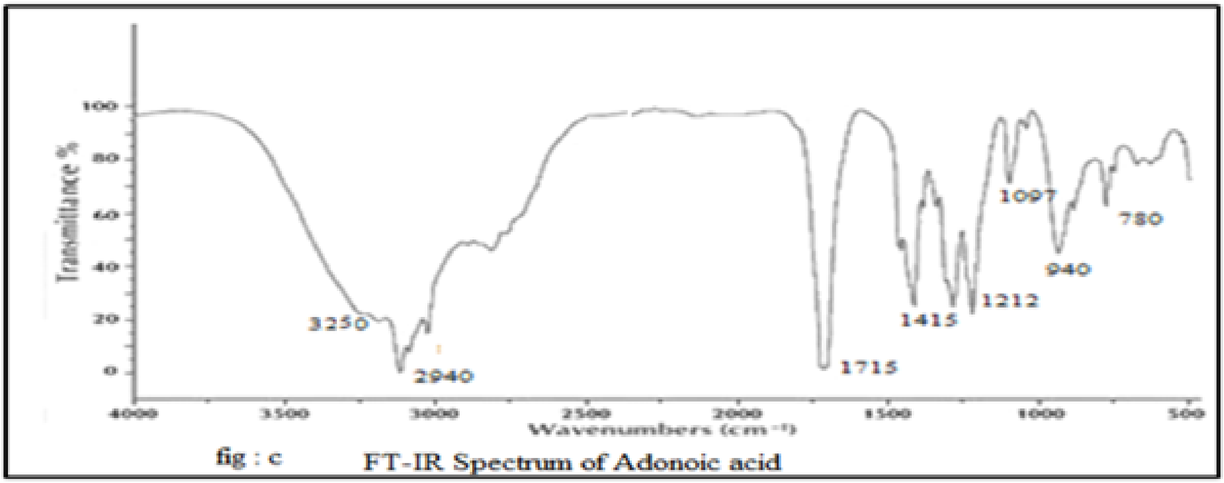


fig : c FT-IR Spectrum of Adonoic acid

Results

The oxidation of adonitol was investigated at different initial concentration of reactants.The rate (-dc/dt) of reaction in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of chloramine T which is written as [CAT]. The values of first order rate constant (K_1) was calculated as

$$K_1 = \frac{-dc/dt}{[CAT]}$$

The kinetics of oxidation of adonitol was investigated at initial concentration of the reactants (Tab. 1). The first order dependence of CAT at different concentration which is showed by plot of (–dc/dt) versus [CAT] (fig.d). The rate of reaction was found to be highly influenced by [Ru (III)] (tab. 1). The plots of (–dc/d)t against Ru(III) were linear passing through origin suggesting first order dependence of reaction on the catalyst and at the same time it also shows that reaction does not proceed with measurable rate in the absence of Ru(III)(fig.e). The insignificant effect of an increase in substrate concentration on the reaction rate indicated zero order w.r.t. adonitol.

Table-1: Effect of variation of [CAT] and Ru (III) on the reaction rate at 40^0C

[CAT]X10^3 mol dm^{-3}	**Ru(lll) X 10^6 Mol dm^{-3}S^{-1}**	**[ADT]X10^3 M**	**(-dc/dt) X 10^7**	**K$_1$X 10^4 S^{-1}**
0.83	1.0	1.0	4.5	5.4
1.00	1.0	1.0	5.5	5.5
1.25	1.0	1.0	6.6	5.4
1.67	1.0	1.0	8.8	5.4
2.5	1.0	1.0	13.3	5.3
5.0	1.0	1.0	27.7	5.4
1.0	9.6	1.0	4.8	5.0
1.0	14.4	1.0	7.3	5.0
1.0	19.2	1.0	10.0	5.2
1.0	24.0	1.0	13.0	5.4
1.0	28.8	1.0	16.0	5.5
1.0	33.6	1.0	19.0	5.6
1.0	1.0	3.34	2.2	
1.0	1.0	4.00	2.3	
1.0	1.0	5.00	2.5	
1.0	1.0	6.67	2.5	
1.0	1.0	10.00	2.7	
1.0	1.0	20.00	2.7	

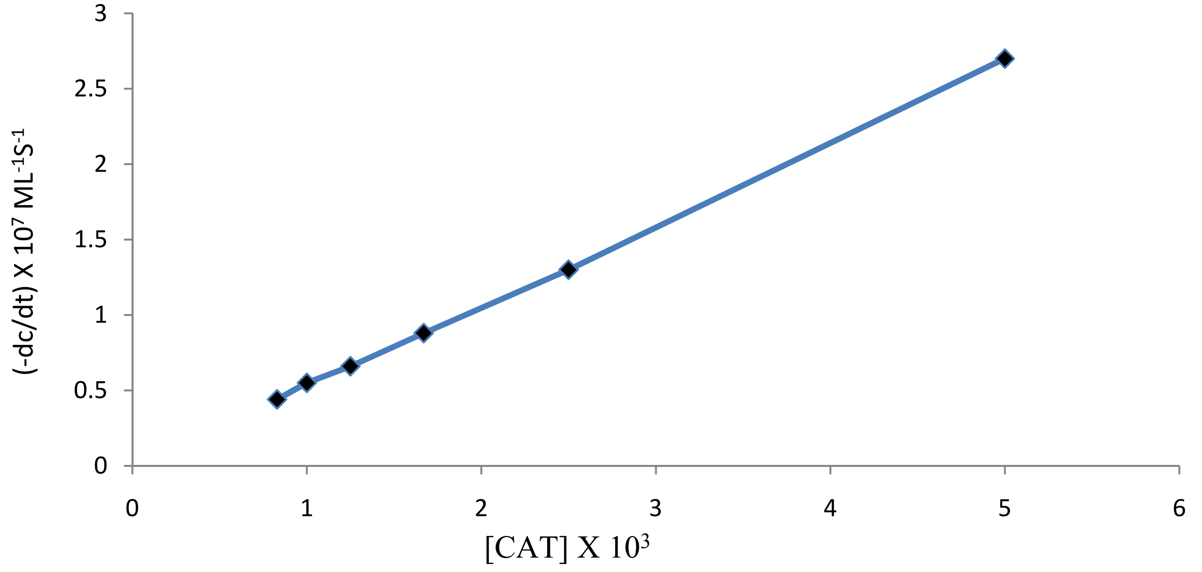


Fig.d Plot of (-dc/dt)X10^7 ML^{-1}S^{-1} vs. [CAT]X10^3 M at 40^0C under experimental condition of Table 1.

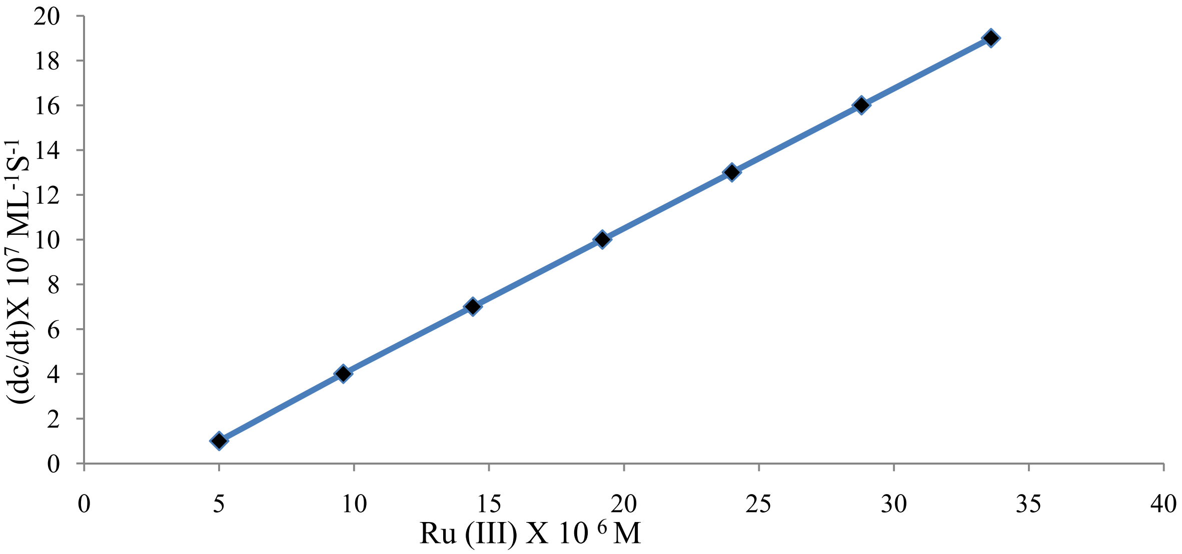


Fig.e Plot of Ru (III) X 10 ^{6} M vs. (dc/dt)X 10^7 $ML^{-1}S^{-1}$ at 40^0 C under experimental condition of table 2.

Table 2: Effect of variation of $HClO_4$, KCl, $Hg(OAc)_2$ and $NaClO_4$ on the reaction rate at 40^0C

[$HClO_4$]X10^3Mol	[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	1.0	1.0	1.0	4.6
1.0	1.0	1.0	1.0	5.0
1.25	1.0	1.0	1.0	5.5
1.67	1.0	1.0	1.0	5.5
2.5	1.0	1.0	1.0	6.3
5.0	1.0	1.0	1.0	6.6
1.0	0.83	1.0	1.0	4.5
1.0	1.0	1.0	1.0	5.0
1.0	1.25	1.0	1.0	4.7
1.0	1.67	1.0	1.0	4.6
1.0	2.5	1.0	1.0	5.5
1.0	5.0	1.0	1.0	5.5
1.0	1.0	0.83	1.0	5.0
1.0	1.0	1.0	1.0	4.6
1.0	1.0	1.25	1.0	5.0
1.0	1.0	1.67	1.0	5.5
1.0	1.0	2.5	1.0	5.5
1.0	1.0	5.0	1.0	5.8
1.0	1.0	1.0	0.83	6.3
1.0	1.0	1.0	1.0	6.4
1.0	1.0	1.0	1.25	6.7
1.0	1.0	1.0	1.67	6.7
1.0	1.0	1.0	2.5	7.0
1.0	1.0	1.0	5.0	7.2

The kinetic results observed in the oxidation of adonitol indicates that on increasing the Perchloric acid the value of (-dc/dt) increases with concentration.Table 2 shows the effect of successive addition of mercuric acetate; KCl and change in ionic strength μ of the medium (affected by addition of $NaClO_4$) showed effect on reaction rate. The negligible effect of mercuric acetate excluded the possibility of its involvement either as a catalyst or an oxidant. Hence the function of mercuric acetate is to act as scavenger, for any Cl^- ion formed in the reaction. Reaction shows no effect of chloride ion the reaction rate. From $NaClO_4$ variation (0.83×10^{-3} to 5.0×10^{-4} $Moldm^{-3}$)showed insignificant effect on the rate of oxidation, suggesting involvement of at least one neutral molecule in the rate determining step of the reaction. The reaction was studied at different temperatures and the rate constants measured at 30, 35, 40, 45 and 50^0C (Table 3) and specific rate constants were used to draw a plot of Log K vs 1/T, which was linear (fig.f). It is led to compute activation parameters in the oxidation of adonitol (Table 4). The kinetic results obtained for the oxidation of adonitol suggested that the oxidation reaction follow a mechanism.

Table 3: Effect of Temperature variation on the reaction rate

T^0C	$(-dc/dt) \times 10^7$
30^0	1.7
35^0	2.6
40^0	4.2
45^0	6.5
50^0	9.8

Table-4: Values of Activation Parameters on the reaction rate

Substrate	Parameters
Ea ($KJmol^{-1}$)	71.94
Log A	12.62
ΔS*($K^{-1}Jmol^{-1}$)	-7.28
ΔH* ($KJmol^{-1}$)	69.34
ΔG* ($KJmol^{-1}$)	3.71
ΔF*	2.34

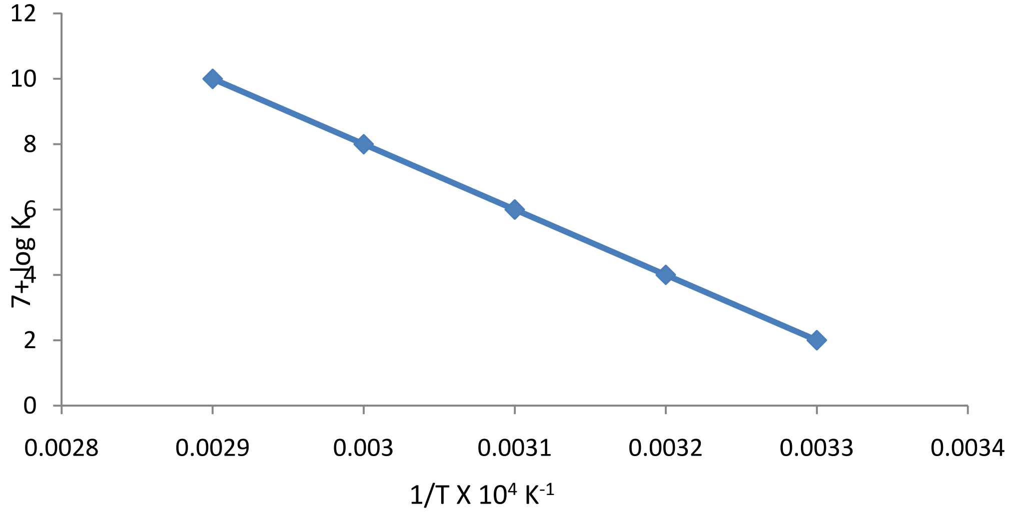


Fig.f Plot between 7+log K vs. $1/T \times 10^4 K^{-1}$ for oxidation of adonitol at 40^0C

Discussion

The number of possible chloro species of Ru (III) present in the solution can be represented by the general formula [Ru (III) (6 – x) (H_2O) Cl_n] $^{3-x}$ where n = 1- 6. All these species are highly pH dependent. The species present in the pH range, studied is however $[RuCl_2(H_2O)_4]^+$ This was confirmed by the reported absorption spectra of Ru (III) solution from 1 x 10^{-3} M to $1x10^{-6}$ M in the pH range 1.00 to 3.00 at constant ionic strength (μ=0.1 M KNO_3). These studies have been shown that octahedral complex species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^+$ do not exist in an the aqueous solution $RuCl_3$. The study on oxidation state Ru(III) exist in acidic medium.

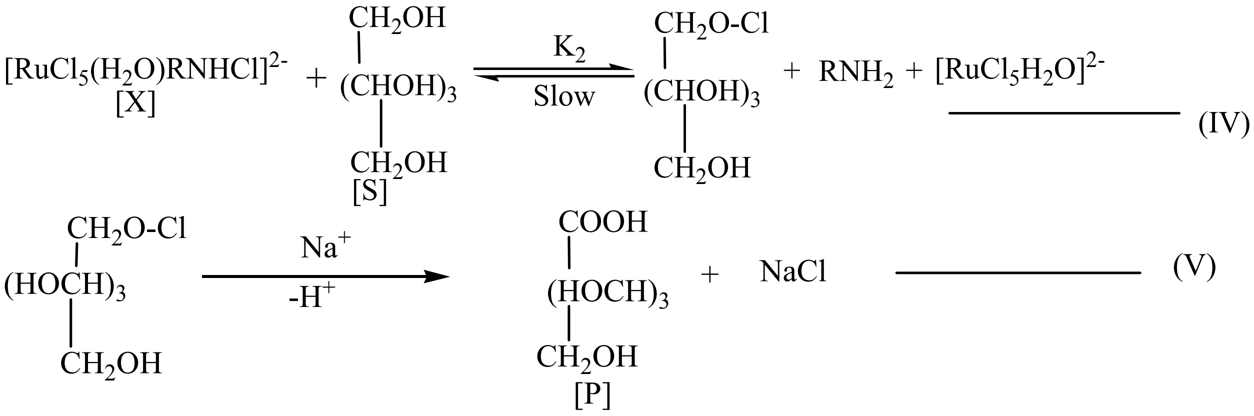
$$[RuCl_6]^{3-} + [H_2O] \rightleftharpoons [RuCl_5\,(H_2O)]^{2-} + Cl^- \;\ldots\ldots\ldots\ldots.. (1)$$

The mechanism of catalysis depends on the nature of substrates, the oxidants and experimental conditions. Chloramine-T (CAT) behaves as a strong electrolyte and ionizing agent. The reactive species of CAT and Ruthenium Chloride are RNClNa and $[RuCl_5\,(H_2O)]^{2-}$ in the acidic medium respectively. In acidic solution of CAT, quick formation of RNHCl has been reported. The above statements suggest the following reaction scheme which gives us the details of various steps in the reaction.

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

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

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



$$\underset{[X]}{[RuCl_5(H_2O)RNHCl]^{2-}} + \underset{[S]}{CH_2OH\text{–}(CHOH)_3\text{–}CH_2OH} \underset{\text{Slow}}{\overset{K_2}{\rightleftharpoons}} CH_2O\text{-}Cl\text{–}(CHOH)_3\text{–}CH_2OH + RNH_2 + [RuCl_5H_2O]^{2-} \text{ ———— (IV)}$$

$$CH_2O\text{-}Cl\text{–}(HOCH)_3\text{–}CH_2OH \xrightarrow[-H^+]{Na^+} \underset{[P]}{COOH\text{–}(HOCH)_3\text{–}CH_2OH} + NaCl \text{ ———— (V)}$$

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).

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

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

Hence,

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

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

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

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

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

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

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

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

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

On comparing ion equation (3) to (5)

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

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

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

We get

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

$$= K_1[RNHCl]\;[Ru(III)]_T \quad\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(7)}$$

According to Eq. (7), when rate constant values are plotted against [CAT] and Ru (III) straight line with positive intercepts were obtained which prove the validty of the rate law (7) and hence proposed mechanism. From intercept of each plot of fig. d and fig. e, the values of rate constant, K_1 have been calculated and recorded in table 1 and 2. These results support the mechanism for the oxidation of reducing sugar. Linear plot with positive intercepts indicates the retarding effect of CAT] and Ru (III) and positive effect on $[H]^+$ on the rate of reaction.

Conclusion

The experimental results as shown revealed that the reaction rate increases when the concentration of the catalyst [Ru(III)] is increased. The rate law is in conformity with all kinetic observation for the catalytic effect Ru (III) on the oxidation of adonitol by CAT has been studied in acidic medium. The reactive species of the catalyst have been identified by absorption spectra.

Oxidation products were identified by spectral analysis and activation parameters have been evaluated. The high positive value of change in free energy of activation (ΔG*) indicates highly solvated transition state, while fairly negative value of change in entropy of activation (ΔS*) suggest the formation of an activated complex with reduction in degree of freedom of molecules. The observed results have been explained by a plausible mechanism and related rate law has been deduced. Therefore, it is concluded that Ru (III) act as an efficient catalyst for the oxidation of adonitol.

References

[1] Y.Lakshman Kumar, R. venkata Nadh and P.S. Radha Krishna Murti, Russian Journal of Physical Chemistry A, 2016, 90(2), 300-307.
[2] Jensuwe Oltmanns, Stefan Palkovitis, Regina, Palkovits, Applied Catalysis A, 2013, 456, 168-173.
[3] Shiela Srivastava and Parul Srivastava, Pelgia Research Library,2010, 1(1), 13-19.
[4] Amrita srivastava and Swarn Lata Bansal, International Journal of chemical and physical sciences, 2015, 4(5), 39-48.
[5] Bharat Singh, Aniruddh K. Singh, Chhaya Singh, Ashish and Kumud Lata Singh, International Journal of pure and applied chemistry,2011,6(1), 23-29.
[6] Shiela Srivastava, Transition Metal Chemistry, 1999, 24, 683-685.
[7] Sheila Srivastava, Parul Srivastava, Vandana Gupta and Arti Jaiswal, Chemistry International, 2015, 3(1), 19-24.
[8] S.Ignatius Arockiam, A. Peterpascal Regis, Int. J. of Innovative Research in science, Engineering and Technology, 2014, 3(9), 15931-15935.
[9] Brian A. Burt, JADA, Vol. 137, (2006), 190-196.
[10] S.Srivatava, Arti Jaiswal and pushpanjali Singh, J. chem. Tracks, 2011, 13(1), 173-178.
[11] N.K.Soni, Riya Sailani, C.L. Khandelwal, P.D. Sharma, Transition metal chemistry, 2014, 39, 41-45.
[12] Srivastava, Lakshmi Chaudhary & Kulina Singh, International J. of Research in Physical Chemistry, 2012, 2(2), 6-10.
[13] Rajeswari V. Hosahalli, Anita P. Savanur Sharanappat, Nandibeworr, Shivamurti A. Chimatadar, Wiley inter science, 2010, 10, Doi 10, 1002.
[14] R.A.Singh, Kamini Singh,& S. K. Singh, J. Chem. Pharm. Res., 2010, 2(3), 684-690.
[15] Chandra Kumar Singh, Search and Research, 2012, 3(2), 39-44.
[16] S. Srivastava and Sangeeta Srivastava, Asian J. of Chemistry, 2008, 20(8), 6228-6234.
[17] S. Srivastava, Pushpanjali Singh, Bulletin of the Catalysis Soc. of India, 2008, 7, 12-19.
[18] Usha Kushwaha, Amita Singh, Anil Kumar, A.K. Singh and Firoz khan, Journal of chemical and Pharmaceutical Research 2012, 4(6), 3144-3153.
[19] E.O.Odebunmi and S.O.Owalude, Iranian Chemical Society, 2008, 5(4), 623-630.
[20] Neelum Kambo and Santosh Kumar Uppadhya, Transition Metal Chemistry, 2000, 25, 461-464.
[21] Arti Gupta, Abhishek Pandey, Anjali Pandey and Roli Srivastava, Journal of Chemical and Pharmaceutical Research, 2015, 7(7), 979-984.
[22] S. Srivastava, V. Gupta, Oxidation Communication, 2004, 27(4), 813-814.
[23] Sheila Srivastava, P.Singh, Oxidation Communication, 2010, 33(2), 408-415.
[24] Aftab Aslam Parwaz Khan, Anish Khan, Abdullah M. Asiri, Ajaya Kumar Singh, Int. J. Electrochem. Sci., 2015, 10, 759 – 774.
[25] A. Srivastava, Neelam, International Journal of Applied Research, 2015, 1(10), 380-384.
[26] H. P. Jayadevappa and G. Nagendrappa, Int. J. of Analytical, Pharmaceutical and Biomedical Sciences, 2013, 2(2), 49-55.
[27] Bharat Singh, Aniruddh K. Singh, Chhaya Singh, Ashish and Kumud Lata Singh, International Journal of pure and applied chemistry, 2011, 6(1), 23-29.

[28] Ajaya Kumar Singh, Bhawana Jain, Reena negi, Yokraj Katre, S.P. Singh, The Open Catalysis Journal, 2009, 2, 12-20.
[29] S. Srivastava, R. Patel, Pankaj Singh, Bulletin of the cata. soc. of Ind., 2013, 12, 28-34.
[30] Puttaswamy and N. Suresha, Indian Journal of Chemistry, 2008, 47 A, 1649-1655.