Kinetics and Mechanism of Ru(III) Catalysed Oxidation of Xylitol by Chloramine-T in Perchloric Acid Medium

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Abstract

The kinetics of the Ru(III)catalyzed oxidation of xylitol by an acidified solution of Chloramine-T in the presence of $Hg(OAc)_2$ as a scavenger, have been studied in the $30^0$to 45 °C range. The rate is first order with respect to chloramines -T and in Ru(III) but zero order with respect to the substrate and to $HClO_4$. The influence of $Hg(OAc)_2$, ionic strength and Cl^-on the rate was found to be insignificant. A transient complex formed between Ru(III) andchloramine-T. In a slow and rate determining step complex reacts with the polyhydric alcohol to give the product and the catalyst is regenerated. Activation parameters have been calculated and a suitable mechanism is proposed.

Keywords: *Kinetics, oxidation, mechanism, xylitol, chloramines-T, Ruthenium (III) chloride*

Introduction

This research paper describes an iodometrically investigation of Ru(III) used as a nontoxic and homogenous catalysis oxidation of xylitol by CAT in acidic standard kinetics. The Ru (III) Catalyst[1-3]is used in oxidation by Chloramine-T with number of compounds like aspirin[4],glycine[5], mannitol[6]and fructose[7]etc. Ru(III) catalyzed oxidation of some polyhydroxy alcohols by sodium periodatehas been reported.[8-10]Ru (III) catalyst mechanism is complicated due to formation of different intermediate product. The mechanism of catalyst depends on the nature of substrate, oxidant and on the experimental conditions.

Aryl N-halosulfonamidesare used as versatile reagents as they react with variety of functional groups performing a wide range of transformations.[11] They act as mild oxidants in both acid and alkaline solutions due to the presence of strongly polarized N- linked halogen in +1 state. Oxidation kinetics of many organic substrates was studied by aryl N-halosulfonamides. A prominent member of this group Chloramine-T (CAT)is a well-known analytical reagent.[12-14]The kinetic and the mechanistic aspects of many of its reactions are well documented.[15-17]

Xylitol is a carbohydrate, included in the group of the polyhydroxylated compounds. Xylitol ($C_5H_{12}O_5$) is a 5 Carbon polyhydric alcohol.[18,19] It is produced commercially by chemical reduction (hydrogenation) of D-xylose derived from hemicellulose-xylan hydrolyses of substrates.[20]The properties of xylitol such as anti-carcinogenic, sugar substitute and higher sweetening capacitythan sucrose make it valuable contender

for wide range of applications in food pharmaceutical, cosmetics and synthetic resin industries. It has many applications in food and chemical industries. It can replace glucose in the fermentation process for the production of penicillin. It has therapeutic effects on diabetes: it is able to reduce the levels of sugar in blood.

In view of the above facts, we have reported for the first time, the results of detailed investigations on the kinetic and mechanistic aspects of oxidation of xylitol by CAT in acid medium at 313K. The objective of the present research is mainly to unfold the mechanistic picture of CAT redox system in acid medium through kinetic studies and to know the relative reactivity of xylitol drug towards CAT in acid medium.

Experimental

Materials:

Aqueous solutions of xylitol (E. Merck), Chloramine-T (BDH, AR), $NaClO_4$ and $Hg(OAc)_2$ (E.Merck) were prepared by dissolving weighed samples in triply distilled H_2O. A $RuCl_3$ (Sigma Chemical Company) solution was prepared in HCl of known strength. All other reagents were of analytical grade. Reaction vessels were painted black to prevent photo- chemical decompositions.

Kinetics:

The requisite volumes of all reagents, including substrate, were thermo-stated at 35 ± 0.1 °C to attain equilibrium. A measured volume of chloramines-T solution, maintained separately at the same temperature, was poured rapidly into the reaction vessel. Progress of the reaction was followed by assaying aliquots of the reaction mixture for chloramines-T, iodometrically using starch indicator, after suitable time intervals.

Stoichiometry

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of oxidant [CAT] over substrate [xylitol] in different ratio at room temperature for 48 h and estimation of unconsumed oxidant [CAT] in different sets showed that one mole of xylitol and consume two mole of [CAT].This result showed 1:2 stoichiometry.

$$C_5H_{12}O_5 + 2RNHCl + H_2O \longrightarrow C_5H_{10}O_6 + RNH_2 + 2HCl$$

Where R = $CH_3C_6H_4SO_2$, whose oxidation products xylonic acid, were detected by conventional methods.

Product analysis:

The reaction mixture containing a large excess of [CAT], i.e., 2 times over [xylitol] in a blackened vessel was allowed to stand for 48 hours at room temperature for completion of the reaction. The reaction products were analyzed by different spectral technique as UV, IR spectroscopy. The product was identical to an authentic sample of xylonic acid.

Spectral Analysis:

Electronic spectra were measured on a Jasco V630 UV–VIS spectrophotometer in the range of 600–180 nm in methanol solutions. The reaction mixture of oxidant [CAT] and Ru(III) catalyst in the presence of HCl showed the absorption band 290 nm while the set of reaction mixture such as Ru(III), mercuric acetate, perchloric acid, CAT ($2.5x10^{-3}$mol dm^{-3}) to [Xylitol] ($5x10^{-2}$mol dm^{-3}) were taken in the reaction vessel and kept for two days at room temperature. The spectra were taken at different concentrations (reaction mixture).A peak was observed at λmax 230 nm indicating acid formation. This might be due to the formation of hydrochloride and it was consumed to give the products.

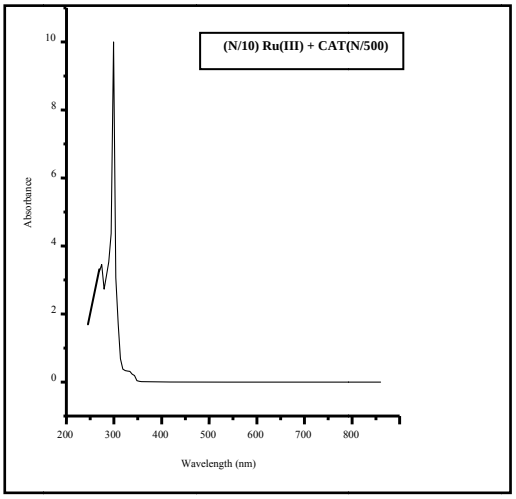


Figure: 1

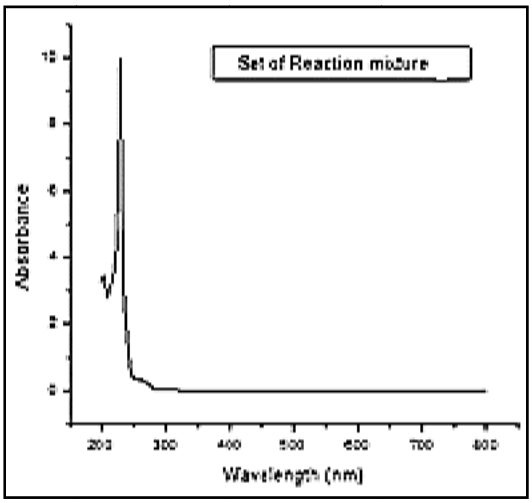


Figure: 2

An infrared spectrum has been used in order to identify the nature of reactive intermediates and reaction products (in solution) and to follow their stretching and bending modes. This spectrum shows typical and broad O-H stretch which is superimposed upon C-H stretch. The sharp –OH absorption band around 3600 cm^{-1} can be observed in dilute solution. This coupled with C=O stretch around 1700 cm^{-1} shows that the compound is carboxylic acid. There is saturation in the compound as shown by presence of C-H stretch around 2900 cm^{-1}.The C-C and C-H bending around 1150 cm^{-1} and 900 cm^{-1}show the presence of saturated aliphatic acid.

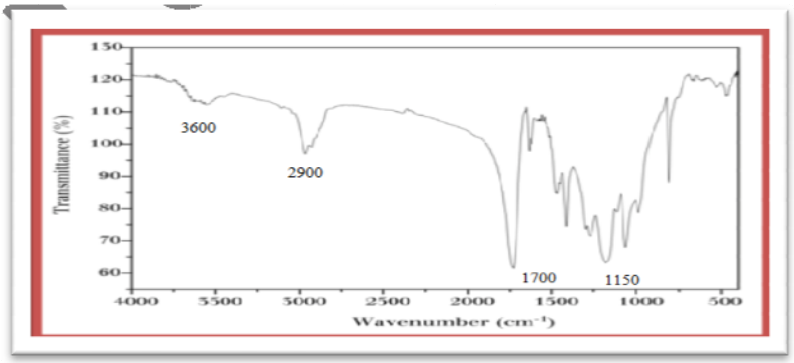


Figure: 4

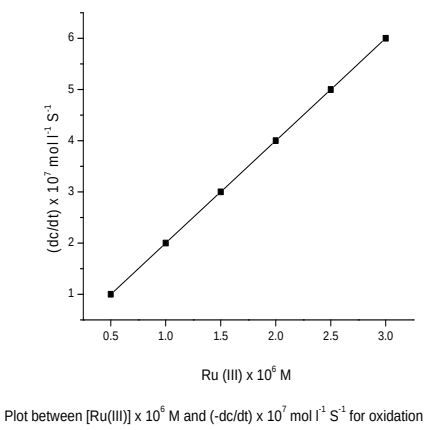
Result and Discussion:

The kinetics of oxidation of xylitol was investigated at several initial reactant concentrations (Table 1) by Chloramine-T in the presence of Ru(III) chloride as a homogenous catalyst have been studied at constant temp of 40^0C. First order constants K_1, were calculated from the plots of CAT versus time(Figure 6).Values of K_1 were constant at all initial concentrations of CAT; thus the reaction exhibits first order dependence on oxidant.

The first order rate constant remained nearly the same at different concentrations of xylitol showing zero order dependence. Variation in the perchloric acid concentration did not bring about significant changes in K_1 values, establishing that the reaction is zeroth order in H^+. The reaction was markedly influenced by increases in Ru(III) concentration, and a linear relationship between K_1 values and Ru(III) was observed (Figure 5).

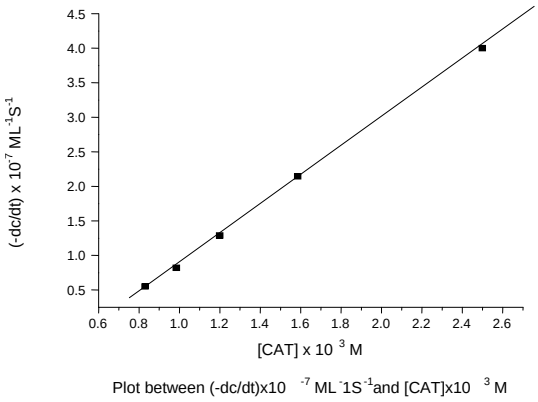
Table 1 Effect of variation of oxidant, Ru (III) and Xylitol at 40^0C temp.

[CAT] X 10^3mol dm^{-3}	Ru(III) x 10^6Mol dm^{-3} s^{-1}	[Xylitol] X 10^3mol dm^{-3}	(-dc/dt) X 10^{-7}	K_1 X 10^4 S^{-1}
0.83	1.0	1.0	0.55	0.67
1.00	1.0	1.0	0.74	0.67
1.25	1.0	1.0	1.25	0.67
1.67	1.0	1.0	2.16	0.67
2.50	1.0	1.0	4.16	0.67
5.0	1.0	1.0	16.6	0.66
1.0	1.0	1.0	2.1	0.23
1.0	1.5	1.0	3.1	0.23
1.0	2.0	1.0	4.1	0.23
1.0	2.5	1.0	5	0.22
1.0	3.0	1.0	6	0.22
1.0	3.5	1.0	7	0.22
1.0	1.0	0.83	0.25	-
1.0	1.0	1.00	0.25	-
1.0	1.0	1.25	0.27	-
1.0	1.0	1.67	0.23	-
1.0	1.0	2.50	0.25	-
1.0	1.0	5.00	0.25	-



Plot between [Ru(III)] x 10^6 M and (-dc/dt) x 10^7 mol l^{-1} S^{-1} for oxidation of D-Xylitol

Figure: 5



Plot between (-dc/dt)x10 $^{-7}$ ML^{-1}1S^{-1}and [CAT]x10 ^{3} M

Figure: 6

Experimental data (Table 2) showed negligible effect of ionic strength of the medium on the rate, and the reaction is unaffected by chloride ion. The negligible effect of $Hg(OAc)_2$ excludes the possibility of its involvement either as a catalyst or as an oxidant. Hence its function is to act as a scavenger for any chloride ion formed in the reaction. The kinetic studies were also made in the $30^0 \pm 50°C$ range (Table 3) and activation parameters were calculated (Table 4). The reactive species of Chloramine-T, in acidic medium, is OCl^- ion.

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

$[HClO_4]$ X 10^3mol	[KCl] x 10^3Mol	$[Hg(OAc)_2]$x10^3mol	$[NaClO_4]$ x 10^3 mol	-(dc/dt) X 10^{-7}
0.83	1.00	1.00	1.00	2.5
1.00	1.00	1.00	1.00	2.4
1.25	1.00	1.00	1.00	2.3
1.67	1.00	1.00	1.00	2.2
2.50	1.00	1.00	1.00	2
5.00	1.00	1.00	1.00	2
1.00	.83	1.00	1.00	1.53
1.00	1.00	1.00	1.00	1.50
1.00	1.25	1.00	1.00	1.50
1.00	1.67	1.00	1.00	1.36
1.00	2.50	1.00	1.00	1.36

1.00	5.00	1.00	1.00	1.30
1.00	1.00	.83	1.00	2
1.00	1.00	1.00	1.00	2.2
1.00	1.00	1.25	1.00	2.2
1.00	1.00	1.67	1.00	1.8
1.00	1.00	2.50	1.00	2
1.00	1.00	5.00	1.00	2
1.00	1.00	1.00	.83	1.36
1.00	1.00	1.00	1.00	1.33
1.00	1.00	1.00	1.25	1.34
1.00	1.00	1.00	1.67	1.34
1.00	1.00	1.00	2.50	1.36
1.00	1.00	1.00	5.00	1.25

Table 3 Effect of the temperature on the Reaction Rate

T^0C	dc/dt	Kr x 10^2
30^0	1.4	0.56
35^0	2.2	0.88
40^0	3.0	1.20
45^0	4.2	1.68
50^0	5.4	2.16

Table 4 Values of Activation Parameter

Substrate	Ea ($KJmol^{-1}$)	log A	$\Delta H^*(KJmol^{-1})$	$G^*(KJmol^{-1})$	$\Delta S^*(K^{-1}Jmol^{-1})$	$\Delta F^*(KJmol^{-1})$
Xylitol	54.55	9.57	53.83	31.41	-65.63	34.01

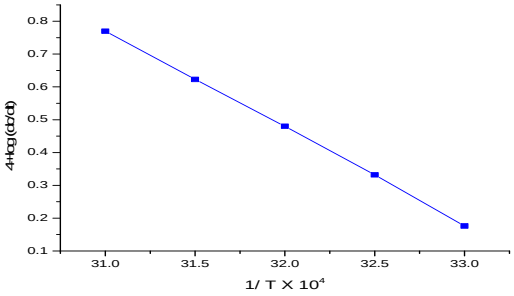


Figure: 7

Discussion and Mechanism:

On the basis of the above discussion for the Ru(III) catalyzed oxidation of D-Xylitol by CAT in acidic medium. The following reaction steps are suggested.

$$RNClNa \underset{}{\overset{(\text{ fast})}{\rightleftharpoons}} RNCl^- + Na^+ \qquad \text{(l)}$$

$$RNCl^- + H^+ \xrightarrow{(\text{fast})} RNHCl^- \qquad \text{(ll)}$$

$$\underset{[Y]}{RNHCl + RuCl_5(H_2O)} \underset{K\text{-}1}{\overset{K1}{\rightleftharpoons}} \underset{[X]}{\left[RuCl_5(H_2O)RNHCl\right]^{2-}} \qquad \text{(lll)}$$

$$2\underset{[X]}{\left[RuCl_5(H_2O)\,RNHCl\right]^{2-}} + \underset{[S]}{\begin{array}{l}CH_2OH\\|\\(CHOH)_3\\|\\CH_2OH\end{array}} \underset{\text{slow}}{\overset{K_2}{\rightleftharpoons}} \begin{array}{l}CH_2\text{-}O\text{-}Cl\\|\\(CHOH)_3\\|\\CH_2OH\end{array} + 2\,RNH_2 + \left[2(RuCl)_5\,H_2O\right]^{2-} \qquad \text{(IV)}$$

$$\begin{array}{l}CH_2OCl\\|\\(CHOH)_3\\|\\CH_2OH\end{array} \xrightarrow[-H^+\ (Fast)]{2Na^+} \begin{array}{l}COOH\\|\\(CHOH)_3\\|\\CH_2OH\end{array} + 2NaCl \qquad \text{(V)}$$

Step (4) is slow and rate determine step rate of reaction. The rate of reaction is term of consumption of concentration of $[RNCl^-]$ ions may be written as equation (1)

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

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

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

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

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

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

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

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

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

$$== [Y]\left\{1 + \frac{K_1[RNHCl]}{K_{-1} + K_2[S]}\right\}$$

$$== [Y]\left\{\frac{K_{-1} + K_2[S] + K_1RNHCl}{K_{-1} + K_2[S]}\right\}$$

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

On comparing ion equation (3) and (5)

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

$$== \frac{K_1[RNHCl][Ru(lll)]_T[S]}{K_{-1} + K_1[RNHCl] + K_2[S]} \quad \text{——————} (6)$$

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

We get

$$\frac{d[RNHCl]}{dt} === \frac{K_2K_1[RNHCl][Ru(III)_T][S]}{K_2[S]} \quad \text——————} (7)$$

$$=== K_1[RNHCl][Ru(lll)]_T \quad \text——————} (8)$$

The rate law (8) is in agreement with all observed kinetics.

Conclusion

From observed kinetic data the following conclusion can be drawn:

i). $CH_3C_6H_4SO_2NCl$- is reactive species of Chloramine -T in acidic medium.

ii). There is formation of most reactive activated complex [RuCl5(H2O)] between reactive species of Ru(III) chloride and reactive species of Chloramine T (CH3C6H4SO2NHCl).

iii). Mercuric acetate as one of the reactants plays the role of inhibitor in addition to its role as Cl- as scavenger.

iv). The rate of oxidation of xylitol did not depend on the ionic strength of the medium of the reaction, indicating that a neutral molecule is involved at the transition state.

v). The observed negative value of entropy of activation for xylitol supports the formation of a rigid activated complex as proposed in step (III) of the mechanism.

vi). The reaction mechanism involves formation of an intermediate complex between a Ru(III) chloride ions and a neural polyhydroxy alcohol molecule which dissociates in a slow step to give the products.

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