

Ruthenium (III) Catalysed Oxidation of D-Sorbitol by Chloramine T in Perchloric Acid Medium: A Kinetic and Mechanistic Approach

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Abstract

The kinetics of Ru (III) catalysed oxidation of sorbitol by acidic solution of Chloramine T in the presence of mercuric acetate as scavenger is investigated in the temperature range 30^o-50^o C. First order kinetics in the lower concentration range of CAT was observed to tend to zero order at its higher concentration. The reaction follows zero order kinetics in sorbitol while it is first order in Ru (III). Increase in [H⁺] and [Cl⁻] showed positive effect while successive addition of sodium perchlorate showed negligible effect on the reaction rate. The main product of oxidation is corresponding acid. Cationic Cl⁻ has been proposed as the real oxidising species. Various thermodynamic parameters have been computed. A suitable mechanism in agreement with the kinetic observations has been derived.

Keywords: Kinetics, Ru (III) chloride, Oxidation, Chloramine T, Acidic medium

Introduction

Sugar alcohols (also called polyhydric alcohols, polyalcohols, alditols or glycitols) are organic compounds, typically derived from sugars, comprising a class of polyols. Sorbitol, less commonly known as glucitol, is a sugar alcohol with a sweet taste which the human body metabolizes slowly^{1,2}. It also occurs naturally in many stone fruits and berries from trees of the genus Sorbus. It can be used as a laxative via an oral suspension or enema. It can be obtained by reduction of glucose, changing the aldehyde group to a hydroxyl group. Most sorbitol is made from corn syrup, but it is also found in apples, pears, peaches, and prunes. It is converted to fructose by sorbitol-6-phosphate 2dehydrogenase. It is identified as a potential key chemical intermediate for production of fuels from biomass resources. Complete reduction of sorbitol³ opens the way to alkanes, such as hexane³, which can be used as a biofuel. Hydrogen required for this reaction can be produced by aqueous phase reforming of sorbitol.

Ruthenium trichloride is the best starting material for the oxidation of compounds. Like osmium, ruthenium^{4,5} exhibits a wide range of oxidation states in its complexes (VIII to -II), and all of these may be reached from RuCl₃, since, although it is homogenous catalyst⁶ in the various redox reactions⁷⁻⁹. Chloramine T (CAT) is mild oxidising agent, chlorinating and analytical agent¹⁰⁻¹³ has been extensively used for catalysed and uncatalysed oxidation of variety of organic compounds. CAT has been developed as an oxidimetric titrant for determination of certain sugar alcohols.

The kinetics and mechanism of oxidation of sugar alcohols have been studied in acidic and alkaline media¹⁴⁻¹⁷, employing different transition metal ions¹⁸⁻²⁰, complex ions and hydrogen peroxide as oxidants. The results show that the mechanism may depend on the nature of the oxidant and the substrate. In some cases the mechanism may involve the formation of an intermediate complex, in others the formation of free radicals, while still in others, the formation of transition state. A survey of representative studies on the oxidation of polyhydric alcohols²¹⁻²² by transition metals are given, with a special attention to the reaction mechanisms and elucidate the activation parameters on their catalytic

reactivity. Hence we felt it would be worthwhile to investigate the oxidative behaviour of CAT with sorbitol to explore the kinetics and mechanistic aspects of the Ru (III) chloride catalysed reaction. This study will enable to understand the biological reaction in living systems and with also help to understand the catalytic activity of Ru (III) along with oxidative capacity of CAT in acidic medium. We have investigated the oxidation of sorbitol with Ru (III) by chloramine T in acidic medium.

Experimental

Materials

The chemicals reagents used in this study were obtained from Aldrich chemical company. They were of analytical reagent grade and used with purification. Ruthenium (III) stock solution was prepared by dissolving a known weight of RuCl₃ (s.d fine chem, Mumbai, India) in 0.10 moldm 10HCl. Dilute solution of ruthenium (III) was made from the stock solution as required. Stock solutions of sorbitol, potassium chloride, perchloric acid, mercuric acetate, sodium perchlorate and chloramine T were made in double distilled water. Fresh solutions were also prepared when needed from its components in double distilled water. All other reaction vessels were also coated black from outside to avoid any photochemical degradation. NaClO₄ (AR) and H₂SO₄ (AR) were used to provide the required ionic strength and acidity, respectively.

Kinetics

A thermostatic water bath was used to maintain the desired temperature. Aliquots of the reaction mixture were placed in the thermostate-controlled water bath, which was pre-equilibrated at 35°C. Requisite volume of sorbitol 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 pipetted 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 in measured aliquots of the reaction mixture withdrawn at regular intervals of time. The kinetic runs were carried out at 35°C.

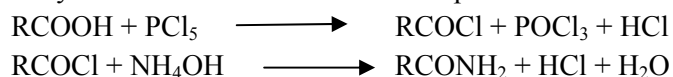
Stoichiometry

Stoichiometry of the reaction was determined by equilibrating varying ratios of CAT to sorbitol at 35°C for 48 hours under the kinetic conditions. Estimation of unconsumed CAT revealed that two moles of CAT were required to oxidise one mole of sorbitol according to the equation (1)



Where R stands for (CHOH)₄ CH₂OH. The corresponding mono carboxylic acid (gluconic acid) was detected by conventional method.

Kept the reaction mixture for 48 hours under kinetic conditions and then added PCl₅ to it. Refluxed till a clear solution is obtained. Cooled and added 4-5 ml of concentrated ammonia solution, heated it on water bath for 4-5 minutes, cooled and filtered the precipitated solid. Washed with water, recrystallized it and determined its m.p. 90°C.



Results and Discussion:

Ru (III) catalysed oxidation of sorbitol by CAT was studied at several initial concentrations of reactants (Table 1). First order kinetics in CAT was obtained at each initial concentration of reactants. Which is also evident from graph (Fig:1) drawn between $(-dc/dt)$ vs. $[CAT]$. Insignificant effect was observed on the concentration of sorbitol. It is indicating thus zero order in sorbitol. The reaction was observed to be very sensitive to $[Ru(III)]$. A plot of $(-dc/dt)$ vs. $[Ru(III)]$ (Fig:2) gives the straight line, which resemble clearly with average value of first order rate constant of $[CAT]$. Their degree of closeness in first order rate constants obtained graphically and by $(-dc/dt)/[Ru(III)]$ clearly confirms first order dependence on $[Ru(III)]$.

Table-1: Effect of variation of $[CAT]$ and Ru (III) on the reaction rate at $40^{\circ}C$

$[CAT] \times 10^3 \text{ Mol dm}^{-3}$	$Ru(III) \times 10^6 \text{ Mol dm}^{-3} \text{ S}^{-1}$	$[SL] \times 10^3 \text{ M}$	$(-dc/dt) \times 10^7$	$K_1 \times 10^4 \text{ S}^{-1}$
0.83	1.0	1.0	1.90	2.28
1.00	1.0	1.0	2.40	2.40
1.25	1.0	1.0	3.12	2.49
1.67	1.0	1.0	3.85	2.30
2.50	1.0	1.0	5.80	2.32
5.0	1.0	1.0	12.40	2.48
1.0	1.0	1.0	2.50	2.50
1.0	1.5	1.0	4.00	2.26
1.0	2.0	1.0	5.24	2.26
1.0	2.5	1.0	6.25	2.50
1.0	3.0	1.0	6.89	2.30
1.0	3.5	1.0	8.15	2.32
1.0	1.0	0.83	2.30	-
1.0	1.0	1.00	2.45	-
1.0	1.0	1.25	2.48	-
1.0	1.0	1.67	2.52	-
1.0	1.0	2.50	2.57	-
1.0	1.0	5.0	2.60	-

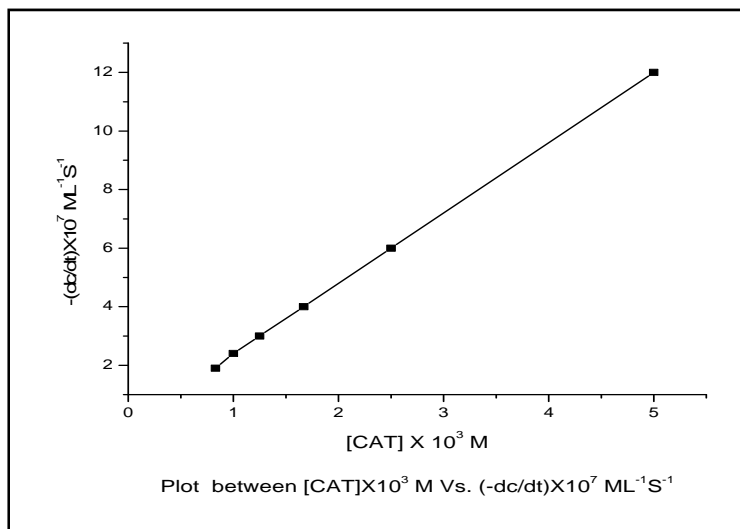


Figure 1

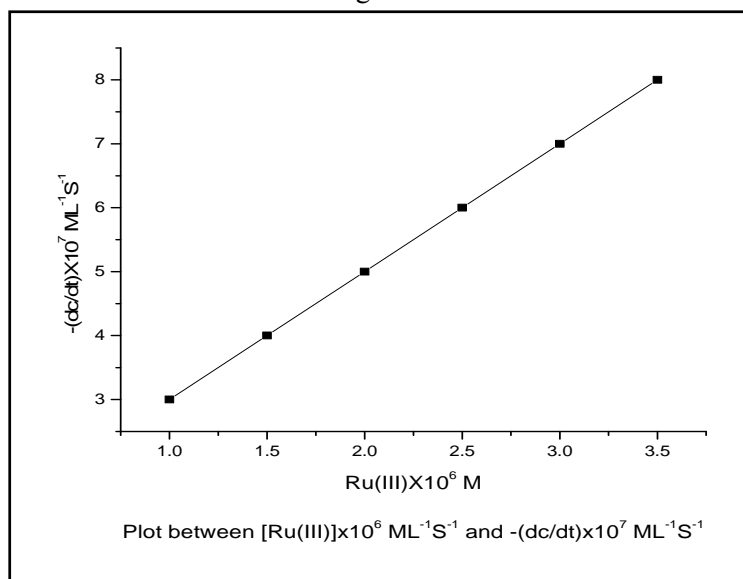


Figure 2

It was also observed that on increasing $[H^+]$ in the reaction mixture, the values of rate constant increased and indicating thereby positive effect of $[H^+]$. The effect of ionic strength (μ) variation on the rate of reaction was studied by carrying out investigation in the presence of different amounts of sodium perchlorate. The results indicated negligible effect of μ on the reaction rate.

A kinetic result obtained on varying the concentration of chloride ions and shows positive effect of chloride ions variations. The reaction rate increased with an increase in Potassium chloride concentration in the reaction mixture while mercuric acetate addition was found to have negligible effect (table 2). Zero effect of mercuric acetate eliminates the possibility of its involvement in CAT oxidation and thus it only acts as scavenger for any Cl^- formed in the reaction and rules out the possibility of parallel oxidation of Cl_2 which would have been formed by interaction $NaCl$ and RNH_2 .

Table 2: Effect of HClO₄, KCl, Hg(OAc)₂ and NaClO₄ on the reaction rate at 40⁰C

[HClO ₄] $\times 10^3$ Mol	[KCl] $\times 10^3$ Mol	[Hg(OAc) ₂] $\times 10^3$ Mol	[NaClO ₄] $\times 10^3$ Mol	(-dc/dt) $\times 10^7$ ML ⁻¹ S ⁻¹
0.83	1.0	1.0	1.0	2.50
1.00	1.0	1.0	1.0	2.58
1.25	1.0	1.0	1.0	2.63
1.67	1.0	1.0	1.0	2.70
2.50	1.0	1.0	1.0	2.73
5.0	1.0	1.0	1.0	2.80
1.0	0.83	1.0	1.0	2.48
1.0	1.00	1.0	1.0	2.52
1.0	1.25	1.0	1.0	2.58
1.0	1.67	1.0	1.0	2.55
1.0	2.50	1.0	1.0	2.60
1.0	5.0	1.0	1.0	2.65
1.0	1.0	0.83	1.0	2.52
1.0	1.0	1.00	1.0	2.55
1.0	1.0	1.25	1.0	2.58
1.0	1.0	1.67	1.0	2.55
1.0	1.0	2.50	1.0	2.56
1.0	1.0	5.0	1.0	2.60
1.0	1.0	1.0	0.83	2.54
1.0	1.0	1.0	1.00	2.57
1.0	1.0	1.0	1.25	2.53
1.0	1.0	1.0	1.67	2.50
1.0	1.0	1.0	2.50	2.48
1.0	1.0	1.0	5.0	2.45

Effect of Temperature variation on the reaction rate

The reactions were studied at five different temperatures in table 3. The rate constant at these temperatures led to compute E_a , ΔS^* , ΔH^* , ΔG^* , F^* in the oxidation of sorbitol and their activation parameters have been recorded in table 4. The rate measurements were taken at 30-50⁰ C and specific rate constants were used to draw a plot of log k versus 1/T, which was linear in fig.3. The moderate ΔH^* and ΔS^* values are favourable for electron transfer reaction. The values of ΔH^* was due to energy of solution changes in the transition state. The negative value of ΔS^* suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an outer sphere mechanism. This conclusion is supported by earlier observations. The activation parameters evaluated for the catalysed reaction explain the catalytic effect on the reaction.

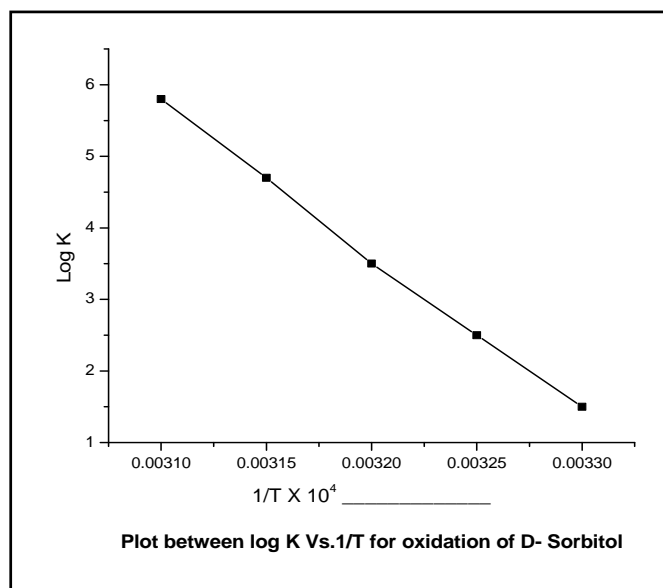


Fig:3

Table-3: Effect of temperature variation

T ⁰ C	(-dc/dt)X10 ⁴ S ⁻¹
30 ⁰	1.5
35 ⁰	2.5
40 ⁰	3.5
45 ⁰	4.7
50 ⁰	5.8

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

Activation Parameters	Values
Ea (KJmol ⁻¹)	54.45
Log A	5.60
ΔS*(K ⁻¹ Jmol ⁻¹)	-244
ΔH*(KJmol ⁻¹)	57.06
ΔG*(KJmol ⁻¹)	19.32
F*	21.92

Mechanism

Kinetic observations show that the reactions under investigation are complex reaction, which usually take place in more than one step. In such reactions as in the present work, there is every possibility for the formation of complex between different reactants of the reactions.

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

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

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

We get

$$\frac{d[\text{RNCl}^-]}{dt} = \frac{K_2 K_1 [\text{RNHCl}][\text{Ru(III)}]_T [\text{S}]}{K_2 [\text{S}]} = K_1 [\text{RNHCl}] [\text{Ru(III)}]_T \quad (7)$$

According to Eq. (7), when rate constant values are plotted against $[\text{CAT}]$ and Ru(III) straight line with positive intercepts were obtained which prove the validity of the rate law (7) and hence proposed mechanism. The rate law is in agreement with all observed.

Conclusion

At the end of research work, it was found that

- paraTolueneSulphonamide is the reactive species of Chloramine T in acidic medium.
- There is a formation of most reactive activated complex $[\text{RuCl}(\text{H}_2\text{O})_5]$ between reactive species of Ru (III) chloride and reactive species of chloramine T in acidic medium.
- Mercuric acetate as one of the reactants plays the role of inhibitor in addition to its role as Cl^- ions scavenger.
- The positive values of free energy of activation (ΔG^*) indicates highly solvated transition state, while fairly high negative values of entropy of activation (ΔS^*) suggest the formation of an activation complex with reduction in the degree of freedom.
- The rate law is in conformity with all kinetic observations and proposed mechanistic steps are supported by negligible effect of ionic strength.

Acknowledgement

We appreciate the support of Chemistry department, University of Lucknow, Lucknow towards the successful completion of this research work.

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