

Ruthenium(III) Catalyzed Oxidation of Mannitol by N-chlorophthalimide

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Abstract: Kinetic investigation in Ru(III) catalysed oxidation of mannitol by N-chlorophthalimide in aqueous acetic acid medium in presence of HCl have been carried out. The influence of Ru(III) shows a first-order dependence on [NCP] and fractional-order each on (Ru(III)) and [H⁺]. The rate was verified for Michaelis-Menten type kinetics. The variation of ionic strength and phthalimide (reaction product) have negligible effect on rate. The negative effect with acrylonitrile could also be observed. On the basis of observed results, two schemes of scanty mechanism are proposed. One as acid dependent and another acid independent paths. Activation parameters for the reaction have been evaluated at different temperatures in conformity with the derived rate law.

Key words: Mannitol, N-chlorophthalimide, Ruthenium(III) chloride, kinetics, oxidation.

1. INTRODUCTION

Mannitol is related to polyhydric alcohols and is derived from sugar with general formula HOCH₂(CHOH)_nCH₂OH (where n= 4 for mannitol). This is obtained from natural products. Mannitol possess sweetness and causes reduction in calorie, non-carcinogenicity^[1] and non-alcoholic beverage. This type of common sugar alcohols have six-carbon chain in the structure and derived from hexoses (six carbon sugar). It is differentiated from other sugar alcohols by the relative orientation of the OH groups, attached to C- atoms i.e. exhibited stereochemical properties. Many reviews are documented for the oxidation of sugar alcohols with different oxidants viz. Ce(IV)^[1] catalysed by Ru(III)^[2] and QCC.^[3] In the recent past, trend of N-halogenoxidant which has been widely used in the estimation of organic substrates.^[4-8] N-chlorophthalimide is low cost selective potential oxidant with nitrogen Cl⁺ and N-anion act as both bases and nucleophiles has been successfully employed in the kinetic oxidation of alcohols,^[9] carbohydrates,^[10] and amino acids,^[11,12] etc. The efficiency of Ru(III) as homogeneous catalyst can be visualized from the oxidation studies of organic substrates such as carbohydrates,^[13] acid,^[14] alcohols,^[15] widely in acidic medium. This prompted me in present investigation to report the mechanistic behaviour of catalyst, substrate, and reacting species on the rate of reaction.

2. Materials and Methods

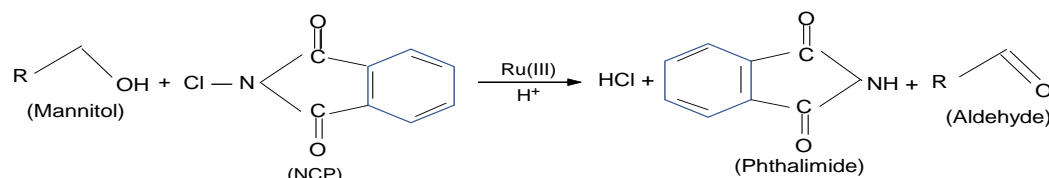
The oxidant NCP (Across) A.G. sample was used in the form of solution in 100% acetic acid (B.D.H.) and its strength was checked iodometrically.^[16] The standard solution of mannitol (Sigma-Aldrich India) was used in doubly distilled water was employed in all kinetic runs. The solution of Ru(III) chloride (Johnsons-Matthay) was prepared in HCl (N/55.55). The solutions of oxidant, substrate and catalyst are kept away from the photochemical effect. Some useful solution of the participating reagents were also freshly prepared and used in standardized form.

Kinetic measurements

All the kinetic study was performed in black painted flask at 303K under pseudo-first order conditions by maintaining large excess of mannitol over oxidant (NCP). The content containing mixture of required volume of solutions of mannitol, and Ru(III) in 20% acetic acid and H⁺ and oxidant NCP in another flask in one vessel were equilibrated at reaction temperature, a requisite quantity of pre-equilibrated (303 K). The standard solutions of NCP was added to this mixture. All the solutions in order to maintain the experimental temperature were kept in a thermostated bath along with reaction mixture. The reaction rate was estimated iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals. Duplicate kinetic runs show indicated that rate constant (k_{obs}) were reproducible to within ± 4%.

4. Stoichiometry and Product analysis

The stoichiometry of the reaction was determined by equilibrating reaction mixture containing 10 to 15 times more [NCP] over [mannitol] and Ru(III) in 20% acetic acid and [H⁺] for a day at 303 K. The unreacted [NCP] measured revealed that one mole of mannitol reacted with one mole of [NCP] for complete oxidation.



where, $\text{R} = \text{CH}_2\text{OH}-(\text{CHOH})_4$ for mannitol.

The mannitaldehyde product was analysed by TLC method and forming its 2,4-DNP derivative and quantitative yield was assigned. The reaction completely rules out the presence of free radicals when solution was tested with acrylamide / BHT.

The effect of [NCP] has been investigated in Ru(III) catalysed reaction, the plot of $\log [\text{NCP}]$ vs. time was found to be linear showing first-order dependence of the reactions rate for NCP as from the slopes of such plots, first-order rate constant (k_{obs}) evaluated.

The rate constant have been studied for the different concentrations of mannitol and plots of $1/k_{\text{obs}}$ vs. $1/[\text{mannitol}]$ was linear intercepting Y-axis with positive slope less than unity (Fig. 1). Thus, showing a fractional-order dependence on rate [mannitol] (Table 1). The dependence of reaction rate on H^+ concentration, primary salt sodium chloride and reductant product of oxidant, phthalimide have been investigated at their different initial concentrations and keeping the concentration of other reactants constant. There was no significant change in rate constant was observed with variation of acid and others kinetic parameters.

Table 1: Variation of [mannitol] on rate

[NCP] = 3.33×10^3 (mol dm⁻³); [H⁺] = 0.20 (mol dm⁻³);
 [Ru(III)] = 2.0×10^5 (mol dm⁻³) = 2.0 (1, 2); CH₃COOH-H₂O = 20%, (v/v);
 Temperature = 303 K

10^2 [mannitol] (mol dm ⁻³)	$10^4 k$ (s ⁻¹)
1.25	0.77
2.00	1.23
2.50	1.56
3.33	1.83
4.00	2.52
5.00	2.95

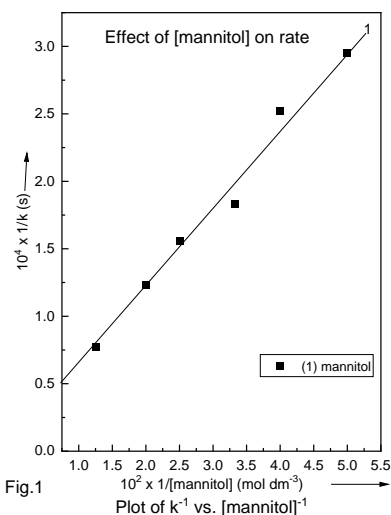


Fig.1

[NCP] = 3.33×10^3 (mol dm⁻³); [H⁺] = 0.20 (mol dm⁻³);
 [Ru(III)] = 2.0×10^5 (mol dm⁻³); CH₃COOH-H₂O = 20%. (v/v);
 Temperature = 303 K

The H^+ indicated fractional-order dependence that obeys $k_{\text{obs}} = a + b [\text{H}^+]$ Benett-Olsen model of [H⁺] ions kinetics. It was also found that ionic strength (μ) of the reaction medium has negligible effect on the reaction rate.

The concentration of Ru(III) was varied while maintaining the concentrations of mannitol and other reagents constant. The plot of $1/k_{\text{obs}}$ vs. $1/\text{Ru(III)}$ shows positive slope less than unity (Fig. 2) indicating fractional-order dependence of rate on [Ru(III)] (Table 2).

Table 2: Dependence of rate on [Ru(III)] catalyst on rate

[mannitol] = 3.33×10^{-2} (mol dm⁻³); [NCP] = 3.33×10^{-3} (mol dm⁻³);
 [H⁺] = 0.20 (mol dm⁻³); CH₃COOH-H₂O = 20%, (v/v); Temperature = 303 K

10^5 [Ru(III)] (mol dm ⁻³)	10^4 k (s ⁻¹)
1.25	1.24
1.50	1.41
2.00	1.83
2.50	2.23
3.33	2.91
5.00	3.85

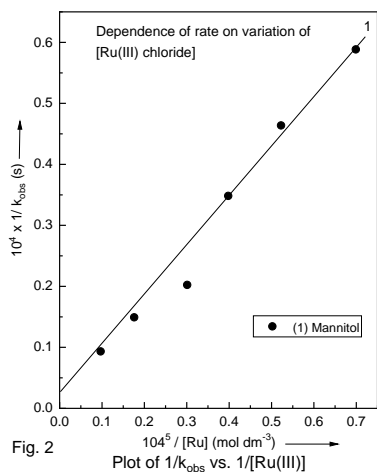


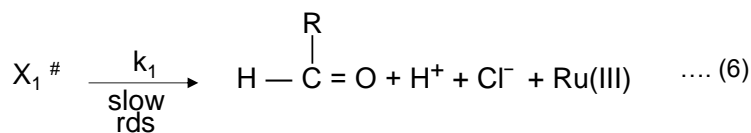
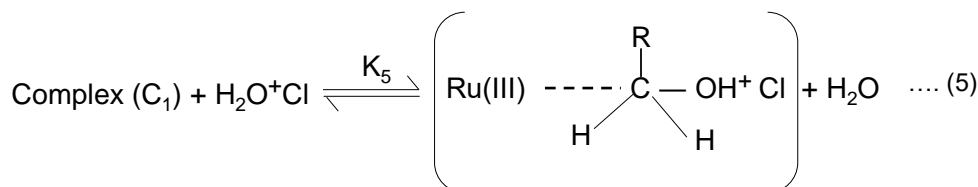
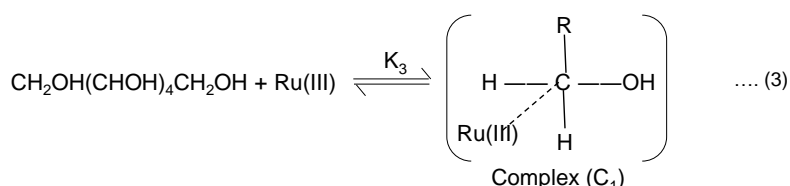
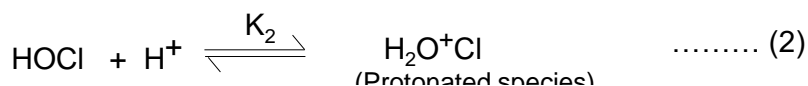
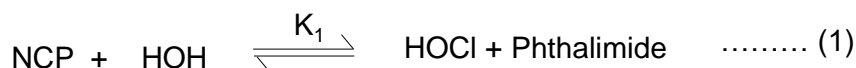
Fig. 2
 [mannitol] = 3.33×10^{-2} (mol dm⁻³); [NCP] = 3.33×10^{-3} (mol dm⁻³);
 [H⁺] = 0.20 (mol dm⁻³); CH₃COOH-H₂O = 20 %, (v/v);
 Temp. = 303 K

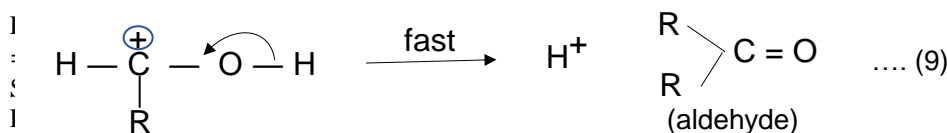
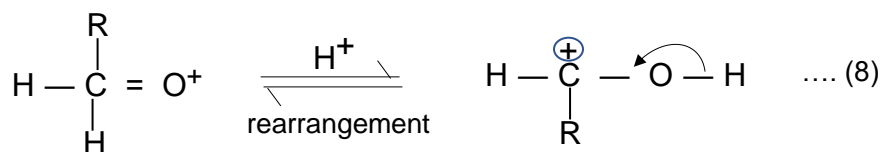
The effect of changing solvent composition (10% to 40%) on the reaction rate was studied. The results suggest that k_{obs} increase with increasing acetic acid constant of the solvent mixture. The plot of $\log k$ vs. $\frac{1}{D}$ was found to be linear with positive slope (Fig. not shown).

HOCl is the reactive oxidizing species because the rate of reaction revealed to be an inverse functions of phthalimide more over H₂O⁺Cl a protonated active species of NCP is probably present under experiment condition.

Mechanism

Reaction path for the Ru(III) catalyzed oxidation of mannitol can be formulated as :





$$\text{Since } [X_1^\ddagger] = \frac{k_1 K_3 K_4 [\text{mannitol}][\text{Ru(III)}][\text{NCP}]}{[\text{phthalimide}]} \quad \dots (13)$$

$$\text{and } [X_2^\ddagger] = \frac{k_2 K_2 K_3 K_4 [\text{mannitol}][\text{Ru(III)}][\text{H}^+][\text{NCP}]}{[\text{phthalimide}]} \quad \dots (14)$$

Applying steady state approximation and substituting the values of $[X_1^\ddagger]$ and $[X_2^\ddagger]$ from equation (13) and equation (14) to equation (12) and on simplification yields the final rate law

$$k_{\text{obs}} = \frac{k_1 K_3 [\text{mannitol}][\text{Ru(III)}](k_1 K_4 + k_2 K_2 K_5 [\text{H}^+])}{[\text{phthalimide}] + K_1 + K_1 K_3 K_4 [\text{mannitol}]x [\text{Ru(III)}]} \quad \dots (15)$$

Equation (15) accounts all the observed kinetic findings of the reactions at low and higher concentrations of the mannitol. The existence of complex was explained by this equation. On adopting certain conditions of the parameters at last also becomes $k_{\text{obs}} = k^1$ (constant).

The negative value of entropy of activation ($-\Delta S^\ddagger = 162.02 \text{ J mol}^{-1} \text{ K}^{-1}$) indicated that complex is more ordered than the reactant at transition state. Other thermodynamic parameters (E_a , ΔH^\ddagger , ΔG^\ddagger) were also determined for the reaction.

Conclusion

The Ru(III) catalysed and N-chlorophthalimide oxidation of mannitol has been studied in aqueous acetic acid medium in presence of HCl. The reaction was sensitized apparently to acidity and followed $k_{\text{obs}} = a + b [\text{H}^+]$ acid dependent and acid independent paths. Consequently, the reacting species of the oxidant NCP, HOCl and $\text{H}_2\text{O}^+\text{Cl}$ were participating in proposed mechanism having stoichiometry (1:1). The study reveals the forming ability of Ru(III) catalyst lead ternary complex with substrate. The first-order dependence [NCP] and fractional-order to mannitol was observed. The derived rate law and other kinetic parameter support the mechanism.

Acknowledgement

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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