



Comparative Study of Kinetics of Catalyzed Oxidation of D (+)galactose and lactose by Ruthenium (III) in Alkaline Medium

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ABSTRACT

Kinetic investigation in Ru(III) catalyzed oxidation of D(+)-galactose and lactose in an alkaline solution of potassium bromate in the presence of mercuric acetate as a scavenger for Br^- ion has been carried out in the temperature range 30-45°C. The rate shows first order dependence with respect to the bromate and zeroth order with respect to the substrate (sugars). The reaction exhibits first order dependence on the catalyst ruthenium(III) and there is inverse order on the rate of reaction. Potassium chloride and acetic acid have a positive effect on the rate. Negligible effect of change in $\text{Hg}(\text{OAc})_2$, ionic strength of the medium and D_2O . $[\text{RuCl}_3(\text{H}_2\text{O})\text{OH}]^-$ and BrO_3^- are the most reactive species Ru(III) chloride and bromated, respectively. Galactonic acid and lactobionic acid have been identified as the main oxidation products of the reaction. Various activation parameters have been calculated and recorded. On the basis of experimental findings, a suitable mechanism consistent with the observed kinetics was proposed and the rate law has been derived on the basis of obtained data.

Key words: Alkaline medium; Kinetics; Oxidation; Potassium bromate; Ru(III) catalyzed; Sugars.

INTRODUCTION

Catalysis by transition metal ions, plays an important role in understanding the mechanistic aspects of a particular redox reaction. Ru(III) acts as an efficient catalyst in many redox reactions, hence the use of ruthenium(III) chloride as homogeneous catalyst in acidic medium. A number of oxidants like potassium bromate¹⁻², N-bromoacetamide³⁻⁵, N-bromosuccinimide^{6,7}, Chloramine-T⁸ and sodium periodate⁹⁻¹⁰ have been earlier used in oxidation of various compounds. The kinetics of redox reactions incorporating certain transition metals ions like Osmium(VIII)¹¹,

ruthenium(VIII)¹², iridium(III)¹³ and palladous ion as homogeneous catalyst has been extremely investigated. However, reactions involving Ru(III)¹⁴⁻¹⁵ have been little investigated and hardly any investigation has so far been reported to explain the catalytic role of ruthenium(III) chloride with potassium bromate as an oxidant in alkaline medium. This prompted us to undertake the present investigation which consists of ruthenium(III) catalyzed oxidation of D(+)-galactose and lactose in nano concentration range by alkaline potassium bromate in the presence of mercuric acetate as a scavenger.

Objectives of the present study are to :

- (i) elucidate a plausible mechanism,
- (ii) identify the oxidation products ,
- (iii) deduce an appropriate rate law,
- (iv) ascertain the various reactive species and
- (v) calculate activation parameters.

EXPERIMENTAL

Material

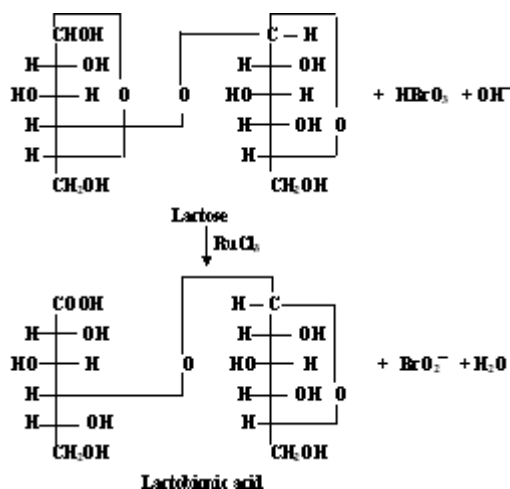
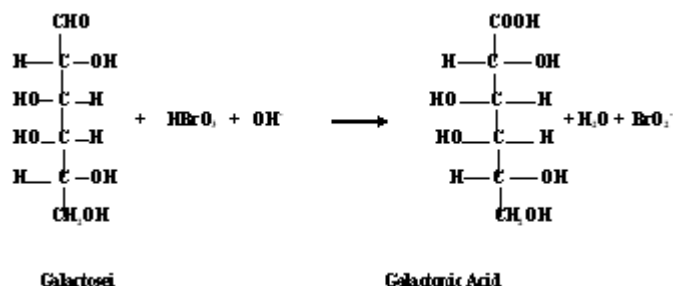
An aqueous solution of D(+)-galactose and lactose (E.Merck), potassium bromate (BDH; AR), NaOH and NaClO₄ (E.Merck) were prepared by dissolving the weighed samples in triply distilled water. NaOH was used as a source of OH⁻ ion. Sodium perchlorate was used to maintain the ionic strength of the medium. A solution of RuCl₃ (Johnson Matthey) was prepared in HCl of known strength. Deuterium oxide (D₂O) (purity 99.4%) was supplied by BARC Mumbai, India. All other reagents were of analytical grade and stills employed were of Jenna glass. Reaction vessels were painted black so as to prevent photochemical decomposition, if any.

Kinetics

A thermostatic water bath was used to maintain the desired temperature within $\pm 0.1^\circ\text{C}$. Requisite volume of reagents, including substrate, was taken in a reaction vessel and thermostated at $35 \pm 0.1^\circ\text{C}$ for thermal equilibrium. A measured volume of oxidant solution, which was also maintained separately at the same temperature, was rapidly poured into the reaction vessel. The kinetics was followed by examining desired portions of reaction mixture for oxidant iodometrically using starch as an indicator after suitable time intervals.

Stoichiometry

The stoichiometry of the reaction was determined by equilibrating varying ratios of [bromate] to sugars at 35°C for 48 hrs under kinetic condition. Estimation of unconsumed bromate revealed that, one mole of the substrate consumes one mole of the oxidant. The oxidation of D(+)-galactose and lactose leads to the formation of galactonic acid and lactobionic acid respectively. The stoichiometric determination indicated the following overall reaction:-



Identification of end product formed in the above reaction i.e. corresponding acid¹⁶ was carried out as follows-

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 of FeCl₃ solution. A reddish brown colour ppt. is obtained, which confirms presence of carboxylic group.

RESULTS AND DISCUSSION

Ruthenium(III) catalyzed oxidation of D(+)-galactose and lactose was investigated at several initial reactant concentrations (Table-1). First order kinetics was observed in case of oxidant, i.e. bromate which was also confirmed by a plot of (-dc/dt) versus [Bromate] (Fig.1). The plot obtained is linear with a slope value of 3.33 for D(+)-galactose and 3.36 for lactose, which is similar to the average k_1 3.46 & 3.48 respectively for D(+)-galactose and lactose values. Zero order dependence on substrate was established by varying the amount of D(+)-galactose and lactose at fixed concentration of all other component. Variations in hydroxide ion show negative effect, which means that the rate of the reaction decreases with increase in [OH⁻] concentration while variation of chloride ion concentration shows positive effect (Table-1). The

reaction was markedly influenced by increase in ruthenium(III) concentration. A plot of log (-dc/dt) versus log [Ru(III)] (Fig. 2) gives a slope 1.16 at 35°C for D(+)-galactose and 0.923 at 35°C for lactose which further confirms first order dependence on Ru(III).

Kinetics results (Table-1) show negligible effect of ionic strength of the medium (affected by addition of NaClO₄) and addition of Hg(OAc)₂. The rate measurements were taken at 30^o- 45^o C 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 in Table-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 scavenger¹⁷⁻¹⁹ for any bromide ion formed in the reaction.

Ru(III) chloride has been reported to give a number of possible chloro species dependent on pH of the solution, Ru(III) exists in the following equilibrium under the experimental pH range 10 – 12²⁰. Our experimental data indicate that addition of chloride ion has a positive effect on the reaction velocity.

Table 1.1: Effect of variation of substrate and oxidant on the reaction rates for sugars at 35° C

[Substrate] x 10 ² M	[KBrO ₃] x 10 ³ M	[KCl] x 10 ³ M	[NaOH] x 10 ³ M	[Hg(OAc) ₂] x 10 ³ M	(-dc/dt) x 10 ⁷ ML ⁻¹ s ⁻¹	
					D(+)-galac.	Lactose
0.33	1.00	1.00	1.00	1.25	3.57	3.80
0.40	1.00	1.00	1.00	1.25	3.30	3.75
0.50	1.00	1.00	1.00	1.25	3.40	3.71
0.66	1.00	1.00	1.00	1.25	3.75	3.60
1.00	1.00	1.00	1.00	1.25	3.69	3.60
2.00	1.00	1.00	1.00	1.25	3.48	3.60
1.00	0.83	1.00	1.00	1.25	2.77	2.75
1.00	1.00	1.00	1.00	1.25	3.69	3.60
1.00	1.25	1.00	1.00	1.25	4.40	4.50
1.00	1.66	1.00	1.00	1.25	6.00	5.50
1.00	2.50	1.00	1.00	1.25	8.00	8.57
1.00	3.33	1.00	1.00	1.25	11.42	12.00

[Ru(III)] = 0.096 x 10⁻⁹ M (D(+)-galactose) & 0.0288 x 10⁻⁹ M (lactose).

Table 1.2: Effect of variation of reactants on the reaction rates for sugars at 35° C

[KCl] x 10 ³ M	[NaOH] x 10 ³ M	[Hg(OAc) ₂] x 10 ³ M	[NaClO ₄] x 10 ³ M	(-dc/dt) x 10 ⁷ ML ⁻¹ s ⁻¹ D(+)-galac. Lactose
1.00	1.00	1.25	-	3.57 3.80
1.00	1.00	1.25	-	3.30 3.75
1.00	1.00	1.25	-	3.40 3.71
1.00	1.00	1.25	-	3.75 3.60
1.00	1.00	1.25	-	3.69 3.60
1.00	1.00	1.25	-	3.48 3.60
0.83	1.00	1.25	-	2.84 3.45
1.00	1.00	1.25	-	3.69 3.60
1.25	1.00	1.25	-	3.85 3.71
1.67	1.00	1.25	-	4.00 4.33
2.50	1.00	1.25	-	4.50 4.66
5.00	1.00	1.25	-	4.63 5.00
1.00	0.83	1.25	-	4.15 4.20
1.00	1.00	1.25	-	3.69 3.60
1.00	1.25	1.25	-	3.40 3.50
1.00	1.67	1.25	-	2.85 3.40
1.00	2.50	1.25	-	2.76 3.27
1.00	5.00	1.25	-	2.60 2.92
1.00	1.00	0.83	-	3.50 3.23
1.00	1.00	1.00	-	3.25 3.83
1.00	1.00	1.25	-	3.69 3.60
1.00	1.00	1.67	-	3.70 4.00
1.00	1.00	2.50	-	3.13 3.45
1.00	1.00	5.00	-	3.69 3.60
1.00	1.00	1.25	0.83	3.72 3.70
1.00	1.00	1.25	1.00	3.50 3.63
1.00	1.00	1.25	1.25	3.47 3.75
1.00	1.00	1.25	1.67	3.66 3.55
1.00	1.00	1.25	2.50	3.80 3.60
1.00	1.00	1.25	5.00	3.75 3.68

[KBrO₃] = 1.00 x 10⁻³ M,[Substrate] = 1.00 x 10⁻³ M[Ru(III)] = 0.096 x 10⁻⁹ M (for D(+)-galactose) & 0.0288 x 10⁻⁹ (for lactose).**Table 2: Activation parameters for alkaline bromate oxidation of D(+)-galactose and Lactose**

Substrate	Temperature coefficient	ΔE_a kJ mol ⁻¹	ΔH^* kJ mol ⁻¹	ΔS^* JK mol ⁻¹	ΔG^* kJ mol ⁻¹	Log A	k_r mol ⁻² lit ² sec ⁻¹
D(+) galactose	2.03	57.66	72.70	-15.26	77.40	9.66	0.84
lactose	1.99	54.66	69.92	-15.10	74.57	9.70	2.92

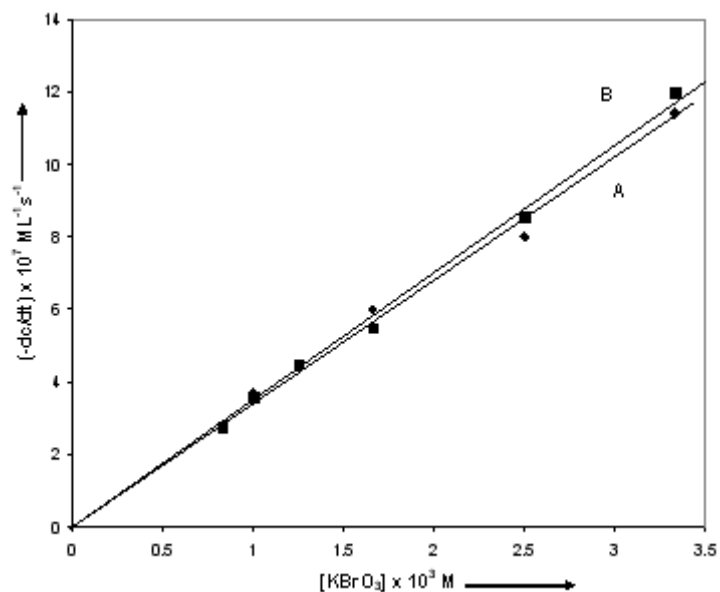


Fig. 1. Plot between $[KBrO_3] \times 10^{-3} \text{ M}$ vs. $(-dc/dt) \times 10^{-7} \text{ ML}^{-1} \text{ s}^{-1}$ for oxidation of D(+)-galactose (A) and lactose (B) at 35° C

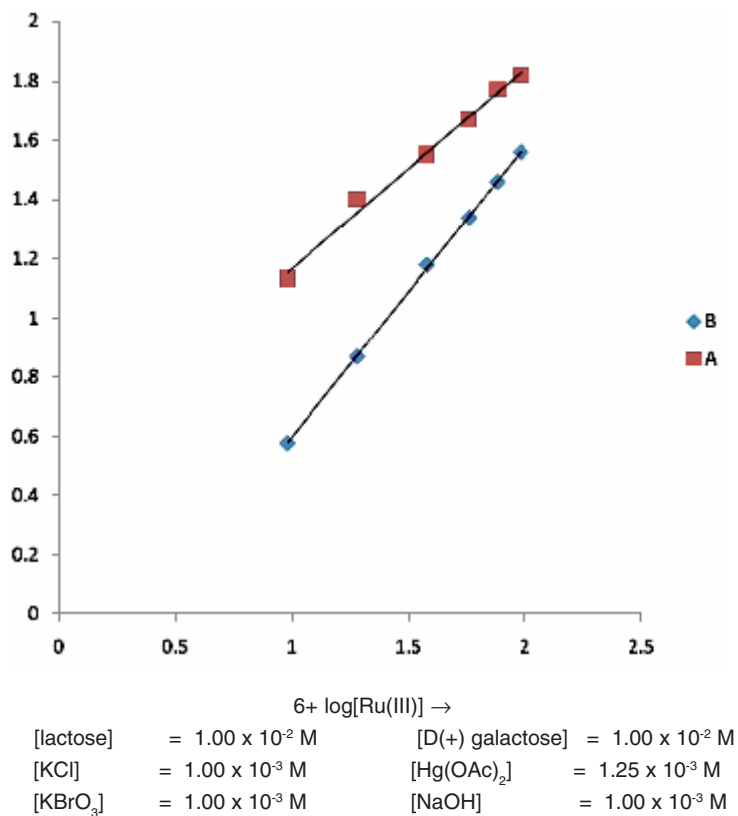


Fig. 2. Plot between $6 + \log [Ru(III)]$ vs. $8 + \log (-dc/dt)$ for oxidation of D(+)-galactose (A) and lactose (B) at 35° C

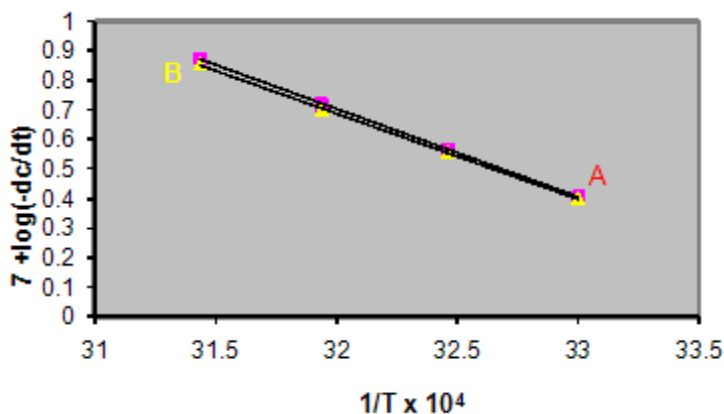
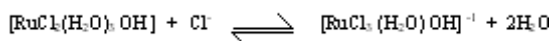
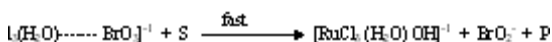
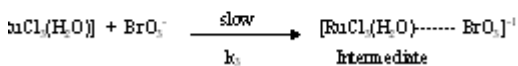
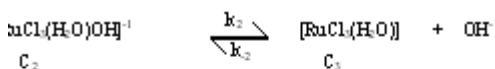
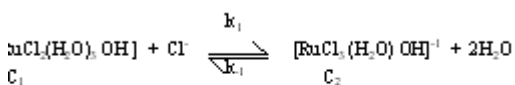


Fig. 3: Plot between $7 + \log(-dc/dt)$ vs. $1/T \times 10^4 \text{ K}^{-1}$ for oxidation of galactose (A) and lactose (B) at 35°C



In alkaline solution of potassium bromate quick formation of BrO_3^- ion has been reported. The above statements lead us to suggest the following reaction scheme, which gives the details of various steps in the reaction.



where

S = substrate

P = corresponding acid products

Considering the above slow steps and applying steady state treatment with a reasonable approximation, the rate law for D(+)-galactose and lactose may be written in terms of consumption of $[\text{BrO}_3^-]$ as equation:-

$$\frac{-d[\text{BrO}_3^-]}{dt} = k_3 [\text{C}_3] [\text{BrO}_3^-]$$

$$\frac{-d[\text{BrO}_3^-]}{dt} = \frac{K_1 K_2 k_3 [\text{Cl}^-] [\text{Ru(III)}]_T [\text{BrO}_3^-]}{[\text{OH}^-] + K_1 [\text{Cl}^-] [\text{OH}^-] + K_1 K_2 [\text{Cl}^-]}$$

where $K_1 = (k_1/k_{-1})$ and $K_2 = (k_2/k_{-2})$

The rate law is in agreement with all observed kinetics. The proposed mechanism is in consistent with the activation parameters given in table-2. The high positive values of change in free energy of activation (ΔG^*) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation (ΔS^*) suggest the formation of an activated complex with reduction in the degree of freedom of molecules.

CONCLUSIONS

The experimental results as shown reveals that the reaction rate doubles when the concentration of the catalyst $[\text{Ru(III)}]$ is doubled. The rate law is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength. From this investigation, it is concluded that BrO_3^- and $[\text{RuCl}_3(\text{H}_2\text{O})_2\text{OH}]^{-1}$ are the reactive species of KBrO_3 and Ru(III) chloride respectively in alkaline medium.

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