

A kinetic study of Ru^{III} catalyzed oxidation of maltose by potassium bromate in alkaline medium

Sheila Srivastava*, Ashish Kumar and Parul Srivastava

Chemical Laboratories, Feroze Gandhi College, Raebareli-229 001, Uttar Pradesh, India

E-mail : she_ila72@yahoo.com

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Abstract : Kinetic investigations in ruthenium(III) catalyzed oxidation of maltose in an alkaline solution of KBrO₃ have been carried out in the temperature range of 30–45 °C. Mercuric acetate is used in the reaction mixture as a scavenger for Br[–] ion to prevent parallel oxidation by bromine. The reaction exhibits first order kinetics. The order of reaction with respect to substrate and catalyst is zero and one respectively. The rate decreases with increasing concentrations of Cl[–] and OH[–] respectively exhibiting negligible effect of mercuric acetate, ionic strength and D₂O. A suitable mechanism in conformity with the kinetic observations has been proposed.

The various thermodynamic parameters were calculated from the rate measurements at 30, 35, 40 and 45 °C respectively.

Keywords : Ruthenium(III) catalysis, maltose, potassium bromate, kinetic study.

Potassium bromate has been used to oxidize various compounds in acidic medium^{1–4}. The utility of Ru^{III} chloride as a non-toxic and homogeneous catalyst has been reported^{6,7}, but scant attention has been paid to explore the catalytic role of ruthenium(III) chloride with potassium bromate as an oxidant in alkaline medium. This fact prompted us to study "The kinetics and mechanism of Ru^{III} catalyzed oxidation of maltose by bromate in alkaline medium and mercuric acetate as a scavenger".

of these respective samples in triply distilled water. NaOH (S.D. fine) was used as a source of OH[–] ions. Ruthenium(III) chloride (Johnson Matthey) solution was prepared by dissolving the sample in HCl of known strength. The reaction stills were painted black so as to prevent photochemical effects, if any.

Table 1. Stoichiometric results

Reactants, mol dm ^{–3} ; NaOH, 1.00; Hg(OAc) ₂ , 1.25; KCl, 1.00; Ru ^{III} , 0.57.6			
[KBrO ₃] × 10 ³ mol dm ^{–3}	[Maltose] × 10 ³ mol dm ^{–3}	[KBrO ₃] [*] × 10 ³ mol dm ^{–3} after 48 h	[KBrO ₃] – [KBrO ₃] [*] [Maltose]
5.00	1.00	3.94	1.06
5.00	2.00	3.08	0.96
5.00	2.50	2.36	1.05
5.00	3.33	1.72	0.98
5.00	4.00	0.96	1.01
10.00	1.00	8.84	1.16
8.00	1.00	7.04	0.96
4.00	1.00	3.10	0.90
3.33	1.00	2.48	0.85
2.50	1.00	1.56	0.94

Experimental

Materials : Aqueous solution of maltose (E. Merck), potassium bromate (B.D.H., A.R.), NaClO₄ and Hg(OAc)₂ (E. Merck), were prepared by dissolving the weighed amount

Table 2. Effect of variation of reactants on the reaction

Reactants, mol dm^{–3}; NaOH, 1.0; Hg(OAc)₂, 1.25; KCl, 1.0; Ru^{III}, 0.057

[Bromate] × 10 ³ mol dm ^{–3}	[Substrate] × 10 ² mol dm ^{–3}	$k \times 10^7$ mol dm ^{–3} s ^{–1}	At 35 °C $k_1 \times 10^4$ s ^{–1}	At 45 °C $k_1 \times 10^4$ s ^{–1}
		35 °C	45 °C	
0.80	2.00	3.20	6.08	4.00
1.00	2.00	4.00	7.84	4.00
1.25	2.00	5.04	9.92	4.03
1.67	2.00	6.74	12.98	4.03
2.50	2.00	9.92	18.42	3.96
3.35	2.00	12.86	25.06	3.83
1.00	0.80	4.15	–	–
1.00	1.00	4.24	–	–
1.00	1.25	4.00	–	–
1.00	1.67	4.08	–	–
1.00	2.50	3.96	–	–
1.00	3.35	3.98	–	–

Table 3. Effect of variation of OH⁻ ion, Cl⁻ ion, mercury(II) acetate and sodium perchlorate at 35 °C

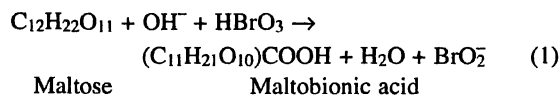
Reactants, mol dm ⁻³ ; KBrO ₃ , 1.00; Ru ^{III} , 0.0576; maltose, 20.00				
[KCl] × 10 ³ mol dm ⁻³	[NaOH] × 10 ³ mol dm ⁻³	[NaClO ₄] × 10 ³ mol dm ⁻³	[Hg(OAc) ₂] × 10 ³ mol dm ⁻³	<i>k</i> × 10 ⁷ mol dm ⁻³ s ⁻¹
1.00	0.80	—	1.25	4.13
1.00	1.00	—	1.25	4.00
1.00	1.25	—	1.25	3.87
1.00	1.67	—	1.25	3.70
1.00	2.50	—	1.25	3.45
1.00	5.00	—	1.25	2.94
0.80	1.00	—	1.25	5.00
1.00	1.00	—	1.25	4.60
1.25	1.00	—	1.25	4.26
1.67	1.00	—	1.25	3.94
2.50	1.00	—	1.25	3.60
5.00	1.00	—	1.25	3.38
1.00	1.00	0.80	1.25	3.95
1.00	1.00	1.00	1.25	4.00
1.00	1.00	1.25	1.25	3.98
1.00	1.00	1.67	1.25	4.12
1.00	1.00	2.50	1.25	4.06
1.00	1.00	5.00	1.25	3.95
1.00	1.00	—	0.80	4.16
1.00	1.00	—	1.00	4.00
1.00	1.00	—	1.25	3.83
1.00	1.00	—	1.67	3.95
1.00	1.00	—	2.50	4.14
1.00	1.00	—	5.00	3.82

Kinetics : A thermostated water-bath was used to maintain the desired temperature to within $\pm 0.1^\circ\text{C}$. Reagents of requisite concentration initially including substrate, were taken in a reaction vessel and then the latter were thermostated at $35 \pm 0.1^\circ\text{C}$ to attain thermal equilibrium. A measured volume of KBrO_3 solution, also maintained at the

same temperature, was rapidly taken out and then poured into the reaction vessel. The kinetics were followed by estimating KBrO_3 iodometrically at different time intervals using starch as an indicator.

Results and discussion

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing excess of bromate over maltose in varying ratios at 50 °C for 48 h and estimation of residual potassium bromate in different sets showed that one mole of maltose consumed one mole of oxidant (Table 1). The product analysis by conventional method⁸ shows the formation of an acid after the reaction. The over all reaction may be represented as in eq. (1),



The negligible effect of $\text{Hg}(\text{OAc})_2$ indicates its role as a scavenger^{9,10}, for any bromide ion formed in the reaction; it thus helps to eliminate the parallel oxidation by bromine likely to be formed due to interaction of Br^- and bromate ion.

Ruthenium(III) chloride has been reported^{5-7,11} to give a number of possible aquo chloro species governed by pH of the solution. The reactive species of ruthenium(III) chloride in alkaline medium has been proposed $[\text{RuCl}_2(\text{H}_2\text{O})_3]^{+1,11}$ which is supported fully by the negative effect of $[\text{Cl}^-]$ and $[\text{OH}^-]$. The following reaction steps are suggested on the basis of above discussion for oxidation of maltose by bromate in presence of ruthenium(III) chloride as a catalyst in alkaline medium.

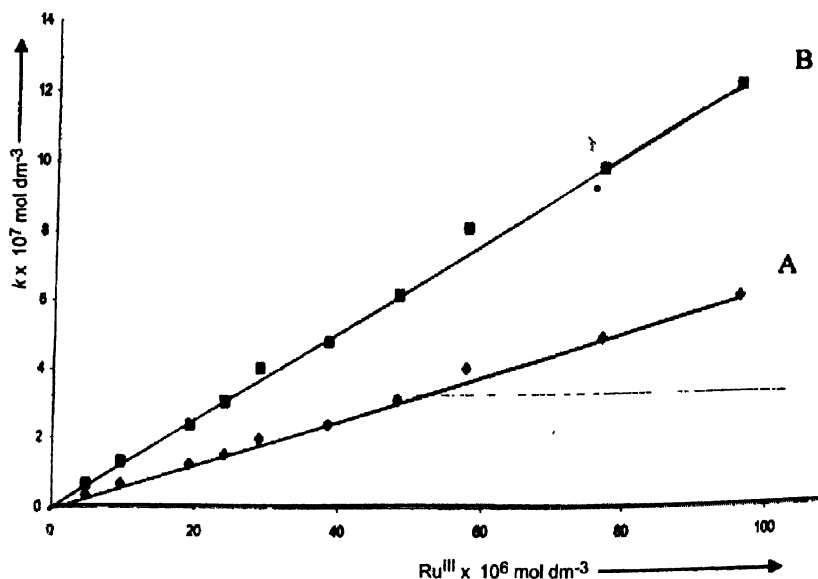


Fig. 1. Plot of $[\text{Ru}^{\text{III}}]$ vs k : (A) 35 °C, (B) 45 °C.

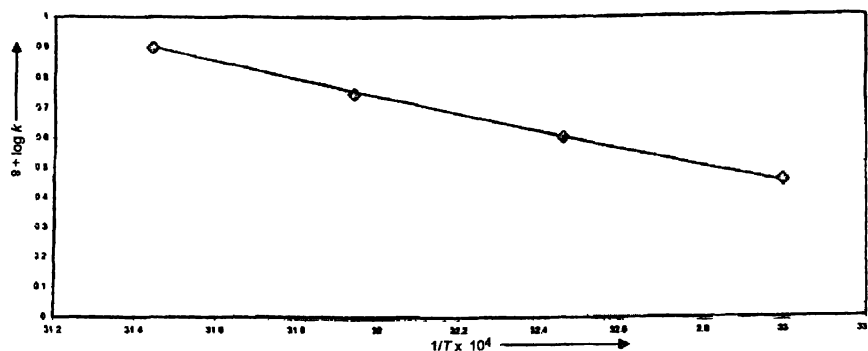
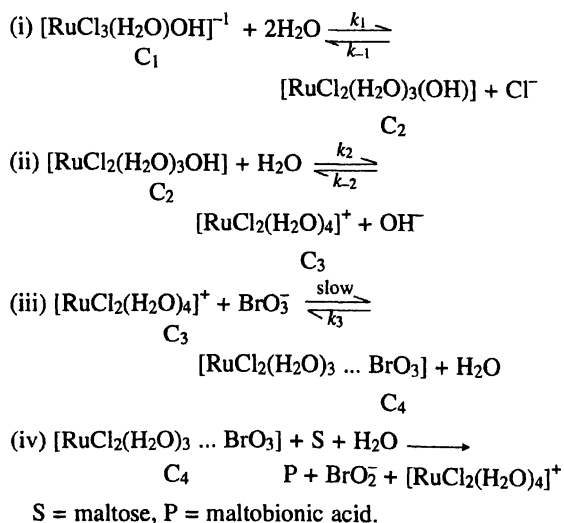


Fig. 2. Plot of log k vs $1/T$.



Considering the above steps and applying the steady state treatment with reasonable approximation, the rate law may be written in terms of consumption of $[BrO_3^-]$ as equation.

$$\frac{-d[BrO_3^-]}{dt} = k_3 [C_3][BrO_3^-]$$

$$\text{or } \frac{-d[BrO_3^-]}{dt} = \frac{k_1 k_2 k_3 [Ru^{III}]_T [BrO_3^-]}{k_{-2} [OH^-] (k_1 + k_{-1} [Cl^-]) + k_{-1} k_2}$$

where $[Ru^{III}]_T = [C_1] + [C_2] + [C_3]$

The kinetic results collected at several concentrations (Table 2) show that the reaction exhibits first order kinetics with respect to $KBrO_3$ which is also evident from k versus $[KBrO_3]$ plot (Fig. 1).

The insignificant effect of an increase in substrate (maltose) concentration on the reaction rate indicated zero order with respect to maltose. First order dependence on Ru^{III} is evident from close resemblance between the slope values (4.2 and 8.0 at 35 and 45 °C for maltose) of k vs Ru^{III} plot (Fig. 2) and average k_1 values (4.00 and 7.84 at 35 and 45 °C respectively).

Negligible effect of variation of ionic strength of the medium and $Hg(OAc)_2$ variation on the reaction rate are clear from the kinetic data in Table 3.

Kinetic result obtained on varying the concentration of chloride ion and OH^- ion indicates negative effect, which means that the rate constant decreases with increase in $[Cl^-]$ and $[OH^-]$.

The rate measurements were taken at 30–45 °C and specific rate constants were used to draw a plot of log k versus $1/T$ (Fig. 2) which was linear. The values of energy of activation (ΔE^*), Arrhenius factor (A), entropy of activation (ΔS^*), and free energy of activation (ΔG^*) were calculated from the rate measurements at 30, 35, 40 and 45 °C and these value have been recorded in Table 4.

Table 4. Activation parameters for alkaline bromate oxidation of maltose

Temp. °C	30	35	40	45
$10^7 k, \text{mol dm}^{-3} \text{s}^{-1}$	2.86	4.00	5.58	7.92
$\Delta E^* = 56 \text{ kJ mol}^{-1}, \Delta H^* = 69 \text{ kJ mol}^{-1}, \Delta S^* = 58 \text{ kJ mol}^{-1}$				

Conclusion

The experimental results as shown reveals that the rate doubles when the concentration of the catalyst $[Ru^{III}]$ is doubled. The rate law is in conformity with all kinetic observations and the proposed mechanistic steps are supported by negligible effect of ionic strength. From this investigation it is concluded that $[RuCl_2(H_2O)_4]^+$ is the reactive species of ruthenium(III) chloride in alkaline medium.

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