



Pelagia Research Library
Der Chemica Sinica, 2010, 1 (1): 13-19



Kinetics and mechanism of oxidation of D-mannitol by potassium bromate in aqueous acidic medium

Sheila Srivastava* and Parul Srivastava

Chemical Laboratories, Feroze Gandhi College, Raebareli, U.P., India

ABSTRACT

Kinetic investigation in Rh(III) catalyzed oxidation of D-Mannitol in an acidified solution of potassium bromate in the presence of Hg(OAc)₂ as a scavenger, have been studied in the temperature range of 30⁰ - 45⁰ C. Increase in concentration of oxidant and H⁺ ion showed fractional positive order and fractional inverse order respectively. The influence of Hg(OAc)₂, ionic strength and Cl⁻ ion on the rate was found to be insignificant. First order kinetics was observed in case of catalyst Rh(III), Rh⁺³ being its reactive species. The order of reaction w.r.t. substrate is zero. The various thermodynamic parameters were calculated from rate measurements at 30, 35, 40 and 45⁰ C respectively. A suitable mechanism in conformity with the kinetic observations has been proposed and the rate law is derived on the basis of obtained data.

Keywords: Kinetics, Oxidation, Potassium bromate, Mannitol, acidic, catalysis, rhodium (III).

INTRODUCTION

Mannitol is found in abundance in nature, particularly in exudates from trees, and in marine algae and fresh mushrooms. It is an isomer of sorbitol and is typically produced today by the hydrogenation of specialty glucose syrups. Mannitol is commercially available in variety of powder and granular forms. In the United States, mannitol is provided by a number of manufacturers, including Cargill, Roquette America, and SPI Polyols. Mannitol is nonhygroscopic (does not pick up moisture). For this reason, it is often used as a dusting powder for chewing gum to prevent the gum from sticking to manufacturing equipment and wrappers. Due to its high melting point (165-169°C), mannitol is also used in chocolate-flavored coating agents for ice cream and confections. It has a pleasant taste, is very stable to moisture pickup and does not discolor at high temperatures, which makes mannitol ideal for use in pharmaceuticals and nutritional tablets.

Potassium bromate has been used to oxidize various compounds in both acidic and alkaline medium [1-6]. Little attention has been paid however, to the reactivity of KBrO_3 in the presence of catalyst [7,8] and nearly no investigation has so far been reported on the catalytic role of rhodium(III) chloride with potassium bromate as an oxidant in acidic medium. This fact prompted us to undertake the present investigation namely, "Acid bromate oxidation of D-Mannitol by acidified KBrO_3 in the presence of Rh(III) chloride as a catalyst and mercuric acetate as a scavenger for bromide ion".

MATERIALS AND METHODS

An aqueous solution of D-Mannitol (E.Merck), potassium bromate (BDH, AR), NaClO_4 and $\text{Hg}(\text{OAc})_2$ (E.Merck) were prepared by dissolving the weighed samples in triple distilled water. Perchloric acid (60%, S. D. Fine) was used as a source of H^+ ion. A solution of RhCl_3 (Sigma Chemical Company) was prepared in HCl of known strength. Deuterium oxide (purity 99.4%) was supplied by BARC (Bombay, India). All other reagents were of analytical grade were available. Sodium perchlorate was used to maintain the ionic strength of the medium. Reaction vessels were painted black so as to prevent photochemical decomposition, if any.

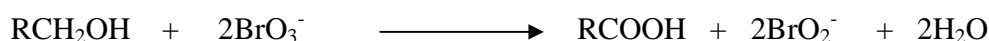
Kinetic Measurements

The requisite volumes of all reagents, including substrate, were thermostated at 35 ± 0.1 °C to attain equilibrium. A measured volume of KBrO_3 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 KBrO_3 , iodometrically using starch as an indicator, after suitable time intervals.

RESULTS

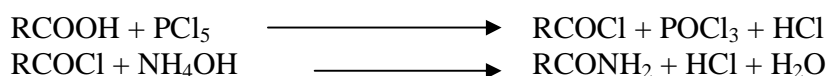
Stoichiometry and product analysis

The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of potassium bromate over D-Mannitol (in varying ratio) at 50° C for 48 hrs. Estimation of residual bromate in different reactions showed that one mole of D-Mannitol consumes two moles of bromate, according to the following stoichiometric equation is represented as follows (1):-



where $\text{R} = \text{CH}_2\text{OH}(\text{CHOH})_n$ for D-Mannitol ($n=4$) whose oxidation product is mannonic acid was detected by measuring the melting point of its amide derivative as follows [9]

Kept the reaction mixture for 48 hours under kinetic conditions and then added PCl_5 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.



Melting point for amide derivative of mannonic acid i.e mannonamide was found to be 110⁰C as against the actual M.P of 109⁰C.

Effect of varying reactant concentrations on the rate

The insignificant effect of an increase in substrate concentration on the reaction rate indicated zero order. It was observed that the value of k_1 (i.e. $-dc/dt / [\text{KBrO}_3]$) were constant at all initial concentrations of KBrO_3 , showing first order dependence on $[\text{KBrO}_3]$ (fig.1). First order dependence on $[\text{Rh(III)}]$ is evident from the close resemblance between the slopes (D- mannitol at 35⁰ C) of $(-dc/dt)$ vs $[\text{Rh(III)}]$ plots (fig.1) and the average values of experimental k_1 value (D- mannitol at 35⁰ C).

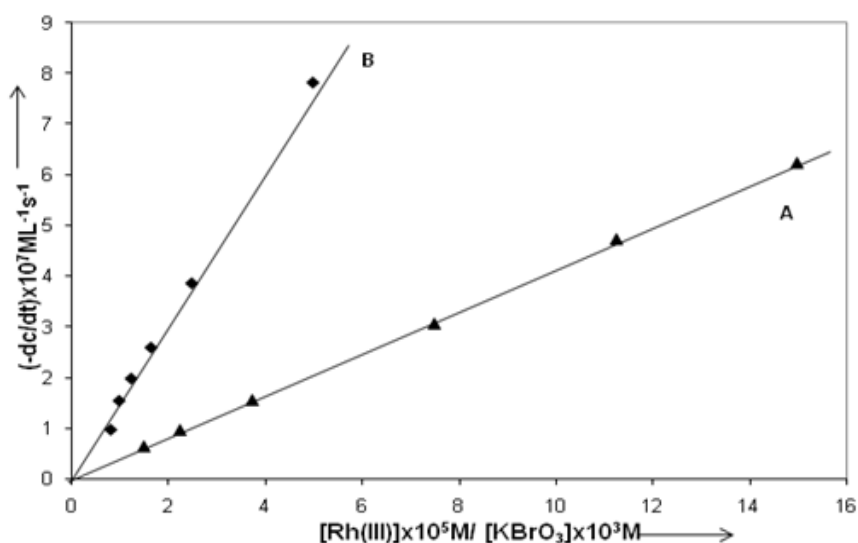


Fig.1 : Plot between $[\text{Rh(III)}] \times 10^5 \text{ mol dm}^{-3} / [\text{KBrO}_3] \times 10^3 \text{ mol dm}^{-3}$ vs. $(-dc/dt) \times 10^7 \text{ mol dm}^{-3} \text{ s}^{-1}$ for oxidation of Glycerol (G') / (G) and D-Mannitol (M') / (M) respectively at 35⁰ C

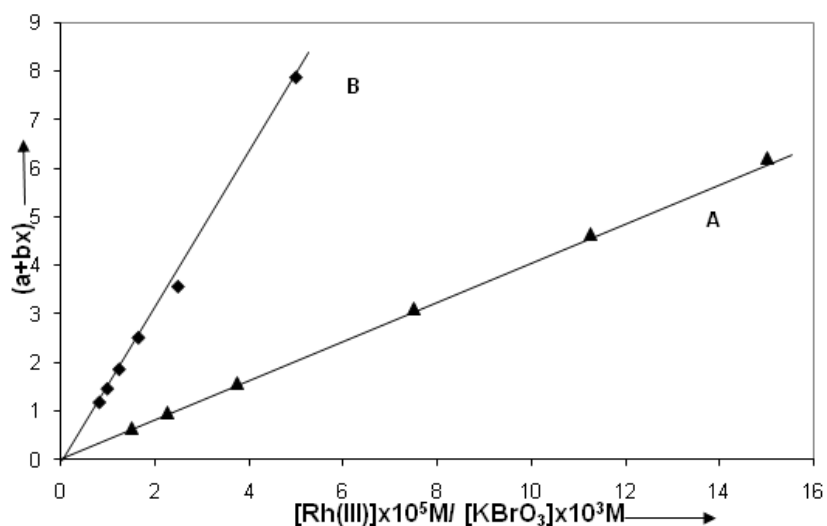


Fig. 2: Plot between $[\text{Rh(III)}] \times 10^5 \text{ mol dm}^{-3} / [\text{KBrO}_3] \times 10^3 \text{ mol dm}^{-3}$ vs. $(a+bx)$ for oxidation of Glycerol (G') / (G) and D-Mannitol (M') / (M) respectively at 35⁰ C

The first order kinetics of $[\text{KBrO}_3]$ and $[\text{Rh(III)}]$ have also been confirmed by 'least square method' (fig.2).

3. Effect of varying concentration of HCl on the rate

At constant $[\text{KBrO}_3]$, $[\text{Substrate}]$, $[\text{Ru(III)}]$, ionic strength and temperature, the rate of reaction did not affect the rate of reaction $[\text{H}^+]$, Table-1. The negligible effect of mercuric acetate excludes the possibility of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without bromate. Hence the role of mercuric acetate here acts as a scavenger [10-12] for any bromide ion formed in the reaction and it helps to the parallel oxidation by Br_2 which would have been formed as a result of interaction between Br^- ion and BrO_3^- ion.

4. Effect of added $[\text{Cl}^-]$ on the rate

The addition of $[\text{Cl}^-]$ in the form of NaClO_4 , keeping $[\text{H}^+]$ constant did not affect the rate of reaction (Table-1).

5. Effect of varying $[\text{Ru(III)}]$ on the rate

The rate measurements were taken at $30^\circ - 45^\circ\text{C}$ and specific rate constants were used to draw a plot of $\log k$ vs $1/T$, which was linear (fig.3).

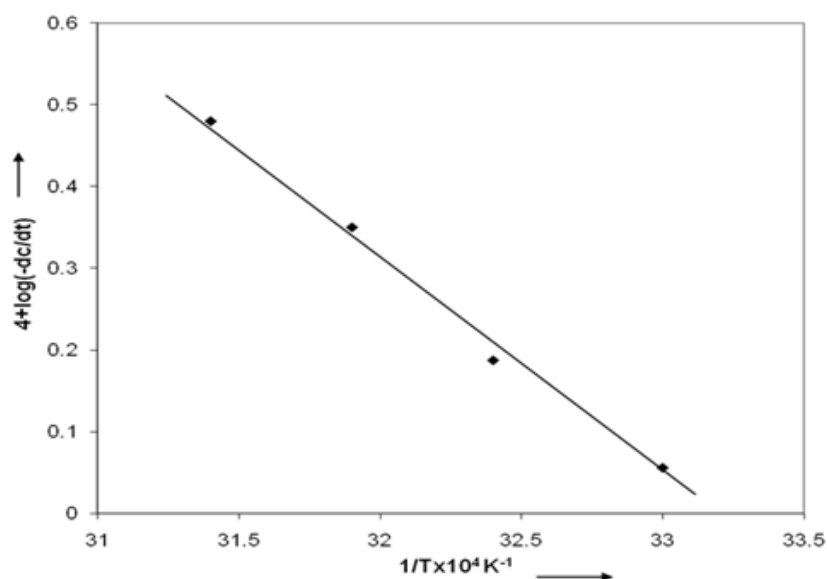
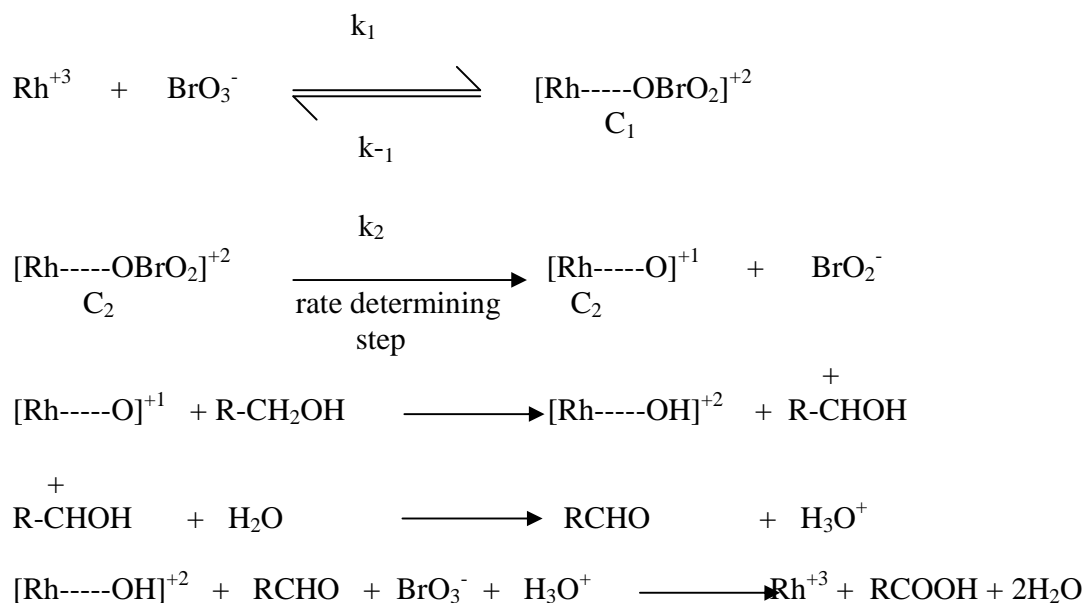


Fig.3: Plot between $7 + \log k$ vs. $1/T \times 10^4 \text{ K}^{-1}$ for oxidation Glycerol (G) and D-Mannitol (M) respectively at 35°C

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 values have been recorded in Table-2.

The reactive species of potassium bromate and Rhodium(III) chloride are HBrO_3 and Rh^{+3} in acidic medium respectively. In acidic solution of KBrO_3 , quick formation of HBrO_3 has been reported. [13]

The above statements lead us to suggest the following reaction scheme which gives us the details of various steps in the title reaction:-



where R = CH₂OH(CHOH)_n for mannitol (n=4).

Now considering the above slow steps and applying steady state treatment with a reasonable approximation, the rate law may be written in terms of consumption of [BrO₃⁻] as equation:-

$$-\frac{d[\text{BrO}_3^-]}{dt} = K_1 k_2 [\text{BrO}_3^-] [\text{Rh}^{+3}]$$

where $K_1 = k_1 / k_{-1}$

The rate law is in agreement with all observed

Table-1: Effect of Variation of Reactants on the Reaction Rates at 35^o C
[Rh(III)] = 3.75 x 10⁻⁵ mol dm⁻³ (D- Mannitol), [KBrO₃] = 1.00 x 10⁻³ mol dm⁻³

[Substrate] x 10 ² mol dm ⁻³	[KCl] x 10 ³ mol dm ⁻³	[HClO ₄] x 10 ³ mol dm ⁻³	[Hg(OAc) ₂] x 10 ³ mol dm ⁻³	[NaClO ₄] x 10 ³ mol dm ⁻³	(-dc/dt) x 10 ⁷ mol dm ⁻³ s ⁻¹ D- Mannitol
0.33	1.00	1.00	1.25	-	1.42
0.40	1.00	1.00	1.25	-	1.26
0.50	1.00	1.00	1.25	-	1.86
0.66	1.00	1.00	1.25	-	1.60
1.00	1.00	1.00	1.25	-	1.30
2.00	1.00	1.00	1.25	-	1.20
1.00	0.83	1.00	1.25	-	1.35
1.00	1.00	1.00	1.25	-	1.20
1.00	1.25	1.00	1.25	-	1.26
1.00	1.67	1.00	1.25	-	1.38
1.00	2.50	1.00	1.25	-	1.48

1.00	5.00	1.00	1.25	-	1.20
1.00	1.00	0.83	1.25	-	1.10
1.00	1.00	1.00	1.25	-	1.20
1.00	1.00	1.25	1.25	-	1.32
1.00	1.00	1.67	1.25	-	1.28
1.00	1.00	2.50	1.25	-	1.39
1.00	1.00	5.00	1.25	-	1.60
1.00	1.00	1.00	0.83	-	1.25
1.00	1.00	1.00	1.00	-	1.28
1.00	1.00	1.00	1.25	-	1.20
1.00	1.00	1.00	1.67	-	1.36
1.00	1.00	1.00	2.50	-	1.42
1.00	1.00	1.00	5.00	-	1.39
1.00	1.00	1.00	1.25	0.83	1.64
1.00	1.00	1.00	1.25	1.00	1.20
1.00	1.00	1.00	1.25	1.25	1.46
1.00	1.00	1.00	1.25	1.67	1.54
1.00	1.00	1.00	1.25	2.50	1.32
1.00	1.00	1.00	1.25	5.00	1.42

Table-2 : Activation parameters for acidic bromate oxidation of D-Mannitol

Parameters	Temp. / °C	D-Mannitol
$k, \times 10^4 s^{-1}$	30	0.86
$k, \times 10^4 s^{-1}$	35	1.20
$k, \times 10^4 s^{-1}$	40	1.78
$k, \times 10^4 s^{-1}$	45	2.46
log A	-	10.36
? $E^*(kJ mol^{-1})$	-	54.57
? $G^*(kJ mol^{-1})$	-	70.32
? $H^*(kJ mol^{-1})$	-	37.72
? $S^*(JK^{-1} mol^{-1})$	-	-12.02

CONCLUSION

The experimental results as shown reveal that the reaction rate doubles when the concentration of the catalyst [Rh(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 which indicates the involvement of an ion in a slow and rate-determining step. 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 degree of freedom of molecules. Positive effect of acetic acid signifies a negative dielectric effect. From this investigation, it is concluded that $HBrO_3$ and Rh^{+3} are the reactive species of $KBrO_3$ and Rh(III) chloride respectively in acidic medium.

REFERENCES

- [1] Sh. Srivastava, R.K. Sharma; *Oxidation Communication*, **2006**, 2, 343-349.
 [2] Sheila Srivastava and Sarika Singh; *J. Indian Chem. Soc.*, **2004**, 18, 295.

-
- [3] Sheila Srivastava, Ashish Kumar and Parul Srivastava; *J. Indian Chem. Soc.*, **2006**, 83, 347-350.
- [4] Sheila Srivastava, Rajendra Kumar Sharma and Sarika Singh; *J. Indian Chem. Soc.*, **2006**, 83, 282-287.
- [5] Ashish Singh , Surya Singh , Ashok Singh , Bharat Singh ; *Trans. Metal Chem.* , **2005**, 30(5), 610-615.
- [6] Iftikhar Ahmed, C. Mohammad Ashraf; *Int. J. Chem. Kinet.* , **2004**, 11, 813-819.
- [7] Saik Sondu , Bangalore , Sethuram and Tageda Navaneeth Rao ; *Transition Metal Chem.* , **1990**,15(1) , 78-80.
- [8] Sheila Srivastava; *Trans. Metal Chem.*, **1999**, 24(6), 683-685.
- [9] F. Feigl, *Spot tests in Organic Analysis*, Elsevier, New York, **1996**.
- [10] Sheila Srivastava, Bharat Singh; *Trans. Metal Chem.*, **1991**, 16, 466.
- [11] N. Venkata Subramanian, V. Thigarajan; *Canadian J. Chem.*, **1969**, 47, 694.
- [12] J. C. Bailor, "Chemistry of Coordination Compound; Reinhold, New York, **1964**, P-4.
- [13] C. S. Reddy, E. V. Sundaram; *J. Indian Chem. Soc.*, **1985**, 62, 209