



Homogeneous catalytic oxidation of some polyhydric alcohols by iridium trichloride

Sheila Srivastava*, Parul Srivastava*, Vandana Gupta and Arti Jaiswal

¹Chemical Laboratories, Feroze Gandhi College, Rae Bareilly – 229001, U.P., India

*Corresponding author's E. mail: she_ila72@yahoo.com (S. S.), parul_9880@yahoo.com (P. S.), Tel: 9956967732

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ABSTRACT

The kinetic investigation for catalyzed oxidation of D-Sorbitol and Glycerol using in Ir(III) in an acidified solution of NBS in the presence of $\text{Hg}(\text{OAc})_2$ as a scavenger for bromide ion has been carried out in the temperature range of 30^o - 45^o C. First order kinetics in the lower NBS concentration range tended to zero order at higher concentration. Increase in concentration of Cl^- and H^+ ion showed fractional inverse order while the order of reaction w.r.t. substrate was zero. Negligible effect of $\text{Hg}(\text{OAc})_2$ and ionic strength of the medium was observed. A suitable mechanism in conformity with the kinetic observations has been proposed and the various activation parameters have been calculated.

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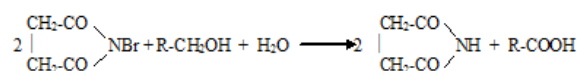
Capsule Summary: The kinetics of D-Sorbitol and Glycerol oxidation using in Ir(III) in an acidified solution of NBS in the presence of $\text{Hg}(\text{OAc})_2$ in the temperature range of 30^o - 45^o C were investigated and Cl^- and H^+ showed significant effect, whereas $\text{Hg}(\text{OAc})_2$ and ionic strength effect was negligible.

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INTRODUCTION

N-bromosuccinimide (NBS) has been used as a brominating and oxidizing agent in synthetic organic chemistry as well as analytical reagent especially in acid medium (Filler, 1963; Kamble et al., 1996ab; Mathur and Narang, 1975; Saroja et al., 1989). Recently, NBS has been used for the bromination of some selected organic substrates in which it is used as source for bromine in radical reactions (such as allylic brominations) and various electrophilic additions. The NBS reaction with organic substrates such as alcohols and amines leads to the products of net oxidation followed by elimination

of HBr (Huang and Fu, 2006; Narender et al., 2004; Shao and Shi, 2006). During the past few decades, there has been an upsurge in the designing of a variety of catalysts to explore their utility in synthetic organic chemistry. A number of transition and platinum group metal ions and their



Scheme 1: Reaction polyhydric alcohol with NBS: Where R = $\text{CH}_2\text{OH}-(\text{CHOH})_4$ for D-Sorbitol and $\text{CH}_2\text{OH-CHOH}$ for Glycerol respectively. The products were identified by TLC method (Feigl, 1996).

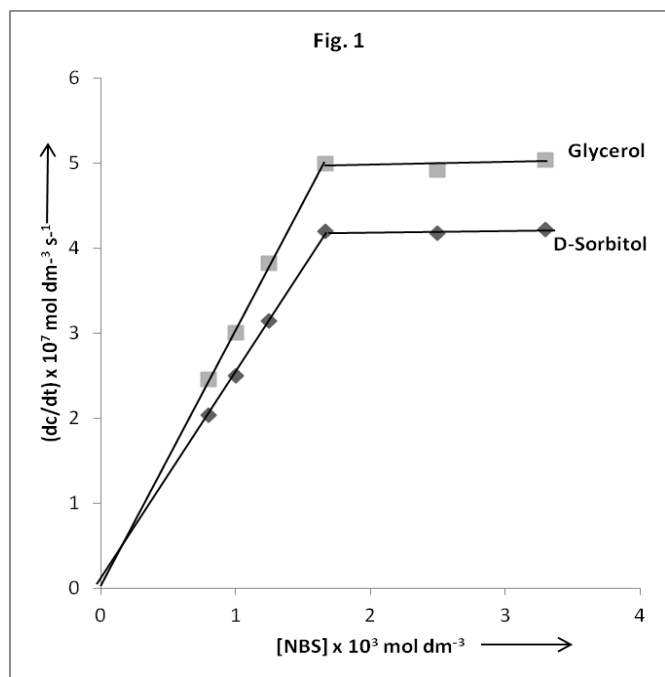


Fig. 1: Plot between $[NBS] \times 10^3 \text{ mol dm}^{-3}$ vs. $(-dc/dt) \times 10^7 \text{ mol dm}^{-3} \text{ s}^{-1}$ for oxidation of Glycerol and D-Sorbitol at 35°C .

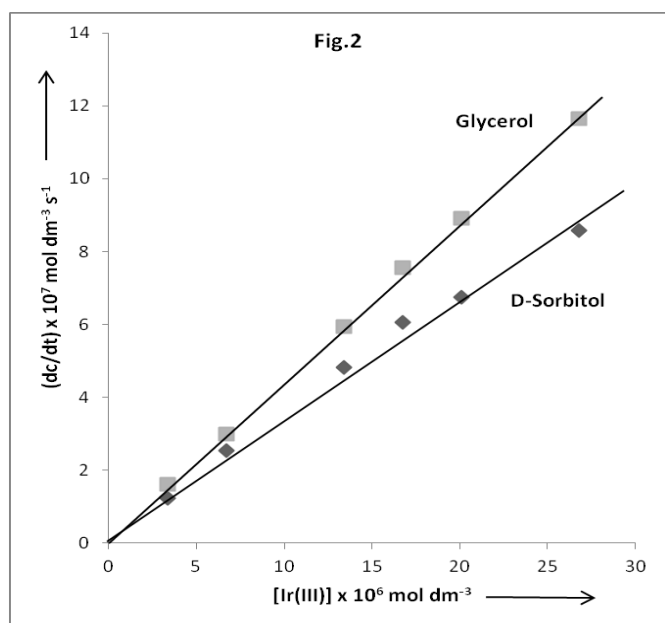


Fig. 2: Plot between $[Ir(III)] \times 10^6 \text{ mol dm}^{-3}$ vs. $(-dc/dt) \times 10^7 \text{ mol dm}^{-3} \text{ s}^{-1}$ for oxidation of Glycerol and D-Sorbitol at 35°C .

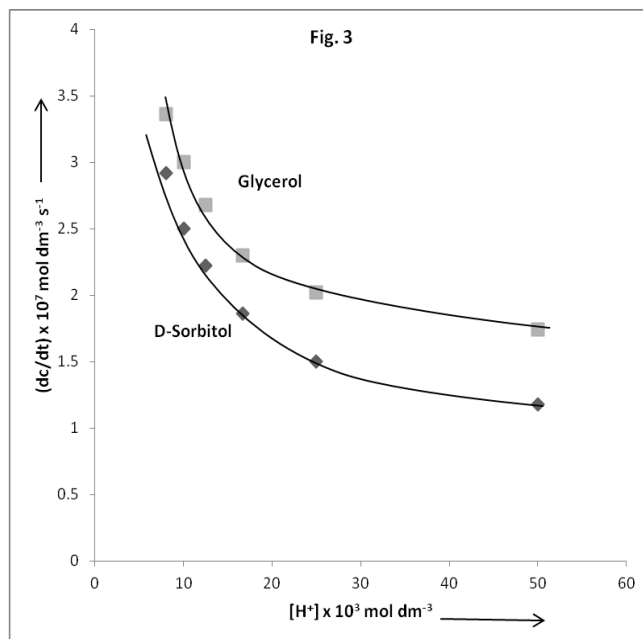


Fig. 3: Plot between $[H^+]$ vs. $(-dc/dt)$ for oxidation of Glycerol and D-Sorbitol at 35°C

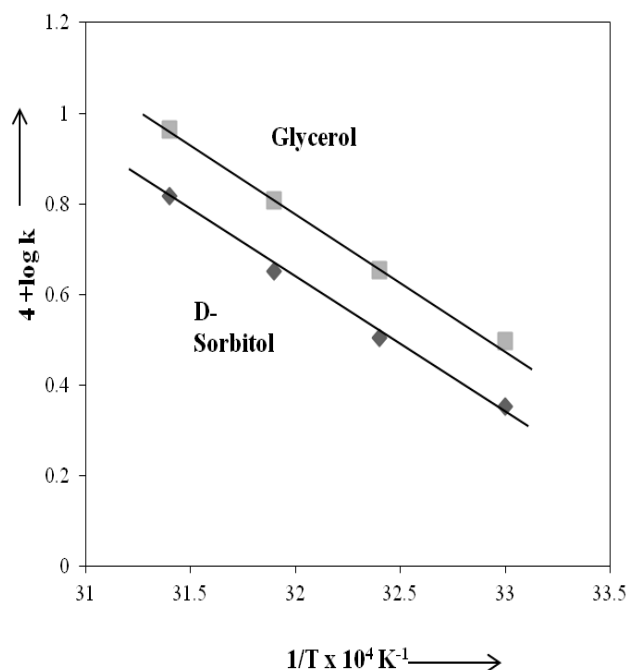


Fig. 4: Plot between $1/T$ vs. $\log k$ for oxidation of Glycerol and D-Sorbitol at 35°C

complexes have been designed and used as catalysts under homogeneous conditions. Little attention has been paid however, to the reactivity of NBS in the presence of catalyst and nearly no investigation has so far been reported on the catalytic role of iridium(III) chloride with NBS as an oxidant in acidic medium. This fact prompted us to undertake the

present investigation namely, "Acidic oxidation of polyhydric alcohols by acidified NBS in the presence of Ir(III) chloride as a catalyst and mercuric acetate as a scavenger for bromide ion".

MATERIAL AND METHODS

Table 1: Effect of Variation of Reactants on the Reaction Rates at 35^o C: [Ir(III)] = 6.67 x 10⁻⁶ mol dm⁻³, [NBS] = 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 Glycerol	(-dc/dt) x 10 ⁷ mol dm ⁻³ D-Sorbitol
1.00	1.00	1.00	1.25	-	3.18	2.38
1.25	1.00	1.00	1.25	-	2.96	2.54
2.00	1.00	1.00	1.25	-	3.00	2.50
2.50	1.00	1.00	1.25	-	3.10	2.56
5.00	1.00	1.00	1.25	-	3.08	2.48
10.00	1.00	1.00	1.25	-	2.98	2.62
1.00	0.83	1.00	1.25	-	3.54	3.02
1.00	1.00	1.00	1.25	-	3.00	2.50
1.00	1.25	1.00	1.25	-	2.66	2.18
1.00	1.67	1.00	1.25	-	2.28	2.78
1.00	2.50	1.00	1.25	-	1.84	1.40
1.00	5.00	1.00	1.25	-	1.46	1.16
1.00	1.00	0.83	1.25	-	3.36	2.92
1.00	1.00	1.00	1.25	-	3.00	2.22
1.00	1.00	1.25	1.25	-	2.68	1.86
1.00	1.00	1.67	1.25	-	2.30	1.50
1.00	1.00	2.50	1.25	-	2.02	1.18
1.00	1.00	5.00	1.25	-	1.74	1.60
1.00	1.00	1.00	0.83	-	3.12	2.44
1.00	1.00	1.00	1.00	-	3.16	2.58
1.00	1.00	1.00	1.25	-	3.00	2.50
1.00	1.00	1.00	1.67	-	2.90	2.60
1.00	1.00	1.00	2.50	-	2.92	2.42
1.00	1.00	1.00	5.00	-	2.88	2.66
1.00	1.00	1.00	1.25	0.83	3.00	2.50
1.00	1.00	1.00	1.25	1.00	3.12	2.40
1.00	1.00	1.00	1.25	1.25	2.96	2.54
1.00	1.00	1.00	1.25	1.67	2.90	2.42
1.00	1.00	1.00	1.25	2.50	3.08	2.60
1.00	1.00	1.00	1.25	5.00	3.20	2.62

The stoichiometry of the reaction was determined by equilibrating varying ratios of [NBS] and substrate i.e. polyhydric alcohols (D-Sorbitol and Glycerol) separately at 50^oC for 48 hrs under kinetic conditions. Estimation of residual NBS in different reactions showed that one mole of polyhydric alcohol consumes two moles of NBS, according to the following stoichiometry is represented in scheme 1.

For NBS in oxidation of D-Sorbitol and Glycerol, the value of (-dc/dt) increases linearly and thereafter when we increase the concentration of NBS, the value of (-dc/dt) tends to attain a constant value, which shows that at low concentration the reaction follows first order kinetics and at higher concentration, it tends to zero-order kinetics. This result is further verified by a plot of (-dc/dt) and the concentration of NBS which give straight line at lower concentration and deviation occurs at higher concentration (Fig. 1). A perusal of the summarized Table 1 clearly shows that the rate of

reaction (-dc/dt) remains almost constant throughout the variation of D-Sorbitol and Glycerol concentration. This indicates zero order rate dependence on D-Sorbitol and Glycerol concentration.

The values of k_1 and (-dc/dt) increase in the same proportion on increasing the concentration of Ir(III). This clearly indicates that the order with respect to [Ir(III)] is one (Fig. 2). First order kinetics of Ir(III) is also confirmed by 'chi-square method' for both D-Sorbitol and Glycerol. The values of first order rate constant (k_1) or (-dc/dt) decreases with increase in the concentration of hydrogen ion, chloride ion and succinimide throughout its variation. This shows negative effect of hydrogen ion concentration on the rate of reaction. Similar result is also obtained by plotting a graph between [H⁺] vs. log (-dc/dt) (Fig. 3).

It is quite clear from the consolidated table the values of (-dc/dt) or first order rate constant k_1 remain almost constant

Table 2: Activation parameters for acidic NBS oxidation of Glycerol and D-Sorbitol

Parameters	Temp. / °C	Glycerol	D-Sorbitol
$k_r \times 10^4 \text{ s}^{-1}$	30	2.10	1.70
$k_r \times 10^4 \text{ s}^{-1}$	35	3.00	2.50
$k_r \times 10^4 \text{ s}^{-1}$	40	4.14	3.40
$k_r \times 10^4 \text{ s}^{-1}$	45	5.92	4.86
Log A	-	11.19	10.13
$\Delta E^*(\text{kJ mol}^{-1})$	-	63.20	57.46
$\Delta G^*(\text{kJ mol}^{-1})$	35	52.52	74.34
$\Delta H^*(\text{kJ mol}^{-1})$	35	55.06	70.31
$\Delta S^*(\text{JK}^{-1} \text{ mol}^{-1})$	35	-8.25	-13.06

on increasing the concentration of mercuric acetate i.e. the rate of reaction remains almost unaffected throughout the variation. Thus, it is clear from the results that mercuric acetate acts as a scavenger. Hence it does not act as catalyst, but acts as a scavenger, to trap the liberated bromide ion in the form of $[\text{Hg}(\text{Br})_4]^{2-}$. Change in ionic strength of the medium did not bring about any appreciable change in the rate of oxidation of substrate.

The rate measurements were taken at 30^o–45^o C and specific rate constants were used to draw a plot of log k vs. 1/T, which was linear (Fig.4). 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^o, 35^o, 40^o and 45^oC and these values have been recorded in Table 2.

The rate law derived on the basis of HOBr as active species of NBS explains all kinetic orders and kinetic effects observed in the present redox system. Hence, HOBr is taken as effective reactive species of NBS.

The reactive species of Iridium(III) chloride is $[\text{IrCl}_5(\text{H}_2\text{O})]^{-2}$ in acidic medium (Gopalkrishnan et al., 1980; Waquar et al., 1990) explains the negative effect of chloride ions. These statements lead to suggest the reaction scheme, which gives the details of various steps in the title reaction (Eqs. 8-9).

CONCLUSIONS

The experimental results as shown reveal that the reaction rate doubles when the concentration of the catalyst $[\text{Ir}(\text{III})]$ 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

HOBr and $[\text{IrCl}_5(\text{H}_2\text{O})]^{-2}$ are the reactive species of NBS and Ir(III) chloride respectively in acidic medium.

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