

# Isoquinolinium chlorochromate mediated oxidation of some diols - A Kinetic Study

<sup>1</sup>Ranjana Tripathi, <sup>2</sup>O.P. Rai

Department of Chemistry  
Govt. P.G. College, (NAAC) Satna (M.P.) India.

**Abstract:** The oxidation kinetics of two diols (1,3-propane diol and 1,4-butane diol) by Isoquinolinium chlorochromate in aqueous acetic acid medium in presence of mineral acid yielded in the formation of corresponding aldehydes as the main product of the oxidation. The reactions exhibit of first-order with respect to [IQCC], however showing fractional-order kinetic with respect to diols and  $k_{obs} = a + b [H^+]$  traits for  $[H^+]$ . The study reveals the existence of symmetrical nature of transition state in the rate-determining step. The solvent effect shows the importance of the cation solvating power. A protonated species of oxidant participate in 1:1 stoichiometry ratio based proposed mechanism involving the proton abstracting mechanism supported by thermodynamic parameters.

**Key words:** Isoquinolinium chlorochromate, 1,3-propane diol, 1,4-butane diol, oxidation, kinetics.

## 1. INTRODUCTION

Over the years, a large number of novel Cr(VI)<sup>[1-5]</sup> oxidants have been introduced especially for complex and highly sensitive substances where great selectivity and effectiveness, coupled with mildness of conditions are required. Isoquinolinium chlorochromate (IQCC) is one of such reagents synthesized recently<sup>[6]</sup>. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agent in terms of the amount of oxidants, and solvent required, short reaction times and high yields. IQCC has been employed as an oxidant for the oxidation of parabromomandelic acid,<sup>[7]</sup> aliphatic aldehydes,<sup>[8]</sup> and sugar alcohols.<sup>[9]</sup> In aqueous acetic acid and DMSO solvent, the kinetics of oxidation of organic diols have been studied by many reagents such as: dihydroxy diperodate argenate(III),<sup>[10]</sup> Mn(II),<sup>[11]</sup> tripropylammonium fluorochromate,<sup>[12]</sup> pyridinium bromochromate,<sup>[13]</sup> QBC,<sup>[14]</sup> and QFC,<sup>[15]</sup> etc. Literature survey reveals that no report is available on the kinetic and mechanistic aspect of oxidation of diols by IQCC, it was observed that by perusal of literature, the oxidation of diol by IQCC through C-H bond fission resulting in the formation of aldehydes. We report in this article, after considering the importance to investigate the oxidation of diols by IQCC with emphasis on structural-reactivity correlation, the mechanistic aspects are discussed.

## 2. EXPERIMENTAL

All the reagents and solvents used were of analytical grade. The diols such as propane-1,3-diol and butane-1,4-diol (BDH) were distilled under reduced pressure before use. The IQCC was prepared by the reported method.<sup>[16]</sup> Its solution was prepared in water and HCl, the purity of this compound was checked iodometrically.

## 3. Kinetic measurements

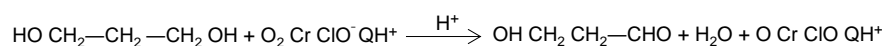
The kinetic measurement of the reaction was investigated under the condition.

$$[\text{diols}] \gg [\text{IQCC}] [\text{H}^+]$$

All the ingredients in definite quantities are kept in thermostat with ( $\pm 0.1^\circ\text{C}$ ) at their experimental temperatures, when both the solutions of oxidant and substrate attain the same equilibrium temperature, they are mixed together and kinetics was monitored by measuring the decrease in [IQCC] iodometrically with the help of hypo solution using starch as an indicator. The values of rate constant are calculated from the integration method and also from the slopes of  $\log [\text{IQCC}]$  versus time plots that showed  $k_{obs}$ , were reproducible to within  $\pm 3\%$ .

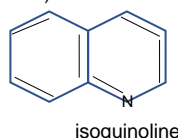
## 4. Results and Discussion

The stoichiometry of IQCC oxidation of propane-1,3-diol and butane-1,4-diol was determined by allowing reaction in thermostat both for 12 h at  $30^\circ\text{C}$ . The excess concentration of IQCC was determined iodometrically. These stoichiometric results correspond to reaction of 1 mole of diol to a 1 mole of IQCC as represented by equation.



(IQCC)

Where, Q = C<sub>9</sub>H<sub>7</sub>N or



The oxidation products of the reaction under investigation obtained as propanaldehyde, and butanaldehyde with yields 89 and 84% respectively and were identified by forming their 2:4 nitrophenyl hydrazone derivatives, characterized by measuring melting points (m.p. 131°C and 117°C) respectively. The above products were also confirmed by TLC method.

The oxidation of diols by IQCC in an atmosphere of nitrogen fails to induce polymerization of acrylonitrile completely discarding the presence of free radicals in the reaction mixture.

The reactions were found to be varied first-order with respect [IQCC] as evidenced by individual kinetic runs. The plots of log [IQCC] versus time was observed linear with unit slope. It shows that the proportionality with respect to oxidant is one and rate is independent of concentration of oxidant.

-dc/dt values increase proportionality with increasing [diol] at low concentration (Table 1) on plotting rate values against [diols], showed straight line passing through origin is obtained in the beginning, but bending towards X-axis at their higher concentration of substrate Plot of k v. [diol] (Fig. 1). The second-order rate constant ( $k_2$ ) values are not fairly constant, these facts confirm that rate of reaction shows not direct proportionality to [diols] and tends to show fraction-order kinetics at higher [diols]. Similar trends was obtained in both the cases.

**Table 1: Dependence of rate on [diols]**

$10^3 \times [\text{IQCC}]$  (mol dm<sup>-3</sup>) = 2.50 (1, 2) ;  $[\text{H}^+]$  (mol dm<sup>-3</sup>) = 0.125 (2), 0.166 (1) ;  
CH<sub>3</sub>COOH-H<sub>2</sub>O %, (v/v) = 30 (1, 2) ; Temperature K = 303 (1, 2)

[diol] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	← 10 <sup>4</sup> k (s <sup>-1</sup> ) →	
	propane 1,3-diol (1)	butane-1,4-diol (2)
1.00	-	1.68
1.25	1.47	-
1.50	-	2.20
1.66	1.91	-
2.00	2.31	2.73
2.50	-	3.02
3.33	3.75	4.41
4.00	4.34	5.20
5.00	4.86	6.12
6.25	5.28	-

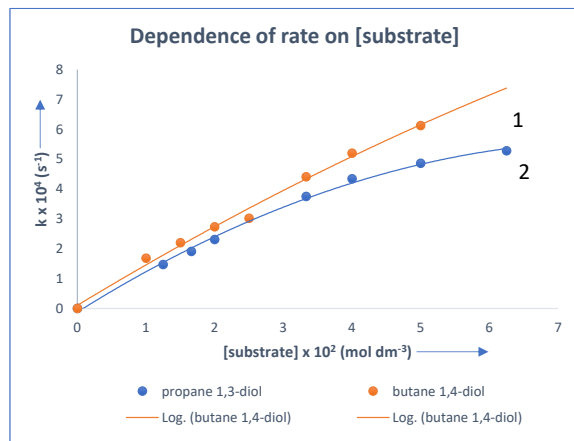


Fig. 1 Pot of k vs. [substrate]

$10^3 \times [\text{IQCC}]$  (mol dm<sup>-3</sup>) = 2.50 (1, 2) ;  
 $[\text{H}^+]$  (mol dm<sup>-3</sup>) = 0.125 (2), 0.166 (1) ;  
CH<sub>3</sub>COOH-H<sub>2</sub>O%,(v/v)=30(1,2);  
Temperature K = 303 (1,2),

The effect of H<sup>+</sup> on the rate was studied by changing the concentration of H<sub>2</sub>SO<sub>4</sub>, it was observed that the rate of reaction increases indicating a direct participation of H<sup>+</sup> in the rate-determining step (Table 2).

**Table 2: Dependence of rate on [H<sup>+</sup>]**

$10^3 \times [\text{IQCC}]$  (mol dm<sup>-3</sup>) = 2.50 (1, 2) ;  $10^2 \times [\text{diol}]$  (mol dm<sup>-3</sup>) = 1.66 (2), 2.0 (1) ;  
CH<sub>3</sub>COOH-H<sub>2</sub>O %, (v/v) = 30 (1, 2) ; Temperature K = 303 (1,2)

[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	← 10 <sup>4</sup> k (s <sup>-1</sup> ) →	
	propane 1,3-diol (1)	butane-1,4-diol (2)
0.080	-	1.46

0.100	-	1.81
0.125	1.96	2.20
0.166	2.31	3.19
0.200	3.16	3.53
0.250	3.82	4.52

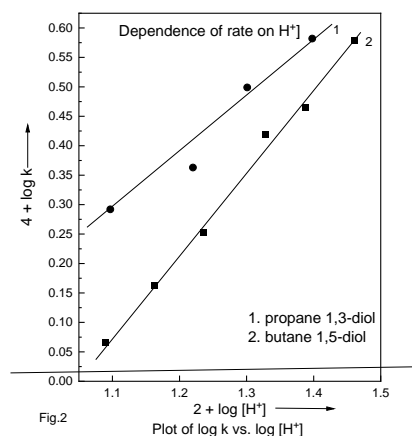


Fig.2

Plot of log k vs. log [H<sup>+</sup>]

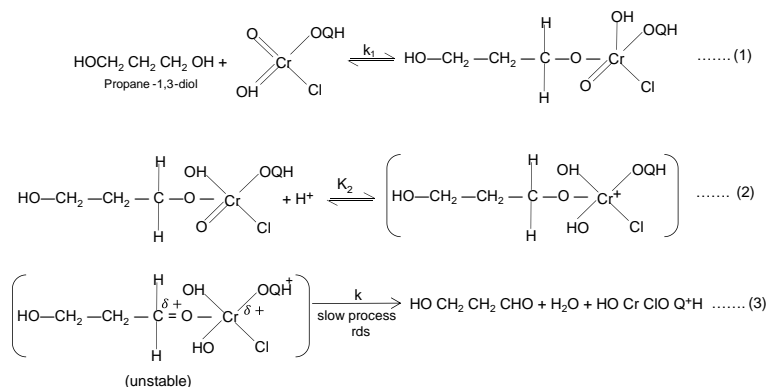
$10^3 \times [\text{IQCC}] \text{ (mol dm}^{-3}\text{)} = 2.50 \text{ (1, 2)}$  ;  
 $10^2 \times [\text{diol}] \text{ (mol dm}^{-3}\text{)} = 1.66 \text{ (2), } 2.0 \text{ (1)}$  ;  
 $\text{CH}_3\text{COOH-H}_2\text{O} \%, \text{ (v/v)} = 30 \text{ (1, 2)}$  ;  
 Temperature K = 303 (1,2)

The plot of log k vs. log [H<sup>+</sup>] (Fig. 2) fairly linear with unit slope indicating first-order dependency on rate leads the reaction is acid catalysed.

Effect of solvent composition were studied on the reaction rate at different compositions of acetic acid and water mixtures. With the increase in the percentage of acetic acid, there is slight enhancement in the reaction rate. The plot of log k vs. 1/D is linear, i.e. decrease in dielectric constant of the medium increases the rate, showing that the reaction is a positive ion-dipole type. The addition Cl<sup>-</sup> ions in the form of NaCl at constant ionic strength ( $\mu$ ) at pre-set conditions did not affect the rate, showing that, it is not involved in a pre-equilibrium to the rate-determining step i.e. a natural species, takes part in the chemical reactions.

### Mechanism

Isoquinolinium chlorochromate species is well specified in the protonated form involving a transfer of hydride from substrate to oxidant in the proposed mechanism.



The rate expression was derived as :

$$\therefore k_{obs} = \frac{k K_1 K_2 [H^+] [\text{diol}]}{1 + K_1 K_2 [H^+] [\text{diol}]} \dots\dots (4)$$

Transforming equation (4) as :

$$\text{or } \frac{1}{k_{obs}} = \frac{1}{k K_1 K_2 [H^+] [\text{Diol}]} + \frac{1}{k} \dots\dots (5)$$

Equation (5) explains Michaelis-Menten types kinetics observed in the reaction between IQCC and diols and all other kinetic parameters.

### Reactivity and Structure

The oxidation rates follow the sequence

butane-1,4-diol > propane,1,3-diol

The oxidation rates based reactivity of the diols are justified by ideally design molecule such as increasing length of carbon chain and long alkyl group to which hydroxyl group is attached. The alkyl group stabilizes the intermediate. The long size of an alkyl group of diols produces more inductive effect which are consistent with their +I effects on the oxidation, Energy of activation ( $E_a$ ) is the measure of reactivity of diol, the more reactive compound is supposed to have lower value of  $E_a$  and less reactive are the higher value ( $E_a$ ) (Table 3). The values of the reactions are well in accordance with the trend.

**Table 3. Thermodynamic and activation parameters for the reaction between diols and IQCC**

Diols	$E_a$ kJ/mol <sup>-1</sup>	A (s <sup>-1</sup> )	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ JK <sup>-1</sup> mol <sup>-1</sup>
Propane-1,3-diol	55.53	$7.98 \times 10^6$	56.03	85.77	94.28
Butane-1,4-diol	54.90	$3.91 \times 10^6$	50.42	85.46	114.72

The observed negative value of  $\Delta E^\ddagger$  causes charge separation which ends being highly solvated, this results in an immobilization of large number of solvent molecules. Thus, the negative values of  $\Delta S^\ddagger$  decrease in the rotational and vibrational degree of freedom of the reacting system due to the formation of a rigid short lived activated complex at the transition state. In an isoentropic reaction, enthalpy of activation determines the reactivity. All the diols examined are oxidised through a common mechanism because they have almost same free energy ( $\Delta G^\ddagger$ ) values. The oxidation of the reaction seems to be take place by enthalpy controlled.

### Conclusion

The oxidation rates of diols follow the sequence butane-1,4-diol > propane-1,3-diol. The oxidation reaction is unaffected by ionic strength in dilute solution and is accompanied by decrease in entropy of activation. The oxidation lead to the formation of corresponding aldehydic compounds. The reaction is first-order with respect to IQCC and satisfied Michaelis-Menten type of kinetics. A hydrogen abstraction mechanism has been proposed.

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### Conflict of Interest

The authors declare conflict of no interest whatsoever.

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