

Kinetics and Mechanism of Ruthenium (III) catalyzed Oxidation of 1, 2, diols (ethane diol) Peroxodiphosphate in HNO₃ Medium

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Abstract:- The Oxidation of some 1,2diol, butane 1,2 diol, 1,2 biphenyl diol by PDP in Nitric acid medium have studied at different temperatures. The reaction Kinetics showed first order dependence on both Oxidant and diol. The probable mechanism consistent with the observed Kinetic data has been proposed. Increasing [H⁺] has decreased the rate of Oxidation at constant Ionic strength and order in [H⁺] was found to be one activation parameters were evaluated Arrhenius and Eyring Theories.

Keywords:- 1,2diols Oxidation mechanism, 1,2 biphenyl diol, Peroxodiphosphate.

I. AIMS AND BACK GROUND

The Kinetics and mechanism of Oxidation of several mono functional Organic compounds by PDP have been very well established¹. Even some of the compounds resistant from Oxidation the compounds resistant from Oxidation to be get Oxidized by PDP on the presence of catalysts like Ag(I), Cu(II), Ru(III), Rh(III) and Os (III)⁶ from the literature Survey it is seen that little attention has been made on the Oxidation of bifunctional compounds by PDP.Hence in continuation of our earlier studies with different bifunctional compounds such as amino acids, amino alcohols etc., We reported here in the Kinetics of Oxidation of such as ethane 1,2, diols, propane ,2 diol, butane 1,2, diol.Since diols are reported to sluggish from Oxidation studies. It is thought worthwhile to study these Oxidations in various acid media in search of their smooth Oxidation to establish a suitable mechanism.However, since our earlier studies shown that PDP in nitric acid medium is a powerful and convenient Oxidant the Oxidation in such medium has been undertaken.

II. MATERIALS AND METHODS

Potassium peroxodiphosphate was used, although the salt contained some impurity of phosphate the later did not interfere in Kinetics of the reaction.The preparation and standardization of other reagents and solution are given elsewhere.Doubly distilled water was employed throughout the study; the second distillation was from alkaline potassium permanganate solution in all glass apparatus.

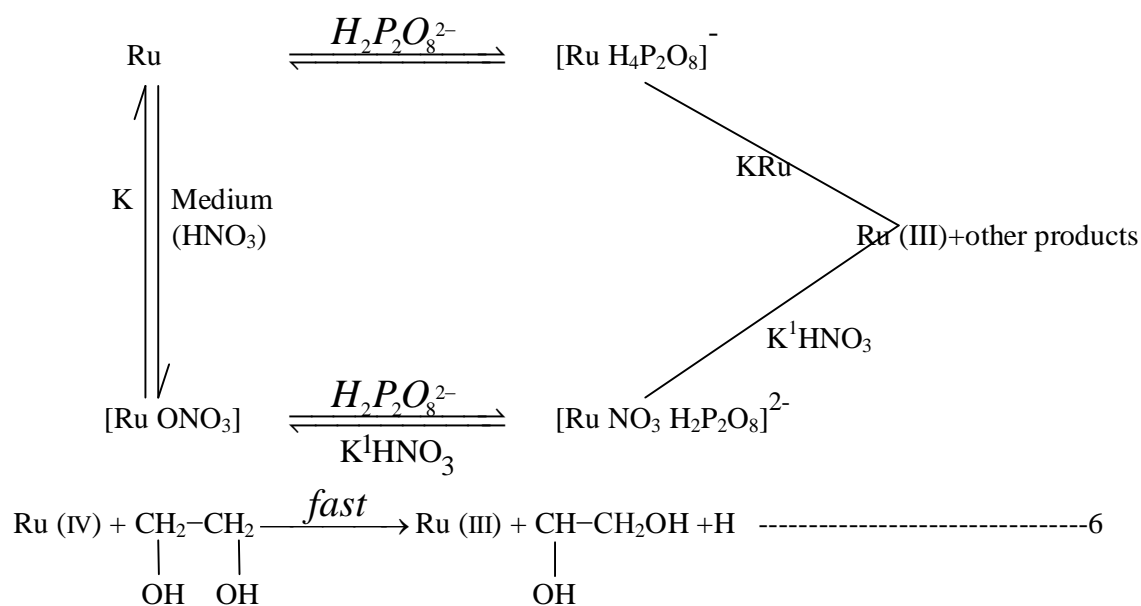
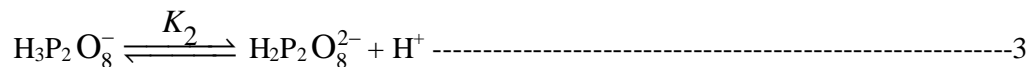
The reactions were conducted in glass stopper Erlenmeyer flasks suspended in a water bath thermo stated at 50 ± 0.1°C stated other reaction mixture except peroxodiphosphate (PDP) were taken in these flasks required volume of PDP was withdrawn from the thermally pre-equilibrated solution and then discharged in to the reaction mixture the time of initiation of the reaction was recorded, when the pipette was half empty of the contents. However reactions were not initiated by diol due to Ru(III) catalyzed decomposition of PDP.

An aliquot sample of (50m³) of the reaction mixture was withdrawn periodically and then discharged into a freshly prepared KI solution (10%), which contained 0.5 mol dm⁻³ HClO₄. A solution of mixed catalyst (IC m³) [Fe(II) + Cu (II)] was added in the end.The liberated iodine was titrated against sodium thiasulphate solution using starch indicator. Diol did not interfere in iodometric analysis of PDP.However, iodine liberated by mixed catalyst was accounted from the subsequent calculation peroxodiphosphate concentration.Stock solution of diols prepared from MERCK chemicals dissolved in double distilled water. The water used for the Kinetics reactions was doubly distilled from a quartz cell.

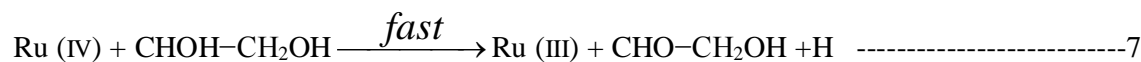
The progress of the reaction was monitored by the recording absorbance due to the liberated iodine, when KI is added to the un reacted PDP spectrometrically using visible spectro photo meter with absorption maximum at 460mm obtained for the reaction mixture under experimental conditions.

The Kinetics of reactions generally followed up to 75% completion of the reaction the ionic strength of the reaction was kept constant using anal grade KNO₃ values of [H⁺] were read from a standard curve of [H⁺] versus [NHO₃] prepared using the results of Kemp and water¹².

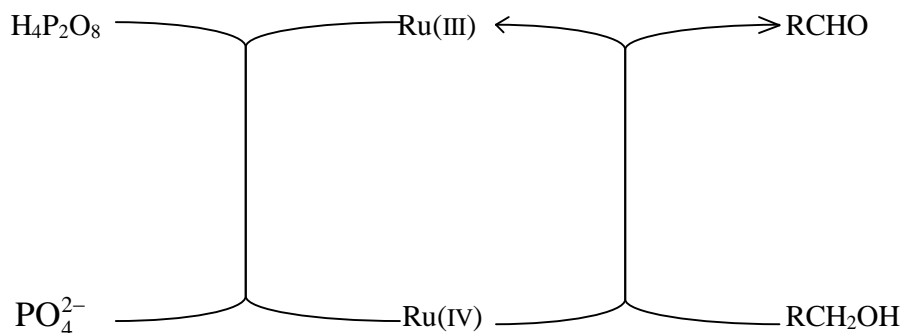
The results were reproducible within the experimental error limits of 3%. The methods of evaluating the rates, orders and Kinetic parameters were the same as reported in our earlier studies. It was observed that the rates of these Oxidation reaction are in the order Butane 1, 2 diol> Propane 1,2, diol> ethane 1,2 diol Based on stoichiometric studies, induced Polymerization with monomers and product analysis. The most probable mechanism for these Oxidation reactions is as shown below in scheme.



If the mechanism is catalyzed with equilibrium step (3) the loss of PDP lead to the rate law (8)



$$-\frac{d[\text{PDP}]}{dt} = \frac{K^1\text{Ru}K^1 + K^1\text{HNO}_3K^1\text{HNO}_3(\text{Ru})[\text{PDF}][\text{H}^+]}{1 + K[\text{NO}_3^-]K_3 + (\text{H}^+)}$$



Where K^{11} is second order rate constant K^1 is observed Pseudo first order rate constant the reactions were studied at different temperatures and the plots of $\log K^1$ versus $1/T$. The activation parameters for all substrated were evaluated

III. STRUCTURE REACTIVITY CORRELATION

The presence of +I.E changes the reactivity of parent compound by altering the availability of electrons at the site of attack of Oxidant from the data in the (table-4). It is evident that the order of reactivity of diols is as follows.

Butane 1,2diol> propane 1,2 diol> ethane 1,2 diol. It is found from the plot of ΔH versus ΔS the values of 'B' i.e. iso Kinetic temperature range (280-303k) and hence reactions are assumed to be enthalpy controlled. Constancy in the calculated values ΔG for the for the Oxidation reactions indicates the probably the same type of mechanism could operate for all the Oxidation reactions.

Table. 1: Order in PDP in the Oxidation of diols PDP in nitric acid medium

[PDP] = $3 \times 10^{-3} \text{ mol dm}^{-3}$ [Diol] = $3 \times 10^{-2} \text{ mol dm}^{-3}$

[HNO₃] = $5 \times 10^{-1} \text{ mol dm}^{-3}$

[Temp] = 298k

Time in minutes	Optical density	1+logabsorbance
0	0.471	0.6730
5	0.432	0.6354
15	0.375	0.5740
20	0.340	0.5314
25	0.300	0.4771
30	0.294	0.4683
35	0.280	0.4471
40	0.270	0.4431

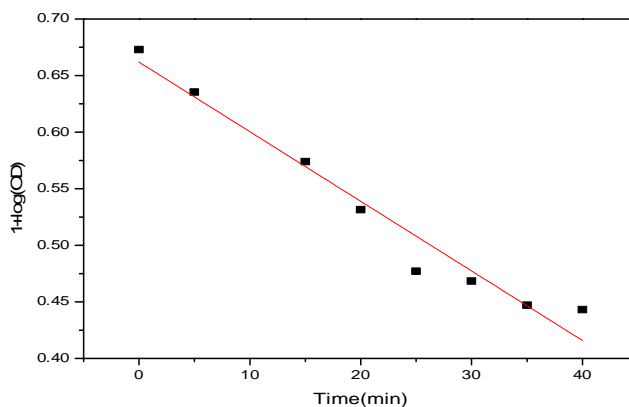


Fig 1: Order in [PDP] in PDP – Diol reaction conditions are same as in Table 1

Table. 2: Effects of [Propane 1,2diol] on Oxidation of diols by PDP in aqueous nitric acid medium
 [PDP] = $3 \times 10^{-3} \text{ mol dm}^{-3}$
 [H⁺] = $5 \times 10^{-1} \text{ mol dm}^{-3}$
 [Temp] = 298K

2 + log (Diol)	1.578	1.602	1.788	1.858	1.903	1.958
4 + log K¹ (Ethane Diol)	0.510	0.558	0.625	0.713	0.758	0.854
4 + log K¹ (Propane Diol)	1.31	1.358	1.425	1.513	1.558	1.654
4 + log K¹ (1,2 Butane Diol)	1.51	1.558	1.624	1.711	1.753	1.851

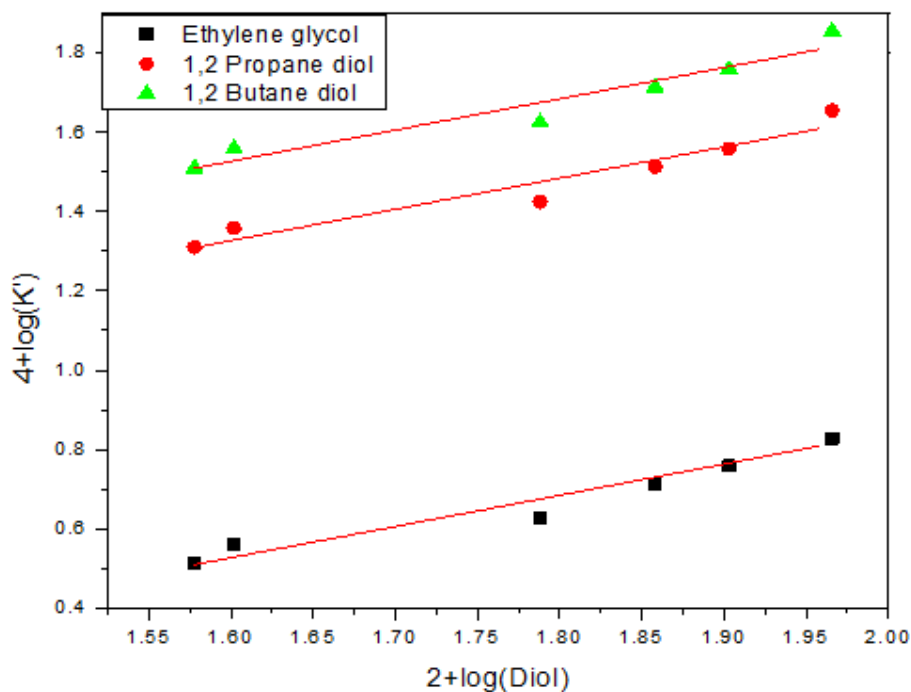


Fig. 2: Effect of [Diol] in PDP – Diolreaction conditions are same as in Table 2

Table. 3: Effect of [H⁺] on Oxidation of propane 1,2diol by PDP in aqueous nitric acid medium
 [PDP] = $3 \times 10^{-3} \text{ mol dm}^{-3}$
 [H⁺] = $5 \times 10^{-1} \text{ mol dm}^{-3}$
 [Temp] = 298k

Table. 4: Effect of [H⁺] on Oxidation of propane 1,2diol by PDP.
 [PDP] = $3 \times 10^{-3} \text{ mol dm}^{-3}$ [Diol] = $3 \times 10^{-2} \text{ mol dm}^{-3}$

1 + log [H⁺]	1.24	1.18	1.09	0.604	0.302	1.186
4 + log K	0.578	0.549	0.508	0.389	0.298	0.276

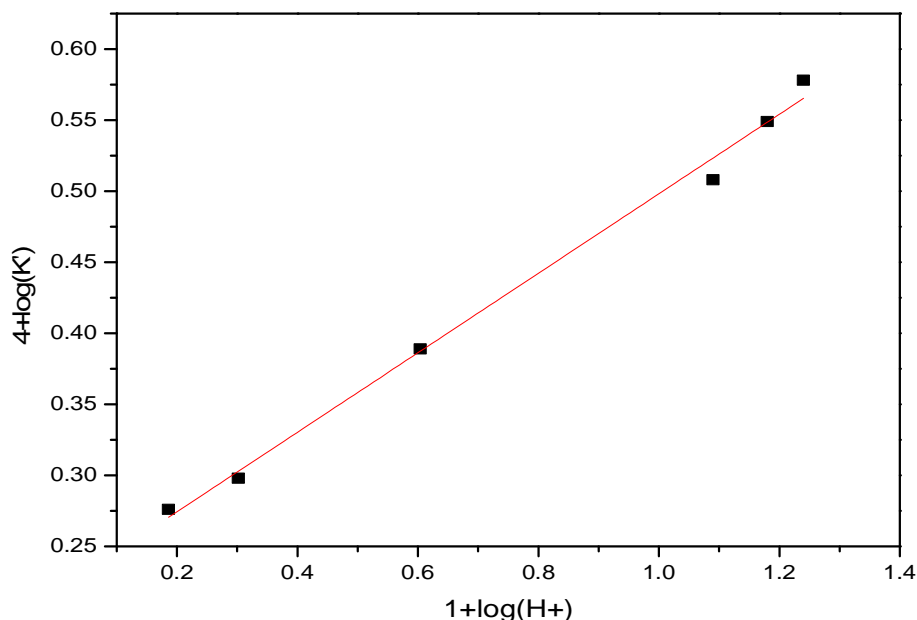


Fig. 3: Effect of [HNO₃] in PDP – Diol reaction conditions are same as in Table 3

Table. 5: Kinetic and thermo dynamic parameters at 303k for the Oxidation of diols by PDP in HNO₃ medium.

[PDP] = $3 \times 10^{-3} \text{ mol dm}^{-3}$
 [Diol] = $3 \times 10^{-2} \text{ mol dm}^{-3}$
 [H⁺] = $5 \times 10^{-1} \text{ mol dm}^{-1}$

Diol	$K \times 10^3$	ϵ	ΔG^*	ΔH^*	ΔS^*
	($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	exp	KJmol^{-1}		$\text{JK}^{-1} \text{ mol}^{-1}$
Propane 1,2 diol	9.80	81.3	88.2	78.6	33.9

IV. CONCLUSIONS

The presence of positive inductive effect changes the reactivity of parent compound by altering the availability of electrons at the site of attack of Oxidant. From the data in Table 4, it is evident that the order of reactivity of the diols is as follows. Butane 1,2diol > propane 1,2 diol > ethane 1,2 diol. It is found from the plot of ΔH versus ΔS the values of 'B' i.e. iso Kinetic temperature 332k. It is higher than the experimental temperature range (283-303k) hence the reactions are assumed to be enthalpy controlled constancy in the calculated values of ΔG for the Oxidation reactions indicates that probably the same type of Mechanism is operative of all the Oxidation reactions.

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