

# To study thermodynamic parameters of oxidation of 2 – Hydroxy – 1 – Naphthalidene Anil & Substituted Anils by $Ce^{4+} \rightarrow Ce^{3+}$ Redox system in aqueous Sulphuric acid medium at variable temperatures.

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**Abstract** :- Oxidation of 2 – Hydroxy – 1 – Naphthalidene anil & Substituted anils by The kinetics of oxidation of the Schiff base & its substituted anils by  $Ce^{4+} \rightarrow Ce^{3+}$  Redox system in aqueous Sulphuric acid medium has been studied. The study is carried out at five variable temperatures & thermodynamic parameters,  $\Delta H$ ,  $\Delta G$ ,  $\Delta E$  &  $\Delta S$  have been calculated & reported. The frequency factor (A) also determine & a suitable possible mechanism has been suggested on the basis of kinetic results.

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## I. Introduction

Chemical Kinetics deals with chemically interacting system as the interaction continues with observable, macroscopic changes in the properties of the system which are time dependent. It probes details of these energy barrier by examining the dependence of rates of chemical reaction on composition, pressure & temperature.

Chemical kinetics<sup>1</sup> compliments thermodynamic parameters such as change in energy of activation ( $\Delta E_a$ ) change of enthalpy ( $\Delta H$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta G$ ), frequency factor (A) for oxidation of 2 – Hydroxy – 1 – Naphthalidene Anil & Substituted Anils by cerium (IV) in aqueous sulphuric acid medium at variable temperatures was author's aim.

## II. Experimental

All the reagents used were of A.R. grade. Double distilled water was used throughout the experiments &

absolute alcohol used as a solvent which was prepared by standard methods<sup>2</sup>. 0.025 M Solution of ceric sulphate was prepared & standarised by known methods<sup>3</sup>. All Schiff base were dissolved in glacial acetic acid & known excess amount of standardized  $Ce^{4+}$  ion solution was thermostated.

All kinetic measurements were performed at five variable temperatures. The course of reaction was followed by determining concentration of unreacted  $Ce^{4+}$  ions in the reaction mixture by titrating it against standard FAS solution. Such titrations were carried out at regular intervals. Thermodynamical parameter such as  $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ ,  $\Delta E$ , etc<sup>4-5</sup>. Were studied for four different ligands.

## III. Results & Discussions

### Determination of Thermodynamic Parameter

Oxidation of 2 – Hydroxy – 1 – Naphthalid eneanil [ $L_1$ ].

Temp °k	$K \times 10^{-2}$ Min <sup>-1</sup>	$\Delta H$ KJ mole <sup>-1</sup>	$\Delta G$ KJ mole <sup>-1</sup>	$\Delta S$ Jdeg <sup>-1</sup> mole <sup>-1</sup>	$A \times 10^3$ Min <sup>-1</sup>	$\Delta E$ KJ mole <sup>-1</sup>
303	1.4212	27.0414	82.460	- 182.901	1.7697	
308	1.6587	26.9998	83.467	- 183.335	1.7072	29.5605
313	1.9946	26.9583	84.385	- 183.471	1.7070	
318	2.2700	26.9167	85.432	- 184.011	1.6252	
323	2.5940	26.8751	86.459	- 184.470	1.5620	

Oxidation of 2<sup>1</sup> – Methoxy – 2 – Hydroxy – 1 – Naphthalideneanil [L<sub>2</sub>].

Temp °k	K × 10 <sup>-2</sup> Min <sup>-1</sup>	Δ H KJ mole <sup>-1</sup>	Δ G KJ mole <sup>-1</sup>	Δ S Jdeg <sup>-1</sup> mole <sup>-1</sup>	A × 10 <sup>2</sup> Min	ΔE KJ mole <sup>-1</sup>
303	1.8147	20.8400	81.845	- 201.333	1.9280	
308	2.0777	20.7988	82.890	- 201.596	1.8995	23.3595
313	2.2613	20.7573	84.057	- 202.236	1.7872	
318	2.5930	20.7157	85.081	- 202.405	1.7794	
323	2.7948	20.6741	86.259	- 203.048	1.6729	

Oxidation of 3<sup>1</sup> – Methoxy – 2 – Hydroxy – 1 – Naphthalideneanil [L<sub>3</sub>].

Temp °k	K × 10 <sup>-2</sup> Min <sup>-1</sup>	Δ H KJ mole <sup>-1</sup>	Δ G KJ mole <sup>-1</sup>	Δ S Jdeg <sup>-1</sup> mole <sup>-1</sup>	A × 10 <sup>1</sup> Min <sup>-1</sup>	ΔE KJ mole <sup>-1</sup>
303	2.908	15.5634	80.656	- 214.828	3.8056	
308	3.172	15.5218	82.883	- 215.211	3.6943	18.0825
313	3.482	15.4803	82.933	- 215.506	3.6220	
318	3.771	15.4387	84.082	- 215.860	3.5275	
323	4.017	15.3971	85.284	- 216.367	3.3713	

Oxidation of 4<sup>1</sup> – Methoxy – 2 – Hydroxy – 1 – Naphthalideneanil [L<sub>4</sub>].

Temp °k	K × 10 <sup>-2</sup> Min <sup>-1</sup>	Δ H KJ mole <sup>-1</sup>	Δ G KJ mole <sup>-1</sup>	Δ S Jdeg <sup>-1</sup> mole <sup>-1</sup>	A × 10 <sup>2</sup> Min <sup>-1</sup>	ΔE KJ mole <sup>-1</sup>
303	1.6593	21.6178	82.070	- 199.511	2.4010	
308	1.8653	21.5762	83.026	- 199.967	2.3103	24.1369
313	2.1011	21.5347	84.249	- 200.364	2.2382	
318	2.3880	21.4931	85.306	- 200.671	2.1918	
323	2.6411	21.4515	86.410	- 201.110	2.1115	

The first order rate constant were determined at five different temperatures. The plot of titre value (Tt) against time are plotted for different temperatures for all substrates L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub>. The energy of activation (Δ E) is determined from the plot of log K<sub>1</sub> against 1/T in each case of each substrates. The energy of activation decreases due to introduction of methoxy group. The frequency factor (A) was determined & its value was very low for all substrate L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> which gives positive evidence for the formation of more rigid activated complex. The entropy of activation (Δ S) values negative for all Substrates L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub> & L<sub>4</sub>. The free energy of activation (Δ G) is nearly same for all four substrates (83 ~ 84kcal). The negative value of

entropy also proves that the formation of more rigid activated complex takes place prior to the rate determining step. The comparasion of all these values of thermodynamic parameter are made in above all tables which is the expected pattern of order. This is because in case of methoxy group as a substituent, the two effects are opposed the inductive effect tending to decrease the electron density on all the ring atoms, the tautomeric effect to increase it specifically.

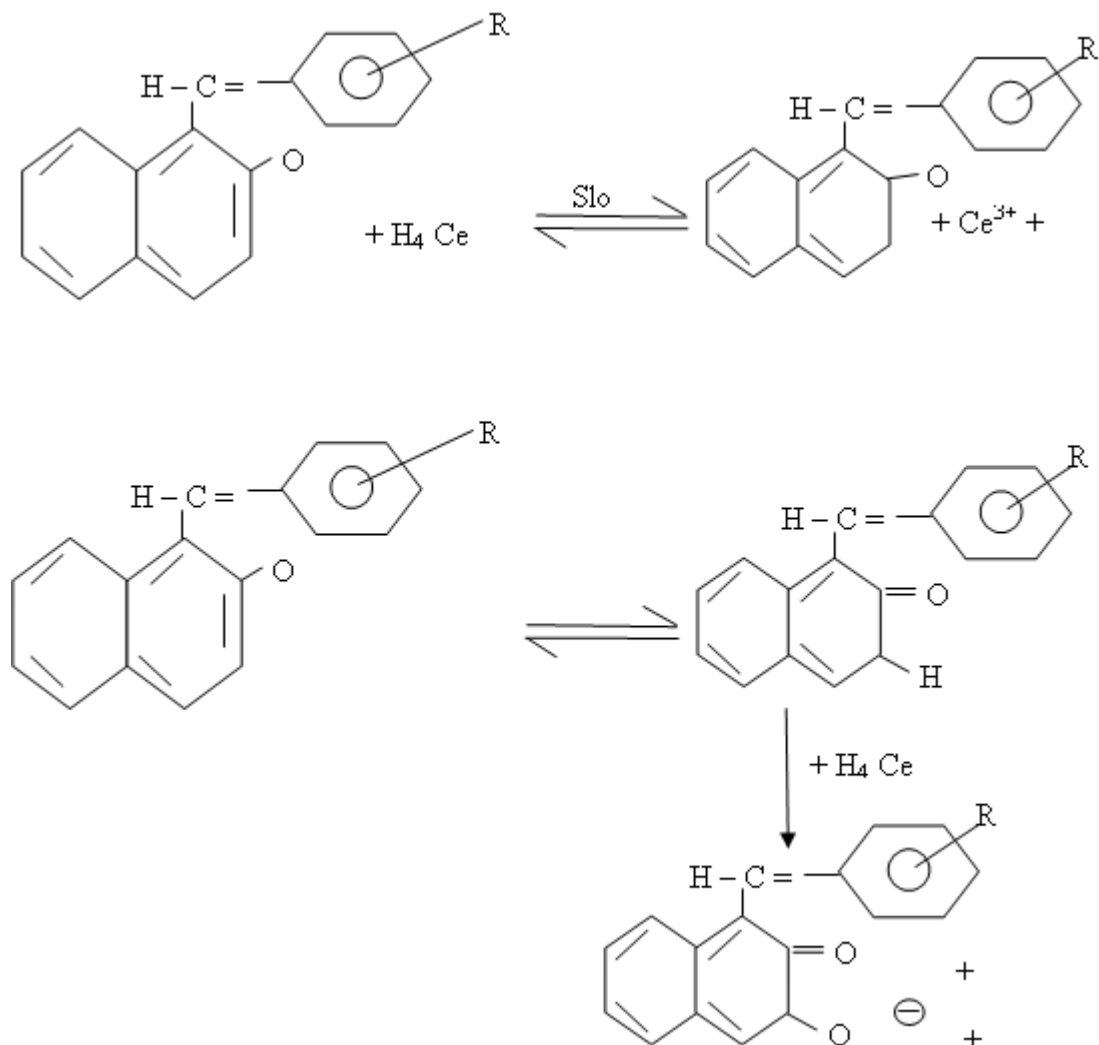
#### IV.Mechanism

The species of cerium (IV) complexes in Sulphuric acid has been widely investigate. The isolation of a number of cerium (IV) complexes from Sulphuric acid has also shown

by G. Hargraves, L.H. Sutcliffe<sup>(10)</sup>. The existence of ceric Sulphate, coupled with the fact that cerium in solution is present only as complex anion, suggests that ceric Sulphate exists as the complex Sulphatoceric acid<sup>(7)</sup>  $H_4Ce(SO_4)_4$  on the basis of observation, the reaction rate of oxidation increases with increase in concentration of sulphuric acid,

$H_4Ce(SO_4)_4$  must be reactive species in the reaction & the action of it on the substrate must be a rate determining step. The mechanism proposed by J.P. Sign & other<sup>3</sup>, Ramesh Yamgar.

For the oxidation of Schiff base is shown as



Where  $R = H, O - OCH_3, m - OCH_3$  or  $p - OCH_3$  followed by fast reaction

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