

**KINETICS OF OXIDATION OF SCHIFF BASES : PART-I.  
5-CHLORO-2-HYDROXY-4-METHYLACETOPHENONEANIL  
BY Ce (IV) IN AQUEOUS SULPHURIC ACID**

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**Abstract :** Kinetics of oxidation of schiff base has been studied by  $Ce^{+4}/Ce^{+3}$  redox system in aqueous sulphuric acid medium. The order of reaction with respect of Ce (IV) as well as schiff base was found to be one. A plot of  $k_1^{-1}$  vs  $[substrate]^{-1}$  was linear with an intercept on the rate axis which suggests the formation of an equilibrium complex between the reactants prior to the rate determining step. The effect of different salts viz. KCl, NaCl and  $NH_4Cl$ , the ionic strength, temperature and solvent on the rate of reaction have also been studied. The thermodynamic parameters viz.  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  and activation energy,  $A$  were also evaluated for the present oxidation process.

**Key words :** 5-Chloro-2-hydroxy-4-methylacetophenoneanil, Ceric sulphate.

**Introduction :**

The kinetic study of several organic substances has been well investigated by using Ce (IV)  $\leftrightarrow$  Ce (III) redox system (1-4). But also studies on the oxidation of schiff base by ceric sulphate in sulphuric acid medium are reported (5-6). The present communication deals with the kinetic study of schiff base, 5-chloro-2-hydroxy-4-methylacetophenoneanil, by ceric sulphate in aqueous sulphuric acid.

**Materials & methods :**

All the chemicals used were of AR grade. The schiff base, 5-chloro-2-hydroxy-4-methylacetophenoneanil(L) was prepared by refluxing 5-chloro-2-hydroxy-4-methylacetophenone and aniline in ethanol for 3-4 hours. It was then purified by recrystallisation and ascertained by TLC method. The stock solutions of ceric sulphate and ferrous ammonium sulphate were prepared in 2N sulphuric acid and standardised by known method (7).

**Kinetic measurements :**

The kinetic study of oxidation of schiff base (L) was carried out at constant desired temperature with the help of an electrically heated thermostat with an accuracy of  $\pm$

0.1 °C. The titrations were carried out by pipette out 5 ml aliquots from the reaction mixture at different intervals of time and the unreacted ceric sulphate was determined by titrating it against standard ferrous ammonium sulphate solution using ferrion as an indicator.

**Results and discussion :**

**Effect of substrate :**

To evaluate the order of reaction with respect to substrate the titrations were carried out at different concentrations of the substrate. The concentrations of oxidant and sulphuric acid were kept constant. The temperature was maintained at 298 K. The results are recorded in Table 1.

The  $k_1$  values are found to be directly proportional to the concentration of the schiff base studied indicating that the reaction follows first order kinetics with respect to Schiff base. The values of  $k_2$  (Second order constant), calculated from  $k_1 / [substrate(L)]$ , are practically constant which also proves the first order dependence of reaction on the Schiff base. Fig.1 shows the plot of  $k_1^{-1}$  vs  $[substrate]^{-1}$  which is linear making an intercept on the rate axis indicating the formation of an equilibrium complex between Ce (IV) and substrate.

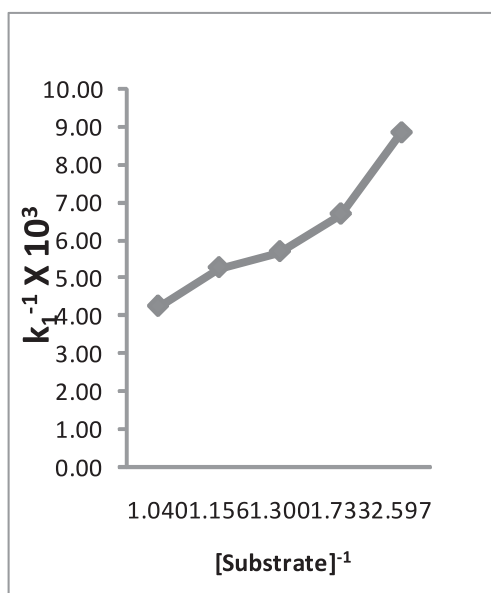


Fig.-1: the plot of  $k_1^{-1}$  vs  $[\text{substrate}]^{-1}$

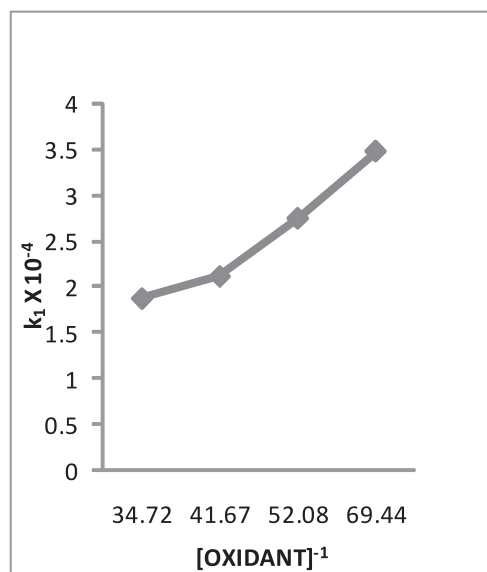


Fig. - 2 : A plot of  $k_1$  against  $[\text{Ce(IV)}]^{-1}$

#### Effect of oxidant :

In order to determine the order of a reaction with respect to oxidant, the reaction was studied at different concentration of the oxidant while keeping (Fig. 2) all other parameters constant. The reaction follows first order kinetics with respect to Ce (IV). The  $k_1$  values are given in Table 2. The value of  $k_1$  decreases with increase in concentration of oxidant which is contrary to our exception.

J. Shorter (8) and other have also observed a similar effect in their studies. This fact shows the formation of an equilibrium complex between the reactants prior to the rate determining step. A plot of  $k_1$  against  $[\text{Ce(IV)}]^{-1}$  is linear with an intercept on the rate axis provides a positive evidence for the formation of complex (Fig. 2)

#### Effect of ionic strength :

The reaction was carried out at five different values of ionic strength for each studied salt and at a constant temperature of 298 K. The concentrations of sulphuric acid, oxidant and substrate were kept constant. The ionic strength of the solution was varied separately with the addition of different salts viz. KCl, NaCl and NH<sub>4</sub>Cl. The results are recorded in Table 3.

The  $k_1$  value decrease with increase in ionic strength of the solution. Thus the retarding effect is observed on

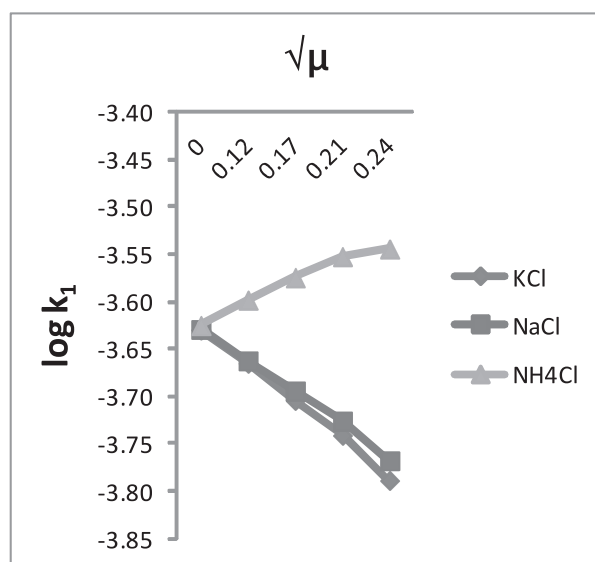


Fig. - 3: The plot of  $\log k_1$  against  $\sqrt{m}$ .

addition of potassium chloride salt. A plot of  $\log k_1$  against  $m$  is a straight line with negative slope (Fig. 3) indicating that the rate determining step of reaction probably involves the ions of opposite charges.

#### Effect of medium :

The reaction was carried out at five different concentration of sulphuric acid keeping all other parameters constant. The values of  $k_1$  are tabulated in Table 4.

The graph of  $k_1$  vs  $[H_2SO_4]^{-1}$  is depicted in Fig. 4.

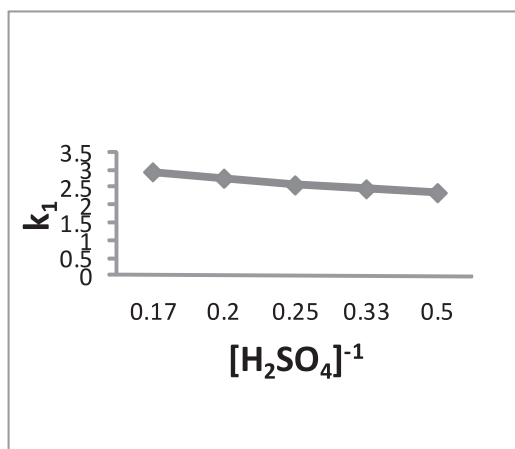


Fig. - 4 : The graph of  $k_1$  vs  $[H_2SO_4]^{-1}$

The results of Table 3 indicate that  $k_1$  increase with increase in concentration of sulphuric acid which is due to the unhydrolysed Ce (IV) species (9) in this reaction.

#### Effect of temperature :

The rate constants were determined at 298K, 303K, 308K, 313K, 318K and 323K and the results obtained are tabulated in Table 4.

The energy of activation ( $\Delta E$ ) is determined from the

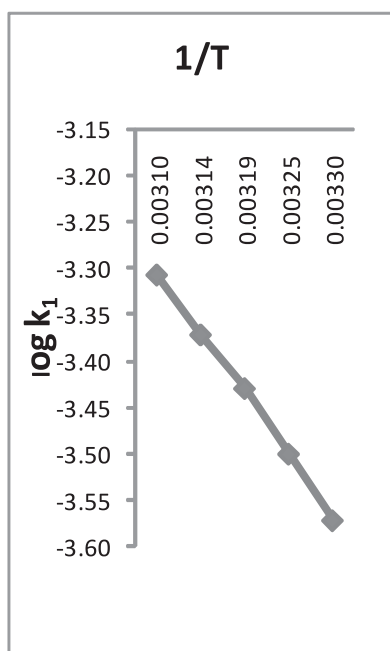
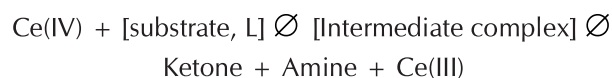


Fig. - 5 : The graph of  $\log k_1$  vs  $1/T$

graph of  $\log k_1$  vs  $1/T$  (Fig.5). Various thermodynamic parameters such enthalpy of activation ( $\Delta H$ ), free energy of activation ( $\Delta G$ ), entropy of activation ( $\Delta S$ ), and frequency factor (A) were calculated and are reported in Table 5.

The low values of (A) and negative value of ( $\Delta S$ ) indicate the formation of a more rigid activated complex / between Ce(IV) and substrate(L).

On the basis of the data obtained, an outline of the steps involved in the oxidation of a schiff base by Ce(IV) is as given below:



#### Conclusion :

These studies can be extended to study the varied drug intermediates and pharmaceutically active and important substances.

#### Acknowledgements :

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Table -1: Effect of concentration of substrate on the Schiff base oxidation by Ce(IV) in aq.  $H_2SO_4$  at 298 K.

$[Oxidant] = 2.40 \times 10^{-2}$  Ionic Strength = 0.288 (KCl)

$[Substrate] \times 10^{-3}$	$k_1 \times 10^{-4} \text{ sec}^{-1}$ (Average)	$k_2 \times 10^{-1} \text{ mole}^{-1} \text{ sec}^{-1}$
0.9615	2.3665	2.4613
0.8650	1.9067	2.2043
0.7690	1.7639	2.2938
0.5770	1.5008	2.6010
0.3850	1.1353	2.9488

Table -2 : Effect of concentration of oxidant on the Schiff base oxidation by Ce(IV) in aq. H<sub>2</sub>SO<sub>4</sub> at 298 K.

[Substrate (L)] = 0.9615 x 10<sup>-3</sup> Ionic Strength = 0.288 (KCl)

[Oxidant] x 10 <sup>-2</sup>	k <sub>1</sub> x 10 <sup>-4</sup> sec <sup>-1</sup> (Average)
1.44	3.4779
1.92	2.7434
2.403	2.1146
2.88	1.8702

Table - 3: Effect of ionic strength on oxidation of Schiff base by Ce(IV) in aq. H<sub>2</sub>SO<sub>4</sub> at 298 K.

[H<sub>2</sub>SO<sub>4</sub>] = 2.0 N

[Oxidant] = 2.40 x 10<sup>-2</sup>

[Substrate(L)] = 0.9615 x 10<sup>-3</sup>

Salt	Ionic strength →	0.288	0.303	0.318	0.333	0.348
KCl	k <sub>1</sub> x 10 <sup>-4</sup> sec <sup>-1</sup>	2.3467	2.1646	1.9778	1.8166	1.628
NaCl	k <sub>1</sub> x 10 <sup>-4</sup> sec <sup>-1</sup>	2.3496	2.1769	2.0231	1.8806	1.7079
NH <sub>4</sub> Cl	k <sub>1</sub> x 10 <sup>-4</sup> sec <sup>-1</sup>	2.3715	2.5252	2.6646	2.8045	2.8556

Table - 4 : Effect of solvent concentration, H<sub>2</sub>SO<sub>4</sub> on the oxidation reaction of Schiff base by Ce(IV) at 298 K..

[Oxidant] = 2.40 x 10<sup>-2</sup>

Ionic Strength = 0.288 (KCl)

[H <sub>2</sub> SO <sub>4</sub> ]	2	3	4	5	6
k <sub>1</sub> x 10 <sup>-3</sup> sec <sup>-1</sup>	2.3665	2.4764	2.5819	2.7731	2.9592

Table - 5 : Determination of thermodynamic parameters for oxidation of Schiff base by Ce(IV) in aq. H<sub>2</sub>SO<sub>4</sub>.

[Oxidant] = 2.40 x 10<sup>-2</sup> M

[H<sub>2</sub>SO<sub>4</sub>] = 2.0 N

[Substrate(L)] = 0.9615 x 10<sup>-3</sup> M

Ionic Strength = 0.288 (KCl)

Temp.(K)	k <sub>1</sub> x 10 <sup>-4</sup> sec <sup>-1</sup>	ΔE in KJ /mole	ΔH in KJ /mole	ΔG in KJ /deg/mole	ΔS KJ /mole	A, sec <sup>-1</sup>
298	2.3665	24.2472	21.7696	95.9582	-241.7686	4.097 x 10 <sup>3</sup>
303	2.6857		21.7280	96.1630	-241.8170	
308	3.1624		21.6864	97.3515	-241.6915	
313	3.7168		21.6449	98.5948	-241.4038	
318	4.2432		21.6033	99.7930	-241.1514	
323	4.9164		21.5617	99.9702	-241.0657	

From Graph, ΔE<sub>a</sub> = 24.2355

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