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Kinetic study of oxidation of schiff bases: Part-V. 5-Chloro-2-Hydroxy-4-Methylacetophenone- 2'-Bromoanil by CE (IV) in acidic medium

*Mahajan Hemant A., #Yamgar R. S., *Patil C. J. and *C. A. Nehete

*Department of Chemistry, Smt. G. G. Khadse College, Muktainagar, Dist. Jalgaon-425 306, MS, India. (hamahajan6@gmail.com)
 # Patkar-Varde College, S. V. Road, Goregaon (W), Mumbai – 400 062.

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ABSTRACT

Oxidation of Schiff base and its kinetics have been studied by Ce^{+4}/Ce^{+3} redox systems 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 $[CHMA2BA]^{-1}$ 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. ΔE, ΔH, ΔG and ΔS and activation energy, "A" were also evaluated for the present oxidation process. On the basis of experimental data a possible mechanism is suggested for the oxidation of CHMA2BA.

Key words: 5-Chloro-2-hydroxy-4-methylacetophenone-2'-bromoanil (CHMA2BA), Ceric sulphate, oxidation mechanism, kinetics and thermodynamics.

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INTRODUCTION

The kinetic study of several organic substances has been well investigated by using Ce (IV) $\rightarrow$ Ce (III) redox system[1-4]. Also the studies on oxidation of Schiff base by Ceric sulphate in Sulphuric acid medium are reported[5-6]. Recently, we have reported the kinetic study of the ketoanil viz. 5-Chloro-2-hydroxy-4-methylacetophenone-anil (CHMAA)[7] and their chloro derivatives[8-10] by Ce(IV) $\rightarrow$ Ce(III) redox couple. Our present communication deals with the kinetic study of Schiff base, CHMA2BA, by Ceric sulphate in aqueous Sulphuric acid.

MATERIALS AND METHODS

Experimental: All the chemicals and reagents used were of synthetic and AR grade respectively. The Schiff base was synthesized as per the method suggested by G. Reddelien[11]. The Schiff base (CHMA2BA) was prepared by taking equimolar mixture of 5-chloro-2-hydroxy-4-methylacetophenone (CHMA) and 2-bromoaniline (2BA) were placed in 500 ml round bottom flask. Anhydrous Zinc chloride(0.5 gm) was then added(as dehydrating agent). The mixture was then heated to 160°C for 30 min. in an oil bath. Then temperature was raised to 180°C and kept for 5 min. It was then cooled and the Schiff base was extracted with Chloroform. The solvent chloroform was distilled off from the extract, gave the final product which was then recrystalised from ethanol and ascertained by TLC monitoring. Stock solutions of Ceric sulphate and Ferrous ammonium sulphate were prepared in 2N sulphuric acid and standardized by reported method[12].

Kinetic measurements: Oxidation of substrate i.e CHMA2BA, and its kinetics was carried out at constant desired temperature with the help of an electrically heated thermostat with an accuracy of ± 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 Ferroin as an indicator.

Method of calculations of the rate constant
For the unimolar quantities of reactants, value of first order rate constant were calculated using relation

$$k1 = (2.303/t) \log\left[\frac{a}{a-x}\right]$$

For the equi-molar quantities of reactants, value of second order rate constant were calculated using relations

$$k2 = (1/at) \left[\frac{x}{a-x}\right]$$

RESULTS AND DISCUSSION

Effect of substrate: To evaluate the order of reaction with respect to substrate, (CHMA2BA) 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.

Table-1: Effect of concentration of Schiff base (CHMA2BA) on oxidation process by Ce(IV)in aq. H_2SO_4 at 298 K.
[Oxidant] = 2.40 x 10^{-2} M   Ionic strength = 0.288 (KCl)

[CHMA2BA] x 10^{-3} M	k_1 x 10^{-4} sec^{-1} (Average)	k_2 X 10^{-1} mole^{-1} sec^{-1}
0.9615	1.656	1.72230
0.8650	1.4568	1.6841
0.7690	1.3923	1.8105
0.5770	1.2756	2.2107
0.3850	1.0258	2.6644

The k_1 values are found to be directly proportional to concentration of Schiff base studied indicating that reaction follows first order kinetics with respect to Schiff base, CHMA2BA and are in the range of 1.0258 x 10^{-4} sec^{-1} to 1.656 x 10^{-4} sec^{-1}. The values of k_2 (Second order constant), calculated from k_1/ [CHMA2BA], are practically constant which also proves first order dependence of reaction on the Schiff base. Fig. 1 shows the plot of k_1^{-1} Vs [CHMA2BA]$^{-1}$ which is linear making an intercept on rate axis indicating formation of equilibrium complex between Ce (IV) and CHMA2BA. Observed results and nature of curve is in concurrence with earlier from our laboratory[7-10] reports.

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 and ranges from 2.0925 x 10^{-4} sec^{-1} to 1.2705 x 10^{-4} sec^{-1}. The value of k_1 decreases with increase in concentration of oxidant which is contrary to our expectation. The results and nature of curve observed is in concurrence with earlier from our laboratory[7-10] reports. J Shorter[13] 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 [Ce(IV)]$^{-1}$ is linear with an intercept on the rate axis provides a positive evidence for the formation of complex (Fig. 2)

Table-2: Effect of concentration of oxidant on CHMA2BA oxidation process by Ce(IV)in aq. H_2SO_4 at 298 K.
[CHMA2BA] = 0.9615 x 10^{-3} M   Ionic strength = 0.288 (KCl)

[Oxidant] x 10^{-2} M	k_1 x 10^{-4} sec^{-1} (Average)
1.440	2.0925
1.920	1.7521
2.403	1.4458
2.880	1.2705
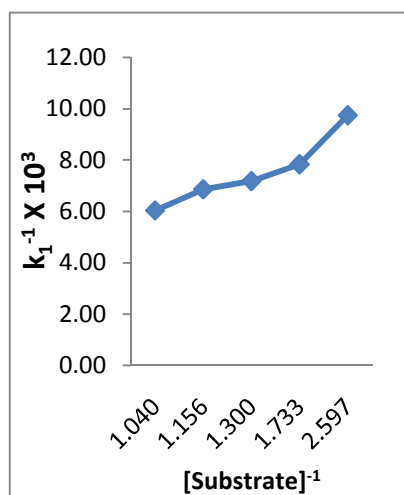
Fig.1:The plot of k_1^{-1} Vs $[CHMA2BA]^{-1}$ i.e [substrate]$^{-1}$
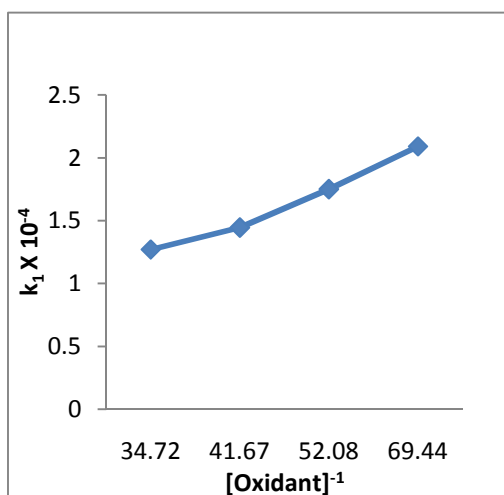
Fig.2: A plot of k_1 against $[Ce(IV)]^{-1}$ i.e [oxidant]$^{-1}$

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_4Cl. The results are recorded in Table 3.

The k_1 value decreases with increase in ionic strength of the solution. Thus the retarding effect is observed on addition of Potassium chloride salt and Sodium chloride whereas this effect shows reversal in case of Ammonium chloride. A plot of log k_1 against $\sqrt{\mu}$ is a straight line with negative slope (Fig. 3) indicating that the rate determining step of reaction probably involves the ions of opposite charges. Similar results were reported from our laboratory for the oxidation of Schiff bases from this laboratory[7-10].

**Table-3: Effect of ionic strength on oxidation of CHMA2BA by Ce(IV) in aq. H_2SO_4 at 298 K.**

$[H_2SO_4]$ = 2.0 N

[Oxidant] = 2.40 x 10^{-2} M   [CHMA2BA] = 0.9615 x 10^{-3} M

Salt	Ionic strength→	0.288	0.303	0.318	0.333	0.348
KCl	k_1 x 10^{-4} sec^{-1}	1.656	1.4215	1.2998	1.1525	0.9926
NaCl	k_1 x 10^{-4} sec^{-1}	1.6389	1.4188	1.3105	1.2257	1.1368
NH_4Cl	k_1 x 10^{-4} sec^{-1}	1.6405	1.7012	1.7490	1.8912	1.9425

Effect of cation size: Reaction was carried out using three different electrolytes having different cation in acidic medium. Rate increases with increase in the size of cation and decreases with decrease in the size of cation of the electrolyte.

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 and the values ranges from 1.656 x 10^{-3} sec^{-1} to 2.183 x 10^{-3} sec^{-1}.

Table-4: Effect of solvent concentration (H_2SO_4), on the oxidation reaction of CHMA2BA at 298 K.

[Oxidant] = 2.40 x 10^{-2} M   Ionic strength = 0.288 (KCl)

$[H_2SO_4]$ N	2.0	3.0	4.0	5.0	6.0
k_1 x 10^{-3} sec^{-1}	1.656	1.9205	2.0565	2.1308	2.1834
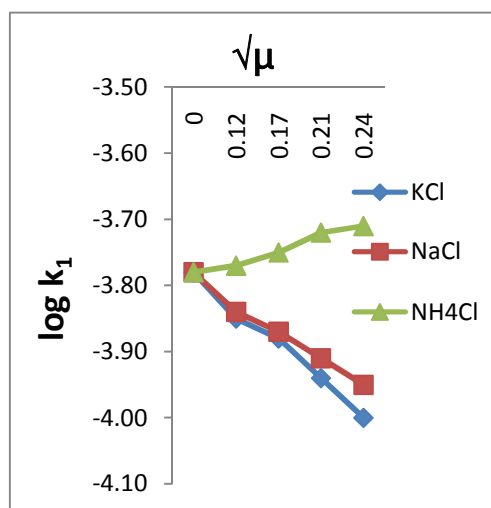
Fig. 3: The plot of log k_1 against $\sqrt{\mu}$.
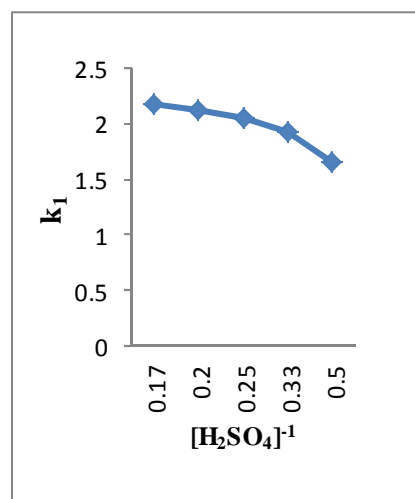
Fig. 4: The graph of k_1 Vs $[H_2SO_4]^{-1}$

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[7-10, 14] in this reaction.

Effect of temperature:
The kinetic parameters (rate constants) were determined at 298K, 303K, 308K, 313K, 318K and 323K, at constant $[CHMA2BA] = 0.9615 \times 10^{-3}$ M, in 2.0 N H_2SO_4 and the results obtained are tabulated in Table 5. The second order rate constant (Table 1) depends on the reaction temperature[7-10].

Table-5: Determination of kinetic and thermodynamic parameters for oxidation of CHMA2BA by Ce(IV) in aq. H_2SO_4.

[Oxidant] $=2.40 \times 10^{-2}$ M   [CHMA2BA] $= 0.9615 \times 10^{-3}$ M
[H_2SO_4] $= 2.0$ N   Ionic strength $= 0.288$ (KCl)

Temp.(K)	$k_1 \times 10^{-4}$ sec^{-1}	[1]ΔE in KJ /mole	ΔH in KJ /mole	ΔG in KJ /deg/mole	ΔS KJ /mole	A sec^{-1}
298	1.656		16.0725	94.5686	-266.86	
303	1.8612		16.0310	95.9029	-259.00	
308	2.1167	18.550	15.9894	97.1979	-262.41	0.2957
313	2.3824		15.9478	98.5099	-263.27	
318	2.6678		15.9063	99.8263	-267.81	
323	2.9526		15.8647	101.1653	-26381	

[1]*Note: From Graph, ΔE = 18.956 KJ/mol, which approximately matches to the experimental values.*
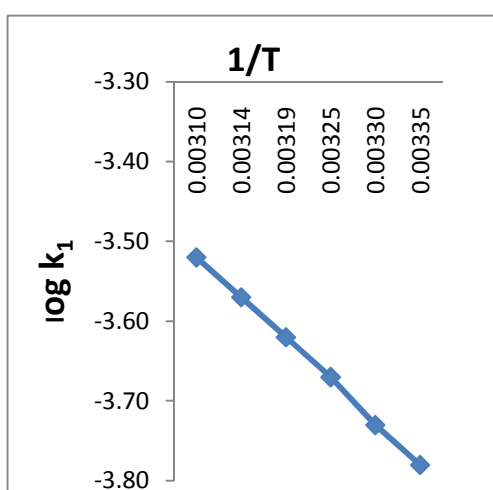
Fig.5: The graph of log k_1Vs 1/T

The thermodynamic parameters viz. energy of activation (ΔE) is determined
from the graph of log k_1 Vs 1/T (Fig.5). Various thermodynamic parameters
such as energy of activation (ΔE), enthalpy of activation (ΔH), free energy of activation (ΔG), entropy of activation(ΔS),and frequency factor (A) were calculated and are reported in Table 5.

The thermodynamic parameters such as (ΔH) and (ΔS) are important in controlling the rates of reaction. The low values of (A) and negative value of (ΔS) indicate the formation of a more rigid activated complex between Ce(IV) and CHMA2BA is less probable and rate is slower. The negative value of entropy indicates that there is formation of

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rigid transition state. Relatively small values of (ΔH) and negative value of (ΔS) are consistent with the reaction which generally proceeds through highly organized transition state[10, 15].

If both the reactants are likely charged, the charge density on the surface in the transition state will be more and hence there can be increase in salvation leading to a negative (ΔS) value[10, 16].This observation is supported by our earlier report[7-10] from our laboratory by the oxidation of Schiff bases by using the same reagent.

Mechanism of the Oxidation of the Schiff base under study:
On the basis of the data obtained, the mechanism of the oxidation of a Schiff base by Ce(IV) may be given below**:**

   Ce(IV)   +   [substrate i.e CHMA2BA]   →   [Intermediate complex]   →   Ketone   +   Amine +   Ce(III)
Which is similar to our earlier report[7-9] in case of the similar compounds by Ce(IV).

The species of cerium complexes in sulphuric acid has been widely investigate[4, 6, 17-19]. The isolation of number of cerium (IV) complexes from sulphuric acid has also shown by G. Hargraves L. H. Sutcliffe[3, 7]. 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[18], $H_4Ce(SO_4)_4$ which must be reactive species in the reaction and the action of it, on the substrate may be a rate determining step[10]. Specifically the possible mechanism of oxidation of the CHMA2BA may be written as given in **Scheme-1**.

Scheme-1.
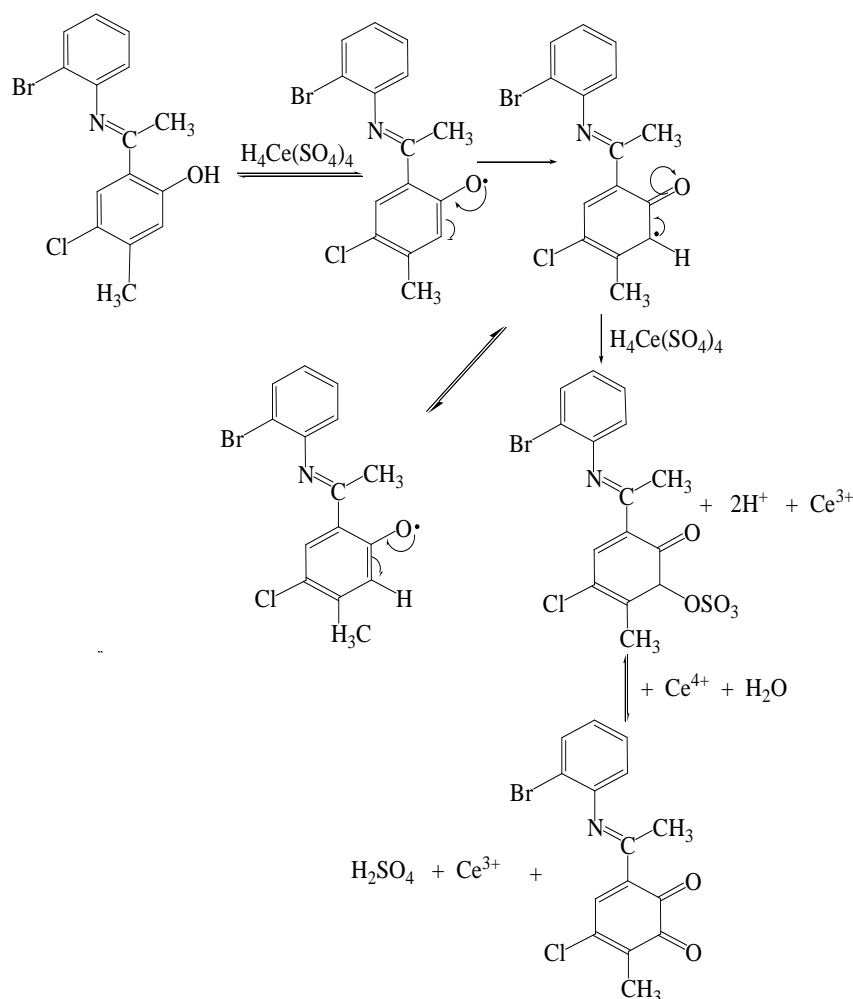
The kinetics of oxidation of 2-Hydroxy-naphthalidene-anil and its substituted derivatives in the aniline part have been studied in aqueous Sulphuric acid medium by Ce^{4+} to Ce^{3+} and reported the similar type of the reaction mechanism[7-10].

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CONCLUSION

This study can be extended to varied drug intermediates, pharmaceutical actives (API) and can be applied to important organic substances bearing similar type of functional groups. From the obtained experimental data, the probable reaction mechanism can be ascertained.

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