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# Kinetic study of oxidation of Schiff bases: Part-III. 5-Chloro-2-hydroxy-4-methylacetophenone-3'-chloroanil by Ce (IV) in acidic medium

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## ABSTRACT

*Oxidation of schiff base and its kinetics 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 $[CHMA3CA]^{-1}$ 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. $\Delta E$, $\Delta H$, $\Delta G$ and $\Delta S$ 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 CHMA3CA.*

**Key words:** 5-Chloro-2-hydroxy-4-methylacetophenone-3'-chloroanil(CHMA3CA), Ceric sulphate, oxidation, mechanism, kinetics and thermodynamics.
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## INTRODUCTION

Schiff bases of acetophenone are of importance in many fields of chemistry. Recently, Schiff bases from varied acetophenone derivatives are reported in the literature[1-2]. The thermal characteristics i.e TGA-DSC data has also been reported[3] for the complexes prepared from aromatic ketonic derivative. The kinetic study of several organic substances has been well investigated by using Ce (IV) $\rightarrow$ Ce (III) redox system[4-6]. Also the studies on oxidation of schiff base by ceric sulphate in sulphuric acid medium are reported[7-8]. Recently, we have reported[9-10] the kinetic study of the keto-substituted-anils by Ce(IV) $\rightarrow$ Ce(III) redox couple. Our present communication deals with the kinetic study of schiff base, CHMA3CA, by ceric sulphate in acidic medium.

## MATERIALS AND METHODS

**Experimental:** All the chemicals and reagents used were of synthetic and AR grade respectively. The schiff base (CHMA3CA) was prepared from 5-Chloro-2-hydroxy-4-methylacetophenone (CHMA) and 3-Chloroaniline(3CA) as per the previously reported[9-10]. It was then purified by recrystallization using ethanol and ascertained by TLC indicated single spot product. Stock solutions of ceric sulphate and ferrous ammonium sulphate were prepared as per method reported[11].

**Kinetic measurements:** Oxidation of substrate i.e CHMA3CA, and its kinetics was carried out as per the method reported[9-10].

**Method of calculations of the rate constant**
The calculations were carried out as per the method reported earlier [10].

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## RESULTS AND DISCUSSION

**Effect of substrate:** To evaluate the order of reaction with respect to substrate, (CHMA3CA) 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 (CHMA3CA) 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)*

| [CHMA3CA] x $10^{-3}$ M | $k_1$ x $10^{-4}$ sec$^{-1}$ (Average) | $k_2$ X $10^{-1}$ mole$^{-1}$ sec$^{-1}$ |
|---|---|---|
| 0.9615 | 1.3888 | 1.4443 |
| 0.8650 | 1.2173 | 1.4066 |
| 0.7690 | 1.1762 | 1.5290 |
| 0.5770 | 1.0543 | 1.8274 |
| 0.3850 | 0.8169 | 2.1239 |

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, CHMA3CA and are in the range of 0.8169 x $10^{-4}$ sec$^{-1}$ to 1.3888 x $10^{-4}$ sec$^{-1}$. The values of $k_2$ (Second order constant), calculated from $k_1$ / [CHMA3CA], 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 [CHMA3CA]$^{-1}$ which is linear making an intercept on rate axis indicating formation of equilibrium complex between Ce (IV) and CHMA3CA. Observed results and nature of curve is in concurrence with earlier[9-10] 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 0.9424 x $10^{-4}$ sec$^{-1}$ to 1.7300 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[9-10] reports. 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 CHMA3CA oxidation process by Ce(IV)in aq. $H_2SO_4$ at 298 K.**

*[CHMA3CA] = 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 | 1.7300 |
| 1.920 | 1.4200 |
| 2.403 | 1.0910 |
| 2.880 | 0.9424 |
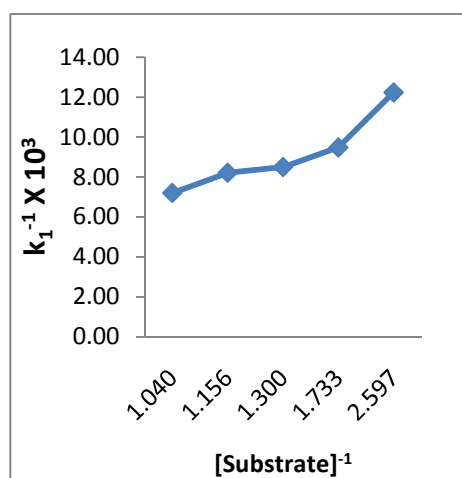


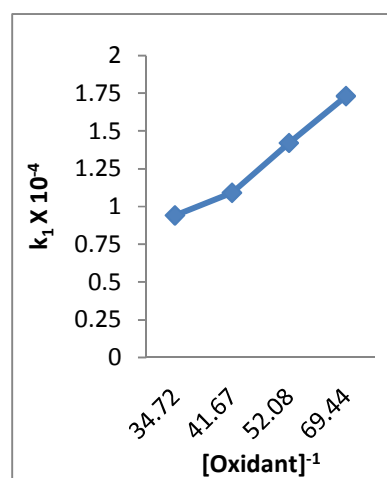**Fig.1:The plot of $k_1^{-1}$ vs [CHMA3CA]$^{-1}$ i.e [substrate]$^{-1}$**          **Fig.2: A plot of $k_1$ against [Ce(IV)]$^{-1}$ i.e [oxidant]$^{-1}$**

**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$_4$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 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 √μ 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 for the oxidation of Schiff bases from this laboratory[9-10].

**Table-3: Effect of ionic strength on oxidation of CHMA3CA by Ce(IV) in aq. H$_2$SO$_4$ at 298 K.**

*[Oxidant] = 2.40 x 10$^{-2}$ M          [H$_2$SO$_4$] = 2.0 N          [CHMA3CA] = 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$^{-1}$ | 1.3919 | 1.2384 | 1.1044 | 0.9537 | 0.8252 |
| NaCl | k$_1$ x 10$^{-4}$ sec$^{-1}$ | 1.3900 | 1.2733 | 1.1640 | 1.0723 | 0.9327 |
| NH$_4$Cl | k$_1$ x 10$^{-4}$ sec$^{-1}$ | 1.3694 | 1.5142 | 1.6099 | 1.7075 | 1.8280 |

**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$_2$SO$_4$]$^{-1}$ is depicted in Fig. 4 and the values ranges from 1.0767 x 10$^{-3}$ sec$^{-1}$ to 07587 x 10$^{-3}$ sec$^{-1}$.
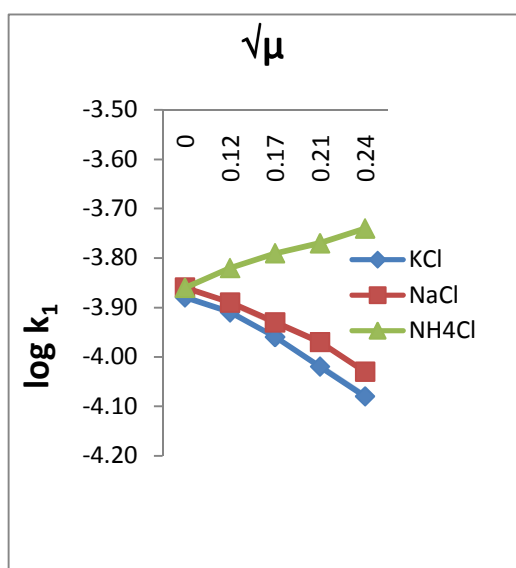


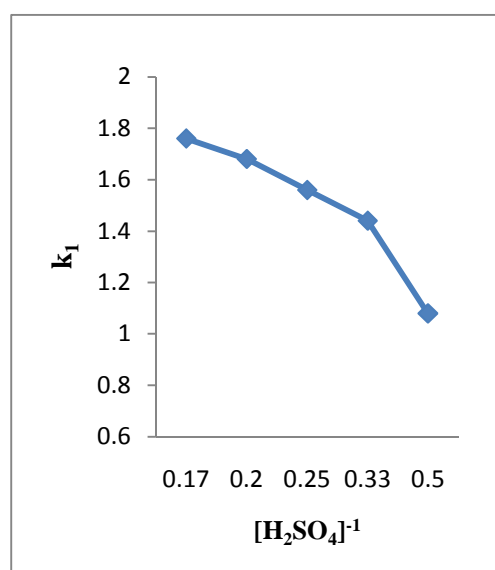Fig. 3: The plot of log k$_1$ against √μ.



Fig. 4: The graph of k$_1$ vs [H$_2$SO$_4$]$^{-1}$

The results of Table 4 indicate that k$_1$ increase with increase in concentration of sulphuric acid which is due to the unhydrolysed Ce (IV) species[9, 12] in this reaction.

**Table-4: Effect of solvent, H$_2$SO$_4$ concentration on the oxidation reaction of CHMA3CA by Ce(IV) at 298 K.**

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

| [H$_2$SO$_4$]  N | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
|---|---|---|---|---|---|
| k$_1$ x 10$^{-3}$ sec$^{-1}$ | 1.0767 | 1.4387 | 1.5653 | 1.6830 | 1.7587 |

**Effect of temperature:**
The kinetic parameters (rate constants) were determined at 298K, 303K, 308K, 313K, 318K and 323K, at constant [CHMA3CA] = 0.9615 x 10$^{-3}$ M, in 2.0 N H$_2$SO$_4$ and the results obtained are tabulated in Table 5. The second order rate constant (Table 1) depends on the reaction temperature[13].

The thermodynamic parameters viz. energy of activation ($\Delta E$) is determined from the graph of log $k_1$ vs 1/T (Fig.5). Various thermodynamic parameters such as energy of activation ($\Delta E$), enthalpy of activation ($\Delta H$), free energy of activation ($\Delta G$), entropy of activation ($\Delta S$), and frequency factor (A) were calculated and are given in Table 5.

**Table-5: Determination of kinetic and thermodynamic parameters for oxidation of CHMA3CA by Ce(IV) in aq. H$_2$SO$_4$.**

*[Oxidant] =2.40 x 10$^{-2}$ M            [CHMA3CA] = 0.9615 x 10$^{-3}$ M*
*[H$_2$SO$_4$] = 2.0 N                     Ionic strength = 0.288 (KCl)*

| Temp.(K) | $k_1$ x 10$^{-4}$ sec$^{-1}$ | [1]$\Delta$E in KJ /mole | $\Delta$H in KJ /mole | $\Delta$G in KJ /deg/mole | $\Delta$S KJ /mole | A, sec$^{-1}$ |
|---|---|---|---|---|---|---|
| 298 | 1.3888 | | 16.1868 | 95.3486 | -265.4205 | |
| 303 | 1.4786 | | 16.1454 | 96.4788 | -265.0654 | |
| 308 | 1.7690 | 18.6684 | 16.1039 | 97. 6321 | -264.7107 | 10.874 |
| 313 | 2.0520 | | 16.0623 | 98.8837 | -264.5792 | |
| 318 | 2.2355 | | 16.0207 | 100.2928 | -264.9367 | |
| 323 | 2.5726 | | 15.9792 | 101.5214 | -264.8074 | |

[1]*Note: From Graph, $\Delta E = 18.6594$ KJ/mol, which approximately matches to the experimental values.*

The thermodynamic parameters such as ($\Delta H$) and ($\Delta S$) are important in controlling the rates of reaction. The low values of (A) and negative value of ($\Delta S$) indicate the formation of a more rigid activated complex between Ce(IV) and CHMA3CA is less probable and rate is slower. The negative value of entropy indicates that there is formation of rigid transition state. Relatively small values of ($\Delta H$) and negative value of ($\Delta S$) are consistent with the reaction which generally proceeds through highly organized transition state[14].
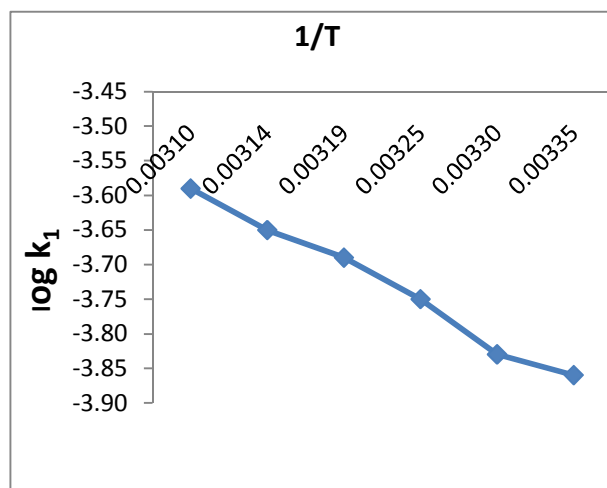


**Fig.5: The graph of log k$_1$vs 1/T**

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 ($\Delta S$) value[15]. This observation is supported by our earlier report[9] 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 CHMA3CA]   $\rightarrow$   [Intermediate complex]   $\rightarrow$   Ketone   +   Amine +   Ce(III)**

which is similar to our earlier report[9] in case of the similar compounds by Ce(IV).

The species of cerium complexes in sulphuric acid has been widely investigate[6, 8, 16-19]. The isolation of number of cerium (IV) complexes from sulphuric acid has been earlier reported[9-10]. 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[17], H$_4$Ce(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[19, 20]. Specifically the possible mechanism of oxidation of the CHMA3CA may be written as given in **Scheme-1**.
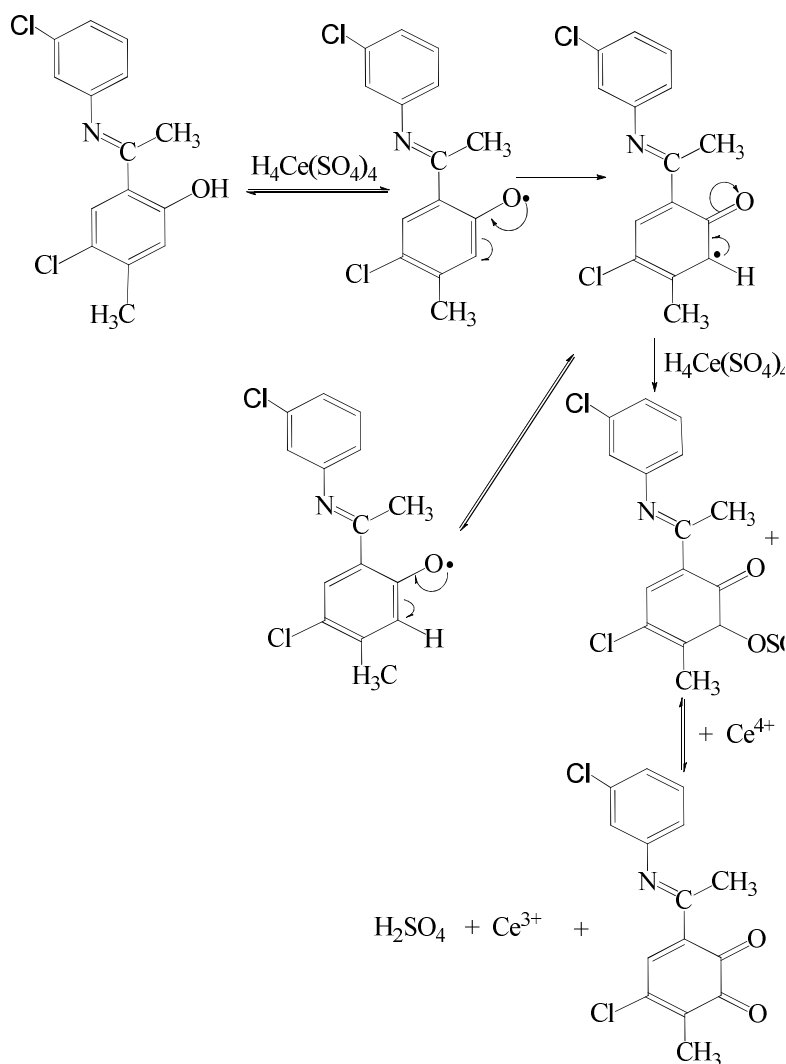
**Scheme-1**

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[21].

**CONCLUSION**

This study can be extended, to study the varied drug intermediates and pharmaceutical actives and important substances involving similar functional groups and based on the experimental data reaction mechanism can be assertain.

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