

Cooxidation of Dibenzalacetone with Oxalic Acid by Pyrazinium Chlorochromate

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Abstract. Oxidation of dibenzalacetone with pyrazinium chlorochromate in presence of oxalic acid has been studied at 313 K. Various reaction parameters such as effect of varying oxidant, substrate, Hydrogen ion concentration, catalyst, solvent composition, ionic strength, effect of Mn^{2+} , effect of Al^{3+} and effect of temperature were studied to determine the kinetics of the reaction. Our study revealed that the reaction followed first order dependence with respect to oxidant and catalyst. The reaction followed fractional order kinetics with respect to substrate and H^+ . Increase in ionic strength was found to have no effect on the reaction rate and decrease in the dielectric constant of the medium decreases the reaction rate. Increase in the concentration of manganous sulphate retarded the reaction rate which confirmed the two-electron transfer involved in the mechanism. There was no possibility of free radical mechanism, which was confirmed by the addition of acrylonitrile shows no significant effect on the reaction rate indicating the non-involvement of free radical reaction.. Based on the experimental observations a mechanism and rate law has been derived. Moreover, the oxidation product was found to be chalcone epoxide, which was characterized by IR spectrum.

1. Introduction

A good number of Cr(VI) complexes are being used in the oxidation of organic compounds. Pyridinium halochromate[1], pyridinium dichromate [2], bipyridyl chlorochromate[3], Quinolinium dichromate [4], Quinaldinium fluorochromate [5] are some of them. These are used for the regiospecific and chemospecific oxidative degradation of functional groups in highly sensitive systems. It has been observed that, with pyridinium halochromates the mode of oxidation depends on the anion attached to Cr(VI) species. The oxidation of aryl methyl sulphides by pyridinium dichromate is found to proceed by a nonradical polar mechanism. while, when potassium dichromate[6] is used, the reaction follows a radical mechanism, involving cation radical as the reaction intermediate. The modes of oxidation of lower oxyacids of phosphorous by pyridini that ,though the oxidizing species in all these cases is Cr(VI) the mode of oxidation is different when different complexed Cr(VI) is used as oxidant. Pyrazinium chlorochromate is reported to be a mild oxidant for selective oxidation in synthetic organic chemistry.

Literature survey reveals that there is less kinetic and mechanistic studies involving chalcones or phenyl styryl ketones were done. The utility of chalcones due to their usefulness as in synthesis of various heterocyclic compounds, as plant origin [8] and exhibit antimalarial [9], antibacterial [10], antifibrogenic [11], anticancer [12], antitrichomonal [13], antiinflammatory [14], antileishmanial [15], cytotoxic and anti-Trypanosoma cruzi [16] activities. Chalcones or phenyl styryl ketones are of great interest because they have a unique structural feature of having a $>C=O$ functional group in conjugation with $>C=C<$ and the whole molecule is in conjugation.

Dibenzylideneacetone or dibenzalacetone is a type of chalcone and is often abbreviated as DBA. It is an organic compound with the formula $C_{17}H_{14}O$. It is a bright yellow solid, insoluble in water, but soluble in ethanol .

In the present investigations the kinetic and mechanistic study of the oxidation of dibenzalacetone with oxalic acid was studied in aqueous acetic acid medium. Chalcones are oxidized by different oxidizing agents and in all these reactions either =C=O instead of =C=O= is attacked by various oxidants that have been used for oxidation of chalcones [17-23] The present work reports the Co-oxidation of dibenzalacetone with oxalic acid in aqueous acetic acid medium and evaluates the reaction constants and Mechanistic aspects are also discussed..

2. Experimental Methods

2.1: Materials:

Sodium hydroxide (NaOH), Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), Benzaldehyde($\text{C}_7\text{H}_6\text{O}$), acetone, ($\text{C}_3\text{H}_6\text{O}$) pyrazine ($\text{C}_4\text{H}_4\text{N}_2$) chromium trioxide (CrO_3) Hydrochloric acid (HCl), Sodium perchlorate, (NaClO_4), perchloric acid, (HClO_4), sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3$,manganous sulphate, MnSO_4 acrylonitrile $\text{C}_3\text{H}_3\text{N}$, potassium iodide (KI) and starch ($\text{C}_6\text{H}_{10}\text{O}_5$)_n were all of AnalaR grade and were used as such.

Water (H_2O) and acetic acid(CH_3COOH) solvents are used. These solvents are purified by the following methods,

Purification of acetic acid by Weissberger method:

The procedure followed for the purification of acetic acid was essentially similar to that of Weissberger[24]. Glacial acetic acid (AR) 2 litre was partially frozen and about one litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30 g) for 4 h and fractionally distilled. The portion distilling between $116\text{--}118^\circ\text{C}$ was collected, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractionated again after treating with chromium trioxide (30 g). The fraction boiling at $116\text{--}118^\circ\text{C}$ was collected and kept in brown bottles.

Purification of Water by deionized method:

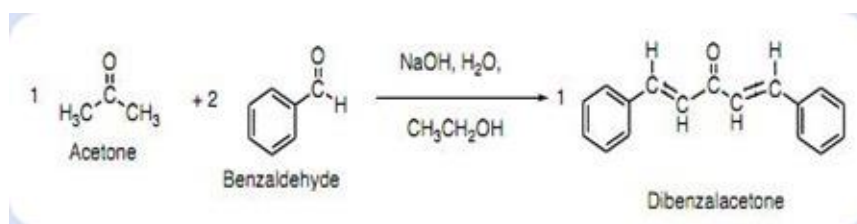
Deionised water was distilled twice in 'corning' glass vessels, the second distillation being from alkaline potassium permanganate and was used throughout the kinetic measurements.

2.2: Preparation of Pyrazinium Chlorochromate [25]

Pyrazinium chlorochromate was prepared by the addition of pyrazine (0.7g) in aqueous HCl (0.8ml MCI in 16ml H_2O) to a cooled solution of chromium trioxide (0.9g chromium trioxide in 0.8ml HCl of 8ml H_2O). The solution was stirred at 0°C with 20min. After stirring, a bright-orange crystal was formed and it's collected in a sintered crucible. Then, it was recrystallized with minimum amount of acidified water and dried for one hour in vacuum (yield 80%).The solid was not appreciably hygroscopic and can be stored for extended periods at room temperature without change. The pyrazinium chlorochromate formed was confirmed with its physical constant (m.p. $148\text{--}150^\circ\text{C}$) and further analyzed through IR and UV spectrum.

2.3: Preparation of Dibenzalacetone: [25]

A cold solution of 8 g of sodium hydroxide in 250 ml of water and 70 ml of ethanol was placed in a 500 ml round bottom flask equipped with mechanical stirrer and it was surrounded by ice water bath. The temperature of the solution was maintained at $20\text{--}25^\circ\text{C}$ and stirred vigorously. To the above solution one half of previously prepared mixture (8.8 g of pure benzaldehyde and 2.4 g of acetone) was added. A flocculant precipitate was formed in 2-3 minutes. The remaining portion of benzaldehyde - acetone mixture was added after 15 min. The precipitate was filtered off and washed well with cold water to eliminate the alkali as completely as possible. The solid was dried at room temperature to constant weight and 9 g of crude dibenzalacetone (93%) with m.p. $105\text{--}108^\circ\text{C}$ were obtained. It was recrystallised from ethyl acetate. The compound melted at 107°C [m.p. $105\text{--}108^\circ\text{C}$].



2.4: Kinetic measurements

The reaction was carried out under pseudo-first order conditions [dibenzalacetone] $\gg$ [Pyrazinium chlorochromate] in 55% (v/v) aqueous acetic acid containing perchloric acid. The course of the reaction was followed spectrophotometrically (ELICO SL207 MINISPEC) at 470 nm for upto 80% of the reaction. The pseudo-first order rate constants k_1 computed from the linear plots of log absorbance versus time by the least squares method, were reproducible within $\pm 2\%$.

2.5: Stoichiometry and product analysis:

The reaction mixture containing an excess of pyrazinium chlorochromate over dibenzalacetone were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unchanged pyrazinium chlorochromate showed that one mole of dibenzalacetone consumed one mole of the pyrazinium chlorochromate.

The product chalcone epoxide was identified by its physical constant (m.p. 132°C) and was further confirmed by FT-IR spectrum.

3. Results and Discussions

Kinetics and mechanism of oxidation of dibenzalacetone by Pyrazinium chlorochromate:

3.1. Effect of varying the [oxidant]

In this study [oxidant] mentioned by [pyrazinium chlorochromate]. The reaction was investigated with varying concentration of Pyrazinium chlorochromate, keeping the concentration of dibenzalacetone always in excess and perchloric acid constant. The reaction was found to be first order with respect to the dibenzalacetone. Pyrazinium chlorochromate as evidenced by the linear plot of log (titre) versus time (Figure. 1). This was further confirmed by the constancy of the pseudo-first order rate constants at various initial concentration of the dibenzalacetone (Table - 1)

Table - 1

[Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$
 [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$
 $[\text{H}^+]$ = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$

Solvent = 55% acetic acid – water (v/v)
 Temperature = 313 K

[Oxidant] $\times 10^3$ mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
0.50	4.54
1.00	4.52
1.50	4.54
2.00	4.53
2.50	4.55

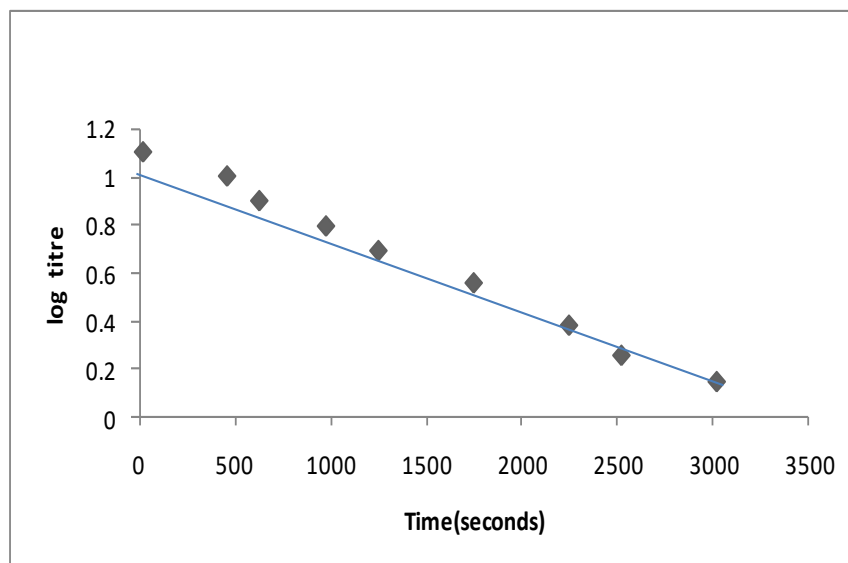


Figure 1. Plot of log (titre) *versus* time

3.2. Effect of varying the [Substrate]

At constant concentration of oxidant and H^+ , the reaction was carried out varying the concentration of the substrate. The pseudo-first order rate constants increase with increase in the concentration of substrate and the plot of $\log k_1$ *versus* [substrate] gave a straight line with a slope of 0.35 (Figure. 2) showing a fractional order dependence on substrate (Table – 2). It was also verified by Michaelis - Menten plot[26,27] (Figure. 3)

Table - 2

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$

Solvent = 55% acetic acid – water (v/v)

[Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$

Temperature = 313 K

$[H^+]$ = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$

[Substrate] x 10^2 mol dm^{-3}	k_1 x 10^4 s^{-1}
0.50	3.71
1.00	4.54
1.50	5.45
2.00	5.98
2.50	6.49

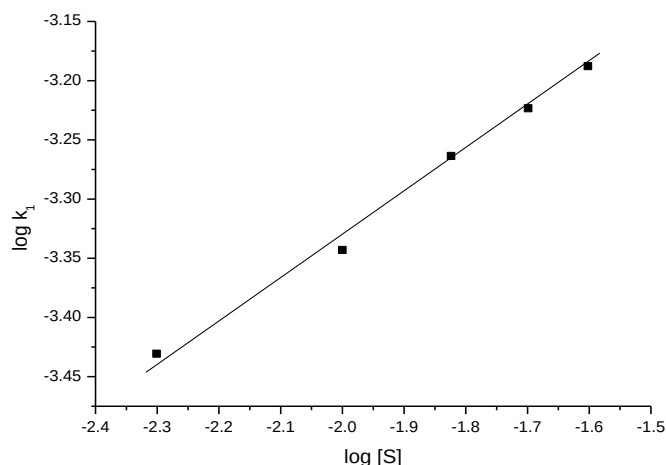


Figure 2. Plot of $\log k_1$ versus $\log [S]$

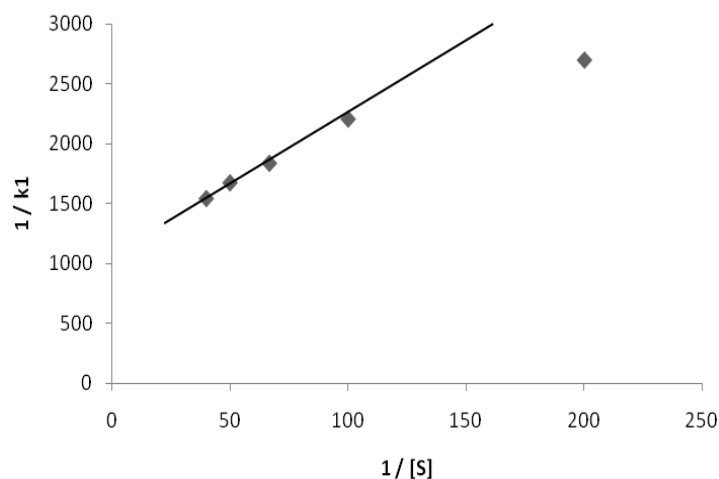


Figure 3. Plot of $1/k_1$ versus $1/[S]$

3.3. Effect of varying the $[H^+]$

The effect of change in acidity on the rate of the reaction the rates were measured at different perchloric acid concentration at constant [substrate], [oxidant] and temperature. The rate constants increase with increase in the concentration of perchloric acid (Table - 3). The plot of $\log k_1$ versus $\log [H^+]$ gave a straight line with a slope of 0.63 indicating fractional order dependence of $[H^+]$ (Figure. 4).

Table - 3

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$

[Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$

[Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$

Solvent = 55% acetic acid – water (v/v)

Temperature = 313 K

$[H^+] \times 10^2$ mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
3.50	2.99
5.25	3.73
7.00	4.54
8.75	5.12
10.25	5.99

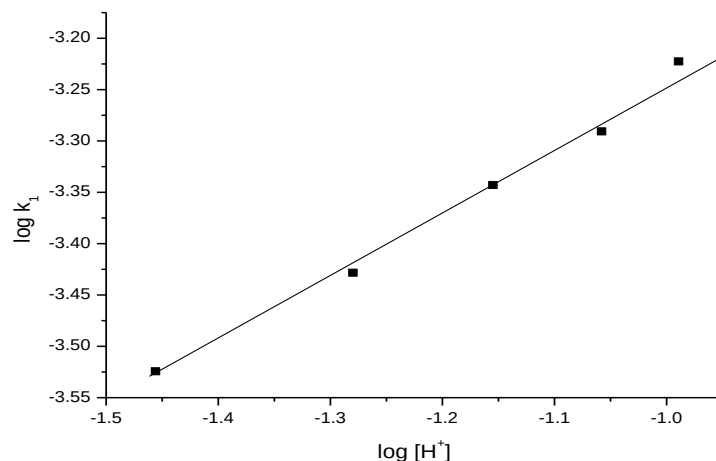


Figure 4. Plot of $\log k_1$ versus $\log [H^+]$

3.4. Effect of varying the [Catalyst]

The reaction was carried out with varying concentration of oxalic acid, keeping all the other factors constant. The rate constants were found to increase with increase in the concentration of [oxalic acid] (Table- 4). The reaction shows unit order dependence with respect to oxalic acid as evidence by the plot of $\log k_1$ versus $\log [\text{catalyst}]$ which was linear with slope of unity ($r = 0.999$) (Figure. 5)

Table - 4

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$

Solvent = 55% acetic acid – water (v/v)

[Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$

Temperature = 313 K

$[H^+]$ = $7.0 \times 10^{-2} \text{ mol dm}^{-3}$

[Catalyst] x 10 ³ mol dm ⁻³	k ₁ x 10 ⁴ s ⁻¹
1.50	1.66
3.00	3.14
4.50	4.54
6.00	6.38
7.50	7.55

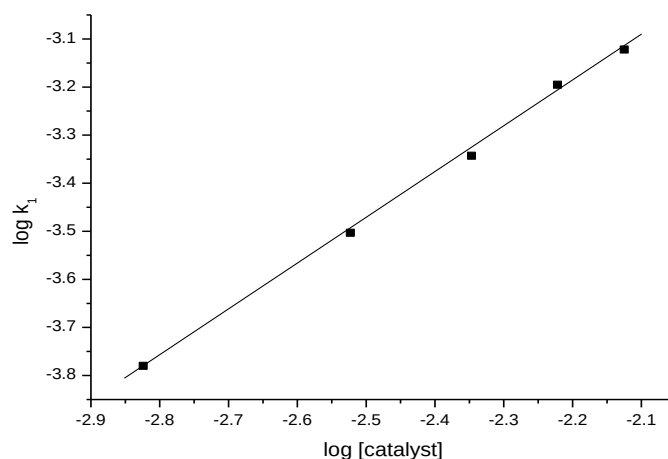


Figure 5. Plot of $\log k_1$ versus $\log [\text{Catalyst}]$

3.5. Effect of varying the ionic strength

The effect of ionic strength on the reaction rate was studied with varying concentrations of sodium perchlorate keeping all other factors constant. The results indicated that ionic strength no appreciable on the reaction rate (Table – 5) which confirmed by the participation of an ion and neutral molecule in the rate controlling step[28].

Table - 5

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$
 [Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = 55% acetic acid – water (v/v)
 [H⁺] = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313 K

$[\text{NaClO}_4] \times 10^3$ mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
0.00	4.54
0.50	4.56
1.00	4.57
1.50	4.53
2.00	4.56

3.6. Effect of varying solvent composition

The reactions were carried out at four different percentage of acetic acid- water mixtures and keeping the other factors constant (Table -6). It was observed that an increase in the percentage of acetic acid considerably increased the rate of the reaction. This suggests the involvement of an ion-dipole interaction in the rate determining step[29]

Table - 6

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$
 [H⁺] = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313 K
 [Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$

% acetic acid-water (v/v)	$k_1 \times 10^4$ s^{-1}
50	3.98
55	4.54
60	5.01
65	5.32
70	5.74

3.7. Effect of varying the [acrylonitrile]

The reaction was studied with varying concentration of acrylonitrile, keeping all the other factors constant. (Table – 7). The clear mixture containing dibenzalacetone and pyrazinium chlorochromate when allowed to stand with a drop of acrylonitrile [30] no turbidity is formed suggesting the

noninvolvement of free radicals in this reaction In this effect varying the concentration of acrylonitrile the rate of the reaction does not change, There is no effect on rate constant.

Table - 7

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$
 [Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = 55% acetic acid – water (v/v)
 [H⁺] = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313 K

[acrylonitrile] x 10 ² mol dm ⁻³	k ₁ x 10 ⁴ s ⁻¹
0.00	4.54
0.50	4.51
1.0	4.53
1.5	4.50
2.0	4.52

3.8. Effect of varying the [Mn²⁺]

The reaction was followed with varying concentrations of Mn²⁺ ions keeping all the other factors constant. the reaction rate decreases with increasing the concentration of Mn²⁺ ions confirming the involvement of two electron process in this reaction [31-33] (Table – 8).

Table - 8

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ Solvent = 55% acetic acid – water (v/v)
 [Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313 K30
 [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$

[Mn ²⁺] x 10 ³ mol dm ⁻³	k ₁ x 10 ⁴ s ⁻¹
0.00	4.54
0.50	4.19
1.00	3.82
1.50	3.54
2.00	3.81

3.9. Effect of varying the [Al³⁺]

The reaction was carried out with varying concentration of Al³⁺ ion, keeping all the other factors constant. There was an increase in the rate with the increasing concentration of Al³⁺ ion. The addition of Al³⁺ ion has noticeable catalytic effect on the reaction rate (Table – 9)

Table - 9

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$
 [Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = 55% acetic acid – water (v/v)
 [H⁺] = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313 K

$[\text{Al}^{3+}] \times 10^3$ mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
0.00	4.54
0.50	4.62
1.00	4.92
1.50	5.23
2.00	5.53

3.10. Effect of varying the temperature

The reaction has been studied at four different temperatures keeping other factors constant. The pseudo-first order rate constants are given (Table - 10). The activation parameters were calculated from the least square procedure of a linear plot of $\ln(k/T)$ versus $1/T$ of Eyring's equation[34] (Figure. 6). The negative value of entropy of activation $\Delta S^\ddagger$ indicate a polar transition state with extensive charge separation which promote high degree of solvation of the transition state compared to the reactant. Additionally, the enthalpy and entropy changes (ΔH and ΔS) were obtained using the van't Hoff equation.[35]

The van't Hoff graphs were obtained by plotting $\ln(K_C)$ vs. $1/T$. [36,37]. The positive value indicate the endothermic process .

$$\ln K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Table - 10

[Pyrazinium chlorochromate] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ [Catalyst] = $4.50 \times 10^{-3} \text{ mol dm}^{-3}$
 [Substrate] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ Solvent = 55% acetic acid – water (v/v)
 [H⁺] = $7.00 \times 10^{-2} \text{ mol dm}^{-3}$

Temperature K	$k_1 \times 10^4$ s^{-1}
303	2.62
313	4.54
323	6.48
333	9.53

$$\begin{aligned}\Delta H^\ddagger &= 28.03 \text{ kJ mol}^{-1} \\ \Delta S^\ddagger &= -135.57 \text{ JK}^{-1} \text{ mol}^{-1} \\ \Delta G^\ddagger &= 70.47 \text{ kJ mol}^{-1} \text{ at } 313 \text{ K}\end{aligned}$$

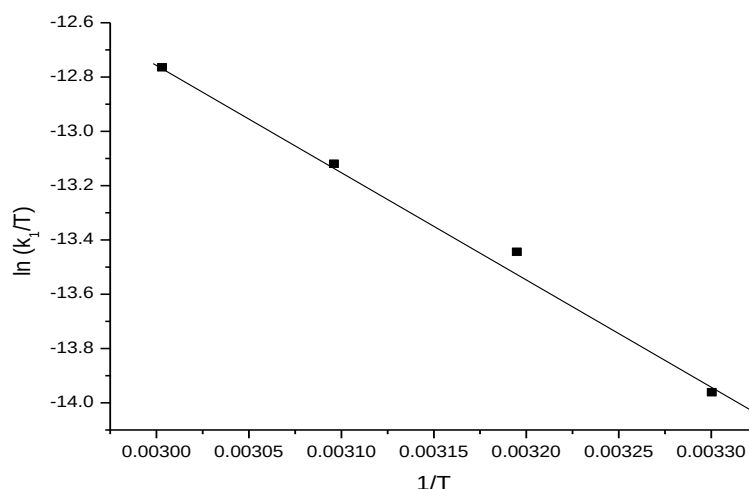
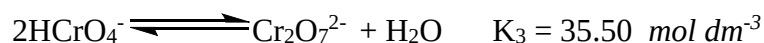
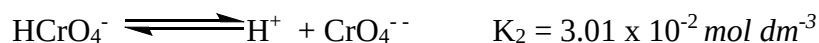


Figure 6. Plot of $\ln(k_1/T)$ versus $1/T$

3.11. Mechanism

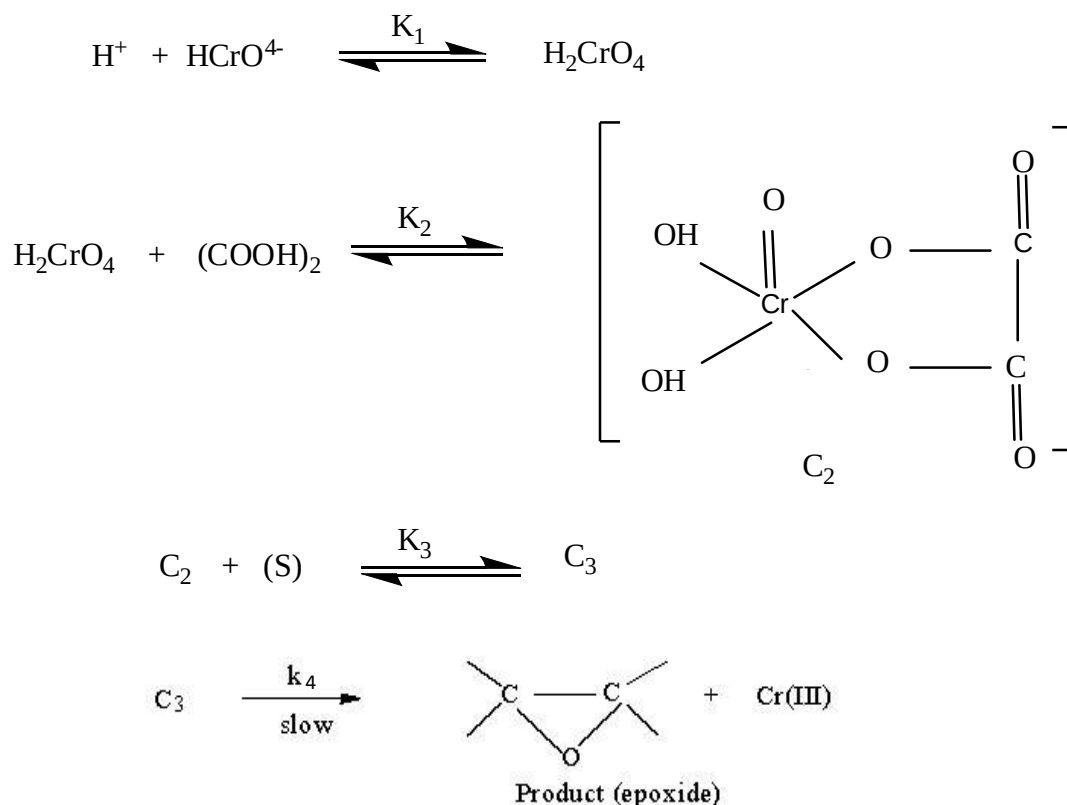
Based on the reaction is showing first order dependence with respect to oxidant and catalyst and fractional order with respect to substrate and $[H^+]$ ion.

The oxidation by Cr(VI) will vary with nature of the Cr(VI) species used and the solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ions the following equilibria are existing[38].



Here the dimerization equilibrium is of considerable importance. In water the dichromate ion will be predominating species only at the concentration of Cr(VI) is greater than about 0.05 mol dm^{-3} . In this case, as the concentration of Cr(VI) is less than 0.05 mol dm^{-3} monomeric form predominates and the active oxidizing species is $HCrO_4^-$. The reaction is acid catalyzed one.

The rates were found to increase with the increase in the percentage of acetic acid. i.e., with decrease in dielectric constant of the medium. The enhanced oxidizing ability is attributed to the formation of acetochromate ion. The acetyl group enhances the electron accepting power of chromium thereby facilitating the reaction.[39] The reaction mixture when allowed to stand with acrylonitrile does not induce polymerization suggesting the absence of free radical pathway. The added Mn^{2+} ions retard the rate of the reaction. The addition of Al^{3+} has noticeable catalytic effect on the reaction rate. Based on the above observations, the mechanism and rate law was proposed (Scheme- IV).



3.12. Rate Law

Hydrogen ion react with chromium species to form Protonated chromium species and then reacts with oxalic acid to form complex (C₂). complex react with dibenzalacetone to form complex (C₃). Complex (C₃) in slow step to form chalcone epoxide as product.

Based on the above mechanism the rate law will be derived. The rate dependent on the rate constant k₄.

$$\text{rate} = k_4 [\text{C}_3]$$

$$= \frac{K_3 k_4 [\text{S}] \text{C}_2}{\{1 + K_3 [\text{S}]\}}$$

$$= \frac{K_2 K_3 k_4 [\text{S}] \text{C}_1 [\text{ox}]}{\{1 + K_3 [\text{S}]\}}$$

$$= \frac{K_1 K_2 K_3 k_4 [\text{S}] [\text{ox}] [\text{Cr(VI)}] [\text{H}^+]}{\{1 + K_3 [\text{S}]\} \{1 + K_1 [\text{H}^+]\}}$$

$$\begin{aligned}
 &= \frac{K_1 K_2 K_3 k_4 [S] [ox] [Cr(VI)] [H^+]}{\{1 + K_3 [S] K_1 [H^+] + K_3 [S] + K_1 [H^+]\}} \\
 &= \frac{K_1 K_2 K_3 k_4 [S] [ox] [Cr(VI)] [H^+]}{\{1 + K_1 [H^+]\} \{1 + K_3 [S]\}} \\
 k_{obs} &= \frac{K_1 K_2 K_3 k_4 [S] [ox] [H^+]}{\{1 + K_1 [H^+] + K_3 [S]\}}
 \end{aligned}$$

Conclusion

Oxidation of dibenzalacetone with pyrazinium chlorochromate in presence of oxalic acid has been studied at 313 K. Various reaction parameters such as effect of varying oxidant, substrate, Hydrogen ion concentration, catalyst, solvent composition, ionic strength, effect of Mn^{2+} , effect of Al^{3+} and effect of temperature were studied to determine the kinetics of the reaction. Our study revealed that the reaction followed first order dependence with respect to oxidant and catalyst. The reaction followed fractional order kinetics with respect to substrate and H^+ . Increase in ionic strength was found to have no effect on the reaction rate and decrease in the dielectric constant of the medium decreases the reaction rate. Increase in the concentration of manganous sulphate retarded the reaction rate which confirmed the two-electron transfer involved in the mechanism. There was no possibility of free radical mechanism, which was confirmed by the addition of acrylonitrile shows no significant effect on the reaction rate indicating the non-involvement of free radical reaction.. Based on the experimental observations a mechanism has been proposed and rate law has been derived. Moreover, the oxidation product was found to be chalcone epoxide, which was characterized by IR spectrum.

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