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Research Article

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Oxidation of Distyryl ketone by Quinaldinium fluorochromate: A Kinetic and mechanistic study

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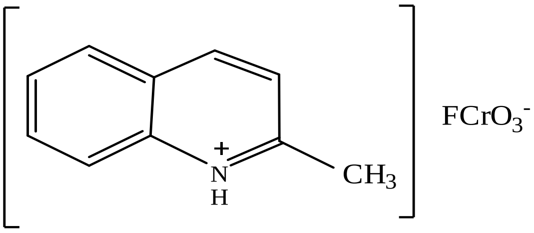
ABSTRACT

The kinetics of oxidation of distyryl ketone by quinaldinium fluorochromate has been studied in aqueous acetic acid medium. The order of the reaction is found to be one with respect to oxidant and hydrogen ion. The order with respect to substrate is found to be fractional. The rate increases with increase in the percentage of acetic acid. Variation of ionic strength has no effect on the reaction rate. The reaction does not induce the polymerization of acrylonitrile. The products of oxidation have been found to cinnamic acid and phenyl acetaldehyde. The reaction rate has been determined at different temperatures and the activation parameters also calculated. A suitable mechanism consistent with the observed kinetics has been proposed.

Keywords: Oxidation, Kinetics, Distyryl ketone, Quinaldinium Fluorochromate.

INTRODUCTION

Quinaldinium fluorochromate (QnFC) has been used in oxidation of many organic substrates. QnFC [1] is a mild, efficient and stable oxidizing agent. It is a bright yellow crystalline solid. The structure of QnFC is given below



Quinaldinium Fluorochromate

Quinaldinium fluorochromate oxidises anthracene into anthraquinone in the presence of dichloromethane. Chalcones are of interest because they have a unique structural feature having a > C = O functional group in conjugation with > C = C < and the whole molecule is in conjugation. Chalcones are oxidized by different oxidizing agents and in all these reactions either the > C = C< or > C = O group of the chalcone is attacked by the oxidant [2-11]. Chalcones are natural substance found in a number of plants. They display many biological activities [12] viz., antiviral, anti inflammatory, antimicrobial [13], antimitotic, antitumor, cytotoxicity, analgesic, anticancer [14] antipyretic properties. Literature survey reveals that there are no kinetic and mechanistic studies involving this useful compound with chalcones. Recently [15] the kinetics of of mechanism of oxidation of substituted dibenzalacetones by Cr(VI) has been reported. This investigation was undertaken to gain a clear understanding of the mechanism of the quinaldinium fluorochromate oxidation of distyryl ketone.

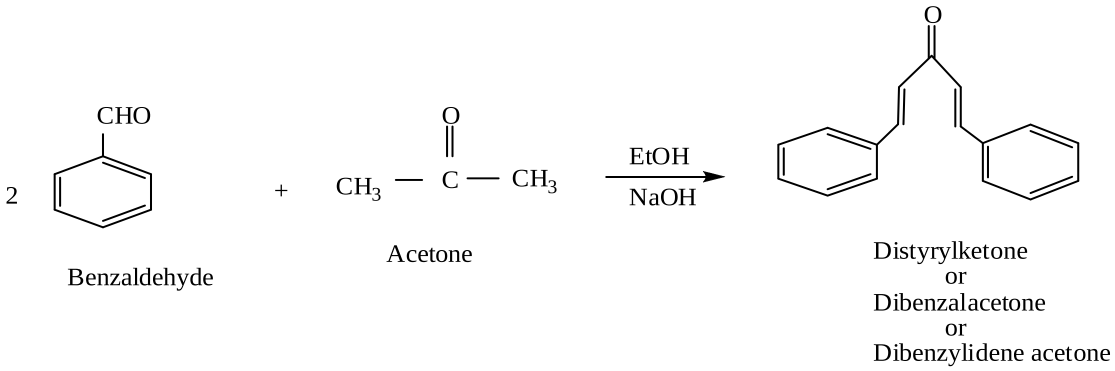
EXPERIMENTAL SECTION

Preparation of quinaldinium fluorochromate [1]

Chromium trioxide (7 g) was dissolved in 8 ml of water in a polythene beaker and 11 ml of 40% hydrofluoric acid were added with stirring at room temperature. A clear orange red solution was formed, 9 ml of quinaldine were added drop-wise with stirring. The mixture was heated on a water bath for about 15 min, then cooled to room temperature, and allowed to stand for 1 h. The bright yellow crystalline quinaldinium fluorochromate was isolated by filtration. It was recrystallized from water and dried in vacuo for about 2 h. The compound melted at (147° C) [lit m.p 146-148° C] and further analysed through spectral data.

Preparation of Distyryl ketone or Dibenzalacetone or Dibenzylideneacetone

A cold solution of 8 g of sodium hydroxide in 250 ml of water and 70 ml of ethanol were 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 20-25° 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 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.pt 105-108° C was obtained [16]. It was recrystallised from ethyl acetate. The compound melted at 107° C [lit m.p 105-108° C].



Acetic acid

Glacial acetic acid (AR) (2 litre) was partially frozen and about 1 litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30g) for 4h and fractionally distilled [17]. The distilled portion was collected between 116-118°C, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractioned again after treating with chromium trioxide (30g). The boiled fraction was collected 116-118°C and kept in brown bottles.

All other chemicals were used as AR grade. Triply distilled water was used for the preparation of solutions.

Kinetic measurements

The kinetic experiments were conducted in aqueous acetic acid (80% v/v) at 313 K. The reaction mixture was consisted of Chalcone (Dibenzalacetone) = 1.00×10^{-3} mol dm^{-3} QnFC=1.00×10^{-5} mol dm^{-3} and $HClO_4 = 4.20 \times 10^{-1}$ mol dm^{-3}. The temperature was maintained constant within ± 0.2°.

The reaction was carried out under pseudo- first order conditions by maintaining the substrate concentration in excess of quinaldinium fluorochromate. Known volumes of substrate, water and acetic acid were mixed to bring the percentage of acetic acid to the desired value and thermostated. The reaction was started by adding the oxidant to the mixture and aliquots were removed at definite time intervals and the decrease in [QnFC] by digital photoelectric colorimeter at 470 nm. The reactions were followed up to 70% completion. The rate constants were obtained from the slope of the plot of log absorbance *versus* time by the least square method. The results were reproducible within ±1.

Product analysis

The reaction mixture containing DBA(Chalcone) (0.1 M) in acetic acid and QnFC (0.1M) in acetic acid was added and the medium was maintained using perchloric acid, Then the reaction mixture was slightly warming and it was kept aside for about 48 hr for the completion of reaction. After 48 h, the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ethereal layer was washed with water for several times and kept on a water bath for ether evaporation and cooled to get the product. Cinnamic acid and phenyl acetaldehyde were identified as products.

Cinnamic acid and phenylacetaldehyde were identified as products and were detected by TLC and compared with those of the authentic samples. The presence of phenyl acetaldehyde among the reaction product was also detected by preparing their 2,4 - dinitrophenyl hydrazine derivatives. cinnamic acid [18] and phenyl acetyadehyde, was further identified and confirmed by using IR , GC-MS and H^1 NMR spectrum.

RESULTS AND DISCUSSION

Effect of quinaldinium fluorochromate

The kinetic data reveals that the oxidation of distyryl ketone by quinaldinium fluorochromate is first order with respect to the oxidant. The plot of log absorbance *versus* time is linear indicating that the order with respect to quinaldinium fluorochromate is unity. The pseudo-first order rate constants were found to be independent of initial concentration of quinaldinium fluorochromate (Figure. 1).

Table -1 Effect of [DBA] and [QnFC] in the Oxidation of Chalcone by Quinaldinium Fluorochromate

$[HClO_4] = 4.20 \times 10^{-1}$ mol dm^{-3} Temperature = 313 K
$AcOH-H_2O$ = 80 -20 (% v/v)

[QnFC] 10^5 mol dm^{-3}	[DBA] 10^3 mol dm^{-3}	k_{obs} 10^4 s^{-1}
0.60	1.00	4.74
1.19	1.00	4.87
1.79	1.00	4.76
2.38	1.00	4.86
2.98	1.00	4.81
1.19	0.50	4.02
1.19	1.00	4.87
1.19	1.50	5.45
1.19	2.00	5.88
1.19	2.50	6.42

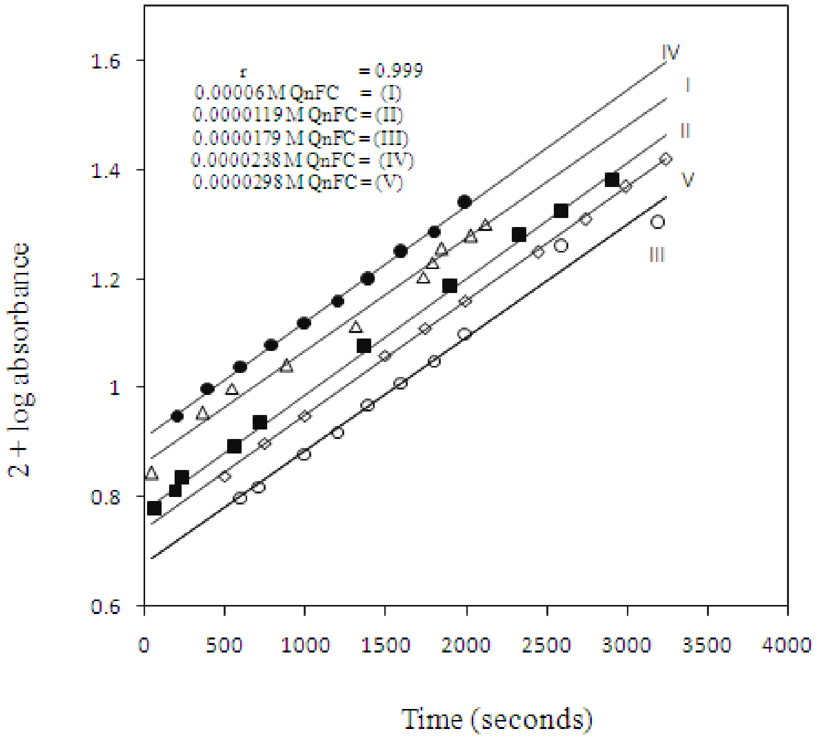


Figure .1 Plot of log absorbance *versus* time

Effect of distyryl ketone

At constant [QnFC], the rate constants are increased with increase in the concentration of the substrate **(Table - 1)**. A plot of log k_1 *versus* log [substrate] with a slope was 0.30. It was further supported by the fact that the double reciprocal plot of k_{obs} *versus* [substrate] gave a straight line with a definite intercept indicating the Michaeli's-Menten type of kinetics in this reaction (Figure. 2).

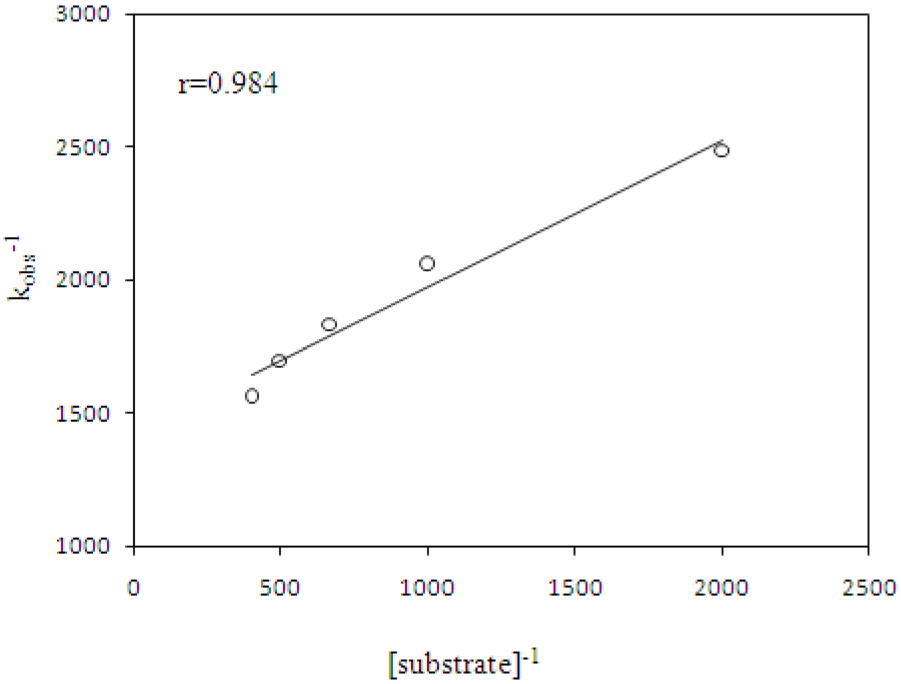


Figure .2 Plot of 1/k *versus* 1/substrate

Effect of Hydrogen ion concentration

The effect of acidity was studied by varying the concentrations of perchloric acid and rate constants were found to increased with increase in the concentration of perchloric acid **(Table - 2)**. The reaction was found to be first order in $[H^+]$ as evidenced by the slope (1.07) of the plot of log k_1 *versus* log $[H^+]$ in (Figure. 3)

Table -2 Effect of hydrogen ion concentration

$[QnFC] = 1.00\times10^{-5} mol\ dm^{-3}$ Temperature = 313 K
$[DBA] = 1.00\times10^{-3} mol\ dm^{-3}$ AcOH-H_2O = 80 :20 (% v/v)

$[H^+]\times10^1$ *mol dm⁻³*	$k_1\times10^4$ s^{-1}
2.53	3.23
4.20	4.87
5.07	6.02
6.30	8.31
7.60	10.71

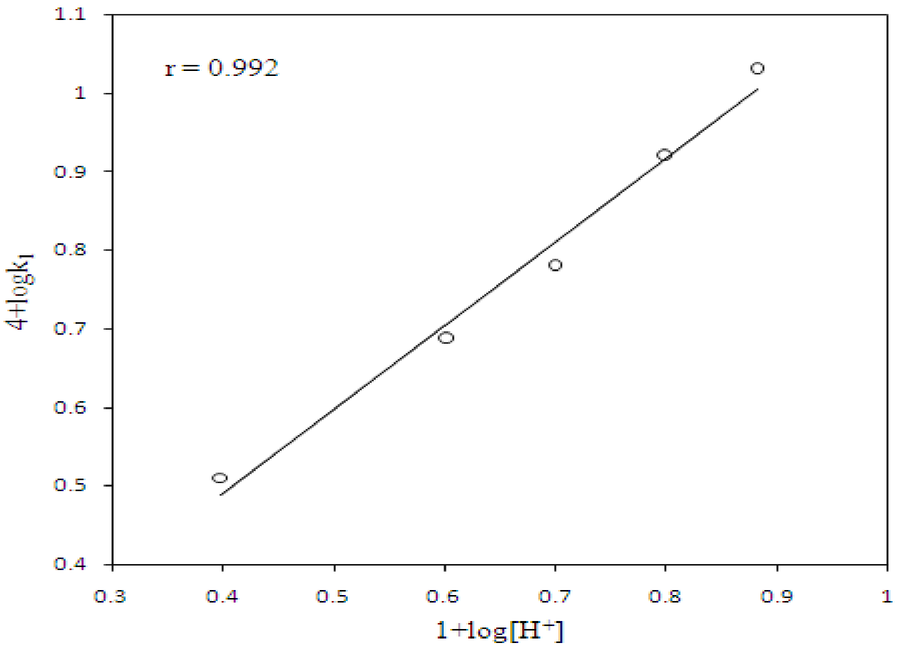


Figure .2 Plot of log k_1 *versus* log $[H^+]$

Effect of solvent composition

Increase in the percentage of acetic acid of the medium increases the rate of the oxidation process **(Table - 3)**. This is normally observed in the oxidation reactions of Cr(VI). Further correlation of log k_{obs} with the reciprocal of the dielectric constant of the medium gives linear plot (Figure. 4) suggesting an ion- dipole interaction [19-21] between distyrylketone and the oxidant.

Table – 3 Effect of solvent composition

$[QnFC] = 1.00\times10^{-5} mol\ dm^{-3}$ $[H^+] = 4.20\times10^{-1} mol\ dm^{-3}$
$[DBA] = 1.00\times10^{-3} mol\ dm^{-3}$ Temperature = 313 K

$AcOH-H_2O$ (% v/v)	ε	$k_1 10^4$ s^{-1}
70-30	28.31	3.74
75-25	24.61	4.16
80-20	20.92	4.87
85-15	17.22	6.45
90-10	13.54	9.64

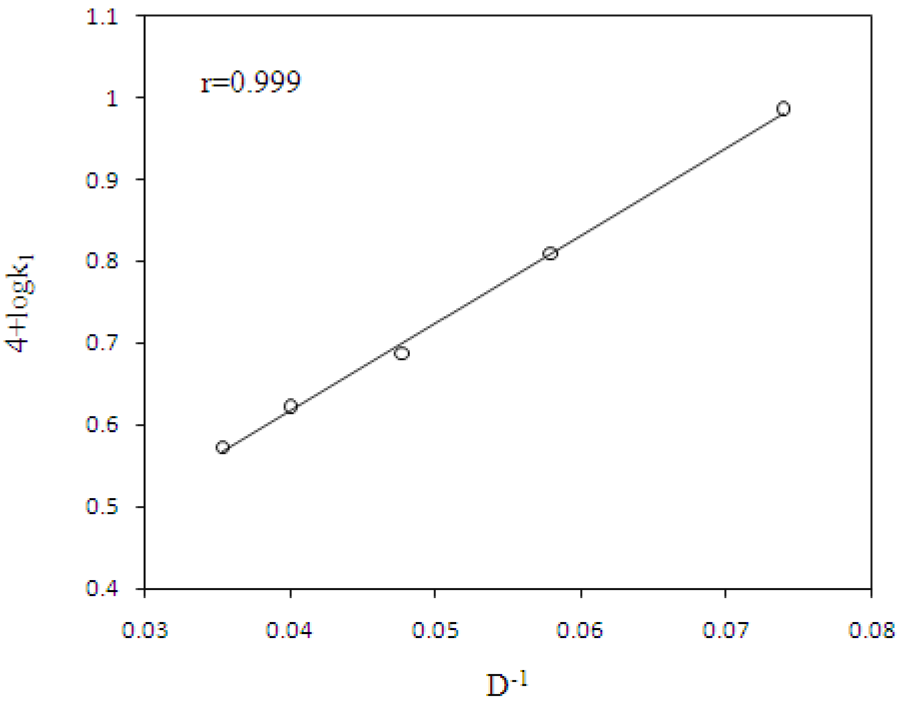


Figure. 4 Plot of log k_1 *versus* D^{-1}

Effect of $NaClO_4$ and acrylonitrile

There was no appreciable change in the rate with the change of ionic strength indicating the involvement of neutral molecules in the rate determining step [22].

The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway [23].

Effect of $MnSO_4$

The reaction was followed with varying concentrations of Mn^{2+} ions keeping all the other factors constant. There was an appreciable decrease [24, 25] in the rate with increasing the concentrations of Mn^{2+} ions confirming the involvement of two electron transfer process in the reaction **(Table - 4)**.

Table – 4 Effect of varying manganous sulphate

$[QnFC] = 1.00\times10^{-5}$ mol dm^{-3} *$[H^+] = 4.20\times10^{-1}$ mol dm^{-3}*
$[DBA] = 1.00\times10^{-3}$ mol dm^{-3} *Temperature = 313 K*
$AcOH-H_2O$ = 80 : 20 (% v/ v)

$[MnSO_4]\times10^6$ *mol dm^{-3}*	$k_1\times10^4$ *s^{-1}*
0.00	4.87
0.50	4.80
1.00	3.92
1.50	2.50
2.00	1.72

Effect of temperature

The reaction has been carried out at four different temperatures 303 K, 313 K, 323 K and 333 K respectively, keeping all other factors constant**(Table - 5)** .The thermodynamic parameters have been computed from the linear plot of ln(k_2/T) *versus* 1/T of Eyring's equation [26] (Figure. 5)

$\Delta H^{\#} = 39.30\ kJ\ mol^{-1}$
$\Delta S^{\#} = -125.06\ J\ K^{-1} mol^{-1}$
$\Delta G^{\#} = 78.44\ kJ\ mol^{-1}$ at 313 K.
$Ea = 41.90\ kJ\ mol^{-1}$ at 313 K.

Table – 5 Effect of varying temperature

[QnFC] = 1.00×10^{-5} mol dm^{-3} *[H$^+$] = 4.20×10^{-1} mol dm^{-3}*
[DBA] = 1.00×10^{-3} mol dm^{-3} *AcOH-H$_2$O = 80 :20 (% v / v)*

Temperature K	$k_1\ 10^4$ s^{-1}
303	3.37
313	4.87
323	8.85
333	14.74

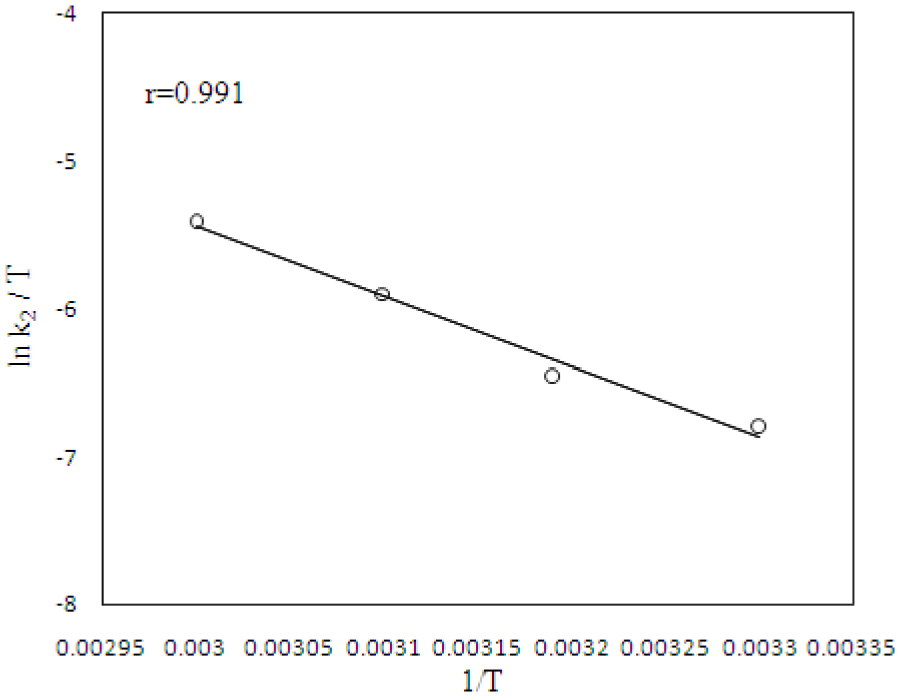
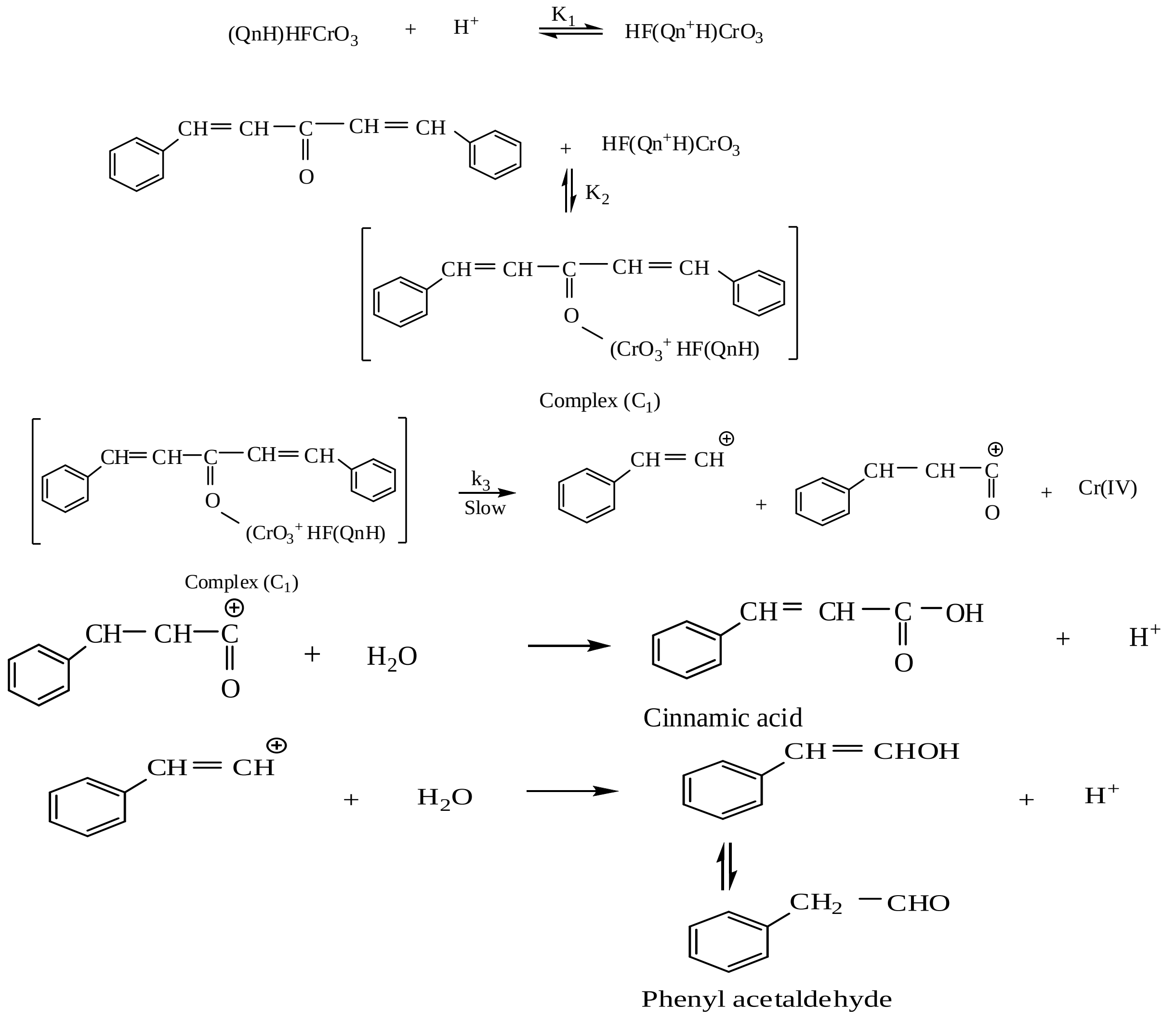


Figure. 5 Plot of ln k_2/ T *versus* 1/T

Mechanism and rate law

From the above observations, it is clear that the reaction is showing unit order with respect to oxidant and [H$^+$] ion and fractional order with respect to substrate. The intermediatary of Cr(IV) during Cr(VI). Oxidation is normally demonstrated by the effect of added Mn(II). The addition of Mn(II) leads to decreased in the rate of oxidation of distyryl ketone because Mn(II) removes Cr(IV) formed [27]. In the present study in consideration of the above datas, the following mechanism is proposed for the oxidation of distyryl ketone by quinaldinium fluorochromate.



Scheme - 1

Rate law

These above observations suggest that the rate law can be shown as

$$\text{Rate} = k_3 C_1 = \frac{k_3K_2[\text{OxH}^+][\text{S}]}{1+K_2[\text{S}]} = \frac{k_3K_1K_2[\text{Ox}][\text{H}^+][\text{S}]}{1+K_2[\text{S}]}$$

CONCLUSION

The oxidation of Chalcones by quinaldinium fluorochromate in aqueous a medium leads to the formation of complex and finally gives the products. The reaction follows simple order kinetics. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

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