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Oxidation of Cinnamic Acid by Quinolinium Fluorochromate

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ABSTRACT

The oxidation of Cinnamic acid with Quinolinium Fluorochromate under pseudo-first order conditions has been studied at 313 K. The reaction shows first order dependence with respect to oxidant, substrate and acid catalyzed by H+. Increase in ionic strength has no effect on the reaction rate and decrease in the dielectric constant of the medium decreases the reaction rate. There is no possibility of free radical mechanism since there is no polymerization of acrylonitrile. Increase in the concentration of manganous sulphate retards the reaction rate which confirms the two electron transfer involved in the mechanism. A possible mechanism has been proposed in the formation of Benzaldehyde and Glyoxalic acid.

Keywords: Oxidation, Cinnamic acid, Quinolinium fluorochromate and Kinetics.

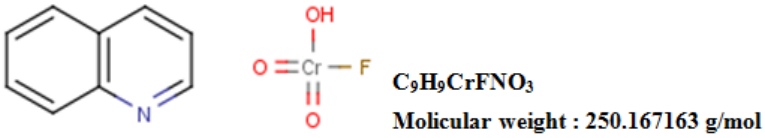
1. INTRODUCTION

Oxidation of alcohols to carbonyl compounds is one of the most important reactions in organic chemistry. The new, mild chromium (VI) oxidizing agent, Quinolinium fluorochromate[1] is an suitable reagent to oxidize various primary and secondary alcohols to the corresponding carbonyl compounds and anthracene to anthraquinone in good yields. Some of the important entries in the list of the reagents are pyridiniumchlorochromate, pyridinium fluorochromate, pyridinium dichromate, pyridiniumbromochromate, Quinoliniumchlorochromate and proliniumchloro-chromate.

However, most of the reagents have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, tedious work-up procedures, or requirement of large excess of reagent. In extension of our studies on development of new reagents based on chromium (VI), we present here Quinolinium fluorochromate (QFC) as a mild and efficient oxidant for alcohols.

The oxidation of maleic, fumaric, crotonic and cinnamic acids by quinolinium fluorochromate (QFC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding epoxide. Quinolinium fluorochromate has advantages in terms of ease of preparation, lower acidity, reaction period and yield of products. This reagent is very stable and can be stored for longer periods without much loss in activity and hence turns out to be a very useful reagent in synthetic organic chemistry. The possible structure of QFC is given below:

Structure of Quinolinium fluorochromate [QFC]



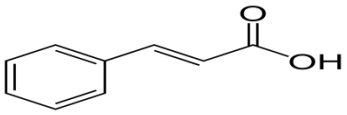
$C_9H_9CrFNO_3$

Molicular weight : 250.167163 g/mol

Cinnamic acid

Cinnamic acid is an organic compound with the formula $C_6H_5CHCHCO_2H$. It is a white crystalline compound that is slightly soluble in water, and freely soluble in many organic solvents. Classified as an unsaturated carboxylic acid, it occurs naturally in a number of plants. It exists as both a cis and a trans isomer, although the latter is more common.

Structure of Cinnamic acid



The kinetics of oxidation of cinnamic acids by pyridiniumbromochromate (PBC) in the presence of oxalic acid has been studied in acetic acid-water (60:40%) medium. [2]The oxidation of maleic, fumaric, crotonic and cinnamic acids by tetraethylammoniumchlorochromate (TEACC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding epoxide[3]. The kinetics of oxidation of cinnamic acid by BPCC in aqueous acetic acid (50%-50% v/v) in the presence of sulphuric acid has been studied[4].

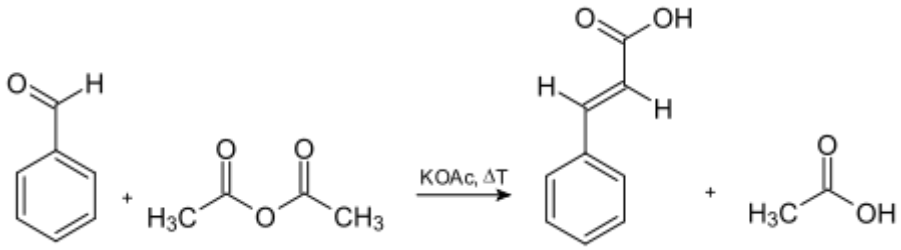
2. EXPERIMENTAL METHODS

2.1 Preparation of Quinolinium fluorochromate [QFC][5]

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 quinoline were added drop wise with stirring .the mixture was heated on a water bath for about 15 min, then cool to room temperature, and allowed to stand for 1 hr the bright Quinolinium fluorochromate was isolated by filtration .it was recrystallized from water and dried in vacuo for about 1 hr . the compound melted at (147^0c) and further analysed through spectral data.

2.2 Preparation of Cinnamic acid

The original synthesis of Cinnamic acid involves the Perkin reaction, which entails the base-catalysed condensation of acetic anhydride and benzaldehyde. Rainer Ludwig Claisen described the synthesis of cinnamate esters by the reaction of benzaldehyde and esters. The reaction is known as the Aldol condensation (with accompanying hydrolysis of the anhydride). It can also be prepared from cinnamaldehyde and benzal chloride.



Synthesis of Cinnamic acid via Perkin reaction

2.3 Acetic acid

The procedure followed for the purification of acetic acid was essentially similar to that of Weissberger6. Glacial acetic acid (AR) two liter was partially frozen and about one liter 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 116-118°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 116-118°C was collected and kept in brown bottles.

2.4 Water

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

2.5 Other reagents

Sodium perchlorate, perchloric acid, sodium thiosulphate, manganoussulphate, acrylonitrile, potassium iodide and starch were all of Analar grade and were used as such.

2.6 Kinetic measurements

Solutions of Cinnamic acid in acetic acid and other reagent like Quinolinium fluorochromate, perchloric acid solutions in doubly distilled water were prepared. In all the reactions pseudo - first order conditions were maintained. The kinetic measurements were made using digital photoelectric colorimeter (Equiptronics EQ 450)λ_{max}= 470 nm as follows.

All the solutions were kept in a thermostat constant temperature for half an hour for each run. The temperature was controlled using Raagaa thermostat to an accuracy of± 0.1˚C. Then the reaction was started by adding a known volume of Quinolinium fluorochromate into the reaction flask. Immediately 1 ml of aliquot (approximate) was transferred in to the quartz cuvette, which had already been kept and thermostated in the instrument. The reactions were followed by determining the concentration of the unreacted Quinolinium fluorochromatefor known intervals of time.

2.7 Stoichiometry

The kinetics of reaction was to establish the stoichiometry of the reaction and identify any side reactions. The stoichiometry of the reaction [QFC]:[Cinnamic acid] was determined by taking excess of [QFC] over [Cinnamic acid] and allowing the reaction to go for completion. After sufficient length of time, all the substrate has completely reacted to Quinolinium fluorochromate. Leaving behind the unreacted Quinolinium fluorochromate. The unreacted Quinolinium fluorochromate was estimated iodometrically. The estimation of unreacted Quinolinium fluorochromate showed that one mole of substrate consumed by one mole of oxidant. The stoichiometry between Cinnamic acid and QFC was found to be 1:1.

2.8 Product analysis

The reaction mixture containing Cinnamic acid (0.1 M) in acetic acid and QFC (0.1M) in acetic acid was added and the medium was maintained. Then the reaction mixture was slightly warmed and was kept aside for about 48 h for the completion of reaction. After 48 h, the reaction mixture was kept on a water bath for ether evaporation and cooled to get the product. Benzaldehyde and glyoxalic acid were identified as products.

The product Benzaldehyde (C_7H_6O) was identified by its physical constant (m.p.-57.12° C) and was detected by comparing with those of the authentic samples. The presence of Benzaldehyde among the reaction products was also detected by on oxidation, benzaldehyde is converted into the odorless benzoic acid, which is a common impurity in laboratory samples. Benzyl alcohol can be formed from benzaldehyde by means of hydrogenation. Reaction of benzaldehyde with anhydrous sodium acetate and acetic anhydride yields cinnamic acid, while alcoholic potassium cyanide can be used to catalyze the condensation of benzaldehyde to benzoin. Benzaldehyde undergoes disproportionation upon treatment with concentrated alkali (Cannizzaro reaction): one molecule of the aldehyde is reduced to the corresponding alcohol and another molecule is simultaneously oxidized to benzoate.

The product Benzaldehyde (Plate-I) was confirmed through IR-spectral data which showed a peak at 1710-1665 cm^{-1} corresponding to unsaturated aldehyde and C-H bond gives 2827-2745cm^{-1}It was further confirmed by a ^1H NMR spectrum (Plate -II)spectrum for benzaldehyde, with a sharp peak at about 10 ppm and a collection of peaks between 7 to 8 ppm.

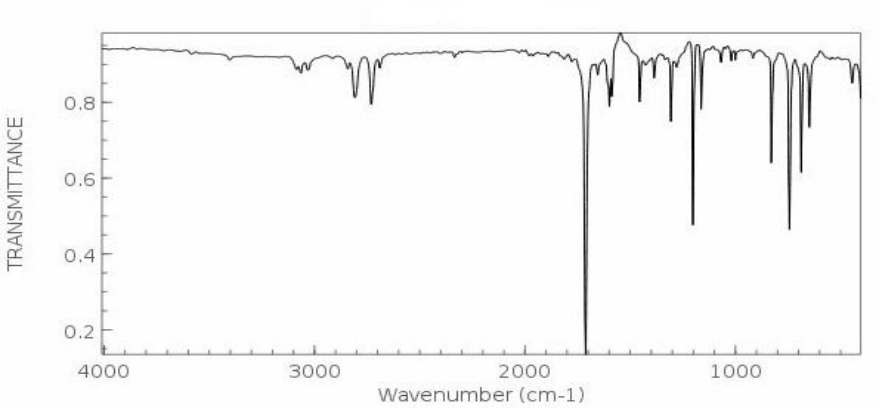


Plate-I: IR Spectrum of Benzaldehyde

A doublet of doublets should be seen around 7.5 corresponding to hydrogens meta to the aldehyde. With further distance from the aldehyde, these hydrogens should be more shielded than the ortho hydrogens and therefore have peaks toward 7 ppm. The doublet of doublets coupling arises from coupling with the ortho hydrogens as well as the para hydrogen. Probably toward the 8 ppm region corresponding to the hydrogens ortho to the aldehyde group. Since they are the closest to the aldehyde, these hydrogens should be the most deshielded and show peaks toward the end of the benzene region. They are also coupled by their neighboring hydrogens to produce a doublet. Finally, a triplet should be seen near 7 ppm corresponding to the hydrogen para to the aldehyde. At this position, the hydrogen should feel the least effect of the aldehyde and resonate at 7 ppm. The triplet arises from coupling with the neighboring meta hydrogens.

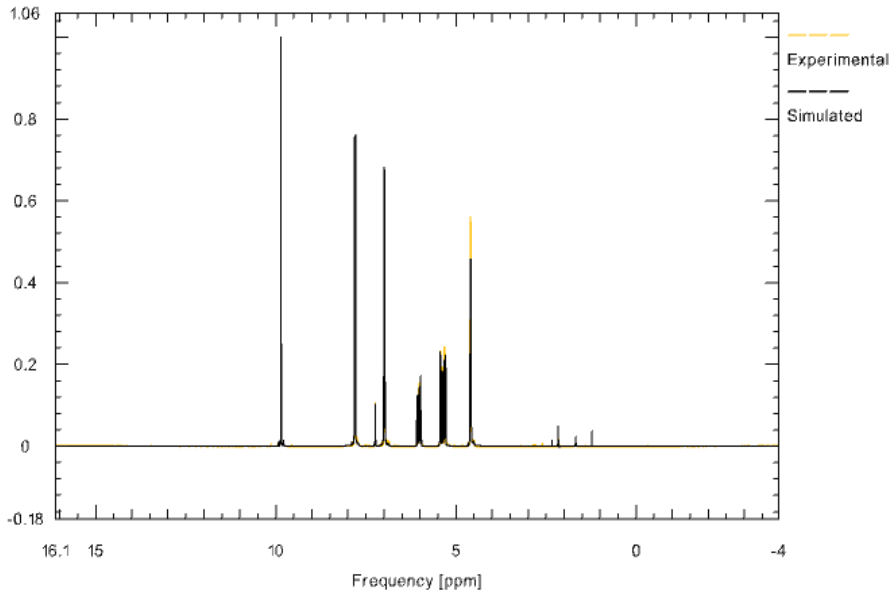


Plate-II : H^1 NMR SPECTRA OF BENZALDEHYDE

Another product glyoxalic acid was confirmed by IR-Spectral data (Plate-III) which showed a peak at 600-900 cm^{-1} corresponding to carboxylic acids group. Carboxylic acids show a strong, wide band for the O–H stretch. Unlike the O–H stretch band observed in alcohols, the carboxylic acid O–H stretch appears as a very broad band in the region 3300-2500 cm^{-1}, centered at about 3000 cm^{-1}. This is in the same region as the C–H stretching bands of both alkyl and aromatic groups.

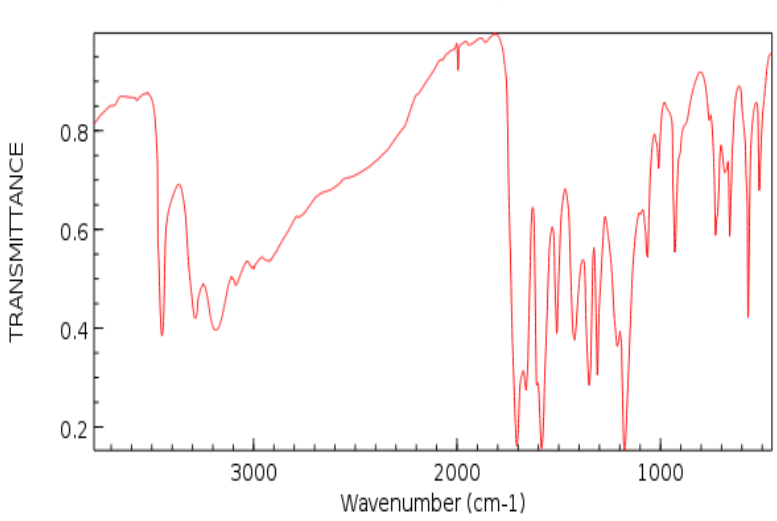


Plate-III: IR Spectrum of Glyoxalic acid

Thus a carboxylic acid shows a somewhat absorption pattern in the region 3300-2500cm^{-1}, with the broad O–H band superimposed on the sharp C–H stretching bands. The reason that the O–H stretch band of carboxylic acids is so broad is because carboxylic acids usually exist as hydrogen-bonded dimers. It was further confirmed by a mass spectrum (Plate -IV)

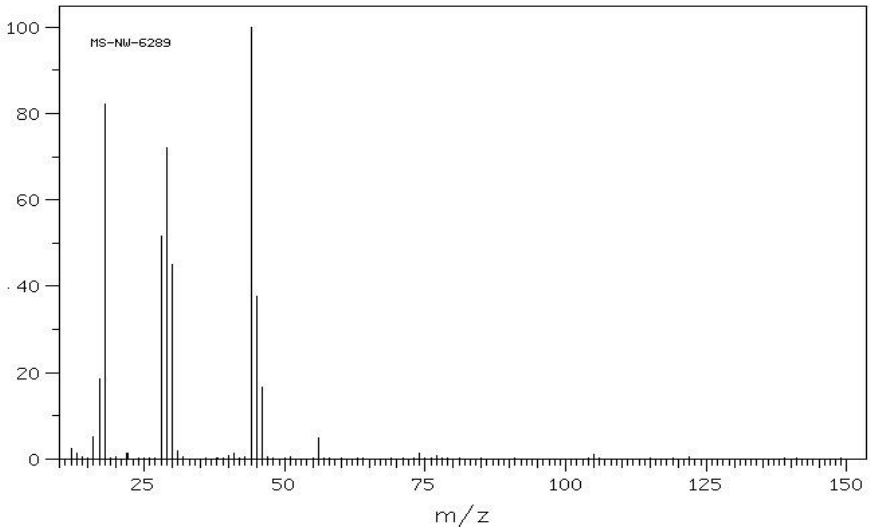


Plate-IV: Mass Spectrum of Glyoxalic acid

3. RESULTS AND DISCUSSION

Kinetics and mechanism of oxidation of Cinnamic acid by Quinolinium fluorochromate in the presence of aqueous acetic acid medium

The kinetics of oxidation of Cinnamic acid by Quinolinium fluorochromate in the presence of Percholric acid was studied at 313K. The results were discussed below.

3.1 Effect of varying the [QFC]

The reaction was investigated with varying concentrations of QFC at constant Cinnamic acid and Perchloric acid. The reaction was found to be first order with respect to the oxidant as evidenced by the linear plot of plot of log absorbance *versus* time (Fig.1) and also from the constancy of the first order rate constant.

Table-1

[Cinnamic acid]=$2.0\times10^{-2} moldm^{-3}$ AcOH-H_2O = 70:30(%)

$[H^+]$ =$3.0\times10^{-1} moldm^{-3}$ Temperature=313K

[QFC]× $10^{-3} mol\ dm^{-3}$	$k_1\times10^4 s^{-1}$
0.50	17.89
1.00	17.89
1.50	17.88
2.00	17.87
2.50	17.88

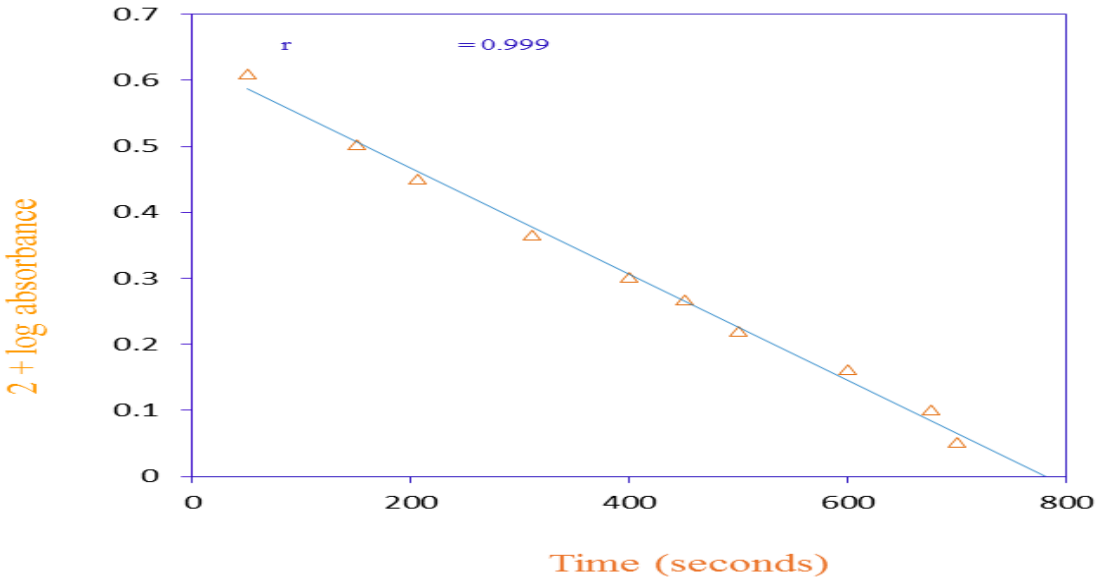


Fig.1 Plot of log absorbance *versus* time

3.2 Effect of varying the Substrate [Cinnamic acid]

The reaction was carried out by varying the concentration of cinnamic acid keeping the other variables constant. The rate of reaction increased with increase in the concentration of Cinnamic acid and the plot of log k_1 *versus* log [Substrate] gave a straight line with a slope of unity (Fig 2) showing a first order dependence on the substrate. This was further well confirmed by the constancy of the specific reaction rate $k_2 = k_1$ /Substrate] (Table 2)

Table-2

[QFC]=1.00×10^{-3} *moldm*$^{-3}$AcOH-H_2O = 70:30(%)

[H^+] =3.0×10^{-1} *moldm*$^{-3}$Temperature=313K

[Cinnamic acid] $\times10^2$ *mol dm*$^{-3}$	$k_1\times10^4$ s^{-1}
1.00	12.30
2.00	17.89
3.00	22.90
4.00	28.39
5.00	37.11

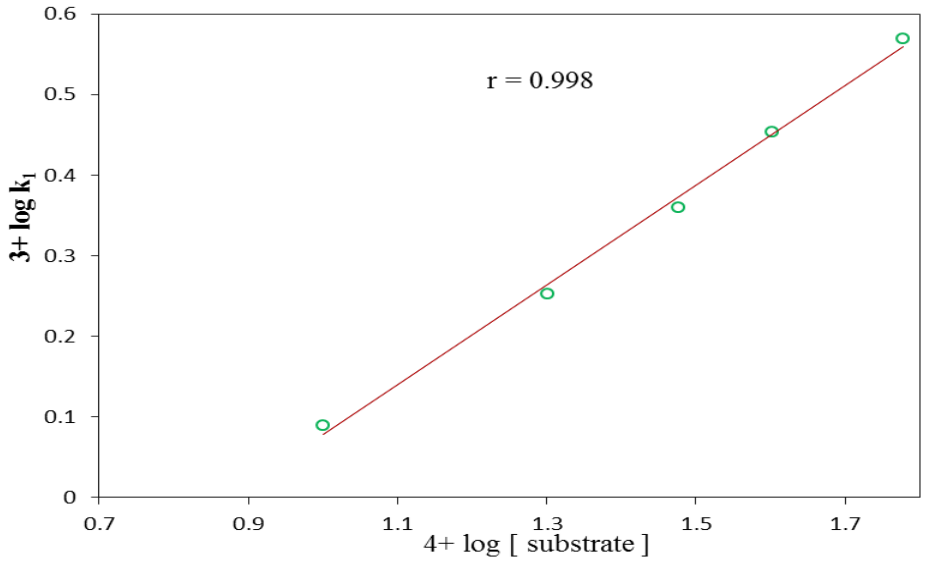


Fig. 2 Plot of log k_1 *versus* log [substrate]

3.3 Effect of varying the ionic strength

The reaction was studied with varying concentration of sodium perchlorate and keeping the other variables constant. The results indicate that ionic strength has negligible effect on the reaction rate, which confirmed the participation of an ion and neutral molecule in the rate determining step[7]

Table-3

[QFC]=1.00×10^{-3} *moldm*$^{-3}$ [H^+] =3.0×10^{-1} *moldm*$^{-3}$

AcOH-H_2O = 70:30(%) [Cinnamic acid]=2.0×10^{-2}*moldm*$^{-3}$

Temperature=313K

[$NaClO_4$] $\times10^4$ *mol dm*$^{-3}$	$k_1\times10^4 s^{-1}$
0.00	17.89
0.50	17.90
1.00	17.91
1.50	17.89
2.00	17.88

3.4 Effect of varying the hydrogen ion concentration

The reaction was followed with different concentration of hydrogen ion keeping the concentration of Quinolinium fluorochromate and substrate constant. The rate has been found to increase with increase in concentration of H^+. A plot of log k_1 *versus* log [H^+] give a straight line (Fig 3). Since the plot of log k_1 *versus* log [H^+] did not give an ideal

slope of unity. It is not possible to take the order with respect to $[H^+]$ as one and it can be concluded that the reaction is simply an acid catalyzed one.

Table-4

[QFC]=1.00×10^{-3} $moldm^{-3}$ AcOH-H_2O = 70:30(%)

[Cinnamic acid]=$2.0\times10^{-2}moldm^{-3}$

Temperature=313K

$[H^+]$ $\times10^1 mol\ dm^{-3}$	$k_1\times10^4 s^{-1}$
1.15	8.12
3.00	17.89
4.50	32.20
6.00	45.64
7.50	51.30

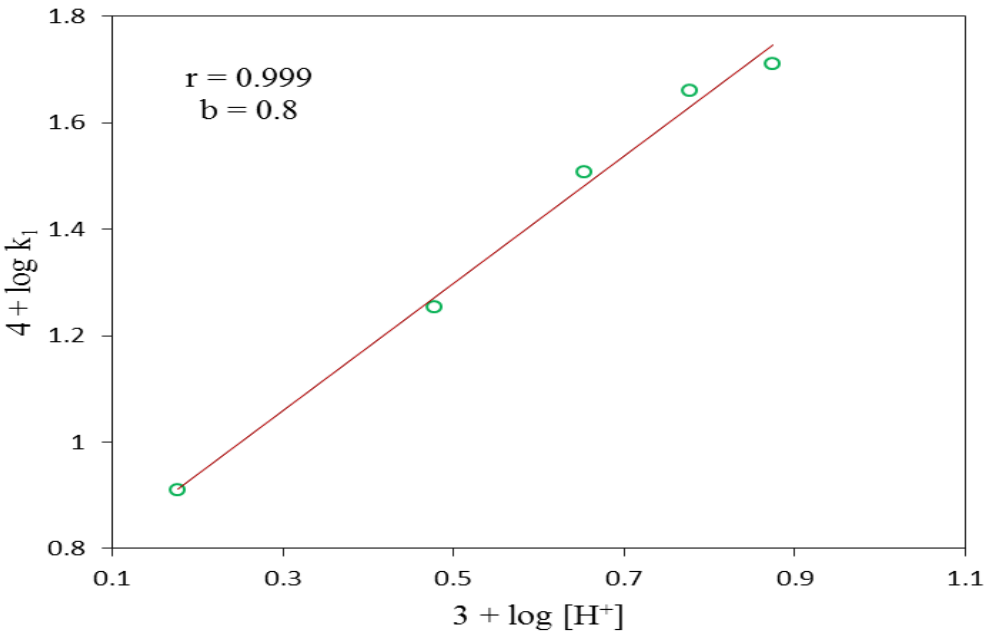


Fig.3 Plot of log k_1 *versus* log $[H^+]$

3.5 Effect of varying the solvent composition

The reaction rate was measured at different acetic acid -water mixtures. It was observed that an increase in the percentage of acetic acid considerably increased in the rate of the reaction. The plot of log k_1 *versus* D^{-1} gave a straight line with a positive slope [8,9](Fig 5)suggests the involvement of an ion –dipole interaction in the rate determining step[10]

Table -6

[QFC]=1.00×10^{-3} *moldm*$^{-3}$[H^+] =3.0×10^{-1} *moldm*$^{-3}$

[Cinnamic acid]=2.0×10^{-2}*moldm*$^{-3}$

Temperature=313K

AcOH-H_2O %(v/v)	E	$k_1\ 10^4\ s^{-1}$
60-40	35.69	10.70
70-30	28.31	17.89
80-20	20.92	19.15

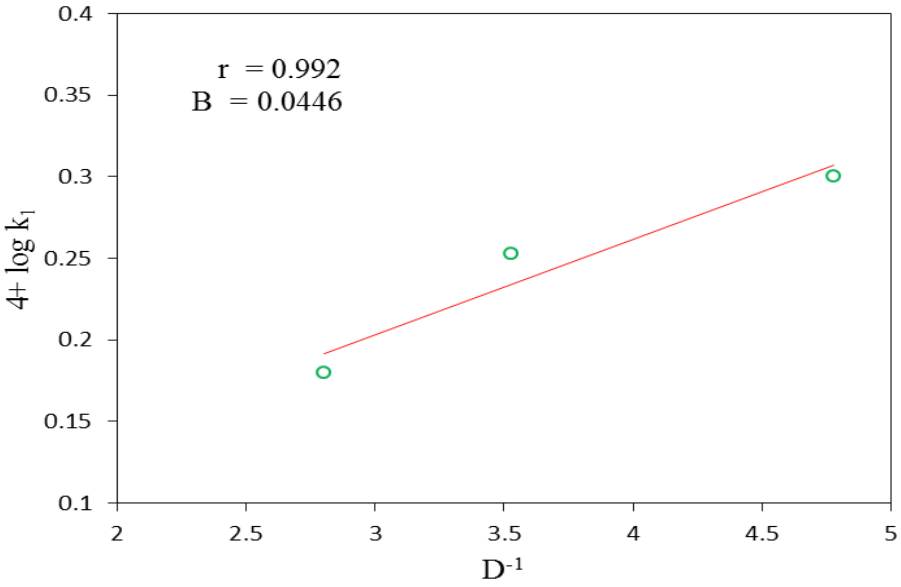


Fig. 5 Plot of log k_1 *versus* D^{-1}

3.6 Effect of added acrylonitrile

The added acrylonitrile has no effect on the reaction mixture indicating the absence of free radical mechanism, no turbidity was obtained.

3.7 Effect of varying the Manganous sulphate

The reaction was carried out with the varying concentrations of Mn^{2+} ions keeping all the other factors constant The added Mn^{2+} ions has decreased the rate of the reaction. It indicates that two electron processes may be involved in the reaction [11-13] (Table 7)

Table-7

[QFC]=1.00×10^{-3} $moldm^{-3}$[H^+] =3.0×10^{-1} $moldm^{-3}$

AcOH-H_2O = 70:30(%) [Cinnamic acid]=$2.0\times10^{-2}$$moldm^{-3}$ Temperature=313K

[$MnSO_4$] $\times10^4$ $mol\ dm^{-3}$	$k_1\times10^4 s^{-1}$
0.00	17.89
0.50	17.76
1.00	17.65
1.50	17.50

3.8 Effect of varying the temperature

The reaction has been studied at six different temperatures keeping all other factors constant .The thermodynamic parameters have been calculated from the least square procedure of a linear plot of $\ln(k_2/T)$ *versus* 1/T (Fig.6) using Eyring's equation[14]

$\Delta H^{\#}$ = 15.69 $kJmol^{-1}$

$\Delta S^{\#}$ = -234.49 $JK\text{-}1mol^{-1}$

$\Delta G^{\#}$ = 89.05 $kJmol^{-1}$

Ea = 18.29 $kJmol^{-1}$

Table-8

[QFC]=1.00×10^{-3} $moldm^{-3}$[H^+] =3.0×10^{-1} $moldm^{-3}$

[Cinnamic acid]=$2.0\times10^{-2}$$moldm^{-3}$

AcOH-H_2O = 70:30(%)

Temperature K	$k_1 10^4 s^{-1}$
303	14.36
308	16.06
313	17.89
318	20.00
323	22.80
328	25.10

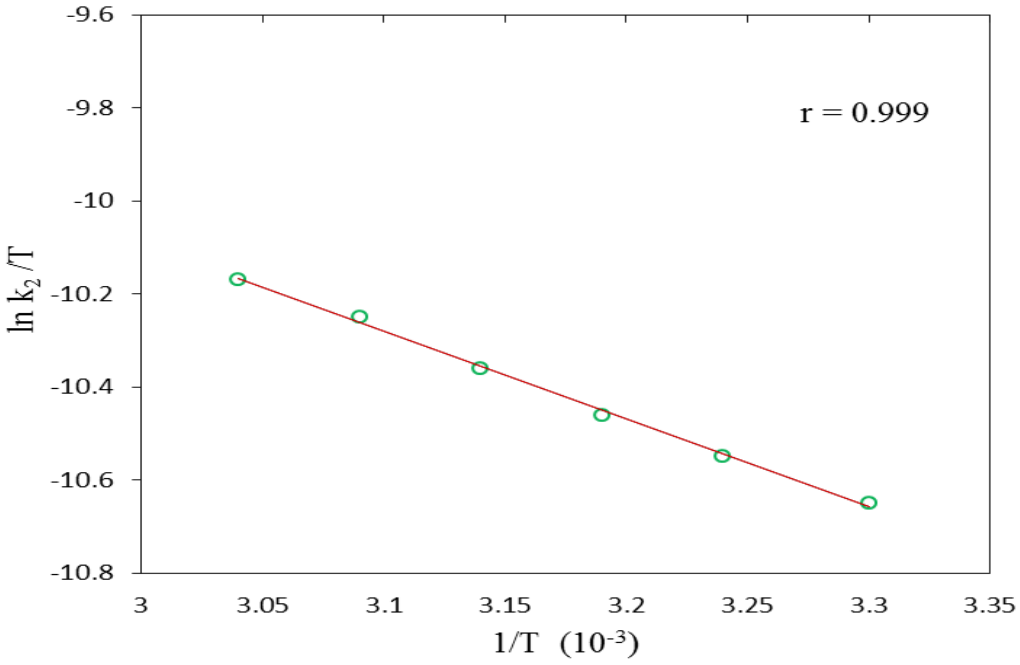


Fig.6 Plot of $\ln k_2/T$ *versus* 1/T

Mechanism and rate law

From the above observation it is clear that the reaction is showing first order with respect to QFC, cinnamic acid and Perchloric acid. The oxidation by Cr(VI) will vary with the 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 are existing,[15]

(i) $H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$ $K_1 = 1.21\ mol\ dm^{-3}$

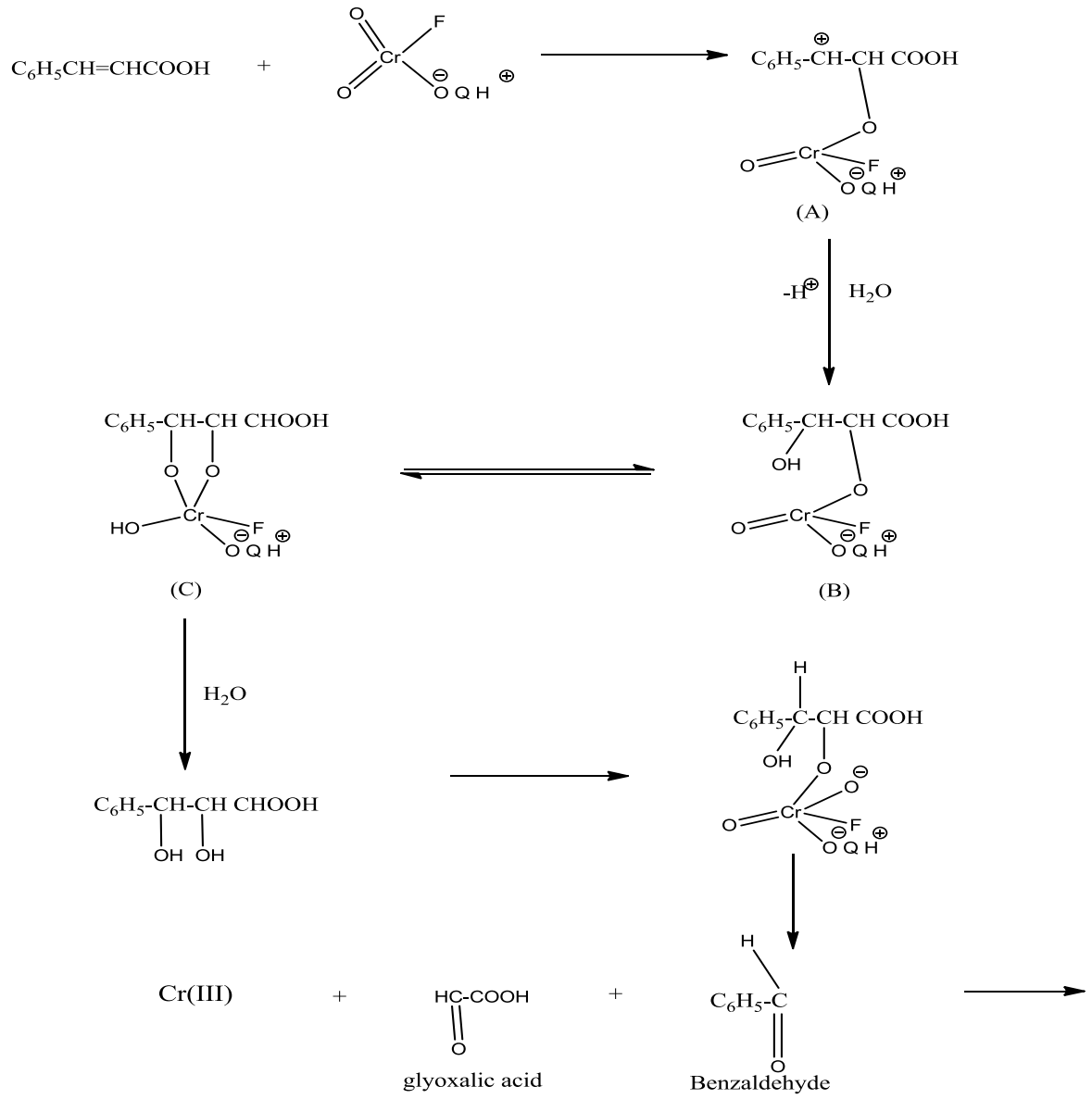
(ii) $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$ $K_2 = 3.0\times 10^{-2} mol\ dm^{-3}$

(iii) $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ $K_d = 35.5$

Here the dimerization equilibrium is of considerable importance. In water the dichromate ion will be predominating species only at the concentrations greater than about 0.05$mol\ dm^{-3}$. In this case as the concentration of Cr(VI) is less than 0.05 $moldm^{-3}$.

The monomeric form predominates and the active oxidising species is $HCrO_4^-$. The reaction is acid catalysed one. The rate increased with decrease in the dielectric constant of the medium and increase in ionic strength has negligible effect on the rate.

The reaction did not induce polymerization of acrylonitrile indicating the absence of free radical path way. The retardation of the rate by addition of Mn^{2+} ions confirmed that a two electron transfer process is involved in the reaction. Based on the above facts the following mechanism was proposed (Scheme 1).



Scheme 1 :- Probable mechanism of oxidation of Cinnamic acid by Quinolinium fluorochromate

Rate Law

The above mechanism leads to the following rate law

$$\text{Rate} = -d[\text{Cr (VI)}]/dt$$

$$= k[\text{Cinnamic acid}][\text{QFC}][H^+]$$ This rate law explains all the experimental facts.

4. CONCLUSIONS

The oxidation of cinnamic acid by quinolinium fluorochromate in aqueous acetic acid medium leads to the formation of benzaldehyde and glyoxalic acid as 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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SUMMARY

1. The rate of oxidation of Cinnamic acid with Quinolinium Fluorochromate under pseudo-first order conditions has been studied at 313 K.
2. The reaction shows first order dependence with respect to oxidant and acid catalyzed by H^+.
3. Increase in ionic strength has no effect on the reaction rate and decrease in the dielectric constant of the medium decreases the reaction rate.
4. There is no possibility of free radical mechanism since there is no polymerization of acrylonitrile. Increase in the concentration of manganous sulphate retards the reaction rate which confirms the two electron transfer involved in the mechanism.
5. Based on the experimental observations a suitable mechanism has been proposed and rate law has been derived.
6. The products of the oxidation reaction are found to be corresponding Benzaldehyde and Glyoxalic acid.