



Oxidation of Substituted Chalcones by Quinaldinium Fluorochromate

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ABSTRACT

The kinetics of oxidation of chalcones by quinaldinium fluorochromate has been studied in aqueous acetic acid medium in the presence of perchloric acid. 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 reaction rates have been determined at different temperatures and the activation parameters calculated. Electron withdrawing substituents are found to enhance the rate of the reaction and electron releasing substituents are found to retard the rate of the reaction and the rate data obeys the Hammett relationship. From the observed kinetic results a probable mechanism has been proposed.

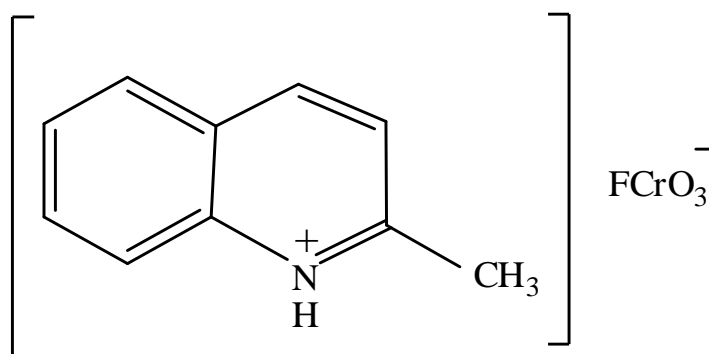
Keywords: Oxidation, Kinetics, Chalcones, Quinaldinium Fluorochromate

1. INTRODUCTION

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of organic compounds. Chromium compounds especially Cr(VI) reagents have been versatile reagents and capable of oxidising almost all the oxidisable organic functional groups. A number of Cr(VI) containing compounds [1-17] have been used to study the kinetics and mechanism of various organic compounds.

The oxidation by fluoro compound involves the formation of a complex between oxidant and substrate which decomposes in the slow step to give products. Oxidation of chloro- and bromo- compounds does not follow such kinetics. These observations suggest 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 an oxidant. Quinaldinium fluorochromate [11] is reported to be a mild oxidant for selective oxidation in synthetic organic chemistry.

The oxidation of the reactive substrate, styryl ketones has been studied extensively with isonicotinium dichromate. This prompted us to investigate the oxidation of chalcones by quinaldinium fluorochromate in aqueous acetic acid medium. Attempts have been made to correlate rate and structure in such a reaction. The probable structure of quinaldinium fluorochromate as shown,



Quinaldinium fluorochromate

2. EXPERIMENTAL

2. 1. Preparation of Dibenzalacetone (Chalcones) [18]

A cold solution of 8g 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 20-25 °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 were obtained. It was recrystallised from ethyl acetate. Substituted dibenzalacetone (distyryl ketones) were prepared by stirring equimolar quantities of substituted benzaldehyde and acetone in the presence of sodium hydroxide in alcohol for about 1 to 2 h. The resulting solution was filtered, washed, dried and recrystallised using suitable solvent. The purity of the distyryl ketones were checked by their melting points.

2. 2. Preparation of Quinaldinium fluorochromate [QnFC] [11]

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 dropwise 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 using water and dried *vacuo* for about 2 h. m.pt. 146-148 °C.

2. 3. 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 (30 g) for 4 h and fractionally distilled. 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 (30 g). 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.

2. 4. Kinetic measurements

The kinetic experiments were conducted in aqueous acetic acid (80 % *v/v*) at 313 K. The reaction mixture consisted of Chalcone (Dibenzalacetone) = 1.00×10^{-3} mol dm⁻³, QnFC = 1.00×10^{-5} mol dm⁻³ and HClO₄ = 4.20×10^{-1} mol dm⁻³. The temperature of the reaction was maintained at the desired value to an accuracy of ± 0.1 °C.

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 .

2. 5. Product analysis

The reaction mixture containing DBA (Chalcone) (0.1 M) in acetic acid and QnFC (0.1 M) in acetic acid was added and the medium was maintained using perchloric acid, then the reaction mixture was slightly warming and 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 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 [19] and phenyl acetyadehyde, was further identified and confirmed by using IR and GC-MS.

3. RESULTS AND DISCUSSION

Rate laws and other data were obtained for all the compounds investigated. Since the results were similar for all the chalcones, only representative data are presented here. The kinetic data reveals that the oxidation of chalcone (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 (Fig. 1).

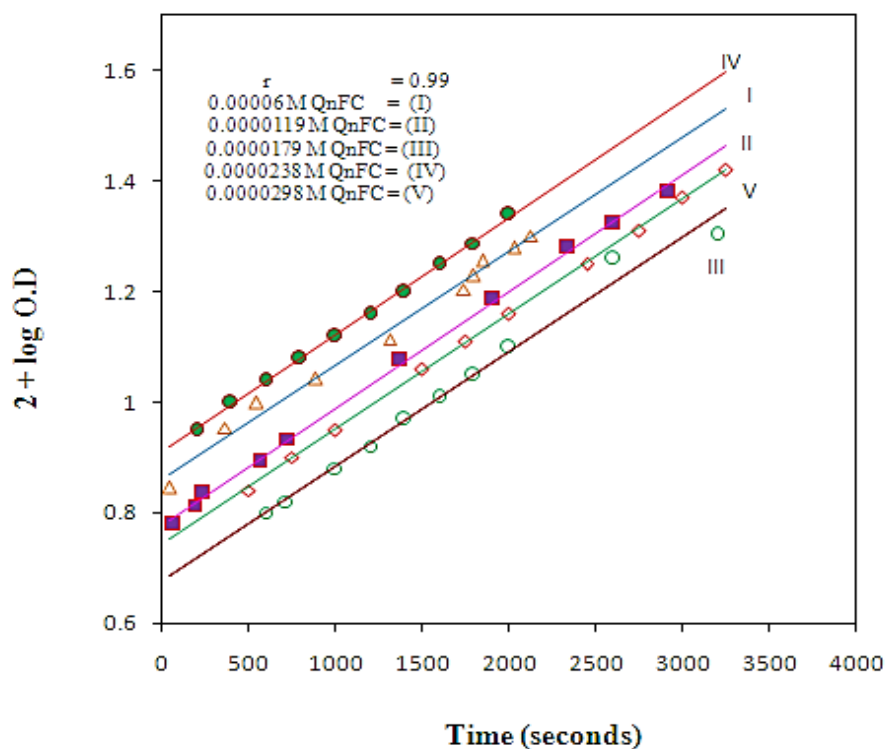


Figure 1. Plot of log absorbance against time at different QnFC in the Oxidation of Chalcones by QnFC.

At constant [QnFC], the rate constants were increased with increase in the concentration of the substrate (Table 1). A plot of $\log k_1$ versus $\log [\text{substrate}]$ 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 Michaelis-Menten type of kinetics in this reaction (Fig. 2).

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

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

[HClO₄] = 4.20 × 10⁻¹ mol dm⁻³ Temperature = 313 K AcOH-H₂O = 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

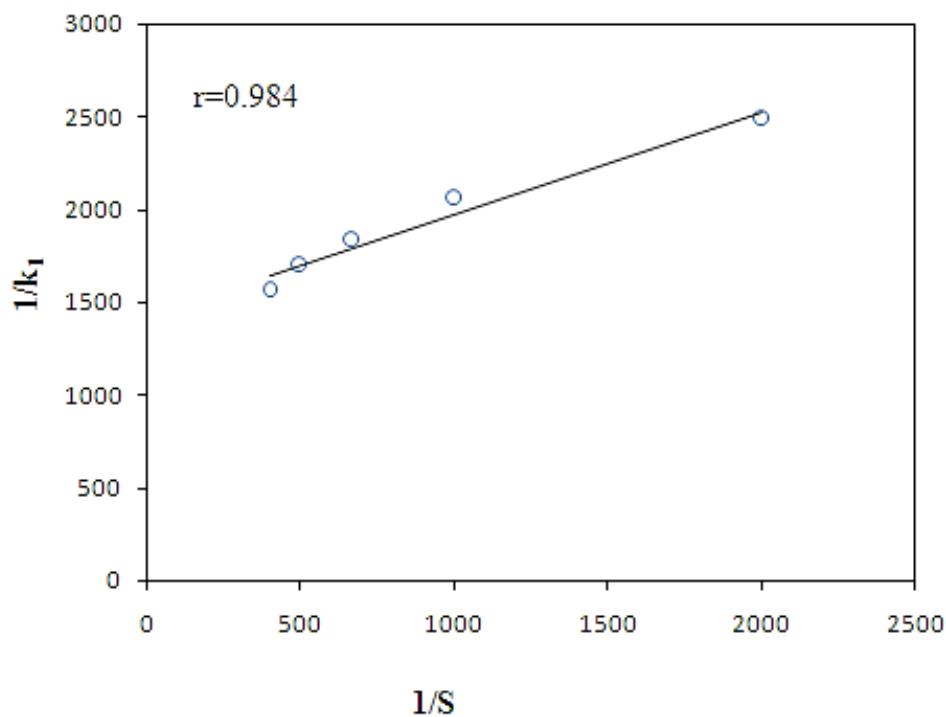


Figure 2. Plot of 1/k₁ against 1/S in the Oxidation of Chalcones by QnFC.

Table 2. Effect of Hydrogen ion concentration on the oxidation of Chalcone by QnFC

[QnFC] = 1.19×10^{-5} mol dm⁻³ Temperature = 313K

[DBA] = 1.00×10^{-3} mol dm⁻³

[HClO ₄] 10 ¹ mol dm ⁻³	k _{obs} 10 ⁴ s ⁻¹
2.53	3.23
4.20	4.87
5.07	6.02
7.60	10.71

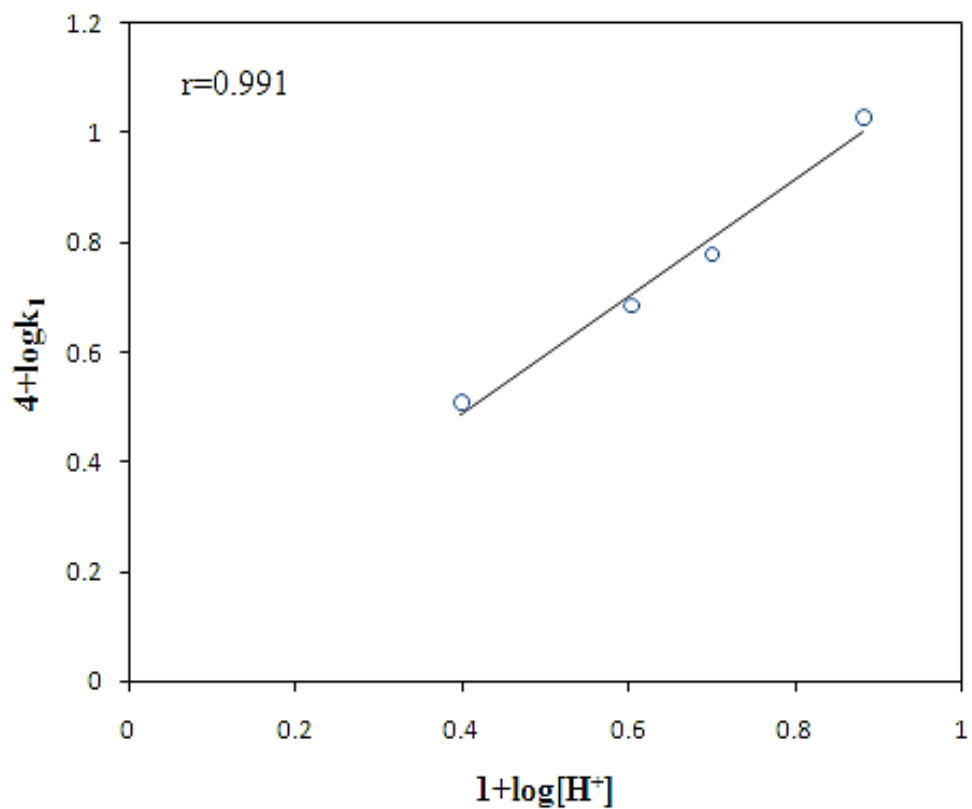


Figure 3. Plot of log k₁ against log [H⁺] in the Oxidation of Chalcones by QnFC.

Table 3. Effect of solvent Composition on the Oxidation of Chalcone by QnFC
 $[QnFC] = 1.19 \times 10^{-5} \text{ mol dm}^{-3}$ $[HClO_4] = 4.20 \times 10^{-1} \text{ mol dm}^{-3}$
 $[DBA] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ Temperature = 313K

AcOH-H ₂ O (% v/v)	D	k ₁ 10 ⁴ s ⁻¹
70-30	28.31	3.74
80-20	20.92	4.87
90-10	13.54	9.64

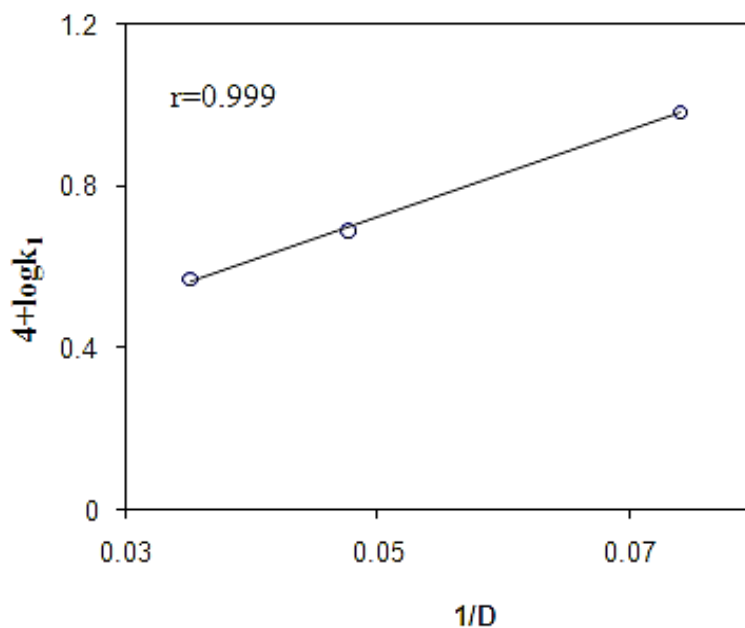


Figure 4. Plot of $\log k_{1(313K)}$ against $1/D$ in the Oxidation of Chalcones by QnFC.

There was no appreciable change in the rate with change of ionic strength indicating the involvement of neutral molecules in the rate-determining step. 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 (Fig. 4) suggesting an ion-dipole interaction [20-22] between chalcone and the oxidant. The reaction does not induce

polymerisation of acrylonitrile indicating the absence of free radical pathway. On the other hand, the addition of Mn^{2+} ion retards the rate of reaction (Table 4).

Table 4. Effect of varying Manganous sulphate
 $[QnFC] = 1.19 \times 10^{-5} \text{ mol dm}^{-3}$ $[HClO_4] = 4.20 \times 10^{-1} \text{ mol dm}^{-3}$
 $[DBA] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ Temperature = 313K

$[MnSO_4] 10^6$ mol dm^{-3}	$k_1 10^4$ s^{-1}
0.00	4.87
0.50	4.80
1.00	3.92
1.50	2.50
2.00	1.72

3. 1. Effect of substituents on the reaction rate

The substituents effect on oxidation process shows that, electron withdrawing substituents are found to enhance the reaction rate and electron releasing substituents are found to retard the rate of reaction [23,24]. Among the substituents used the observed order of reactivity is $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-Br} > m\text{-Cl} > p\text{-Cl} > p\text{-Br} > p\text{-F} > -H > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OCH}_3$. From the series of kinetic runs the rate constant k_1 was estimated and the rate of oxidation of some substituted chalcones have been studied at four different temperatures, viz., 303, 313, 323 and 333 K. The rate constant for all the substituents and activation parameters were evaluated from the Eyring's plots and are listed (Table 5).

Correlation of $\log k_{\text{obs}}$ with Hammett's substituent constant [25,26] σ , gives a good linear plot (Fig. 5) with a positive slope 1.25 ($r = 0.992$). The reaction constant, ρ , obtained from this plot, (eq. 1 to 4) indicates an electron rich at the reaction center of the reaction.

$$\log k_{303 \text{ K}} = 1.39 \sigma - 2.9158 \quad (r = 0.990, n = 11) \quad \dots (1)$$

$$\log k_{313 \text{ K}} = 1.25 \sigma - 2.7939 \quad (r = 0.992, n = 11) \quad \dots (2)$$

$$\log k_{323 \text{ K}} = 1.07 \sigma - 2.6375 \quad (r = 0.993, n = 11) \quad \dots (3)$$

$$\log k_{333 \text{ K}} = 0.92 \sigma - 2.4966 \quad (r = 0.990, n = 11) \quad \dots (4)$$

The fairly high values of enthalpy of activation (ΔH^\ddagger) indicate that the transition state is highly solvated. The negative values of the entropy of activation (ΔS^\ddagger) suggests extensive solvation of the transition state over the reactants.

There exists a linear relationship between ΔH^\ddagger and ΔS^\ddagger as per eq (5) [27],

$$\Delta H^\ddagger = \Delta H^{\ddagger o} + \beta \Delta S^\ddagger \quad \dots (5)$$

where ' β ' is isokinetic temperature. At this temperature all the substituents in a given series have the same reactivity. The β value was obtained from the linear plot of ΔH^\ddagger versus ΔS^\ddagger in

the present case is 387.7 K. This is the above experimental temperature indicating that the reaction is enthalpy controlled.

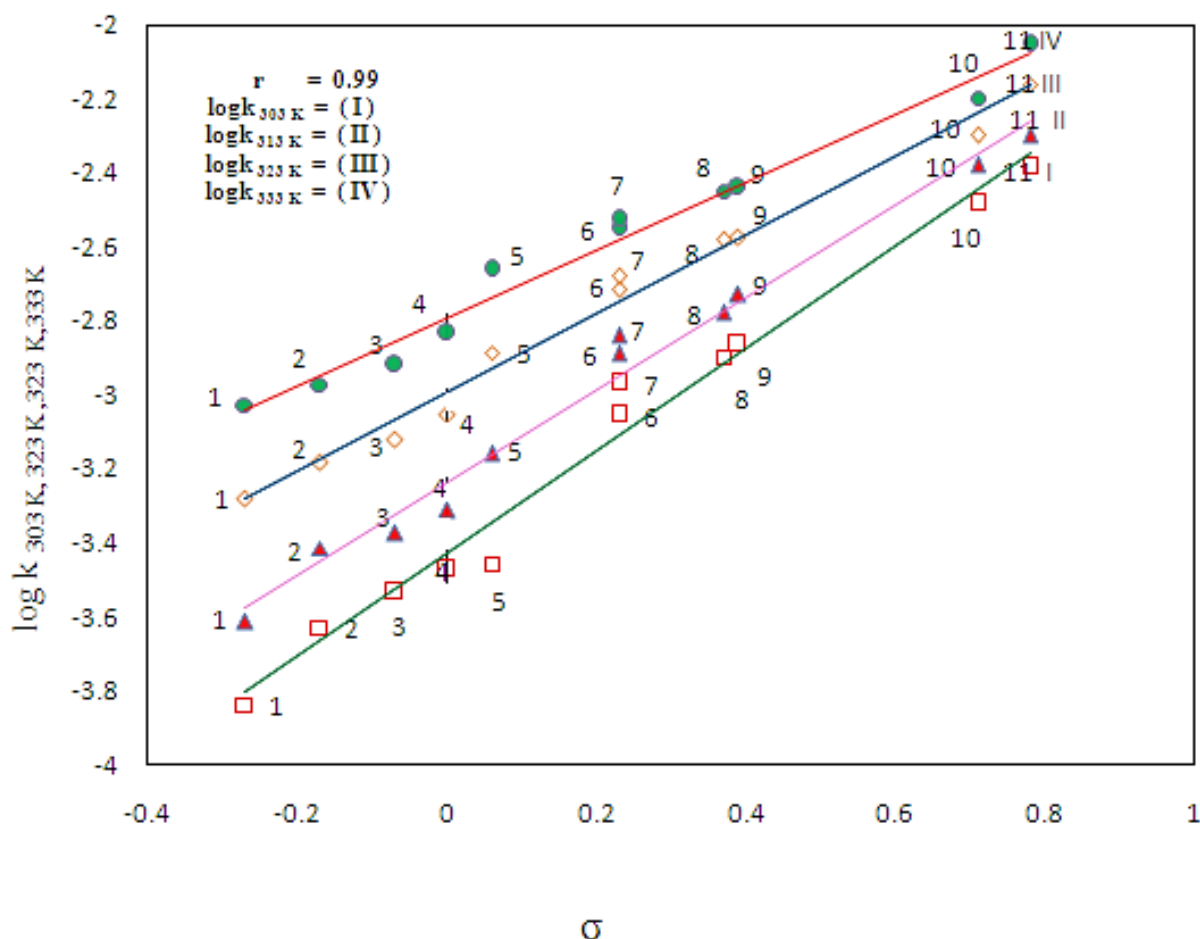


Figure 5. Plot of $\log k_{1(303\text{K},313\text{K},323\text{K},333\text{K})}$ against Hammett's substituent constant σ in the Oxidation of Chalcones by QnFC.

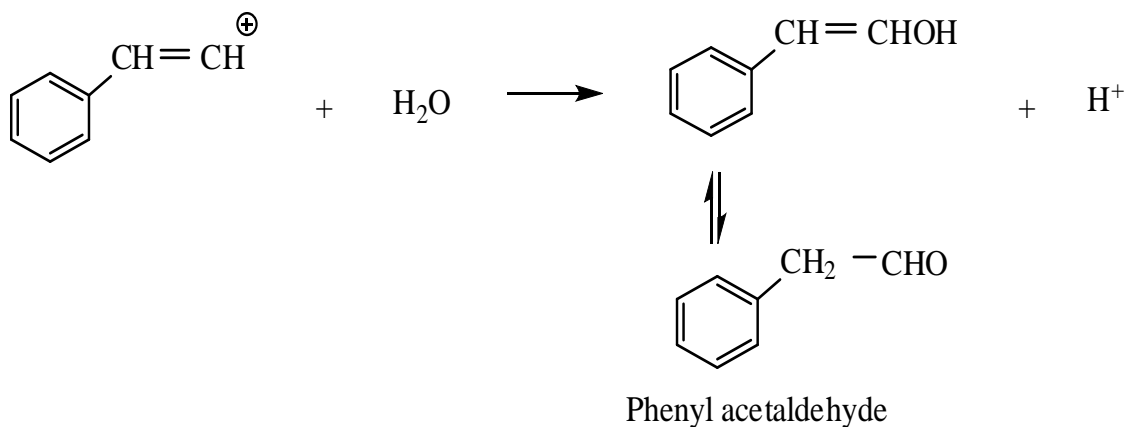
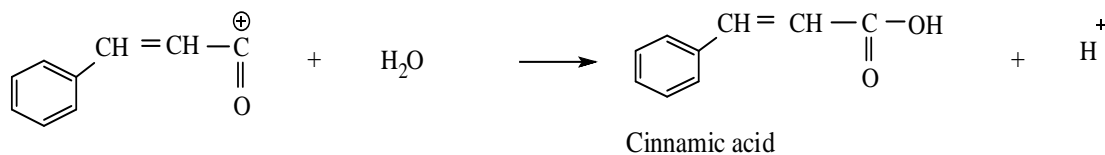
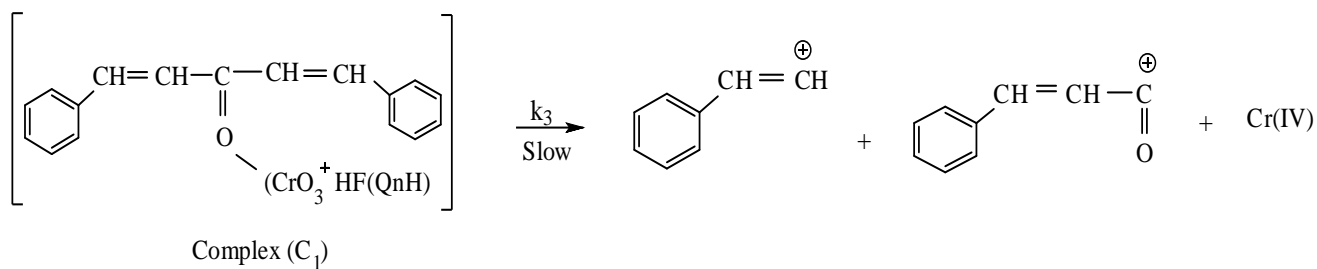
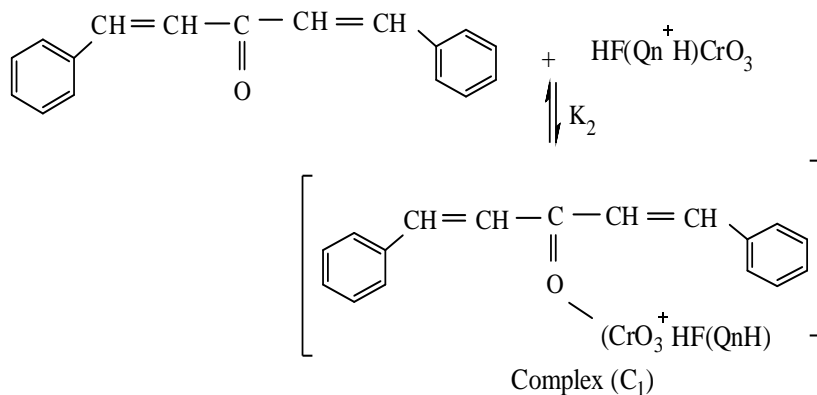
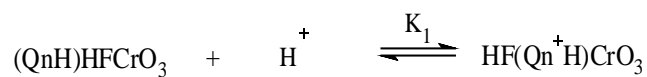
Exner [28,29] criticized the validity of such linear correlation between (ΔH^\ddagger) and (ΔS^\ddagger) as these quantities are dependent on each other. When the measurements at two different temperatures have been made the data can be analysed by the following equation. [30,31].

$$\log(k_1)_{T_1} = a + b \log(k_1)_{T_2} \quad \dots (6)$$

where $T_2 > T_1$

The plots of $\log k_{333\text{K}}$ versus $\log k_{323\text{K}}$ gave straight line $r = 0.998$ and $\log k_{313\text{K}}$ versus $\log k_{303\text{K}}$ gave a straight line $r = 0.996$. The free energy of activation, ΔG^\ddagger , is nearly constant, supporting a unified mechanism with all the substituted chalcones studied. Such a good correlation indicates that the all the substituents follow a common mechanism.

In view of these observations a probable mechanism for the oxidation can be given as shown in Scheme I.



Scheme - 1

Table 5 Thermodynamic Parameters for the Oxidation of Chalcones by Quinaldinium Fluorochromate

$$[\text{DBA}]_{\text{initial}} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{HClO}_4] = 4.20 \times 10^{-1} \text{ mol dm}^{-3}$$

$$[\text{QnFC}]_{\text{initial}} = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{AcOH-H}_2\text{O} = 80-20 (\% \text{v/v})$$

S.No	Substituents	Order with respect to Substrate	$k_{\text{obs}} \times 10^{-4} \text{ s}^{-1}$				ΔH^\ddagger (kJmol ⁻¹)	$-\Delta S^\ddagger$ (Jmol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJmol ⁻¹) at 313K	E_a (kJmol ⁻¹) at 313K	r
			303K	313K	323K	333K					
1	<i>p</i> -OCH ₃	0.56	1.45	2.44	5.24	9.40	50.56	94.85	98.44	53.16	0.993
2	<i>p</i> -CH ₃	0.56	2.35	3.85	6.54	10.70	39.92	125.65	97.25	42.52	0.998
3	<i>m</i> -CH ₃	0.56	2.92	4.22	7.24	12.00	37.36	132.63	97.01	39.96	0.992
4	-H	0.29	3.37	4.87	8.85	14.74	39.30	125.06	96.64	41.90	0.991
5	<i>p</i> -F	0.56	3.49	6.91	13.02	21.85	48.89	92.49	95.72	51.49	0.998
6	<i>p</i> -Br	0.49	8.81	12.92	19.30	28.09	29.90	147.66	94.10	32.50	0.998
7	<i>p</i> -Cl	0.44	10.76	14.48	20.91	29.68	25.88	159.36	93.80	28.48	0.996
8	<i>m</i> -Cl	0.57	12.63	16.63	26.30	35.54	27.09	154.09	93.44	29.69	0.991
9	<i>m</i> -Br	0.56	13.68	18.70	26.58	36.26	24.81	160.79	93.13	27.41	0.998
10	<i>m</i> -NO ₂	0.56	32.96	41.68	50.26	63.48	15.45	184.30	91.05	18.05	0.999
11	<i>p</i> -NO ₂	0.56	41.11	50.11	69.25	88.88	19.41	169.62	90.57	22.01	0.990

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

$$-\frac{d[\text{QnFC}]}{dt} = k_3 C_1$$

$$= \frac{k_3 K_2 [\text{OxH}^+] [\text{S}]}{1 + K_2 [\text{S}]}$$

$$= \frac{k_3 K_1 K_2 [\text{Ox}] [\text{H}^+] [\text{S}]}{1 + K_2 [\text{S}]}$$

4. CONCLUSION

The oxidation of substituted 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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