



OXIDATIVE KINETICS MECHANISM OF SUBSTITUTED CHALCONES BY IMIDAZOLIUM CHLOROCHROMATE

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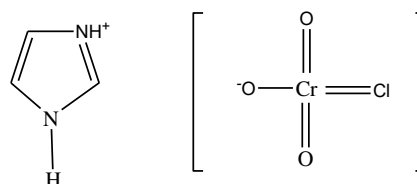
ABSTRACT

The kinetics of oxidation of substituted chalcones by Imidazolium Chlorochromate (ICC) has been studied in 50% acetic acid-50% water medium. The order of the reaction is one with respect to oxidant, hydrogen ion and fractional order with respect to substrate concentration. The rate of the reaction has been conducted at five different temperatures. Thermodynamic parameters have been calculated. A good correlation is found to exist between $\log k_{1(308K)}$ and Hammett constant (σ). For substituted chalcones, the electron withdrawing substituents are found to enhance the rate of the reactions and electron releasing substituents are found to retard the rate of the reaction. The rate data obeys the Hammett relationship. The order of reactivities with substituents is $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-Br} > m\text{-Cl} > p\text{-Cl} > p\text{-Br} > p\text{-F} > -H > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OCH}_3$. The Exner plot of $k_{1(308K)}$ versus $k_{2(313K)}$ is linear and isokinetic temperature is obtained. This supports that all the reactions under this investigation follow a common mechanism. The constant ΔG values are obtained for all the substituted compounds. It also indicates that the substituted compounds are oxidized by same mechanism. Cinnamic acid and Phenyl acetaldehyde was identified as the product of oxidation. Based on the kinetics results, a suitable mechanism has been proposed.

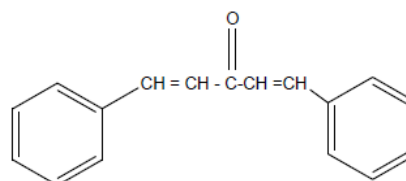
Keywords: Imidazoliumchlorochromate, Chalcones, Kinetics, Oxidation, Mechanism.

1. INTRODUCTION

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds [1]. Chromium especially, Cr (VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidizable organic functional groups [2, 3]. Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry [4]. Imidazolium chlorochromate (ICC) is also one such reagent [5]. Imidazolium chlorochromate has the following advantages over already reported Cr (VI) reagents. (i) quite stable at room temperature (ii) not photosensitive (iii) less hygroscopic and hence a suitable reagent for the oxidation of acid sensitive and ring strained alcoholic as readily soluble in acetic acid [6]. Chalcone are class of natural product and aromatic ketones. Chalcones are oxidized by different oxidizing agents, and in all these reactions either the $>c=c<$ or the $>c=o$ group of the chalcone is attacked by the oxidant [7-8]. Chalcones, either natural or synthetic are known to exhibit various biological activities [9-11].



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 and its structure is given below:



Dibenzylideneacetone or Dibenzalacetone or distyrylketone

2. EXPERIMENTAL

2.1. Material and methods

The solution of the distyryl ketones were freshly prepared in acetic acid and standardized by titrating it against a standard solution of iodine. The chalcones and its derivatives viz, $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-Br} > m\text{-Cl} > p\text{-Cl} > p\text{-Br} > p\text{-F} > -H > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OCH}_3$ were prepared and used. Imidazoliumchlorochromate was prepared by reported method [12], and its melting point ($120\text{-}124^\circ\text{C}$) was checked. Acetic acid was purified [13] by standard method and the fraction distilling at 118°C was collected and saved in brown bottles. All other chemicals used were of AnalaR grade. The solutions were prepared in double distilled water.

2.2. Preparation of Chalcones [11]

A cold solution of 25g of NaOH in 250 ml of water and 200 ml of ethanol was placed in a 200 ml round bottomed flask equipped with mechanical stirrer and it was surrounded by ice 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 of 6.5g [25.5ml, 0.25mol] of pure benzaldehyde 7.3g [9.31 ml of 0.125mol] of acetone was added. A flocculent precipitate was formed in 2-3 min. The remainder of the benzaldehyde acetone mixture was added after 15 minutes. The stirring was continued for a further 30 min.

The precipitate was filtered at the pump and washed well with cold water to eliminate the alkali as completely as possible. The solid was derived at room temperature upon the filter paper to constant weight. 27g of crude dibenzalacetone obtained was recrystallized from ethylacetate (m.p. $105\text{-}108^\circ\text{C}$). 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 recrystallized using suitable solvent. The purity of the distyryl ketones were checked by their melting point.

2.3. Kinetic Measurements

The kinetic studies were carried out under pseudo-first order conditions in 50% (v/v) aqueous acetic acid with the concentration of the chalcones in large excess compared to that of the oxidant. All reactant solutions were placed in a thermostatic water bath for one hour to attain the temperature of 30°C . Appropriate quantities of the reagent solutions were mixed in a 250 cm^3 conical

flask already placed in the thermostatic bath. The reaction rate was followed by measuring the decrease in absorbance at 470nm for up to 80% completion of the reaction by using Systronics UV-vis spectrophotometer. The reactions were followed determining the concentration of the unreacted ICC, at known intervals of time. 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 $\pm 1\%$.

2.4. Stoichiometry

The stoichiometry of the reaction was determined by carrying out several set of experiments with varying amounts of ICC in large excess over chalcone. The estimation of the unreacted oxidant showed that one mole of chalcone consumed one mole of the oxidant.

2.5. Product analysis

To the substrate (0.1 mole) in acetic acid, ICC (0.1mole) in water was added and the medium was maintained in acetic acid using perchloric acid then the reaction mixture was slightly warmed and was kept aside for about 48 hr for the completion of reaction. After 48 hr, the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ether 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 and were detected by TLC and compared with those of the authentic sample. The presence of phenyl acetaldehyde among the reaction product was also detected by preparing their 2,4-dinitrophenyl hydrazine derivatives. Cinnamic acid [13] and phenyl acetaldehyde was further identified and confirmed by using IR and GC-MS.

3. RESULTS AND DISCUSSION

Oxidation of chalcones by imidazoliumchlorochromate has been conducted in 50% acetic acid - 50% water (v/v) medium at 303 K under pseudo-first order condition and the observed results are discussed below.

The reaction was first order with respect to oxidant as evidenced by a good linearity in the plot $\log [\text{absorbance}]$ *versus* time ($r=0.99$). The rate of oxidation increased progressively on increasing the concentration. The plot of $\log k_1$ *versus* $\log [\text{chalcone}]$ gave the slope of 0.53 ($r=0.99$), shows that the oxidation reaction was fractional order with respect to chalcone. It was further supported by the fact that the reciprocal plot of k_{obs} *versus* substrate

gave a straight line with a definite intercept indicating the Michaelis-Menten type of kinetic in this reaction (Fig.1). The rate of the reaction increases with the increasing

$[H^+]$. A plot of $\log k_1$ versus $\log [H^+]$ gave a straight line with a slope of 1.0 ($r = 0.99$), it indicates first order with respect to hydrogen ion concentration (Table 1).

Table 1: Rate data for Oxidation of Chalcone by Imidazolium Chlorochromate at 303K

[Oxidant] 10^4 mol dm^{-3}	[Substrate] 10^3 mol dm^{-3}	$[HClO_4]$ 10^2 mol dm^{-3}	%CH ₃ COOH- %H ₂ O (% v/v)	$[MnSO_4]$ 10^2 mol dm^{-3}	$k_{obs} \cdot 10^3 \text{ s}^{-1}$
2.0	2.5	1.0	50-50	-	2.83
2.5	2.5	1.0	50-50	-	2.81
3.0	2.5	1.0	50-50	-	2.80
3.5	2.5	1.0	50-50	-	2.83
4.0	2.5	1.0	50-50	-	2.82
2.0	2.5	1.0	50-50	-	2.83
2.0	3.0	1.0	50-50	-	3.18
2.0	3.5	1.0	50-50	-	3.38
2.0	4.0	1.0	50-50	-	3.73
2.0	4.5	1.0	50-50	-	4.13
2.0	2.5	1.0	50-50	-	2.83
2.0	2.5	1.5	50-50	-	4.36
2.0	2.5	2.0	50-50	-	5.62
2.0	2.5	2.5	50-50	-	7.96
2.0	2.5	3.0	50-50	-	8.70
2.0	2.5	1.0	50-50	-	2.83
2.0	2.5	1.0	55-45	-	3.63
2.0	2.5	1.0	60-40	-	4.13
2.0	2.5	1.0	65-35	-	5.03
2.0	2.5	1.0	70-30	-	6.11
2.0	2.5	1.0	50-50	0.0	2.83
2.0	2.5	1.0	50-50	0.5	2.52
2.0	2.5	1.0	50-50	1.0	2.03
2.0	2.5	1.0	50-50	1.5	1.76
2.0	2.5	1.0	50-50	2.0	1.67

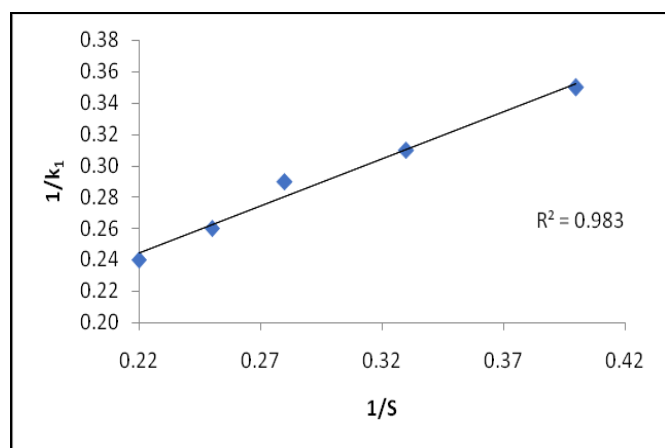


Fig.1: Plot of $1/k_1$ against $1/s$ in the oxidation of Chalcones by ICC

There was no appreciable change in the rate with change of ionic strength indicating the involvement of neutral

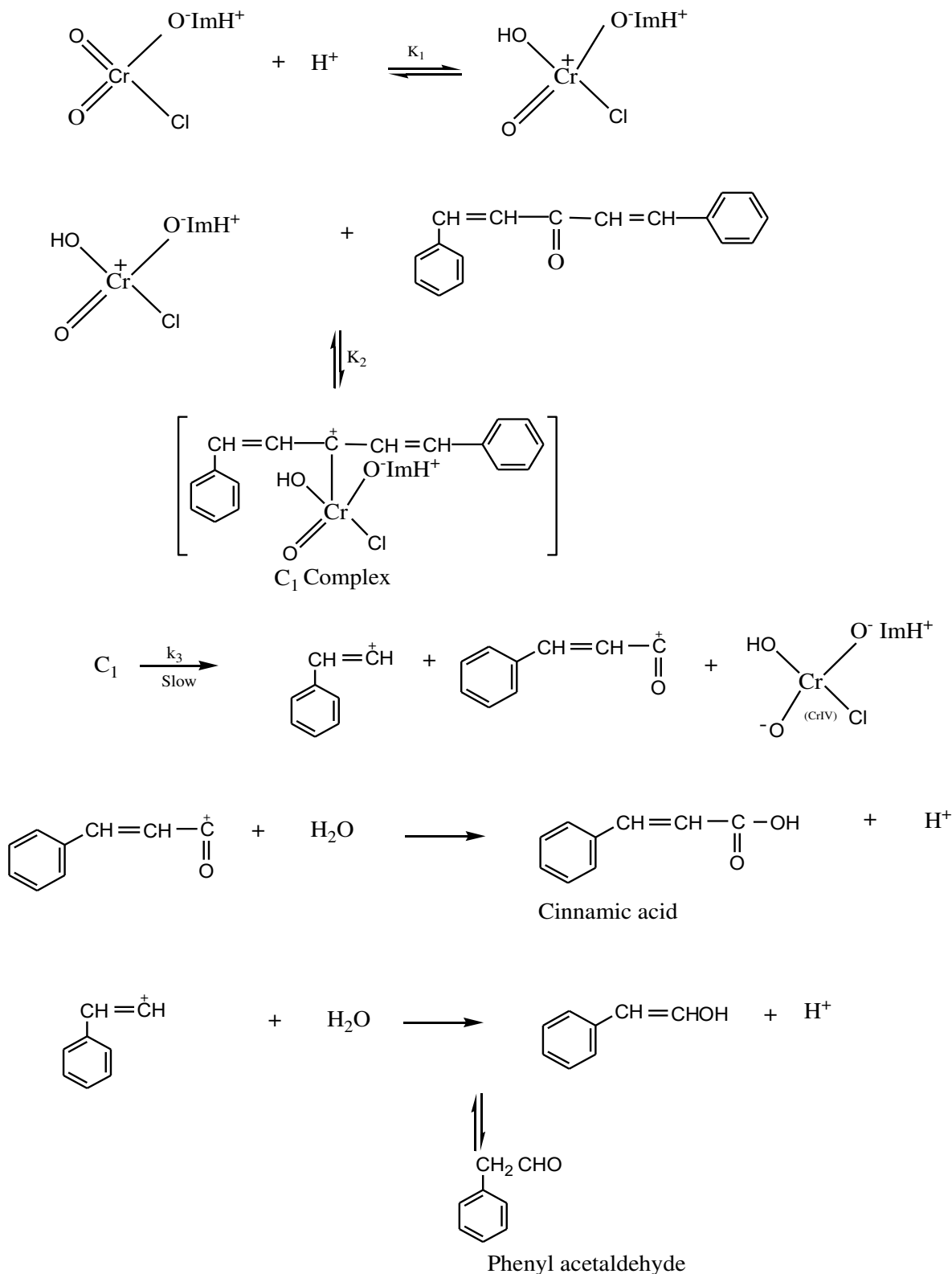
molecule in the rate determining step. The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical path way. The rate constant is decreased by the addition of Mn^{2+} ion. The rate of the reaction increases with decreasing the dielectric constant of the medium suggesting the ion-dipole interaction between the oxidant and chalcone. The rate constants were measured at five different temperatures and the activation parameters were calculated from a plot of $\ln k_2/T$ versus $1/T$ ($r = 0.99$) of the Eyring's equation [14] and it was found to be linear [15].

3.1. Mechanism and rate law

The mechanism of reaction for the oxidation of chalcones by ICC in an acid medium is shown in Scheme-1. The reaction is showing unit order dependence with respect to oxidant and perchloric acid

and fractional order with respect to substrate. It obeys Michaelis- Menten type kinetics. The protonated oxidant is treated with substrate which gives complex

(C₁). The complex C₁ undergoes hydrolysis in presence of water and gives the products such as Cinnamic acid and Phenyl acetaldehyde.



Scheme 1: Mechanism of oxidation of substituted chalcones by ICC

The above mechanism leads to the following rate law

$$\begin{aligned} -\frac{d[\text{ICC}]}{dt} &= k_3 C_1 \\ &= \frac{k_3 K_2 [\text{ICCH}^+] [\text{S}]}{1 + K_2 [\text{S}]} \\ &= \frac{k_3 K_1 K_2 [\text{ICC}] [\text{H}^+] [\text{S}]}{1 + K_2 [\text{S}]} \end{aligned}$$

This rate law explains all the experimental facts

3.2. Effect of substituents on the reaction rate

The kinetics was carried out with a few *meta* and *para* substituted chalcones at 303,308,313,318 and 323K. The observed rate constant increases with increase in temperature for all the compounds. The activation parameters for the oxidation of chalcones by Imidazolium chlorochromate have been evaluated. A plot of $\log k_{(313\text{K})}$ of the substituted chalcones with reaction constant σ gave a good straight line with ρ value 0.56 ($r=0.99$) (Fig.2). The order of the reactivity of chalcones is $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-Br} > m\text{-Cl} > p\text{-Cl} > p\text{-Br} > p\text{-F} > \text{-H} > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OCH}_3$. The plot of $\log (k_1)_{308\text{K}}$ versus $\log (k_2)_{313\text{K}}$ gave a straight line with $r=0.99$. Such a good correlation indicates that all the substituted follow common mechanism (Table 2). The entropy of activation is negative for all the substituted chalcones ranging from -74 to -196 $\text{JK}^{-1}\text{mol}^{-1}$. $\Delta S^\ddagger$ values are negative indicating extensive solvation of transition state over the reactants. Free energy of activation $\Delta G^\ddagger$ values are nearly constant which indicates that all the substituted chalcones are oxidized by the same mechanism. The minimum E_a and $\Delta H^\ddagger$ values support the proposed mechanism.

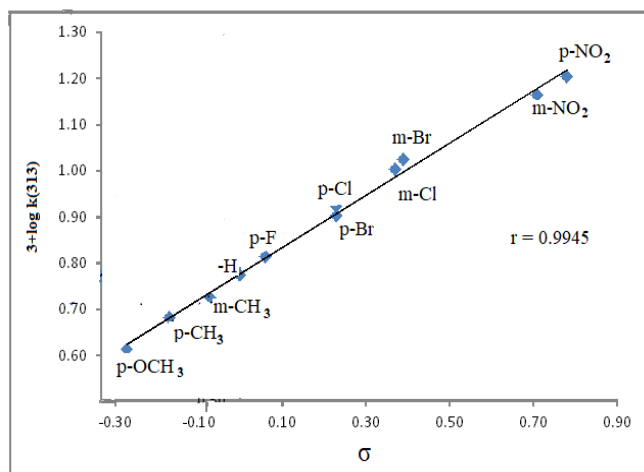


Fig. 2: Hammett's plot

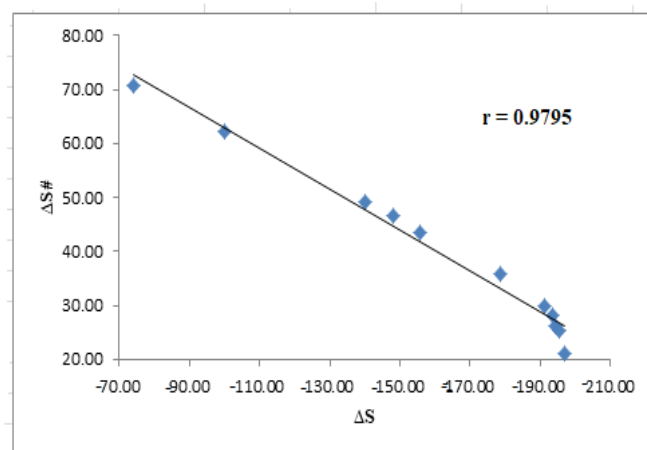


Fig. 3: The plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$

A plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ gave a straight line with a good correlation coefficient 0.98 (Fig. 3). As $\Delta H^\ddagger$ and $\Delta S^\ddagger$ do not vary linearly, no isokinetic relationship is observed. This indicates absence of enthalpy and entropy compensation effect. The validity of the isokinetic relation can be tested graphically by plotting Exner plot. Exner [16-17] criticized the validity of such a linear correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ as these quantities depend on each other when measurement are made at two different temperatures the experimental data can be treated by the following equation.

$$\log k_2 (T_1) = a + b \log k_2 (T_2) \quad \text{where } T_2 > T_1$$

A good correlation coefficient ($r = 0.99$) is obtained when $\log k_2 (308\text{K})$ is plotted against $\log k_1 (313\text{K})$ indicating that the reaction under investigation follows a common mechanism (Fig.4).

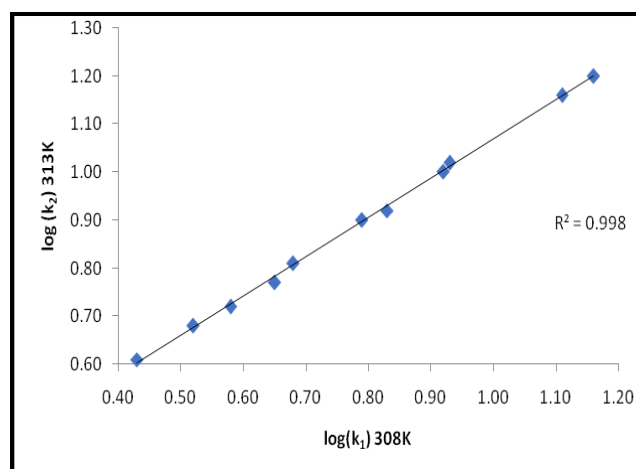


Fig. 4: Exner plot of $\log (k_1)_{308\text{K}}$ versus $\log (k_2)_{313\text{K}}$ for the oxidation of substituted chalcones by ICC

Table 2: Thermodynamic parameters for the oxidation of para and meta substituted chalcones by ICC.

Substituents	$[ICC] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ $[HClO_4] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$					Solvent = 50% AcOH-50% H ₂ O (v/v) $[Chalcones] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$				
	$k_1 \times 10^3 \text{ s}^{-1}$					$\Delta H^\ddagger$ kJ mol^{-1}	$-\Delta S^\ddagger$ $\text{JK}^{-1} \text{ mol}^{-1}$	$\Delta G^\ddagger \text{ kJ mol}^{-1}$ at 308 K	$E_a \text{ kJ mol}^{-1}$ at 308 K	r
	303K	308K	313K	318K	323K					
<i>p</i> -methoxy	1.44	2.69	4.07	6.08	17.37	70.67	-74	93.10	73.19	0.99
<i>p</i> -methyl	1.76	3.31	4.11	6.19	8.57	62.34	-100	92.64	64.86	0.99
<i>m</i> -methyl	2.58	3.73	5.51	7.10	9.32	49.17	-139	91.56	51.69	0.99
-H	2.83	3.80	5.56	7.39	9.37	46.49	-148	91.40	49.01	0.99
<i>p</i> -fluoro	3.95	4.78	6.45	8.91	12.35	43.54	-155	90.72	46.06	0.99
<i>p</i> -bromo	5.12	6.19	8.03	10.77	12.80	35.85	-178	89.94	38.37	0.99
<i>p</i> -chloro	5.92	6.83	8.37	10.83	13.13	29.91	-191	89.67	32.62	0.99
<i>m</i> -chloro	6.64	8.38	10.02	12.62	14.01	28.10	-193	88.60	30.62	0.98
<i>m</i> -bromo	7.14	8.51	10.05	13.48	15.84	26.10	-194	89.13	28.62	0.99
<i>m</i> -nitro	7.62	12.88	14.45	15.86	16.66	25.31	-195	86.04	27.83	0.99
<i>p</i> -nitro	9.09	14.45	15.84	19.06	18.34	21.04	-196	89.16	23.56	0.99

4. CONCLUSION

The mechanism of oxidation of chalcone and substituted chalcones viz *meta* and *para* substituted chalcones by ICC is reported in detail. The reaction is first order with [oxidant] and [H⁺] and fractional order with chalcones. The oxidation of *meta* and *para* substituted chalcones yield the corresponding Phenyl acetaldehyde. The positive ρ value obtained from the Hammett plot reveals that a positively charged reactive intermediate is formed during the oxidation process. Similarly the negative value of $\Delta S^\ddagger$ supports the formation of the activated complex in the slow step. The product of oxidation is Phenyl acetaldehyde. The order of the reactivities with substituents is $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-Br} > m\text{-Cl} > p\text{-Cl} > p\text{-Br} > p\text{-F} > -H > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OCH}_3$. The constancy of $\Delta G^\ddagger$ values indicated that all the substituted chalcones are operative in the same mechanism.

5. ACKNOWLEDGEMENT

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