Kinetics of oxidation of substituted Anilines by Imidazolium chlorochromate

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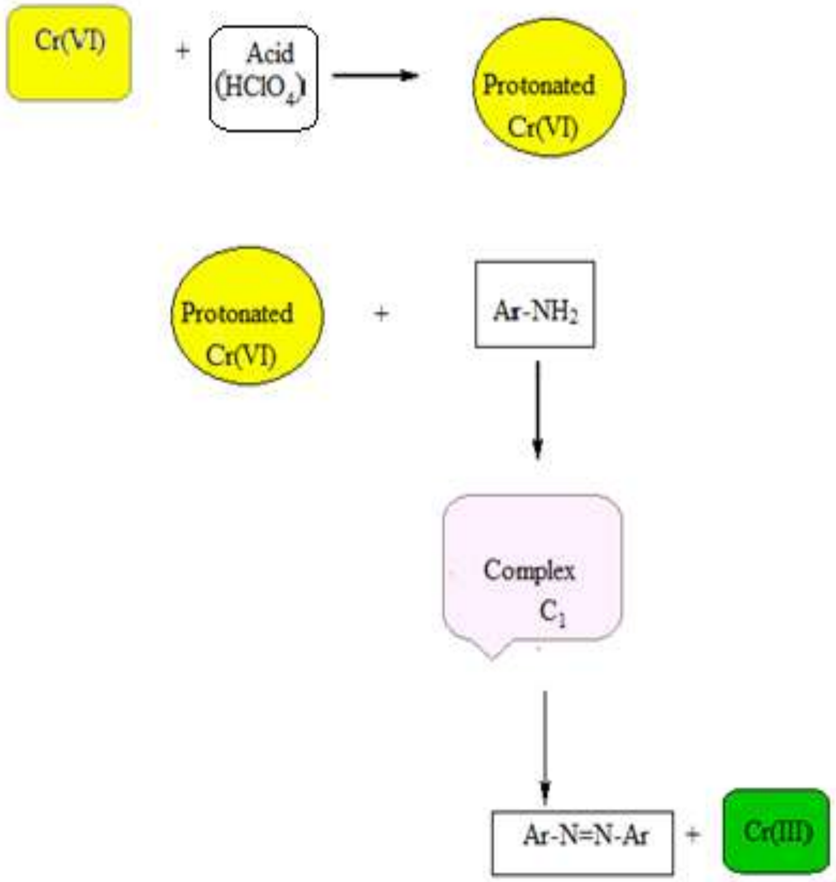
Abstract

The kinetics of oxidation of substituted anilines by imidazolium chlorochromate (ICC) has been studied in 50% acetic acid - water medium. The reaction is first order each in imidazolium chlorochromate, aniline and hydrogen ion concentration. The rate of oxidation increase with decrease in dielectric constant of solvent suggests ion-dipole interaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile and absence of free radical is proved. 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 anilines, the electron withdrawing substituents retard the reaction rate, while the electron releasing substituents enhance the rate of the reaction. The order of reactivities with substituents viz p-OCH_3> p-CH_3>-H >p-Cl>p -Br >m-Cl>m-NO_2 and it is due to the presence of +I and –I effect. Exner plot* $k_{1(308K)}$*versus*$k_{2(313K)}$ *is linear and isokinetic temperature is calculated. This supports that all the substituents under this investigation follows a common mechanism. The constant ΔG values are obtained for all the substituted compounds. It indicates that the substituted compounds are oxidised by same mechanism. Azobenzene has been identified as the product of oxidation. Based on the kinetics results, a suitable mechanism has been proposed.*

Keywords: Imidazolium chlorochromate, Aniline, Kinetics, Oxidation, Activation Parameter.

Graphical Abstract



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 oxidisible 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 of the such reagent[5].

Imidazolium chlorochromate has the following advantages over already reported Cr (VI) reagent: (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]. Anilines (aromatic amines) are the most widespread and principal contaminants of industrial waste waters.

Environmental contaminants were the building blocks for many textile dyes, agro chemicals and other type of synthetic chemicals. The reaction pathways of aromatic amines in natural systems are dominated by redox reaction with soil and sediment constituents. Better understanding of the mechanism of oxidation of such contaminants to harmless products is the important goal for basic research and industrial applications. Hence, in this study, kinetics of oxidation of anilines by imidazolium chlorochromate is carried out[7].

Material and Methods

The anilines and its derivatives viz, p-OCH_3, p-CH_3,-H, p-Cl,p-Br,m-Cl,m-NO_2 were purified and used. Imidazolium chlorochromate was prepared by reported method[5], and its melting point (120-124°C) was checked. Acetic acid was purified[8] by standard method and the fraction distilling at 118°C was collected and saved in brown bottles. All other chemicals used were of AnalaR grades.

Kinetic measurements: The kinetic studies were carried out under pseudo-first order conditions in 50% *(v/v)* aqueous acetic acid medium with the concentration of the aniline in large excess compared to that of the oxidant. All reactant solutions were placed in a thermostated 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 stoppard conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 470 nm for at most 80% completion of the reaction by using systronics UV-Vis spectrophotometer.

The reactions were followed by determining the concentration of the unreacted Imidazolium chlorochromate at known intervals of time. The pseudo-first order rate constants k_1 computed from the linear plots of log absorbance *vs* time by the least squares method were reproducible within ±3%.

Stoichiometry and Product analysis: The stoichiometry of the reaction was determined by carrying out several set of experiments with varying amounts of Imidazolium chlorochromate in large excess over aniline.

The estimation of the unreacted oxidant showed that one mole of aniline consumed one mole of the oxidant. The azobenzene formed as the product of oxidation under kinetic condition was confirmed by TLC, IR as well as GC-MS spectra.

Results and Discussion

Oxidation of anilines by imidazolium chlorochromate has been conducted in 50% acetic acid - 50% water *(v/v)* medium at 308 K under pseudo-first order conditions and the observed results are discussed.

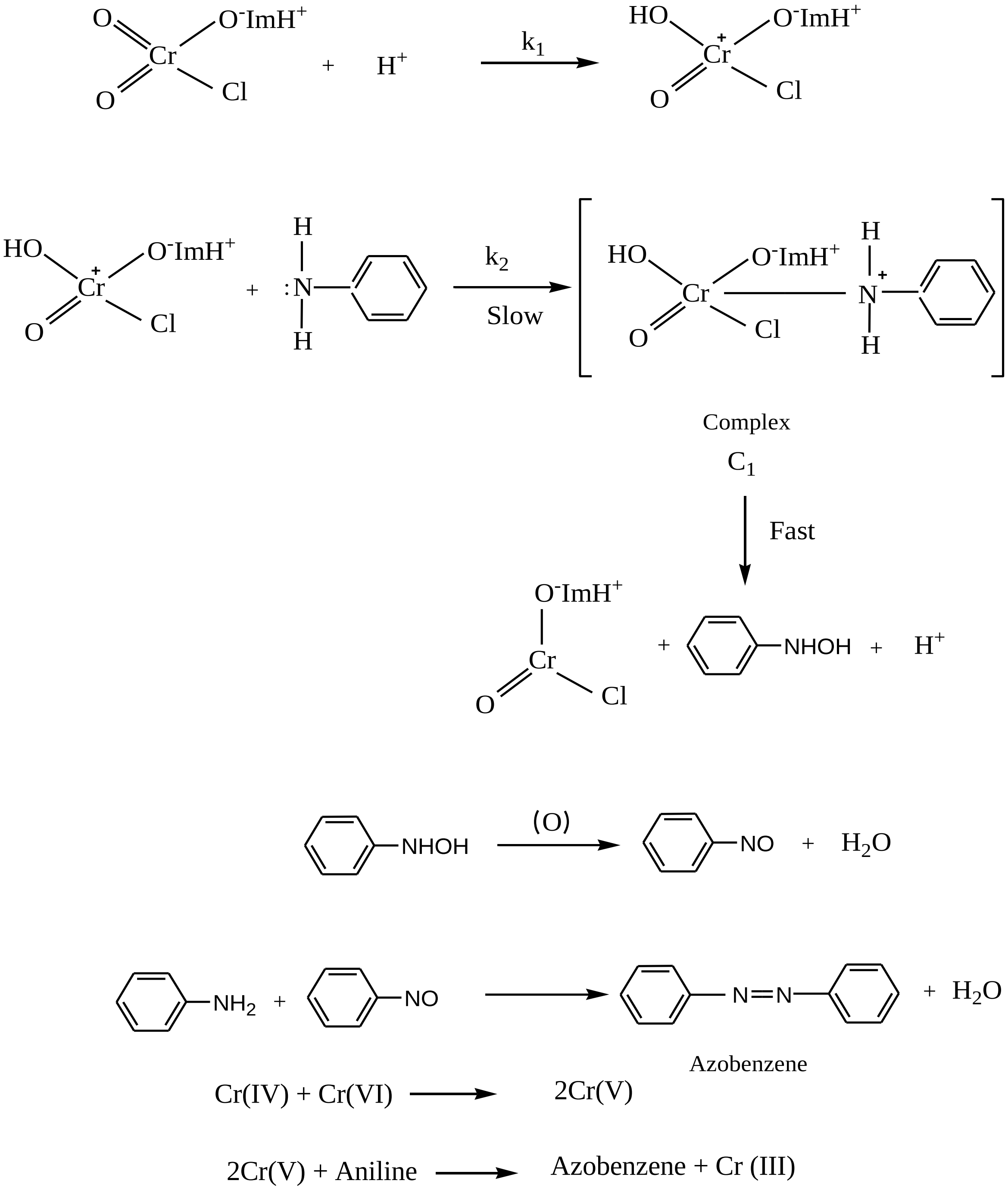
The reaction was first order with respect to oxidant as evidenced by a good linearity in the plot log [ICC] *vs* time (r=0.99). The rate of oxidation increased progressively on increasing the concentration aniline. The plot of log k_1 *vs* log [aniline] gave the slope of 1.03(r= 0.99) shows that the oxidation reaction was first order with respect to aniline.

The rate of the reaction increases with increase the [H^+]. A plot of logk_1 *vs* 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. The rate of the reaction increases with decreasing the dielectric constant of the medium suggesting the ion-dipole interaction between the reactants.

Rate of reaction increases with increase in the concentration of Aniline. The rate constants were measured at five different temperatures and the activation parameters were calculated from a plot of lnk_2/T versus 1/T(r=0.99) of the Eyring's equation[8]and it was found to be linear[9].

Mechanism and rate law: The order with respect to each [Imidazolium ChloroChromate], [H^+] and [aniline] is one. Increasing in ionic strength by the addition of sodium perchlorate has no effect on the rate constants. The rate of oxidation increases with decrease in dielectric constant of solvent suggests ion-dipole interaction in the rate determining step. The reaction did not promote polymerization of acrylonitrile indicating the absence of free radical pathway. The protonated oxidant is formed in the presence of H^+.

The complex C_1 is formed when protonated oxidant react with Aniline. The complex C_1 is dissociated into Cr (IV), phenyl hydroxylamine and H^+ ions. The phenyl hydroxylamine is oxidized to give nitroazobenzene. The nitroazobenzene undergoes the reaction with aniline which forms Azobenzene as a product of oxidation reaction (Scheme).



Scheme 1: Mechanism of oxidation of substituted aniline by Imidazolium Chlorochromate

The above mechanism leads to the following rate law rate:

$$\frac{-d[ICC]}{dt} = k_1k_2[ICC][S][H^+]$$

Effect of Substituents on the reaction rate: The kinetics was carried out with a few meta and para substituted anilines at 303,308,313,318 and 323 K. The observed rate constant increases with increase in temperature for all the compounds. The activation parameters for the oxidation of anilines by Imidazolium chlorochromate have been evaluated. A plot of $\log k_{1\ (303K)}$ of the substituted anilines with reaction constant σ gave a good straight line with ρ value -0.80 (r =0.99). The *σ* value indicates the sensitivity of a reaction to the effects of electronic perturbation. It also provides the information about the nature of the transition state involved during the reaction.

A reaction involving development of positive charge in the transition state is aided by electron- releasing substituents and the *σ* value negative. The presence of electron releasing substituents in the phenyl ring activates the reaction rate while the electron withdrawing substitutent retards in the reaction rate. The order of the reactivity of aniline is *p-*OCH_3 *>p-*CH_3*>- H > p-Cl> p-Br >m-Cl>m-*NO_2 is due to the presence of +I and -I effect.

Table 1
Rate data for oxidation of aniline by imidazolium chlorochromate at 303K

[Oxidant] $10^3 mol\ dm^{-3}$	[Substrate] $10^2 mol\ dm^{-3}$	[$HClO_4$] $10^2 mol\ dm^{-3}$	%CH_3COOH-%H_2O (% v/v)	[$AlCl_3$] $10^2 mol\ dm^{-3}$	$k_{obs}\ 10^4$ s^{-1}
1.5	3.0	0.5	50-50	-	6.24
2.0	3.0	0.5	50-50	-	6.26
2.5	3.0	0.5	50-50	-	6.25
3.0	3.0	0.5	50-50	-	6.23
3.5	3.0	0.5	50-50	-	6.20
1.5	3.0	0.5	50-50	-	6.24
1.5	3.5	0.5	50-50	-	7.24
1.5	4.0	0.5	50-50	-	8.00
1.5	4.5	0.5	50-50	-	9.37
1.5	5.0	0.5	50-50	-	10.72
1.5	3.0	0.5	50-50	-	6.24
1.5	3.0	1.0	50-50	-	7.83
1.5	3.0	1.5	50-50	-	8.10
1.5	3.0	2.0	50-50	-	9.98
1.5	3.0	2.5	50-50	-	10.49
1.5	3.0	0.5	50-50	-	6.24
1.5	3.0	0.5	55-45	-	7.49
1.5	3.0	0.5	60-40	-	8.10
1.5	3.0	0.5	65-35	-	9.48
1.5	3.0	0.5	70-30	-	10.73
1.5	3.0	0.5	50-50	0.0	6.24
1.5	3.0	0.5	50-50	0.5	6.21
1.5	3.0	0.5	50-50	1.0	6.01
1.5	3.0	0.5	50-50	1.5	5.92
1.5	3.0	0.5	50-50	2.0	5.86

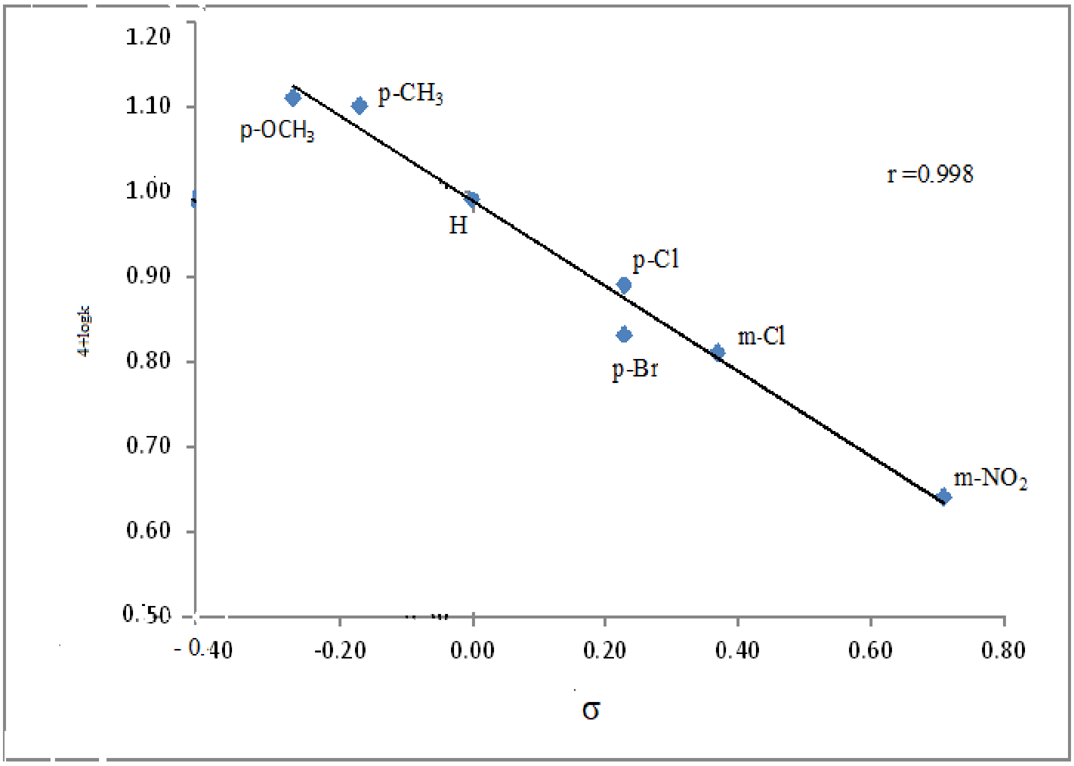


Figure 1: Hammett's plot

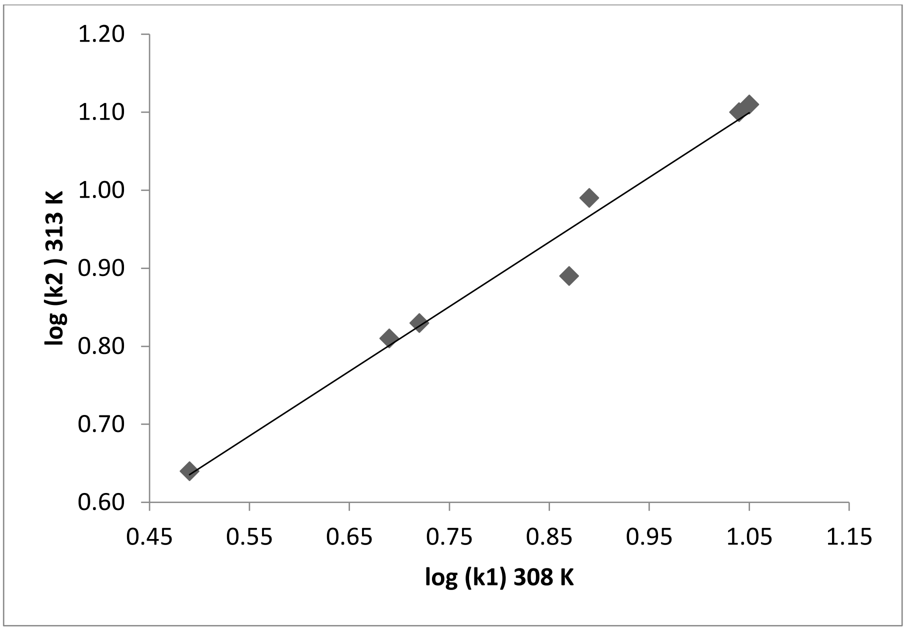


Figure 2: Exner plot of log $(k_1)_{308K}$ *versus* log $(k_2)_{313K}$ for the oxidation of substituted anilines by ICC

Table 2
Thermodynamic parameters for the oxidation of para-meta substituted anilines by ICC.
[ICC] =1.5x10^{-3}*mol dm*$^{-3}$, Solvent=50% AcOH-50%
H_2O *(v/v)*,
[Aniline]=3.0x10^{-2}*mol dm*$^{-3}$, [$HClO_4$] =0.5 x10^{-2}*mol dm*$^{-3}$,
[$AlCl_3$] = 0 x10^{-2}*mol dm*$^{-3}$.

S.N.	**Substituents**	**k_1X10^4*s*$^{-1}$**					**ΔH$^{\#}$ *kJ mol*$^{-1}$**	**-ΔS$^{\#}$ *JK*$^{-1}$ *mol*$^{-1}$**	**ΔG$^{\#}$ *kJ mol*$^{-1}$ at 308 K**	**Ea *kJ mol*$^{-1}$at 308 K**	**r**	***σ***
		303K	**308K**	**313K**	**318K**	**323K**						
1.	*p*–methoxy	9.58	11.22	12.88	15.13	17.37	21.26	-191	83.73	23.78	0.99	-0.27
2.	*p*- methyl	9.48	11.15	12.45	14.59	16.59	22.57	-187	82.06	25.19	0.99	-0.17
3.	H	6.24	7.87	9.71	13.48	15.84	23.15	-179	84.09	26.67	0.99	0.0
4.	*p*-chloro	5.91	7.51	7.76	11.48	14.79	35.56	-161	84.22	38.08	0.99	+0.23
5.	*p*-bromo	4.53	5.24	6.76	8.94	12.58	37.68	-156	84.98	40.20	0.99	+0.23
6.	*m*-chloro	3.97	4.92	5.56	7.45	9.88	40.25	-150	84.16	42.77	0.99	+0.37
7.	*m*-nitro	2.92	3.98	4.36	6.91	9.04	45.15	-139	85.93	47.67	0.99	+0.71

The plot of log $(k_1)_{308K}$ *vs* log $(k_1)_{313K}$ gave a straight line with r=0.99. Such a good correlation indicates that all the substituents follow common mechanism. The entropy of activation is negative for all the substituent anilines ranging from-139 to -191*JK-1mol-1*. ΔS$^{\#}$values are negative indicating extensive solvation of transition state over the reactants. Free energy of activation ΔG$^{\#}$ values are nearly constant which indicates that all the substituted anilines are oxidized by the same mechanism. The minimum E_a and ΔH$^{\#}$ values supports the proposed mechanism.

A plot of ΔH$^{\#}$ *vs* ΔS$^{\#}$ gave a straight line with a good correlation coefficient 0.998. As ΔH$^{\#}$ and ΔS$^{\#}$ do not vary linearly, no isokinetic relationship is observed. This indicates absence of enthalpy and entropy compensation effect.

The reality of the isokinetic relation can be tested graphically by plotting Exner plot. Exner criticized the validity of such a linear correlation between ΔH$^{\#}$ and ΔS$^{\#}$ 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.

$\log k_2 (T_1) = a+b \log k_2 (T_2)$

where $T_2>T_1$.

A good correlation coefficient (r = 0.97) is obtained when $\log k_{2\,(308K)}$ is plotted against $\log k_{1\,(313K)}$ indicating that the reaction under investigation follows a common mechanism.

Conclusion

The mechanism of oxidation of anilines viz. m- and p- substituted anilines by ICC is reported in detail. The reaction is first order each in [Aniline], [ICC] and $[H^+]$. The oxidation of m- and p- substituted anilines gives the corresponding azobenzenes. Since aniline is very harmful to the environment, its removal from the environment is the ultimate goal of basic research. The negative 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 $\Delta S^{\#}$ supports the formation of the activated complex in the slow step. The product of oxidation is azobenzene. A good Hammett plot is obtained in substituted Anilines. The electron withdrawing substituents retards the reaction rate while the electron releasing substituents enhances the rate of the reaction.

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References

1. Muzart J., Chromium- catalyzed oxidation in organic synthesis, *Chem Rev.*, **92(1)**, 113 **(1992)**

2. Kothari A., Kothari S. and Banerji K.K., Kinetics and mechanism of oxidation of alcohols by butyltriphenylphusphonium dichromate, *Indian Journal of Chemistry*, **44A**, 2039 **(2005)**

3. Chimatadar S.A., Salunke M.S. and Nandibewoor S.T., Kinetic and mechanism of oxidation of arsein (III)by quinolium dichromate (QDC) in aqueous perchloric acid, *Indian Journal of Chemistry*, **45A**, 388 **(2006)**

4. Pandurangan A., Murugesan V. and Palanichamy M., Quninolium bromochromate: A new selective and efficiend reagent for the oxidation of alcohols in anhydrous active acid, *J. Indian Chem. Soc.*, **72**, 479 **(1995)**

5. Pandurangan A., Abraham Rajkumar G., Arabindoo Banumathi and Murugesan V., Imidazolium fluorochromate (IFC): A new mild, stable and selective chromium (VI) oxidant, *Indian Journal of Chemistry*, **38B**, 99 **(1999)**

6. Patwari S.B., Khansole S.V. and Vibhute Y.B., Kinetics and Mechanism of oxidation of Aniline And Substituted Anilines By Isoquinolinium Bromochromate in Aqueous Acetic Acid, *Journal of the Iranian Chemical Society*, **9**, 399 **(2009)**

7. Sheik Mansoor S. and Syed Shafi S., Oxidation of Anilines And Some Para- Substituted Anilines by Benzimidazolium Fluorochromate in Aqueous Acetic Acid Medium-A Kinetic And Mechanistic Study, *Arabian Journal of Chemistry*, **7**, 17 **(2014)**

8. Wyne-Jones W.F.K. and Eyring H., The Absolute Rate of Reaction in Condensed Phases, *J. Chem. Phys.*, **3(8)**, 492 **(1935)**

9. Frost A.A. and Pearson R.G., Reaction Kinetic and Mechanism, Wiley Eastern, New York **(1961)**.

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