

REACTIVITY IN THE QUINOLINIUM CHLOROCHROMATE ON THE OXIDATION OF ANILINE IN AQUEOUS ACETIC ACID MEDIUM

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Article Received on
30 April 2015,

Revised on 25 May 2015,
Accepted on 16 June 2015

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ABSTRACT

Oxidation of aniline by quinolinium Chlorochromate (QCC) in aqueous acetic acid leads to the formation of azobenzene. The reaction is first order with respect to both aniline and QCC and is catalyzed by hydrogen ion. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The rate of oxidation decreases with increasing dielectric constant of solvent, indicating the presence of an ion-dipole interaction. The reaction does not induced the polymerization of acrylonitrile. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. The reaction rates have been determined at different temperatures and the activation parameters have been calculated. From the above observation kinetic results a probable mechanism have been proposed.

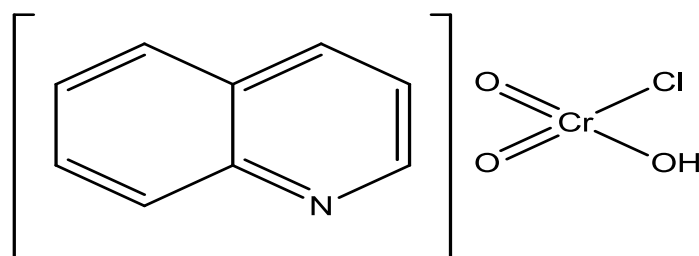
KEYWORDS: Kinetics, Oxidation, Quinolinium Chlorochromate, Aniline, Activation Parameters, Acid catalyst.

INTRODUCTION

A good number of Cr(VI) complexes are being used in the oxidation of organic compounds. Pyridinium halochromate,^[1-4] pyridinium dichromate,^[5-6] bipyridyl chlorochromate,^[7-9] Quinolinium dichromate,^[10] Quinaldinium fluorochromate,^[11] are some of them. These are used for the regiospecific and chemospecific oxidative degradation of functional groups in highly sensitive systems. It has been observed that, with pyridinium halochromates,^[12,13] the

mode of oxidation depends on the anion attached to Cr(VI) species. The oxidation of aryl methyl sulphides by pyridinium dichromate is found to proceed by a nonradical polar mechanism. while, when potassium dichromate,^[14] is used, the reaction follows a radical mechanism, involving cation radical as the reaction intermediate. The modes of oxidation of lower oxyacids of phosphorous by pyridinium fluorochromate,^[15] pyridinium chlorochromate,^[16] and pyridinium bromochromate,^[17] have been studied by Banerji and co-workers. The oxidation by fluoro compound involves formation of a complex between the oxidant and the substrate which decomposes in the slow step to give products. Oxidation of chloro- and bromo- compounds do 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 oxidant. Quinolinium chlorochromate is a mild and selective oxidant. Quinolinium chlorochromate,^[18] is a stable reagent originally introduced as an oxidizing agent for alcohol is used in synthetic organic chemistry,^[19-24] The kinetic mechanistic aspects of oxidation reactions by QCC reports are available in the literature,^[25-30] The kinetics of oxidation of anilines by various oxidizing reagents have been well studied,^[31-33] Anilines are the most widespread and principal contaminates of industrial waste waters. Better understanding of the mechanism of oxidation of such compounds to harmless products.

Structure of Quinolinium Chlorochromate



quinolinium chloro chromate



Molecular Weight = 265.61

Melting Point = 127-130⁰C

EXPERIMENTAL

Materials And Methods

All the chemicals used were analytical grade. Aniline was used after vacuum distillation. Double distilled water was used for all purposes.

Preparation of Quinolinium Chlorochromate [QCC]

Chromium trioxide (7 g) was dissolved in 8 ml of water in a e beaker and 11 ml of 40% hydrochloric acid were added with stirring at room temperature. A clear orange red solution was formed and 9 ml of quinoline 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 quinolinium chlorochromate was isolated by filtration. It was recrystallized from water and dried in vacuo for about 2 h. The compound melted at (128 °C)[lit m.p 127-130 °C],^[34] and further analysed through spectral studies.

Acetic acid

The procedure followed for the purification of acetic acid was essentially similar to that of Weissberger³⁵ Glacial acetic acid (AR) 2 litre was partially frozen and about one litre 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.

Kinetic Measurements

The kinetic experiments were conducted in aqueous acetic acid (50% V/V) at 313K. The reaction mixture consisted of Aniline = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ · QCC = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and $\text{H}_2\text{SO}_4 = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$. The temperature was maintained constant within $\pm 0.2^\circ$.

The reaction was carried out under pseudo- first order conditions by maintaining the substrate concentration in excess of quinolinium chlorochromate. 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 [QCC] by digital photoelectric colorimeter at 470nm. 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 .

Stoichiometry

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

Product analysis

The reaction mixture containing Aniline (0.03 M) in acetic acid and QCC (0.001M) in acetic acid was added and the medium was maintained using sulphuric acid. 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 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. Azobenzene was identified as product.

The product azobenzene was identified by its physical constant (m.p. 68 °C) and was detected by comparing with those of the authentic samples.

The product azobenzene was confirmed through IR-spectral data and further confirmed by mass spectrum

RESULTS AND DISCUSSION

Effect of varying the Oxidant

The reaction was investigated with varying concentrations of QCC at constant aniline and sulphuric acid concentrations. 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 in (Table 1)

Effect of varying the Substrate aniline

The reaction was carried out by varying the concentration of aniline keeping the other variables constant. The rate of reaction increased with increase in the concentration of aniline 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. (Table 2)

Effect of varying the ionic strength

The reaction was studied with varying concentration of sodium sulphate 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,^[36] (Table -3)

Effect of varying the hydrogen ion concentration

The reaction was followed with different concentration of hydrogen ion keeping the concentration of quinolinium chlorochromate 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) with a slope of 1.34 ($r = 0.999$). 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,^[37] (Table 4).

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 (Fig 4) suggests the involvement of an ion -dipole interaction in the rate determining step.^[38-40] (Table 5).

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.

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 process may be involved in the reaction⁴¹⁻⁴³ (Table 6)

Effect of varying the temperature

The reaction has been studied at four different temperatures keeping all other factors constant (Table 7). The thermodynamic parameters have been calculated from the least square procedure of a linear plot of $\ln(k_2/T)$ versus $1/T$ (Fig 5) using Eyring's equation.^[44,45]

$$\Delta H^\ddagger = 18.57 \text{ kJmol}^{-1}$$

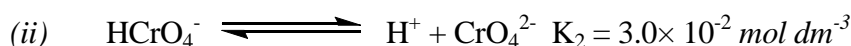
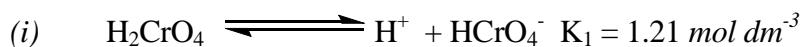
$$\Delta S^\ddagger = -172.72 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta G^\ddagger = 72.62 \text{ kJmol}^{-1}$$

$$E_a = 21.17 \text{ kJmol}^{-1}$$

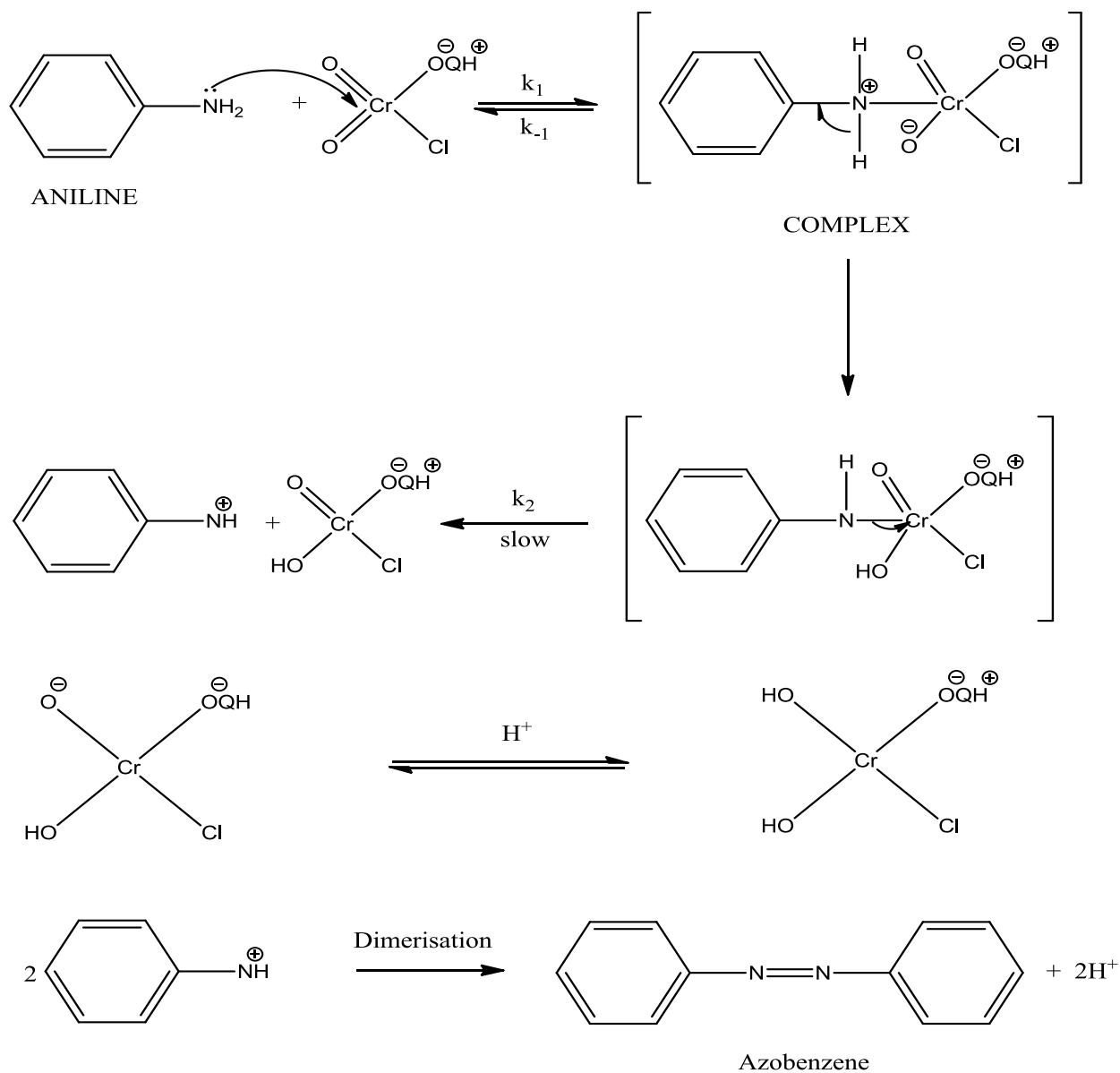
Mechanism and Rate law

From the above observation it is clear that the reaction is showing first order with respect to QCC and aniline. 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,^[46]



Here the dimerisation 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 mol dm^{-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).

Mechanism and Rate law



Scheme:1 Probable mechanism of oxidation of Aniline by Quinolinium chlorochromate

Table-1- Effect of varying the Oxidant

$$[\text{Aniline}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{AcOH-H}_2\text{O} = 50:50(\%)$$

$$[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{Temperature} = 313\text{K}$$

$[\text{QCC}] \times 10^{-3} \text{ mol dm}^{-3}$	$k_1 \times 10^4 \text{ s}^{-1}$
0.50	3.82
1.00	3.85
1.50	3.83

2.0	3.86
2.50	3.84
3.00	3.81

Table-2- Effect of varying the Substrate aniline

[QCC] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ AcOH-H₂O = 50:50(%)
 [H⁺] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313K

[Aniline] $\times 10^2$ <i>mol dm⁻³</i>	$k_1 \times 10^4$ <i>s⁻¹</i>
1.50	1.72
3.00	3.85
4.50	5.75
6.00	7.58
7.50	10.95
9.0	15.83

Table-3- Effect of varying the ionic strength

[QCC] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ [H⁺] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$
 AcOH-H₂O = 50:50(%) [Aniline] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$
 Temperature = 313K

[Na ₂ SO ₄] $\times 10^4 \text{ mol dm}^{-3}$	$k_1 \times 10^4 \text{ s}^{-1}$
0.00	3.85
0.50	3.86
1.00	3.85
1.50	3.89
2.00	3.86
2.50	3.87

Table-4- Effect of varying the hydrogen ion concentration

[QCC] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ AcOH-H₂O = 50:40(%)
 [Aniline] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313K

[H ⁺] $\times 10^2 \text{ mol dm}^{-3}$	$k_1 \times 10^4 \text{ s}^{-1}$
0.5	1.47
1.00	3.85
1.50	5.88
2.00	9.12
2.50	15.84
3.00	19.95

Table -5 - Effect of varying the solvent composition

[QCC] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ [H⁺] = $1.0 \times 10^{-2} \text{ mol dm}^{-3}$
 [Aniline] = $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temperature = 313K

AcOH-H ₂ O %(v/v)	E	k ₁ 10 ⁴ s ⁻¹
30-70	57.85	2.81
40-60	50.46	3.09
50-50	43.08	3.85
60-40	35.69	5.62
70-30	28.31	8.12
80-20	20.92	19.49

Table-6- Effect of varying the manganous sulphate

$$[\text{QCC}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3} \quad [\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{AcOH-H}_2\text{O} = 50:50(\%) \quad [\text{Aniline}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{Temperature} = 313\text{K}$$

[MnSO ₄] × 10 ⁴ mol dm ⁻³	k ₁ × 10 ⁴ s ⁻¹
0.00	3.85
0.50	3.83
1.00	3.80
1.50	3.78
2.00	3.76
2.50	3.75

Table-7- Effect of varying the temperature

$$[\text{QCC}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3} \quad [\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{Aniline}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3} \quad \text{AcOH-H}_2\text{O} = 50:50(\%)$$

Temperature K	k ₁ 10 ⁴ s ⁻¹
303	2.76
308	3.42
313	3.85
318	4.32
323	4.83
328	5.43

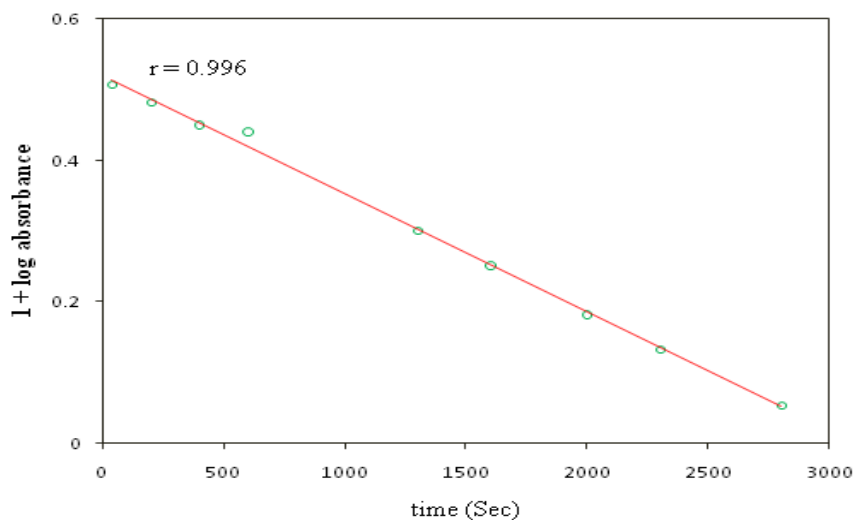


Fig.1 Plot of log absorbance *versus* time

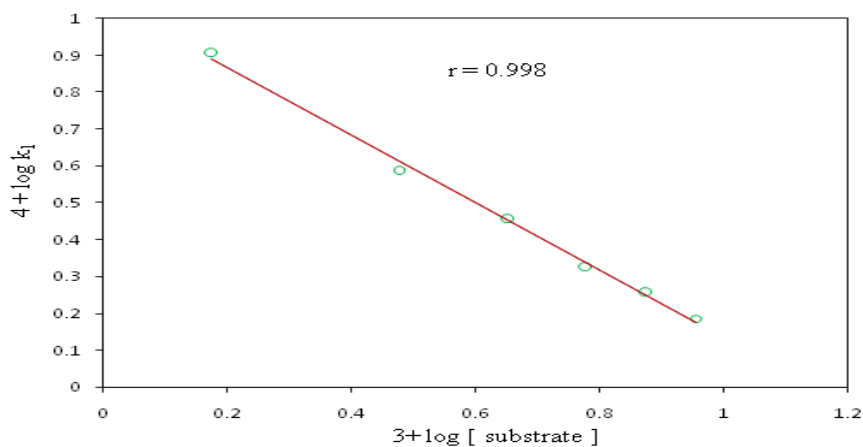


Fig.2. Plot of $\log k_1$ *versus* \log [substrate]

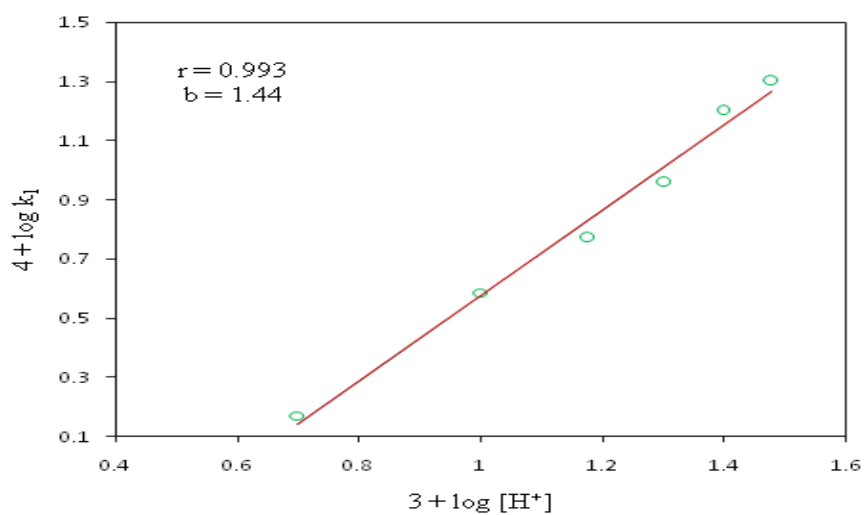


Fig.3 Plot of $\log k_1$ *versus* \log [H⁺]

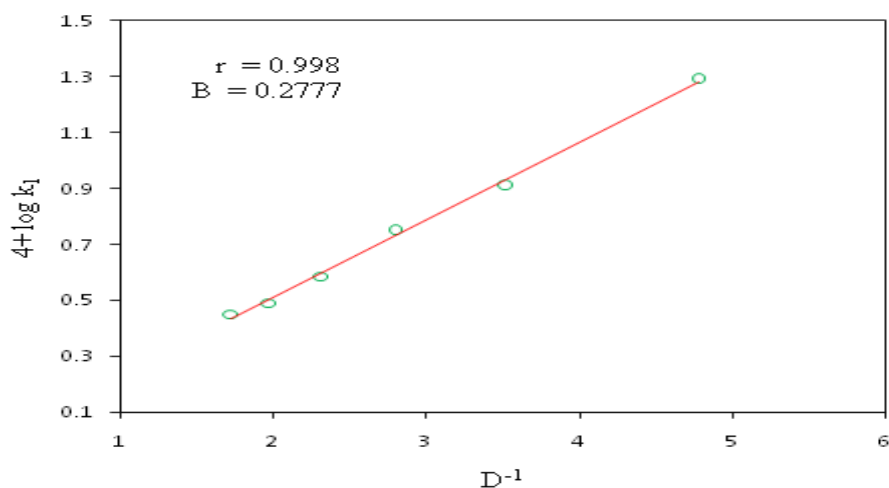


Fig.4 Plot of $\log k_1$ versus D^{-1}

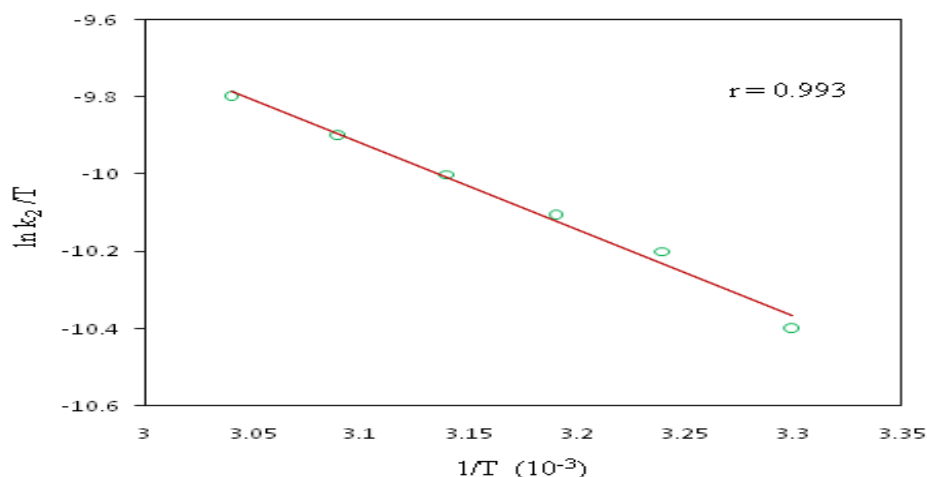


Fig.5 Plot of $\ln k_2/T$ versus $1/T$

CONCLUSION

In this paper we have reported the detail mechanism of the aniline by Quinolinium chlorochromate. The reaction is first order with respect to oxidant and aniline. The reaction is acid catalysed by hydrogen ion concentration. The oxidation of aniline yield by azobenzene. Since aniline is very harmful to the environment, its removal from the environment is the ultimate goal of basic research. For this purpose deep understanding of the mechanism of the process of aniline is needed. The negative value of ΔS^\ddagger provided support for the formation of the activated complex in the slow step.

ACKNOWLEDGEMENT

The authors thank the Principal and Management, Jamal Mohamed College (Autonomous), Tiruchirappalli, Tamilnadu, India for providing necessary facilities and encouragement.

BIBLIOGRAPHY

1. Bhattacharjee. M.N, Chaudhuri. M.K, Dasgupta. H.S and Roy,N;Khathing. D.T, *Synthesis.*, 1952; 588.
2. Corey. E.J and Suggs. J.W, *Tetrahedron Lett.*, 1975; 2647.
3. Narayanan. N and Balasubramanian. T.R, *Ind.J. Chem.*, 1986; 25: 229.
4. Aparna. P, Kothari. S and Banerji .K.K, *Proc.Ind.Acad. Sci .*, 1995; 107: 213.
5. Corey.E.J.and Suggs. J.W. *Tetrahedron Lett.*, 1979; 399.
6. Mangalam. G and Sundaram. S.M, *J.Ind.Chem Soc.*, 1991; 77.
7. Guziec. F.S and Luzzio. F.A, *Synthesis.*, 1980; 691.
8. Mathur. D, Sharma. P.K and Banerjee. K.K, *Ind.J.Chem.*, 1963; 32: 961.
9. Rathore. S, Sharma,P.K and Banerjee,K.K, *Ind .J.Chem.*, 1995; 34: 702.
10. Balasubramanian. K and Prathibha. V, *Ind.J.Chem.*, 1986; 25: 326.
11. Nebahat and BeytiyeOzgun, *Monatshefte fur Chemie.*, 407, (2004).
12. Banerji,K.K, *J.Chem Soc.,Perkin Trans II*, 2065, (1988).
13. Rajasekaran.K, Bhaskaran.T and Sekaran.C.G, *J.Chem Soc., Perkin Trans. II*,1183, (1984).
14. Srinivasan,C, Chellamani. A and Rajagopal. S. *J.Org.Chem.*, 1985; 50: 1201.
15. Monndra,A, Mathur,A and Banerjee,K.K, *J.Chem.Soc.,Dalton Trans*, 2967, (1990).
16. Seth,M, Mathur,A and Banerji,K.K, *Bull. Chem. Soc.*, Japan, 1990; 63: 3840.
17. Anjali grover, Seema varshney and Banerji,K.K.*Ind.J.Chem.*, 1984; 33: 1622.
18. Khansole. S. V, Patwari. S. B, Vibhute. A. Y and Vibhute. Y. B, *Chin. Chem. Lett.*, 2009; 20: 256.
19. Srinivasan. R, Ramesh. C. V, Hadhulatha. W and Balasubramanian. K *Ind. J. Chem.*, 1996; 35(A): 480.
20. Cainelli. G and Cardillo. G, “*Chromium Oxidation in Organic Chemistry*”, Springer Verlag, NewYork, (1984).
21. Corey. E. J, and Suggs. J. W, *Tetrahedron Lett.*, 1975; 16: 2647.
22. Murugesan. V and Pandurangan. A, *Ind. J. Chem.*, 1992; 31: 377.
23. Lonkar. S. M, Mokle. S. S, Vibhute. A. Y, and Vibhute. Y. B., *Der Chemica Sinica.*, 2010; 1(2):119.
24. Vaijyanthi. S. P, Mathiyalagan. N, *Der Chemica Sinica.*, 2011; 2(3): 41.

25. Pandeewaran. M, Johns. B, Bhuvaneswari. D. S and Elango. K. P, *J. Serb. Chem Soc.*, 2005; 70: 145.
26. Saravanakanna.S, Elango. K. P, *Int, H, Chem. Kinet.*, 2002; 34: 585.
27. Ozgun. B and Degirmenbasi, *Monatsh. Chem.*, 2004; 135: 483.
28. Singh. J. V, Mishra, K and Pandey. A, *Oxid. Commun.*, 2003; 26: 235.
29. Singh.J. V, Mishra. K and Pandey. A, *Bull. Polish Acad. Sci.*, 2003; 51: 25.
30. Chaubey. G. S, Kharsyntiew. B and Mahanti. M. K, *J. Phys. Org. Chem. Commun.*, 2003; 17: 83.
31. Exner.O, Streitwiser. R. W and Taft. R. W, "*Progress in physical organic chemistry*", John wiley, New York, 41(1973).
32. Eyring.H, *J.Chem. Phys.*, 1935; 33; 107.
33. Rajalakshmi.K, Ramachandramoorthy.T and Srinivasan,S, *Rasayan J. Chem.*, 2012; 5(1): 28.
34. Kumar rai,K, Kannaujia,R, Karuna Rai and Surjeet Singh, *Orien. J. Chem.*, 2013; 29: 1071.
35. Weissberger, A and Prabhakar. E. S, "*Organic solvents Physical Properties and Methods of Purifications*", 2nd ed., Interscience Publishers Ltd., London (1963).
36. Chockalingam.P, Ramakrishnan,P.S, Arulraj. S. J and Nambi,K, *J. Indian Chem. Soc.*, 1992; 69: 247.
37. Patwari.S. B, Khansole. S. V and Vibhute. Y. B, *J. Iran. Chem. Soc.*, 2009; 6: 399.
38. Rao.C. N, "*A Hand Book of Chemistry and Physics*" Affiliated East-West Press, New Delhi (1967).
39. Amis. E. S, "*Solvent Effects on Reaction Rates and Mechanism*", Academic Press, New York(1967).
40. Quinlan and Amis. E. S, *J. Am. Chem. Soc.*, 1955; 77: 4187.
41. Graham. G. T. E and Westheimer. F. H, *J. Am. Chem. Soc.*, 1958; 80: 3030.
42. Gurusurthy. R and Karunakaran. K, *J. Indian Chem. Soc.*, 1995; 72: 349.
43. Karthikeyan.G, Elango. K. P, Periyasamy. V and Vijayakumar. K, *Asian J. Chem.*, 1995; 7(4): 705.
44. Frost. A and Pearson. R. G "*Kinetics and Mechanism*" Eastern, New Delhi (1970).
45. Eyring.H, *J. Chem. Phys.*, 1935; 33: 107.
46. Wiberg. K. B and Mill.T, *J. Am. Chem. Soc.*, 1958; 80: 3022.