

REACTIVITY IN THE MORPHOLINIUM CHLOROCHROMATE ON THE OXIDATION OF ANILINES

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ABSTRACT

The oxidation kinetics of aniline and some para- and meta- substituted anilines by morpholinium chlorochromate (MCC) has been studied in aqueous acetic acid medium. The reaction is first order with respect to oxidant and fractional order with respect to substrate and $[H^+]$. In the case of substituted anilines, the order with respect to substrate varies depending upon the nature of the substituent present in the ring. In general, the electron withdrawing substituents retard the reaction rate while the electron releasing substituents enhance the rate of the reaction. The products of oxidation are the corresponding azobenzenes. Based on the kinetic results and product analysis, a suitable mechanism has been proposed for the reaction of MCC with anilines.

Keywords: Anilines, Kinetics, Morpholinium chlorochromate, Oxidation, Reaction mechanism

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INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry¹. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest. Morpholinium chlorochromate (MCC) is also one such reagent. The kinetics and mechanistic aspects of oxidation reactions by MCC, reports are available in the literature²⁻⁴. The kinetics of oxidation of anilines by various oxidizing reagents have been well studied^{5, 6}. Anilines are the most widespread and principal contaminants of industrial waste waters. Better understanding of the mechanism of oxidation of such compounds to harmless products.

EXPERIMENTAL

Materials and Methods

All the chemicals used were of analytical grade. The anilines used were with substituents, viz., *p*-OCH₃, *p*-CH₃, *m*-CH₃, *p*-Br, *p*-Cl, *m*-Cl, *p*-NO₂ and *m*-NO₂. The solid anilines were used after recrystallisation and the liquid anilines were used after vacuum distillation. Acetic acid was purified by the standard method and the fraction distilling at 118°C was collected⁷. Double distilled water was used for all purposes. MCC was prepared by the known method and its purity was checked by an iodometric method⁸.

Kinetic Measurements

The reactions were carried out under pseudo-first order conditions by keeping an excess of substrate over MCC. The temperature was kept constant to $\pm 0.1^\circ K$. The progress of the reaction was followed by estimating the unreacted oxidant iodometrically⁹ at 303K, 313K, 323K and 333K. The rate constants, k_1 , were evaluated from the linear plots of $\log [MCC]$ against time. [$r = 0.996$](Fig.1).

Stoichiometry and Product Analysis

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of MCC largely in excess over aniline. The estimation of unreacted MCC showed that 1 mole of MCC reacts with 3 moles of aniline. The reaction mixture from the actual kinetic run after sufficient length of time was extracted with chloroform and dried over anhydrous sodium sulphate. The

chloroform layer was then evaporated in a hot water bath to get the solid product. The oxidative product was azobenzene. m.p. 66°C (lit. 68°C) and UV abs (Et OH) at λ_{max} 320nm.

RESULTS AND DISCUSSION

The kinetics of oxidation of anilines by morpholinium chlorochromate (MCC) in the presence of perchloric acid was studied at 313K. The results are summarized below.

Table-1: Effect of [substrate], [oxidant] and $[\text{H}^+]$ on the reaction rate at 313K
60% acetic acid – water(v/v)

[substrate] $\times 10^2$ mol dm^{-3}	[oxidant] $\times 10^3$ mol dm^{-3}	$[\text{H}^+] \times 10^2$ mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
1.50	1.50	1.50	3.45
2.25	1.50	1.50	3.70
3.00	1.50	1.50	4.04
3.75	1.50	1.50	4.28
4.50	1.50	1.50	4.54
3.00	1.50	0.75	3.77
3.00	1.50	1.50	4.04
3.00	1.50	2.25	4.28
3.00	1.50	3.00	4.51
3.00	1.50	3.75	4.73
3.00	0.50	1.50	4.02
3.00	1.00	1.50	4.03
3.00	1.50	1.50	4.04
3.00	2.00	1.50	4.06
3.00	2.50	1.50	5.08

Table-2: Effect of solvent, $[\text{Mn}^{2+}]$ and $[\text{Al}^{3+}]$ on NaClO_4 on the reaction rate at 313K
[substrate] = $3.00 \times 10^{-2} \text{ mol dm}^{-3}$, [oxidant] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.50 \times 10^{-2} \text{ mol dm}^{-3}$

$[\text{Mn}^{2+}] \times 10^3$ mol dm^{-3}	$[\text{Al}^{3+}] \times 10^3$ mol dm^{-3}	$[\text{NaClO}_4]$ mol dm^{-3}	% acetic acid(v/v)	$k_1 \times 10^4$ s^{-1}
-	-	0.00	-	4.04
-	-	0.50	-	4.07
-	-	1.00	-	4.18
-	-	1.50	-	4.09
-	-	2.00	-	4.07
0.00	-	-	-	4.04
0.50	-	-	-	4.07
1.00	-	-	-	4.28
1.50	-	-	-	4.79
2.00	-	-	-	5.07
-	0.00	-	-	4.04
-	0.50	-	-	3.41
-	1.00	-	-	3.10
-	1.50	-	-	3.41
-	2.00	-	-	3.60
-	-	-	40	2.29
-	-	-	50	3.06
-	-	-	60	4.04
-	-	-	70	4.47
-	-	-	80	4.91

Table-3: Effect of substituent on temperature
 [substrate]= $3.00 \times 10^{-2} \text{ mol dm}^{-3}$, [oxidant]= $1.50 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.50 \times 10^{-2} \text{ mol dm}^{-3}$
 60% acetic acid – 40% water (v/v)

Substituents	$k_1 \times 10^4 \text{ s}^{-1}$				$\Delta H^\ddagger$ kJmol^{-1}	$-\Delta S^\ddagger$ $\text{JK}^{-1} \text{ mol}^{-1}$	$\Delta G^\ddagger$ kJmol^{-1} at 313K	r	Order
	303K	313K	323K	333K					
Parent –H	2.44	4.04	5.82	8.12	30.42	213.61	97.28	0.994	0.40
<i>p</i> -OCH ₃	3.42	5.06	7.16	9.68	26.23	224.84	96.60	0.998	0.25
<i>p</i> -CH ₃	2.84	4.63	6.74	8.95	29.15	216.44	96.90	0.992	0.24
<i>m</i> -CH ₃	2.53	4.12	6.45	8.56	31.53	209.62	97.14	0.992	0.40
<i>p</i> -Br	2.15	3.72	5.62	8.02	33.67	203.88	97.48	0.994	0.40
<i>p</i> -Cl	2.01	3.65	5.43	7.84	34.65	201.05	97.58	0.992	0.35
<i>p</i> -Cl	1.73	3.40	5.06	7.45	37.12	193.98	97.84	0.988	0.34
<i>m</i> -NO ₂	1.29	2.53	4.33	6.36	41.66	181.59	98.50	0.992	0.48
<i>p</i> -NO ₂	1.15	2.47	4.30	6.23	43.05	177.43	98.59	0.989	0.49

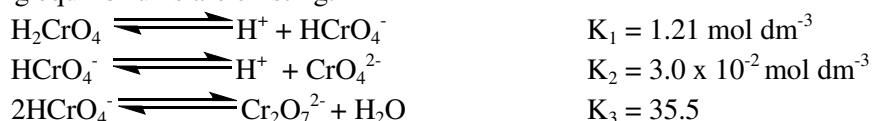
Table-4: Reaction constant for the oxidation of substituted anilines

Temperature, K	ρ	r
303	-0.42	0.993
313	-0.29	0.991
323	-0.21	0.990
333	-0.16	0.994

Mechanism

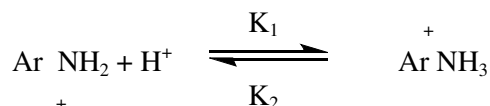
From the above observations it is clear that the reaction is showing first order dependence with respect to oxidant and fractional order with respect to substrate and $[\text{H}^+]$ ion.

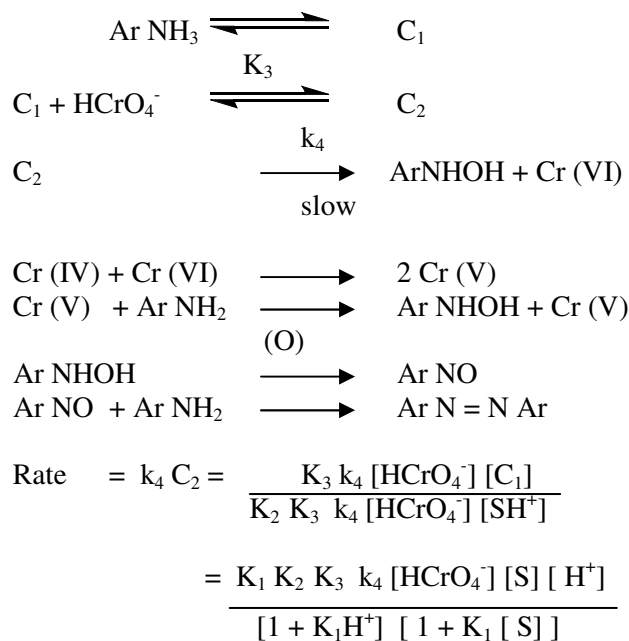
The oxidation by Cr(VI) will vary with nature of the Cr(VI) species used and the solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ions the following equilibria are existing.



Here the dimerization equilibrium is of considerable importance. In water the dichromate ion will be predominating species only at the concentration of Cr(VI) is 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} monomeric form predominates and the active oxidizing species is HCrO_4^- .

The rate increases with decrease in the dielectric constant of the medium and increases in ionic strength has negligible effect on the rate. The rate of the reaction increases linearly with an increase in the hydrogen ion concentration, showing that the reaction proceeds completely an acid catalysed pathway¹⁰. The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway. The addition of Mn^{2+} ion has noticeable catalytic effect on the reaction rate. The addition of Al^{3+} ion decreases the oxidation rate due to the formation of complex between Al^{3+} ion and substrate. Based on the above observations a probable mechanism has been proposed and sustained with rate law (Scheme -1).





Scheme -1

Effect of Substituents

An insight into the nature of the transition state and hence the mechanism can also be gained from an analysis of the substituent effect on the course of the oxidation.

The effect of substituents on the rate of oxidation has been studied by employing a number of *meta*- and *para*- substituted anilines at three different temperatures. The respective rate constant and thermodynamic parameters were calculated using Eyring's plot¹¹ and the values are given in table -3.

More generally, if the Hammett equation is valid at a given temperature, the condition for its validity at any other temperature is a linear relationship between enthalpies called isokinetic relationship. $\Delta H^\ddagger = \Delta H_o^\ddagger + \beta \Delta S^\ddagger$

$\Delta H_o^\ddagger$ is the enthalpy of activation, when $\Delta S^\ddagger = 0$ and usually has no physical significance and β is the isokinetic temperature. A plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ gave a straight line with good correlation coefficient ($r = 0.999$) and $\beta = 367 \text{ K}$ (Fig.2).

The Exner plot of $5 + \log k_{1(333\text{K})}$ versus $5 + \log k_{1(303\text{K})}$ gave a straight line with ($r = 0.992$) (Fig.3). Such good correlation indicates that all the investigated substituted compounds follow a common mechanism^{12,13}.

If this linearity between enthalpies and entropies is true, it should predict a meaningful correlation between $\log k_1$ and σ . When the Hammett equation was applied to this reaction system with the usual substituent constants, σ , excellent linear correlation was obtained with negative ρ values (Fig.4), which indicates that electron-releasing substituents accelerate and electron-withdrawing substituents retard the rate of the reaction. The negative sign of ρ values indicates that an electron-deficient transition state is involved in the mechanism of oxidation (Table-4). From this evident shows that the reaction series is following a common mechanism with the different rate-determining step.

CONCLUSION

In this paper we have reported the detailed mechanism of oxidation of aniline and some *para* and *meta* substituted anilines by MCC. The reaction is first order with [oxidant] and fractional order with [anilines] and $[\text{H}^+]$. The oxidation of anilines yields the corresponding azobenzenes. 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

$\Delta S^\ddagger$ provided support for the formation of the activated complex in the slow step. The constancy of $\Delta G^\ddagger$ values indicated that all the substituted anilines are operative in the same mechanism.

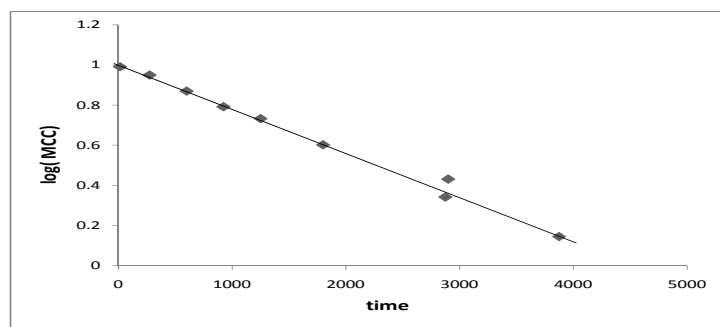


Fig.-1: Plot of log[titre value] versus time
Isokinetic Plot

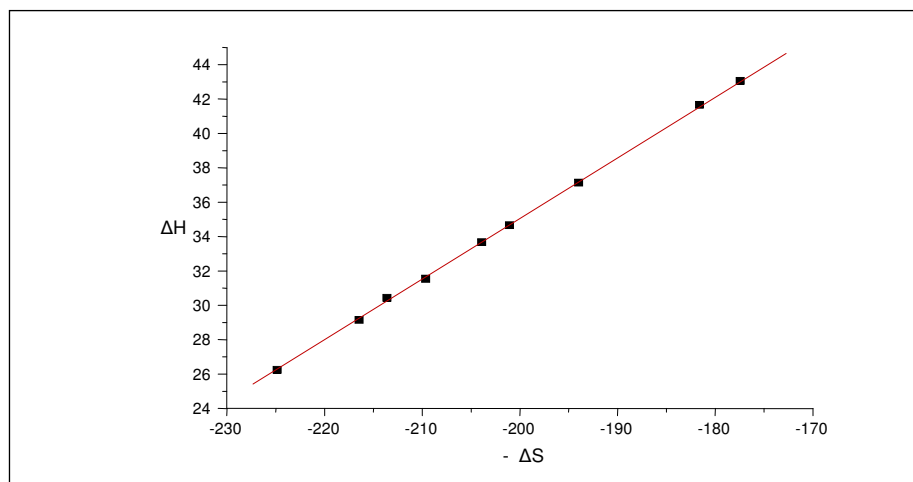


Fig.-2: Plot of ΔH versus $-\Delta S$
Exner Plot

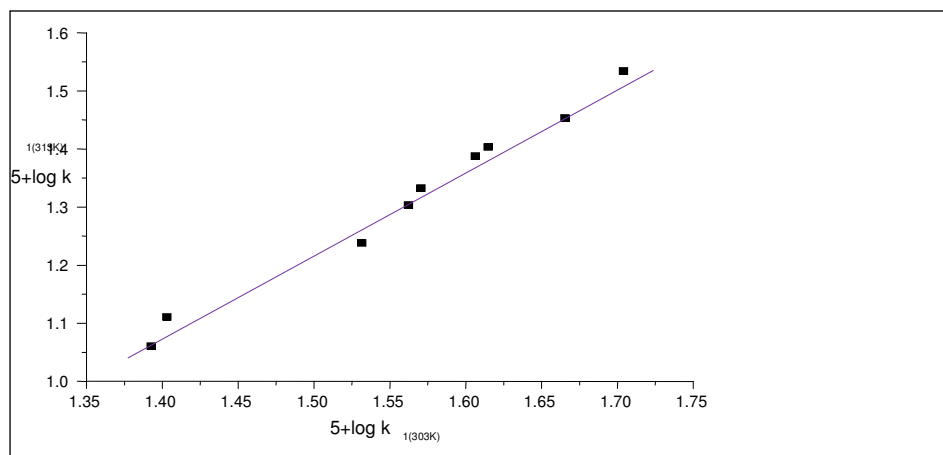
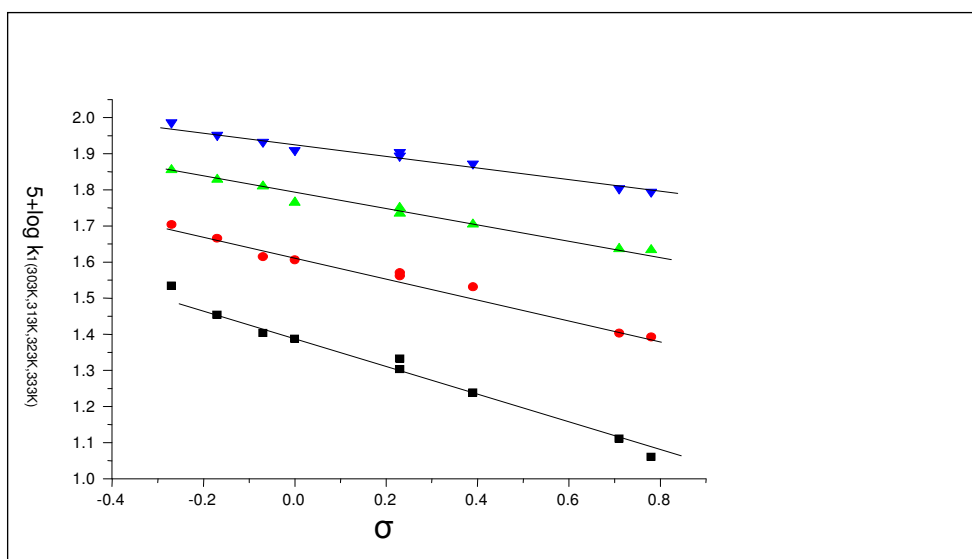


Fig.-3: Plot of $5+\log k_{I(313K)}$ versus $5+\log k_{I(303K)}$

Hammett Plot

Fig.-4: Plot of $5 + \log k_{(303K, 313K, 323K, 333K)}$ versus σ

ACKNOWLEDGEMENTS

The authors thank the Principal and Management of Bishop Heber College(autonomous), Tiruchirappalli, for providing laboratory facilities.

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[RJC-883/2012]

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