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Kinetics of Oxidation of *p*-Chloro Aniline by Chromic Acid

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Kinetics of oxidation of *p*-chloro aniline by chromic acid in 10% acetic acid-water medium have been reported for the first time. The rate of reaction is proportional to the first power of concentration of oxidant and substrate, *i.e.*, amine. The order of reaction with H^+ is one in each case. The reaction velocity increases by increasing percentage composition of acetic acid. The addition of neutral salt on the reaction mixture shows no effect on the reaction rate. The study reveals that the rate of reaction is increased by addition of Ag^+ and Cu^{2+} whereas retarded by Mn^{2+}. Various activation parameters have been computed. Based on above finding a probable reaction mechanism has been proposed. The final product is *p*,*p*′-dichloro azobenzene.

Key Words: Kinetics, Oxidation, *p*-Chloroaniline, Chromic acid.

INTRODUCTION

Recently, we have communicated[1, 2] the results on the kinetics of oxidation of aniline,[1] N-methyl aniline, N,N-dimethyl aniline, *o*-, *m*, *p*-toluidines by chromic acid under various conditions. Several workers have employed chromic acid as an oxidising agent for a variety of compounds such as carboxylic acid[3, 4], alcohols[5, 6], aldehydes[7], ketones[8], hydroxylamine[9, 10], etc.

Although the kinetics of *p*-halo substituted aniline have also been acclaimed in the literature with oxidants such as CAT[11, 12], NBS[13, 14], NCS[15] and Fe(III)-2 spectrophotometrically[16], but the oxidation kinetics of *p*-chloroaniline has not been probed with chromic acid. The present work of oxidation of *p*-chloroaniline with chromic acid has been taken for the first time.

EXPERIMENTAL

All the chemicals used during the investigation were of BDH, E. Merck, S. Merck or AR-grade of extra pure quality.

The oxidant was prepared by dissolving chromium(VI) oxide in conductivity water and standardized iodometrically. *p*-chloro aniline was distilled under reduced pressure and its solution was prepared in distilled water. The other solutions were also prepared in distilled water and standardized accordingly.

The kinetic measurements were initiated by mixing definite volumes of two solutions (both being pre-equilibrated at the reaction temperature) in a thermostat (±0.1°C) containing chromic acid and the organic substrate. The course of reaction was monitored by withdrawing a known aliquot of the reaction mixture at a definite interval of time and the unconsumed chromic acid was estimated iodometrically.

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Integration and Ostwald isolation method were followed in the evaluation of rate constants.

RESULTS AND DISCUSSION

The oxidative feature of the reaction of *p*-chloroaniline with chromic acid has been explored in a binary solvent mixture of acetic acid and water. The dependence of rate on the concentrations of oxidant is incorporated in Table-1. The order of reaction with respect to the concentration of chromic acid and substrate was observed to be one in each case.

The plot of k_1 versus [*p*-chloro aniline] is linear passing through origin showing constancy in first order rate constant.

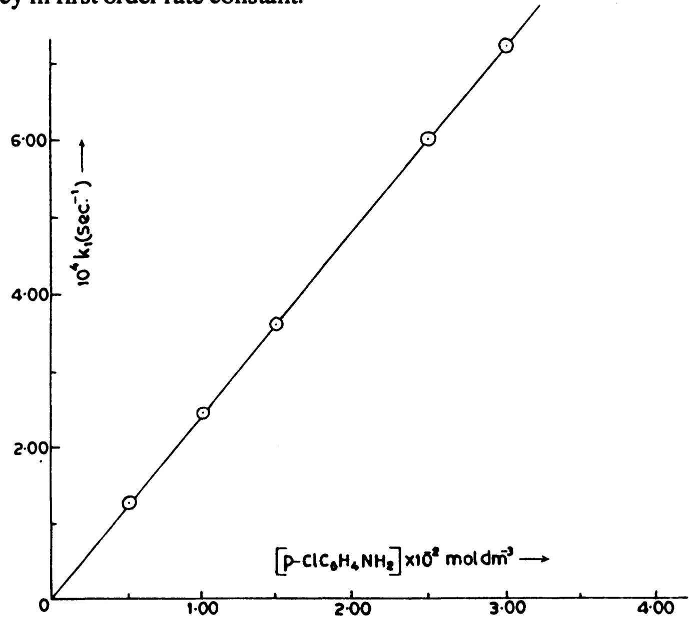


Fig. 1. Dependence of rate on *p*-$CK_6H_4NH_2$ Plot of k_1 Vs [*p*-$ClC_6H_4NH_2$].

TABLE-1

[*p*-chloro aniline] = 1.00×10^{-2} M, Temp. = 303 K, HOAc-H_2O = 10% (v/v)

[Chromic acid] × 10^3 M	1.250	2.000	2.500	4.000	5.000
$k_1 \times 10^4$ s^{-1}	2.249	2.456	2.540	2.895	3.214

[Chromic acid] = 2.00×10^{-3}, Temp. = 303 K, HOAc-H_2O = 10% (v/v)

[*p*-chloro aniline] × 10^2 M	0.500	1.000	1.500	2.500	3.000
$k_1 \times 10^4$ s^{-1}	1.254	2.456	3.608	6.018	7.220

The rate of reaction is influenced by the addition of varying concentration of sulphuric acid. The rate constant increases at higher concentration of H^+.

Variations in the dielectric constant of the medium suggest that pseudo first order rate constant increases with increase in composition of acetic acid. The plot of log k_1 versus $10^3/D$ is linear with positive flow (Table-2). The addition of neutral salt to the reaction mixture shows negligible primary salt effect, whereas the reaction velocities increase by adding Cu^{2+} and Ag^+, however, retarded by Mn^{2+}.

TABLE-2

EFFECT OF SULPHURIC ACID AND CATALYSTS

[*p*-chloro aniline] = 1.00×10^{-2} M, HOAc-H_2O = 10% (v/v), [Chromic acid] = 2.00×10^{-3} M, Temp. = 303 K

$[H_2SO_4] \times 10^3$ M	0.00	1.00	2.00	3.00	4.00
$k_1 \times 10^4$ s^{-1}	2.456	2.488	4.821	7.341	9.631
$[CuSO_4 \cdot 5H_2O] \times 10^3$ M	0.00	0.50	1.00		
$k_1 \times 10^4$ s^{-1}	2.456	3.293	4.146		
$[MnSO_4 \cdot H_2O] \times 10^3$ M	0.00	0.50	1.00		
$k_1 \times 10^4$ s^{-1}	2.456	2.390	2.338		
$[Ag_2SO_4] \times 10^3$ M	0.00	0.50	1.00		
$k_1 \times 10^4$ s^{-1}	2.456	2.582	2.698		

EFFECT OF CONCENTRATION OF SALTS

[*p*-chloro aniline] = 1.00×10^{-2} M, Temp. = 303 K [Chromic acid] = 2.00×10^{-3} M, HOAc-H_2O = 10% (v/v)

$[NaCl] \times 10^3$ M	2.00	4.00	6.00
$k_1 \times 10^4$ s^{-1}	2.453	2.450	2.447
$[KCl] \times 10^3$ M	2.00	4.00	6.00
$k_1 \times 10^4$ s^{-1}	2.452	2.449	2.446

EFFECT OF ACETIC ACID (SOLVENT)

[*p*-chloro aniline] = 1.00×10^{-2} M, Temp. = 303 K, [Chromic acid] = 2.00×10^{-3} M

HOAc-H_2O% (v/v)	10	20	30	40
$k_1 \times 10^4$ s^{-1}	2.456	3.580	5.432	11.040

The reaction is investigated at four different temperatures and the values of various thermodynamic parameters for the said reaction are determined.

Thermodynamic parameters

Various thermodynamic parameters such as activation energy, frequency factor, entropy of activation, free energy of activation and enthalpy of activation have been calculated which are recorded in Table-3.

TABLE-3

VARIOUS THERMODYNAMIC PARAMETERS

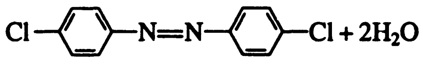
E_a (kJ mol^{-1})	A (sec^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})	ΔS* (J K^{-1} mol^{-1})
51.041 ±0.531	17.981 $\pm 0.137 \times 10^4$	47.243 ±0.578	95.570 ±0.907	–157.945 ±0.581

Stoichiometry and Product Analysis

Stoichiometry of the reaction was determined. It was found that 2 moles of *p*-chloroaniline consume 2 moles of chromic acid. The final product of oxidation of *p*-chloroaniline by chromic acid was *p,p'*-dichloroazobenzene[16, 17]. The final product was identified by Pausacker and Scroggie.[18]

The overall stoichiometric reaction may be represented by the following equation:

$$2ClC_6H_4NH_2 + 2H_2CrO_4 \longrightarrow 2H_2CrO_3 +$$

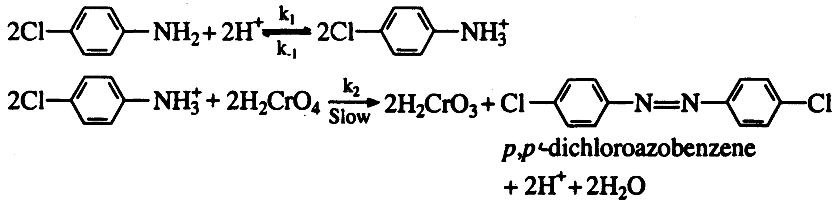


p,p'-dichloroazobenzene

Mechanism and Rate Expression

Amines are basic in nature and hence it is likely that protonation of amines may takes place prior to oxidation and then the protonated amines get oxidised.

Based on above experimental facts the following mechanism proposed as:



In the present investigation, the first step in oxidation of *p*-chloroaniline by chromic acid is the protonation of *p*-chloroaniline. This reacts with H_2CrO_4 to give products. The solvent effect and salt effect substantiate the involvement of an ion and a molecule in the rate determining step.

Taking into consideration the proposed scheme of mechanism the following general mechanism and rate expression is proposed:

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \text{ (Fast)} \tag{1}$$

where S stands for *p*-chloroaniline

$$SH^+ + H_2CrO_4 \xrightarrow[\text{Slow}]{k_2} \text{Products} \tag{2}$$

$$\text{Rate of reaction} = k_2[SH^+][H_2CrO_4] \tag{3}$$

On applying the steady state approximation,

$$-\frac{d}{dt}[SH^+] = O = k_1[S][H^+] - k_{-1}[SH^+] - k_2[SH^+][H_2CrO_4]$$

$$[SH^+] = \frac{k_1[S][H^+]}{k_{-1} + k_2[H_2CrO_4]}$$

Substituting the value of $[SH^+]$ in equation (3), we get

$$\text{Rate of reaction} = \frac{k_2k_1[S][H^+][H_2CrO_4]}{k_{-1} + k_2[H_2CrO_4]}$$

Since $k_{-1} \gg k_2$, therefore

$$\text{Rate of reaction} = \frac{k_2 k_1 [S][H^+][H_2CrO_4]}{k_{-1}}$$

$$= k_2 k [S][H^+][H_2CrO_4]$$

where $k = \frac{k_1}{k_{-1}}$

The derived rate law explains all the observed experimental facts.

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