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Kinetics of Oxidation of *p*-Iodoaniline by Chromic Acid

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The kinetics of the chromic acid oxidation of *p*-iodo aniline have been studied in 10% aqueous acetic acid medium. The order with respect to both oxidant and substrate is one in each case. The order of reaction with H^+ is one in each case. The reaction velocity increases by increasing the percentage composition of acetic acid. The primary salt effect on the rate of oxidation is negligible. The catalysts such as Ag^+, Cu^{2+} show increasing effect whereas Mn^{2+} retards the rate. Various thermodynamic parameters have been evaluated. A probable mechanism has been suggested on the basis of kinetic results.

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

INTRODUCTION

Recently, we have communicated[1–3] the results on the kinetics of oxidation of aniline, N-methyl aniline, N,N-dimethyl aniline, *o*-, *m*-, *p*-toludines by chromic acid under various conditions. Employing chromic acid as an oxidising agent a variety of compounds such as carboxylic acid[4, 5], alcohols[6, 7], aldehydes[8], ketones[9], hydroxylamine[10, 11] etc. have been studied.

Although the survey kinetics of *p*-iodo aniline has also been acclaimed in literature with oxidants such as chloramine-T[12], hexacyanoferrate(III)[13] etc., but the oxidation kinetics of *p*-iodoaniline has not been probed with chromic acid. The present work of oxidation of *p*-iodo aniline with chromic acid has been taken up for the first time.

EXPERIMENTAL

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

The oxidant was prepared by dissolving chromium(VI) oxide in conductivity water and standardized iodometrically. *p*-Iodo 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 progress of the reaction was followed by titrimetric procedure of Wiberg and Mill for the

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estimation of Cr(VI) iodometrically using starch end point in a measured aliquot of the reaction mixture at various intervals.

RESULTS AND DISCUSSION

Effect of oxidant and substrate

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

The plot of k_1 *vs.* [*p*-iodo aniline] is linear passing through origin showing constancy in first order rate constant (Table-1, Fig. 1).

TABLE-1

[*p*-Iodo aniline] = 1.00×10^{-2} M, Temp. = 308 K, $HOAc-H_2O$ = 10% (v/v)

[Chromic acid] × 10^3 M	1.25	2.00	2.50	4.00	5.00
$k_1 \times 10^4$ s^{-1}	1.623	1.754	1.879	2.246	2.634

[Chromic acid] = 2.00×10^{-3} M, Temp. = 308 K, $HOAc-H_2O$ = 10% (v/v)

[*p*-Iodo aniline] × 10^2 M	0.66	1.00	1.50	2.00	3.00
$k_1 \times 10^4$ s^{-1}	1.127	1.754	2.551	3.355	5.132

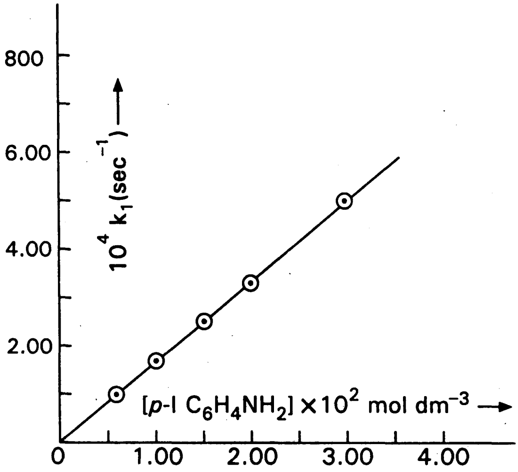


Fig. 1. Dependence of rate on the *p*-I $C_6H_4NH_2$ plot of k_1 *vs.* [*p*-I $C_6H_4NH_2$] [H_2CrO_4] = 2.00×10^{-3} mol dm^{-3}, $HOAc-H_2O$ (v/v) = 10%; Temp. = 308 K

Effect of sulphuric acid, neutral salts, catalysts, acetic acid and temperature

Chromic acid oxidation of *p*-iodo aniline was studied at different initial concentrations of sulphuric acid. The pseudo first order rate constant showed an increase with increase in the concentration of acid (Table-2) suggesting that the reactions under study are acid catalyzed.

The addition of salts like NaCl, KCl to the reaction mixture shows negligible effect on the rate of reaction indicating that the rate determining step involves an ion and a neutral molecule. Similar observations have also been made by Arumugam *et al.*[14] and Agrawal *et al.*[15]

The rate of reaction is influenced by the added catalytic cations like Cu^{2+} and Ag^{+}. However, the rate of reaction is retarded by adding Mn^{2+} (Table-2).

Variation in the dielectric constant of the medium suggests that pseudo first order rate constant increases with increase in composition of acetic acid. The plot of log k *vs.* $10^3/D$ is linear with positive flow (Table-2).

The effect of temperature was also studied and rate constants (k_1) were recorded as 1.234, 1.754, 2.480, 3.562×10^{-4} s^{-1} for *p*-iodo aniline [1.00×10^{-2} M] at 303, 308, 313, 318 K respectively. 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-2
EFFECT OF SULPHURIC ACID AND CATALYSTS

[*p*-Iodo aniline] = 1.00×10^{-2} M, HOAc-H_2O = 10% (v/v), [Chromic acid] = 2.00×10^{-3} M, Temp. = 308 K.

$[H_2SO_4] \times 10^3$ M	0.000	1.000	2.000	3.000	4.000
$k_1 \times 10^4$ s^{-1}	1.754	1.961	3.836	5.727	7.634
$[CuSO_4 \cdot 5H_2O] \times 10^3$ M	0.000	0.500		1.000	
$k_1 \times 10^4$ s^{-1}	1.754	2.469		3.292	
$[MnSO_4 \cdot H_2O] \times 10^3$ M	0.000	0.500		1.000	
$k_1 \times 10^4$ s^{-1}	1.754	1.722		1.697	
$[Ag_2SO_4] \times 10^3$ M	0.000	0.500		1.000	
$k_1 \times 10^4$ s^{-1}	1.754	1.812		1.884	

EFFECT OF CONCENTRATION OF SALTS

[*p*-Iodo aniline] = 1.00×10^{-2} M, Temp. = 308 K, [Chromic acid] = 2.00×10^{-3} M, HOAc-H_2O = 10% (v/v)

$[NaCl] \times 10^3$ M	2.000	4.000	6.000
$k_1 \times 10^4$ s^{-1}	1.751	1.748	1.746
$[KCl] \times 10^3$ M	2.000	4.000	6.000
$k_1 \times 10^4$ s^{-1}	1.750	1.747	1.745

EFFECT OF ACETIC ACID (SOLVENT)

[*p*-Iodo aniline] = 1.00×10^{-2} M, Temp. = 308 K, [Chromic acid] = 2.00×10^{-3} M

HOAc-H_2O % (v/v)	10	20	30	40
$k_1 \times 10^4$ s^{-1}	1.754	2.509	3.890	7.244

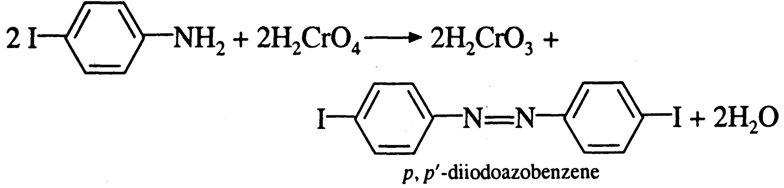
TABLE-3
VARIOUS THERMODYNAMIC PARAMETERS

E_a (kJ mol^{-1})	A (sec^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})	ΔS* (J K^{-1} mol^{-1})
56.947	7.588	54.453	98.008	−140.284
±0.519	$\pm 0.077 \times 10^5$	±0.551	±0.703	±0.083

Stoichiometry and product analysis

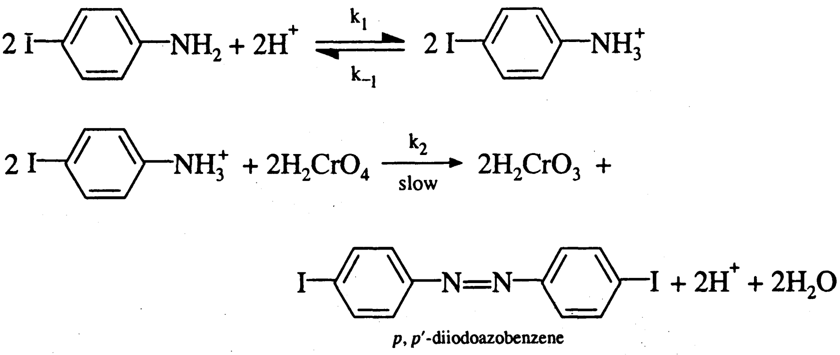
Stoichiometry of the reaction was determined. It was found that 2 moles of *p*-iodo aniline consume 2 moles of chromic acid. The end product of oxidation of *p*-iodo aniline by chromic acid was *p,p'*-diiodoazobenzene[16–18]. The end product was identified by Pausacker and Scroggie[19].

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



Mechanism and rate expression

Based on the above experimental facts the following mechanism is proposed:



In the present investigation, the first step in oxidation of *p*-iodo aniline by chromic acid is the protonation of *p*-iodo aniline. 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 are proposed:

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

where S stands for *p*-iodo aniline.

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

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

On applying the steady state approximation,

$$-\frac{d}{dt}[SH^+] = 0 = k_{-1}[SH^+] - k_2[SH^+][H_2CrO_4]$$

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

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 $k_{-1} \gg k_2$,

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

$$= k_2k[S][H^+][H_2CrO_4]$$

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

The derived rate law explains all the observed experimental facts.

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