Kinetics of Oxidation of Aniline by Chromic Acid

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The kinetics of the chromic acid oxidation of aniline have been studied in 10% aqueous acetic acid medium. The order with respect to both oxidant and substrate is one each, the overall order being two. The rate constant was found to depend upon the concentration of HCl and H_2SO_4 acid. Various thermodynamic parameters have been evaluated. The stoichiometry of the reaction has been determined. *p*-Benzoquinone has been identified as the oxidation product of the reaction. A plausible mechanism consistent with the experimental results has been suggested.

INTRODUCTION

Chromic acid is one of the most versatile of available oxidizing agents, reacting with almost all types of oxidizable groups. Kinetic studies have been extensively carried out for various organic and inorganic compounds by using chromic acid[1–7]. The oxidation of aromatic amines has been studied by different oxidizing agents[8–12]. Further the kinetics of aniline has already been carried out by using different oxidants like hexacyanoferrate(III)[13], periodate[14], H_2O_2, O_3, PbO_2, IO_3^-, BrO_3^-, alkaline $KMnO_4$, N-chlorobenzamide[15] by earlier workers. The kinetics of chromic acid oxidation of some nitrogenous organic compound (aniline) have received no attention earlier. This therefore forms the subject matter of the present paper.

EXPERIMENTAL

Cr(VI) oxide (E. Merck) was twice recrystallized from conductivity water and stock solutions were prepared in conductivity water. The standardization of the Cr(VI) solution was carried out iodometrically. Aniline was distilled under reduced pressure using traces of Zn dust. Glacial acetic acid (S. Merck) was used as the solvent. The reaction was carried out in 10% acetic acid-water (v/v). The other chemicals employed were of B.D.H., E. Merck or S. Merck of analytical grade.

The progress of the reaction was followed by titrimetric procedure of Wiberg

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

RESULTS AND DISCUSSION

Kinetic investigation of the oxidation of aniline by chromic acid was made at several concentration by keeping [chromic acid] constant and varying [aniline] and also at varying [chromic acid] and constant [aniline]. The rate constants obtained are given in Table 1 and Table 2 respectively.

TABLE-1

EFFECT OF VARYING [ANILINE] ON THE RATE OF OXIDATION

[Chromic Acid] = 1.33×10^{-3} M		Temp. = 25°C
[Aniline] M	$k_1 \times 10^3$ min^{-1}	$K_s = k_1 \times 10^3/$[Aniline] litre mole^{-1} min^{-1}
0.8	3.089	0.3861
1.0	4.055	0.4055
1.2	4.992	0.4160
1.4	5.956	0.4254
2.0	8.383	0.4191
3.5	14.695	0.4198

TABLE-2

EFFECT OF VARYING [CHROMIC ACID] ON THE
RATE OF OXIDATION

[Aniline] = 0.8 M	Temp. = 25°C
[Chromic acid] M	$10^3 k_1$ min^{-1}
0.0013	3.089
0.0020	3.614
0.0024	4.137
0.0026	4.430
0.0040	5.646
0.0053	7.186

The order with respect to chromic acid and aniline was observed to be one each, hence the reaction is of total order two.

The rate of reaction increases with increase in concentration of chromic acid.

The active oxidising species of Cr(VI) in the present case is in the form of H_2CrO_4, since at high concentration of chromic acid, the concentration of H_2CrO_4 will increase in the reaction mixture.

Effect of Substrate

The plot of [substrate] versus k gives straight line with unit slope indicating that reaction follows first order kinetics with respect to substrate (Fig. 1). From
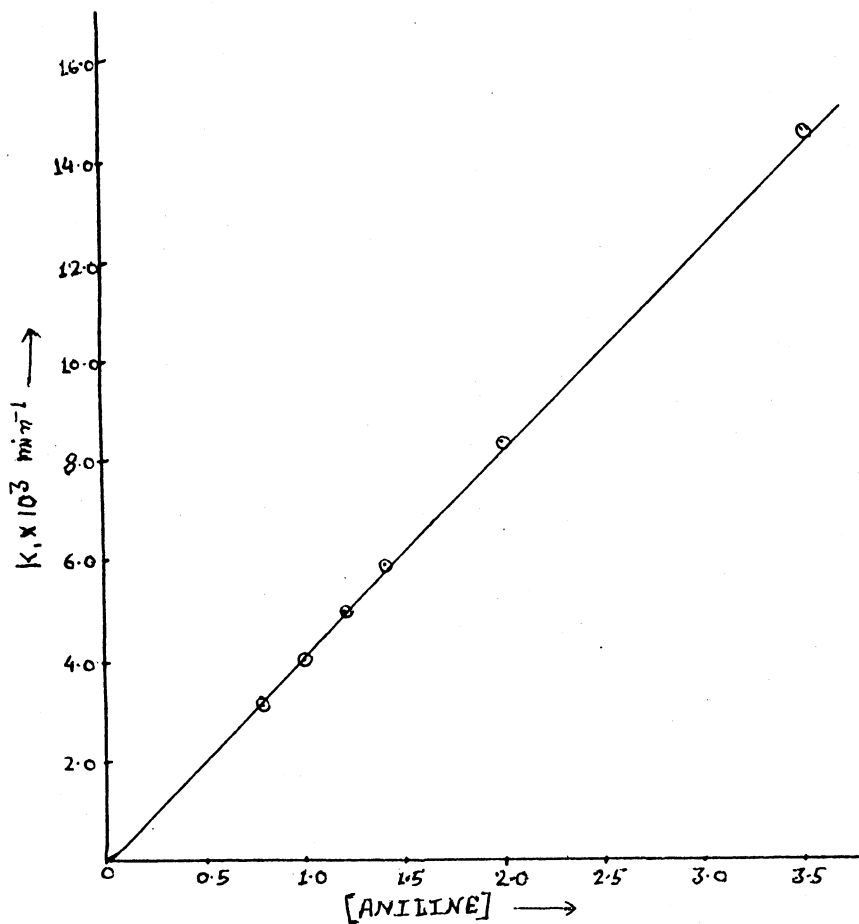
Fig. 1.   Plot of $K_1 \times 10^3$ min^{-1} vs. [aniline] at 25°C

the scrutiny of Table 1 the rate constant increases with increasing concentration of aniline; however, the value of $k_1/$(aniline) remains almost constant, leading to the inference that the order of the reaction with respect to aniline is one.

Effect of Acids

The rate constant was found to depend upon the concentration of HCl and H_2SO_4. With increase is [HCl] and [H_2SO_4] the rate was found to increase at initial stages only up to certain concentration of HCl and H_2SO_4 and the rate constant, thereafter decreased with further increase in [HCl] and [H_2SO_4] [Fig. 2]. The results are recorded in Table 3. Added acids are exerting two opposing effects: on one hand, acids are favouring the protonation of amines, while on the other, these acids are forming species like $HOCrO_2Cl$ and $HOCrO_2OSO_3H$ with chromic acid. These are lesser oxidising agents than chromic acid. It is likely that
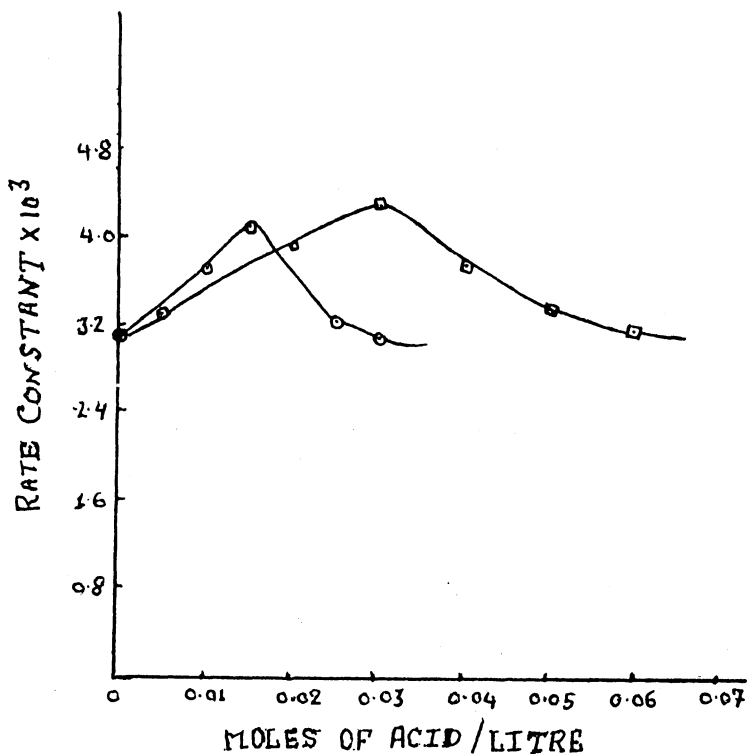
Fig. 2. Plot of rate constant vs. moles of acid lit^{-1} [aniline] = 0.80 M, [chromic acid] = 0.00133 M at 25°C ⊙ H$_2$SO$_4$ and ⊡ HCl

up to rate maxima, the former is predominant. Similar observations have also been reported by Bobtelsky *et al.*[16]

It was observed that HCl had greater influence on the rate of reaction as compared to H$_2$SO$_4$.

TABLE-3

EFFECT OF ACIDS ON THE RATE OF OXIDATION

[Aniline] = 0.8 M	[Chromic Acid] = 1.33 × 10^{-3} M		Temp. = 25°C
[HCl] M	$10^3 \times k_1$ min^{-1}	[H$_2$SO$_4$] M	$10^3 \times k_1$ min^{-1}
0.000	3.0890	0.000	3.0890
0.010	3.6380	0.005	3.3890
0.020	3.9356	0.010	3.7404
0.030	4.3264	0.015	4.0960
0.040	3.7650	0.020	3.5930
0.050	3.4068	0.025	3.2420
0.060	3.1988	0.030	3.1000

Effect of Salts

The added salts like NaCl, KCl, Na_2SO_4, K_2SO_4, to the reaction mixture show negligible effect on the rate of reaction, indicating that the rate determining step involves an ion and a neutral molecule. Similar observations have been also observed by Arumugan et al.[17], and Agrawal et al.[18]. The effects of salts are recorded in Table 4.

Effect of Catalyst

The rate of reaction is influenced by the catalytic cations like Cu^{2+}, Ag^+; however the rate of reaction is retarded by Mn^{2+}.

Effect of the Solvent

The rate of oxidation of aniline increases with increases in percentage of acetic acid (Table 5). This fact can be explained by two reasons: Firstly, increase of percentage of acetic acid decreases the dielectric constant of the medium, and this decrease in dielectric constant is responsible for the increase in the rate of the reactions involving an ion and a dipole. Secondly, acetic acid combines with chromic acid to form acetyl chromic acid or its protonated species which are stronger oxidising agents than chromic acid alone[19]. Similar observations have been reported by Sathyabhama et al.[20]

TABLE-4
EFFECT OF SALTS ON THE REACTION RATE

[Aniline] = 0.8 M   [Chromic Acid] = 1.33×10^{-3} M   Temp. = 25°C

Salt	[Concentration] M	$10^3 \times k_1$ min^{-1}	Salt	[Concentration] M	$10^3 \times k_1$ min^{-1}
NaCl	0.000	3.089	Na_2SO_4	0.000	3.089
	0.004	3.050		0.001	3.027
	0.006	3.035		0.002	2.988
	0.008	3.012		0.003	2.946
KCl	0.000	3.089	K_2SO_4	0.000	3.089
	0.004	3.047		0.001	3.017
	0.006	3.023		0.002	2.979
	0.008	3.003		0.003	2.934

TABLE-5
EFFECT OF SOLVENT COMPOSITION ON THE
RATE OF OXIDANT

[Aniline] = 0.8 M   [Chromic acid] = 1.33×10^{-3} M   Temp. = 25°C

Percentage of Acetic Acid	$10^3 \times k_1$ min^{-1}
10	3.089
20	6.556
30	11.430
40	22.507

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 6.

Stoichiometry and Identification of the Oxidation Product

Stoichiometry of the reaction was determined. It was found that 3 moles of anilines consumed 2 moles of chromic acid. The end product of oxidation of aniline by chromic acid was *p*-benzoquinone[21-25] identified. The overall reaction may be represented by the following empirical equation:
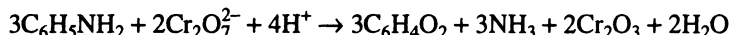
$$3C_6H_5NH_2 + 2Cr_2O_7^{2-} + 4H^+ \rightarrow 3C_6H_4O_2 + 3NH_3 + 2Cr_2O_3 + 2H_2O$$

TABLE-6
VARIOUS THERMODYNAMIC PARAMETERS

[Aniline] = 0.8 M   [Chromic acid] = 1.33×10^{-3} M

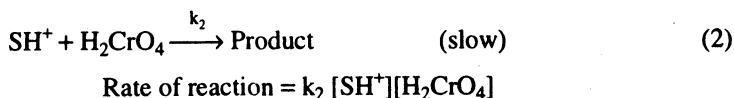| Temp. (°C)	$k_2 \times 10^5$	E_a kcal $mole^{-1}$	$A \times 10^{-4}$ sec^{-1}	ΔS^* e.u.	ΔH^* kcal $mole^{-1}$	$\Delta G\ddagger$ kcal $mole^{-1}$
20	10.81	11.44	2.94	−38.06	10.91	40.84
30	20.36	11.44	2.89	−38.12	11.13	41.54
40	38.36	11.44	2.89	−38.17	11.18	42.25

Kimijima *et al.*[26] have also reported *p*-benzoquinone as the oxidation product of aniline.

Mechanism

Amines are basic in nature and hence it is likely that protonation of amines may take place prior to oxidation and then the protonated amines get oxidised. The tentative mechanism of the oxidation of aniline by chromic acid may be as follows:

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

where S stands for substrate.

$$SH^+ + H_2CrO_4 \xrightarrow{k_2} \text{Product} \qquad \text{(slow)} \qquad (2)$$

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

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

on applying steady-state approximation, we may write

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

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

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

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

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

where $K = \dfrac{k_1}{k_{-1}}$.

The derived rate law explains all the observed experimental facts.

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