Kinetics of Oxidation of Aniline, N-Methylaniline, N,N'-Dimethylaniline by Chromic Acid

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Kinetics of oxidation of aniline by chromic acid has been studied in 10 % aqueous acetic acid and N-methylaniline, while the kinetics of oxidation of N,N'-dimethylaniline have been studied by chromic acid in 1 % aqueous acetic acid. The order with respect to oxidant for aniline, N-methylaniline, N,N'-dimethylaniline is one, zero, zero, respectively. The order with respect to substrate is one in each case. The rates constant were found to depend upon the concentration of HCl and H_2SO_4. The primary salt effect on the rate of oxidation is negligible. The reaction rate increases with the decrease of the dielectric constant of the medium in each case. An addition of Cu^{2+} and Ag^+ ions have marked accelerating effect on all the three reactions, while in case of Mn^{2+} ions the rate is found to decrease in case of aniline and N,N'-dimethylaniline, but increase in case of N-methyl aniline. Thermodynamic parameters were evaluated and mechanisms for the reactions have been proposed. The isokinetic temperature has also been evaluated.

Key Words: N-Methlyamine, N,N'-Dimethylamine, Chromic acid, Aniline, Oxidation.

INTRODUCTION

Reaction involving chromic acid have received little attention. Although some investigations utilizing chromic acid on oxidation kinetics in organic and inorganic compounds are reported in literature[1-9]. Literature survey pertaining to above-titled reaction reveals that no attempt have been made to explore the detailed kinetics study of aniline, N-methyaniline and N,N'-dimethylaniline by chromic acid. Thus, present study devoted to complete, concise and general mechanism of oxidation of these amines in aqueous acetic acid medium.

EXPERIMENTAL

The oxidant solution was prepared by dissolving Cr(VI) oxide (E.Merck) in conductivity water and diluting the solution. The standardization of the Cr(VI) solution was carried out iodometrically. Aniline, N-methylaniline, N,N'-dimethyl-aniline were distilled under reduced pressure using a trace of zinc dust during distillation. Doubly distilled water was used throughout the course of investigation. Glacial acetic acid (E.Merck) was used as a solvent. The reactions were studied in

thermostat ($\pm$ 0.1 °C). The progress of the reaction was followed by titrimetric procedure of Wiberg and Mill[10] for the estimation of Cr(VI) iodometrically using a starch end point in a measure aliquot of the reaction mixture at various intervals.

RESULTS AND DISCUSSION

The kinetic investigation were performed at several initial concentrations of chromic acid for aniline, N-methyaniline and N,N'-dimethylaniline and order of reaction for these reactions are found to be one, zero, zero, respectively (Table-1). The active oxidizing species of Cr(VI) in the present cases in the form of H_2SO_4. Since at high concentration of chromic acid, the concentration of H_2CrO_4 will increase in the reaction mixture.

TABLE-1
EFFECT OF [CHROMIC ACID] ON THE RATE CONSTANT

[Aniline] = 0.8 M, HOAc-H_2O = 10 % (v/v), Temperature = 298 K			
[Chromic acid] $\times 10^3$ M	1.330	2.000	2.400	2.660
$k_1 \times 10^3$ min^{-1}	3.089	3.614	4.137	4.430
[N-Methylaniline] = 1.00×10^{-2} M, HOAc-H_2O = 1 % (v/v), Temperature = 293 K			
[Chromic acid] $\times 10^3$ M	0.400	0.660	1.000	1.330
$k_0 \times 10^6$ mol L^{-1} min^{-1}	1.727	2.582	4.291	8.349
[N,N'-Dimethylaniline] = 1.00×10^{-2} M, HOAc-H_2O = 1 % (v/v), Temperature = 293 K			
[Chromic acid] $\times 10^3$ M	0.400	0.660	1.000	1.330
$k_0 \times 10^6$ mol L^{-1} min^{-1}	1.970	3.559	6.863	10.172

The order of the reactions between chromic acid and aniline, N-methylaniline, N,N'-dimethylaniline are one, zero, zero, respectively. The rate of reactions increases with increase of chromic acid and aniline, methylaniline, N,N'-dimethylaniline concentration in each case (Tables 1 and 2).

TABLE-2
EFFECT OF [SUBSTRATE] ON THE RATE CONSTANT

[Chromic acid] = 1.33×10^{-3} M, HOAc-H_2O = 10 % (v/v), Temperature = 298 K			
[Aniline] $\times$ M	0.800	1.000	1.200	1.400
$k_1 \times 10^3$ min^{-1}	3.089	4.055	4.992	5.956
Chromic acid = 0.66×10^{-3} M, HOAc-H_2O = 1 % (v/v), Temperature = 293 K			
[N-Methylaniline] $\times 10^2$ M	1.000	1.500	1.800	2.000
$k_0 \times 10^6$ mol L^{-1} min^{-1}	4.067	6.573	5.168	9.268
[Chromic acid] = 0.66×10^{-3} M, HOAc-H_2O = 1 % (v/v), Temperature = 293 K			
[N,N'-Dimethylaniline] $\times 10^2$ M	1.000	1.500	1.800	2.000
$k_0 \times 10^6$ mol L^{-1} min^{-1}	3.559	5.714	7.111	8.035

The kinetics of oxidation of aniline, N-methylaniline and N,N'-dimethylaniline by chromic acid were studied over a wide range of hydrochloric acid and sulphuric acid concentration. With increase in [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 (Fig. 1). 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 hand, these acids are forming species like $HOCrO_2OSO_3H$ with chromic acid. These are lesser oxidizing agents than chromic acid. It is likely that up to rate maxima, the former is predominant. Similar observations have also been reported by Bobtelsky et al.[11]. It was observed that HCl had greater influence on the rate of reaction as compared to H_2SO_4.
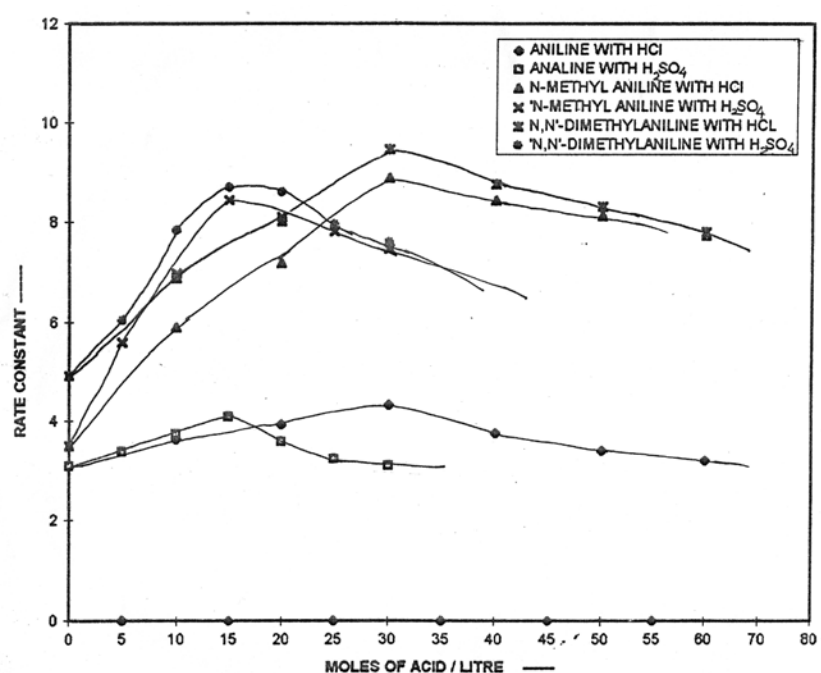

Fig. 1.

The rates of oxidation increase with increase in percentage of acetic acid in case of amine, N-methylaniline and N,N'-dimethylaniline (Table-4). This 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 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 oxidizing agents than chromic acid alone[12]. Similar observations have been reported by Sathyabhama et al.[13].

The added salts line NaCl, KCl, Na_2SO_4 and K_2SO_4 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.

TABLE-3

[Aniline] = 0.8 M, HOAc-H$_2$O = 1 % (v/v),
[Chromic acid] = 1.33 × 10^{-3} M, Temperature = 298 K

[HCl] × 10^{-3} M	k$_0$ × 10^6 mol L^{-1} min^{-1}	[H$_2$SO$_4$] × 10^{-3} M	k$_1$ × 10^3 min^{-1}
0.0	3.089	0.0	3.089
10.0	3.638	5.0	3.389
20.0	3.935	10.0	3.740
30.0	4.326	15.0	4.096
40.0	3.765	20.0	3.593
50.0	3.406	25.0	3.242
60.0	3.198	30.0	3.100

[N-Methylaniline] = 1.00 × 10^{-2} M, HOAc-H$_2$O = 1 % (v/v),
[Chromic acid] = 0.66 × 0^{-3} M, Temperature = 298 K

[HCl] × 10^{-3} M	k$_0$ × 10^6 mol L^{-1} min^{-1}	[H$_2$SO$_4$] × 10^{-3} M	k$_1$ × 10^3 min^{-1}
00.0	3.502	0.0	3.502
10.0	5.906	5.0	5.595
20.0	7.188	10.0	6.979
30.0	8.878	15.0	8.445
40.0	8.431	20.0	8.102
50.0	8.127	25.0	7.821
60.0	7.747	30.0	7.480

[N-N'-Dimethylaniline] = 1.00 × 10^{-2} M, HOAc-H$_2$O = 1 % (v/v),
[Chromic acid] = 0.66 × 10^{-3} M, Temperature = 298 K

[HCl] × 10^{-3} M	k$_0$ × 10^6 mol L^{-1} min^{-1}	[H$_2$SO$_4$] × 10^{-3} M	k$_1$ × 10^3 min^{-1}
0.0	4.925	0.0	4.925
10.0	6.887	5.0	6.042
20.0	8.013	10.0	7.834
30.0	9.461	15.0	8.698
40.0	8.762	20.0	8.602
50.0	8.318	25.0	7.962
60.0	7.809	30.0	7.607

TABLE-4

EFFECT OF SOLVENT COMPOSITION ON THE RATE CONSTANT

[Aniline] = 0.8 M, [Chromic acid] = 1.33 × 10^{-3} M, Temperature = 298 K			
HOAc-H$_2$O % (v/v)	10	20	30	40
k$_1$ × 10^3 min^{-1}	3.089	6.556	11.430	22.507

[N-Methylaniline] = 1.00 × 10^{-2} M, [Chromic acid] = 0.66 × 10^{-3} M, Temperature = 298 K			
HOAc-H$_2$O % (v/v)	10	20	30	40
k$_0$ × 10^6 mol L^{-1} min^{-1}	6.022	7.224	8.324	9.053

[N,N'-Dimethylaniline] = 1.00 × 10^{-2} M, [Chromic acid] = 0.66 × 10^{-3} M, Temperature = 298 K			
HOAc-H$_2$O % (v/v)	10	20	30	40
k$_0$ × 10^6 mol L^{-1} min^{-1}	8.788	10.071	11.234	13.584

The catalytic effect of Cu^{2+}, Mn^{2+} and Ag$^+$ ions is studied in case of oxidation reactions. In the present investigation it has been found that little amount of Cu^{2+} and Ag$^+$ ions have marked accelerating effect on all the three reactions. In case of

Mn^{2+} ions the rate is found to decrease in case of aniline and N,N'-dimethylaniline, but increase in case of N-methylaniline. On the basis of these studies, it has been suggested that Cu^{2+} ion is catalysis is characteristic in case where it can form a complex with substrate. Similarly the possibility, due to which Ag^+ ions can increase the rate of reaction, is the complex formation between Ag^+ ions and the substrate. The retarding effect of Mn^{2+} ions is explained by assuming that in presence of Mn^{2+} ions, two different oxidizing species of chromium are involved. They are Cr(V) and Cr(IV). These species can oxidize Mn^{2+} ion with results, lesser chromium is available for the oxidation of substrate and hence the rate decreases.
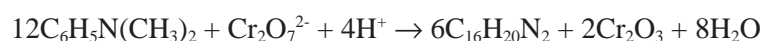
In case, where addition of Mn^{2+} ions increases the rate, it is assumed that the intermediate species of manganese ion *i.e.*, Mn^{3+} and Mn^{4+} are formed which can also bring about the oxidation of substrate.

The values of various Arrhenius and Erying parameters were computed from the study of rate measurement within temperature range at 293, 298, 303, 308 and 313 K, respectively and are reported in Table-5.

TABLE-5

Activation parameters	Aniline	N-Methylaniline	N,N'-Dimethylaniline
E_a (K J mol^{-1})	47.86 ± 0.02316	46.15 ± 0.0673	48.19 ± 0.0122
A (s^{-1})	2.98 ± 0.23680	7.76 ± 0.1439	23.68 ± 0.3592
ΔH^* (KJ mol^{-1})	46.57 ± 0.96340	68.99 ± 1.0943	61.87 ± 0.6966
ΔG^* (KJ mol^{-1})	173.80 ± 0.13940	95.99 ± 0.1624	102.82 ± 1.8584
ΔS^* (KJ mol^{-1})	-159.70 ± 0.19650	-228.03 ± 0.2735	-218.39 ± 0.1930

The stoichiometry of each reaction under investigation has been determined by equilibrating the reaction mixture containing an excess of chromic acid over aniline, N-methylaniline and N,N'-dimethylaniline, respectively in varying ratio at the experimental temperature for 5 d. At the completion of the reaction the unconsumed chromic acid was determined by usual iodometric method. The results of the experiment on stoichiometry indicated that 3 moles of aniline were consumed for 2 moles of the chromic acid, 6 moles of N-methylaniline were consumed for 2 moles of chromic acid, 12 moles of N,N'-dimethylaniline were consumed for 2 moles of the chromic acid, respectively. The stoichiometric equation overall for each reaction under investigation are:

$$3C_6H_5NH_2 + 2Cr_2O_7^{2-} + 4H^+ \rightarrow 3C_6H_4O_2 + 3NH_3 + 2Cr_2O_3 + 2H_2O$$

$$6C_6H_5NHCH_3 + 2Cr_2O_7^{2-} + 4H^+ \rightarrow 3C_{14}H_{14}N_2 + 2Cr_2O_3 + 8H_2O \; k_{-1} + k_2[H_2CrO_4]$$

$$12C_6H_5N(CH_3)_2 + Cr_2O_7^{2-} + 4H^+ \rightarrow 6C_{16}H_{20}N_2 + 2Cr_2O_3 + 8H_2O$$

The oxidation product have been identified to be *p*-benzoquinone[10], N,N'-dimethylaniline quinone diimine[11]. N,N,N',N'-Tetramethyl benzidine quinone diimine[14], respectively for each reaction by the method described by Taylor and Saunders[15].

Mechanism and rate expression

Following mechanism and rate expression are proposed to account for their kinetic results.

For aniline

$$S + H \longrightarrow SH^+ \qquad\qquad \text{fast} \qquad\qquad (1)$$
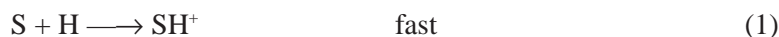
where S stands for substrate

$$SH^+ + H_2CrO_4 \longrightarrow \text{Products} \qquad \text{slow} \qquad\qquad (2)$$

Rate of reaction:

$$K_2[SH^+][H_2CrO_4]$$

or $d/dt[SH^+] + k[S][H^+] - k_{-1}[SH^+] - k_{-2}[SH+][H_2CrO_4]$

On applying steady state approximation, we may write,

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

since $k_{-1} \gg k_2$

Rate of reaction:

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

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

where $k = k_1/k_{-1}$

For N-methylaniline and N,N'-dimethylaniline

$$S + H^+ \xrightarrow[k_{-1}]{k_1} SH^+ \qquad\qquad \text{slow} \qquad\qquad (1)$$

$$SH^+ + H_2SO_2 \longrightarrow H_2CrO_4 + \text{Product} \qquad \text{fast} \qquad\qquad (2)$$

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

Applying stationary state approximation, d/dt [SH$^+$] = 0

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

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

Since $k_2 \gg k_1$

Therefore, $-d/dt[H_2CrO_4] = k_1[S][H^+]$

The derived rate law explains all the observed experimental facts obtained in the oxidation reactions. The order of reactivity observed was in the following sequence:

N,N'-Dimethylaniline > N-Methylaniline > Aniline

Similar results have been reported by Mathani and Gopalan[16] and Rao *et al.*[17] in their work. One of the steps in the reaction is protonation of amines which would naturally increase with the increase in the basicity of the amine and hence rate of the reaction will follow the pattern of the basic nature of the amine. So far as reaction mechanism of oxidation of the anilines is concerned, it involves two steps, first is the protonation of amine and second is the oxidation of the protonated species. The similarity in the mechanism for different anilines is also supported by the thermo-dynamics parameters. However, the kinetic studies lead to the conclusion that in case of anilines, oxidation step is the rate-determining step while in case of secondary and tertiary amines, protonation step is the rate determining step. These can be understood by comparing their relative rates of protonation and oxidation. In case of N-methylaniline and N,N'-dimethylaniline there is greater electron density at the nitrogen atom due to inductive effect and hence their rates of oxidation will be faster thus protonation of these amines may be the rate determining step. However, in case of aniline, the rate of oxidation will be slower because there is no increase of electron density at the nitrogen atom of aniline and hence electrophilic attack of the oxidant will be lesser. Thus the oxidation of protonated aniline is the rate determining step.

The isokinetic temperature β was found to 338.69 K which is in good agreement with the value 343.85 K obtained from Exner plot[18].

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