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Kinetics of Oxidation of N,N′-Dimethylaniline by Chromic Acid

RANVEER SINGH* and K.B.L. SHRIVASTAVA
Department of Chemistry
Government Model Autonomous Science College
Rewa-486 001, India

The kinetics of oxidation of N,N-dimethylaniline by chromic acid have been studied in 1% aqueous acetic acid medium. The order of reaction between chromic acid and N,N-dimethylaniline is zero and one with respect to chromic acid and N,N-dimethylaniline respectively. The rate constant was 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 decrease of the dielectric constant of the medium. Rate increases by the addition of catalyst such as Cu^{2+}, Ag^+ and retarded by the addition of Mn^{2+}. Various thermodynamic parameters have been evaluated. A plausible mechanism constant with the experimental results has been proposed.

INTRODUCTION

Chromic acid is a well known oxidizing agent and has been studied extensively for the oxidation of organic and inorganic compounds[1–5]. The oxidation of aromatic amines has been studied by different oxidizing agents[6–9]. Further the kinetics of N,N-dimethylaniline has already been carried out by using different oxidants like MnO_2,[10] $CuCl_2$,[11] and periodate[12] etc. by earlier workers. The kinetics of chromic acid oxidation of N,N-dimethylaniline have received no attention earlier. This therefore forms the subject matter of the present paper.

EXPERIMENTAL

Standard solution of chromic acid was prepared in distilled water and was standardised iodometrically. The reactions were studied in thermostat (± 0.1°C). The N,N′-dimethylaniline was distilled under reduced pressure using a trace of zinc dust during distillation. Glacial acetic acid was used as the solvent. All the chemicals used during the investigation were either AnalaR, B.D.H., E. Merck or S. Merck of extra pure quality. The progress of the reaction was followed by titrimetric procedure of Wiberg 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.

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*For correspondence: Dr Ranveer Singh, C/o Shri Janardan Singh, beside Post Office Building, Nagara–221 711 (Ballia), India.

RESULTS AND DISUSSION

Kinetic investigation of the oxidation of N,N-dimethylaniline by chromic acid was made at several concentrations by keeping [chromic acid] constant and varying [N,N-dimethylaniline] and also by varying [chromic acid] and keeping [N,N-dimethylanline] constant. The rate constants obtained are given in Table-1. The order of the reaction between chromic acid and N,N-dimethylaniline is zero and one with respect to chromic acid and N,N-dimethylaniline respectively. Hence the total order of reaction is (0 + 1) *i.e.* 1. The rate of the reaction increases with increase of chromic acid and N,N-dimethylaniline concentration.

TABLE-1
EFFECT OF VARYING [REACTANTS] ON THE REACTION RATE

Temperature = 20°C, $HOAc\text{-}H_2O$ = 1% (v/v)

Effect of chromic acid concentration: [N,N-dimethylaniline] = 1.00×10^{-2} M

(Chromic acid) × 10^3 M	0.40	0.66	1.00	1.33
$k_0 \times 10^6$ moles $L^{-1}min^{-1}$	1.97	3.56	6.86	10.17

Effect of N,N-dimethylaniline concentration: [Chromic acid] = 0.66 M

[N,N′-dimethylaniline] × 10^2 M	1.00	1.50	1.80	2.00
$k_0 \times 10^6$ moles $L^{-1}min^{-1}$	3.56	5.71	7.11	8.03

The rate constant was found to depend upon the concentration of HCl and H_2SO_4. 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 and the rate constant, thereafter, decreased with further increase in [HCl] and [H_2SO_4] (Fig. 1). The results are recorded in Table 2.

TABLE-2
EFFECT OF ACIDS ON THE RATE OF OXIDATION

(N,N′-Dimethylaniline) = 1.00×10^{-2} M, $HOAc\text{-}H_2O$ = 1% (v/v)

(Chromic acid) = 0.66×10^{-3} M, Temperature = 25°C

[HCl] M	$k_0 \times 10^6$moles $L^{-1}min^{-1}$	[H_2SO_4] M	$k_0 \times 10^6$moles $L^{-1}min^{-1}$
0.000	4.925	0.000	4.925
0.010	6.887	0.005	6.042
0.020	8.013	0.010	7.834
0.030	9.461	0.015	8.698
0.040	8.762	0.020	8.602
0.050	8.318	0.025	7.962
0.060	7.809	0.030	7.607

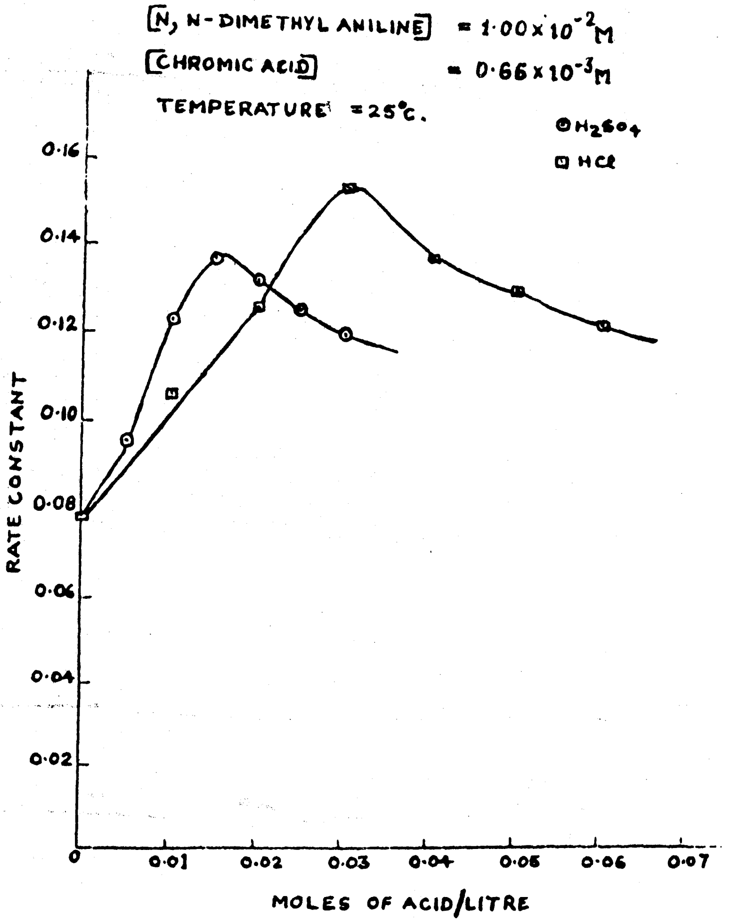

Fig. 1 Plot of rate constant *vs.* moles of acid/litre

Added acids are exerting two opposing effects. On the one hand, acids are favouring the protonation of amines, while on the other, these acids are forming species like $HOCrO_2{\cdot}Cl$ and $HOCrO_2O{\cdot}SO_3H$ with chromic acid. These are lesser oxidising agents than chromic acid. It is likely that up to rate maxima, the former is predominant and after the maxima, the latter becomes predominant. Similar observations have also been reported by Shrivastava *et al.*[1]. It was observed that HCl had greater influence on the rate of reaction as compared to H_2SO_4.

The added salts like NaCl, KCl, Na_2SO_4 and K_2SO_4 to the reaction mixture show negligible effect on the rate of reaction. The rate of reaction is influenced by catalytic cations like Cu^{2+}, Ag^+; however, the rate of reaction is retarded by Mn^{2+} (Table 3). The increase in the percentage of acetic acid in the reaction mixture largely enhances the raction rate. The plot of log k_0 *vs.* percentage composition of acetic acid, *i.e.* 1/D is linear having positive slope, suggesting the reaction is positive ion-dipole type. The kinetics of oxidation of N,N-dimethylaniline by chromic acid have been studied at different temperatures and rate constants and are recorded in Table-3. Various thermodynamic parameters such as activation energy, frequency factor, enthalpy of activation, free energy of activation and entropy of activation have been evaluated, which are recorded in Table-4.

TABLE-3

EFFECT OF CONCENTRATION OF SALTS, CATALYST, SOLVENT AND TEMPERATURE ON REACTION RATE

Temperature = 25°C, HOAc-H_2O = 1% (v/v)

Effect of salts concentration: [N,N′-Dimethylaniline] = 1.00×10^{-2} M

[Chromic acid] = 0.66×10^{-3} M

[NaCl] × 10^3 M	4.00	6.00	8.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	4.88	4.83	4.77
[KCl] × 10^3 M	4.00	6.00	8.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	4.86	4.75	4.68
[Na_2SO_4] × 10^3 M	1.00	2.00	3.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	4.78	4.69	4.58
[K_2SO_4] × 10^3 M	1.00	2.00	3.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	4.75	4.59	4.47

Effect of Catalysts concentration: [N,N′-Dimethylaniline] = 1.00×10^{-2} M

[Chromic acid] = 0.66×10^{-3}M

[$CuSO_4 \cdot 5H_2O$] × 10^3 M	1.00	2.00	3.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	5.38	6.09	6.70
[$MnSO_4 \cdot H_2O$] × 10^3 M	1.00	2.00	3.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	4.41	4.23	4.05
[Ag_2SO_4] × 10^3 M	1.00	2.00	3.00
$k_0 \times 10^6$ moles L^{-1} min^{-1}	4.95	5.34	5.71

Effect of percentage composition of acetic acid: [N,N′-Dimethylaniline] = 1.00×10^{-2} M,

[Chromic acid] = 0.66×10^{-3} M

HOAc-H_2O% (v/v)	10	20	30	40	50
$k_0 \times 10^6$ moles L^{-1} min^{-1}	8.79	10.07	11.23	13.58.	15.02

Effect of temperature: [N,N′-Dimethylaniline] = 1.00×10^{-2} M

[Chromic acid] = 1.66×10^{-3} M

Temperature °C	20	25	30	35	40
$k_0 \times 10^6$ moles L^{-1} min^{-1}	3.56	4.92	6.80	9.37	12.89

TABLE-4
VARIOUS THERMODYNAMIC PARAMETERS

E_a kJ mol^{-1}	A L $sec^{-1}mol^{-1}$	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	ΔS^* JK^{-1} mol^{-1}
48.1900 ± 0.0122	23.6800 ± 0.3592	61.8700 ± 0.6966	102.8200 ± 1.8584	- 218.3900 ± 0.1930

Stoichiometry and Identification of the oxidation product

Stoichiometry of the reaction was determined. It was found that 6 moles of N,N-dimethylaniline were consumed for each mole of the chromic acid. The end-product was identified to be N,N,N′,N′-tetramethyl benzidine-quinone di-imine. The overall reaction may be represented by the following empirical equation:

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

Similar observations have been reported by Mizoguchi *et al.*[13], Galus and Adams[14], Galus *et al.*[15] and Willstatter *et al.*[16].

Mechanism

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

$$SH^+ + H_2CrO_4 \xrightarrow{k_2} H_2CrO_4 + \text{Product (Fast)} \tag{2}$$

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

Applying stationary state approximation,

$$-\frac{d}{dt}[SH^+] = 0$$

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

Therefore

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

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

Since

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

Therefore

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

The derived rate law explains all the observed experimental facts.

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