

Kinetics of oxidation of N-methyl aniline by chromic acid

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Abstract : The oxidation kinetics of N-methylaniline have been studied by chromic acid in acetic acid water medium. The order of reaction between chromic acid and N-Methylaniline has been studied respectively. The rate constant was found to depend upon the concentration of HCl and H₂SO₄ acid. With increase in concentration of acid, the rate was found to increase initially up to a certain specific concentration, then the rate constant decreased with further increase in concentration of acid. An addition of natural salts like NaCl, KCl, Na₂SO₄ and K₂SO₄ shows negligible effect. The effect of solvent has been studied by varying the composition of acetic acid and has obtained increasing effect of the rate. The effect of catalyst such as Ag⁺, Cu⁺⁺ and Mn⁺⁺ shows increasing effect. Various thermodynamic parameters have been evaluated. The stoichiometry of the reaction has been determined. N,N-dimethyl-benzidine quinone dimine has been identified as the oxidation product of the reaction. A plausible mechanism consistent with experimental result has been suggested.

(Keywords : Oxidation kinetics, N,N-dimethyl-benzidine quinone dimine, order of reaction)

Introduction

Chromic acid is one of the most versatile of available oxidizing agents, reacting with all almost all types of oxidizable groups. Kinetic studies have been extensively carried out for various organic and inorganic compounds by using chromic acid¹⁻⁸. The oxidation of aromatic amines have been studied by different oxidizing agents⁹⁻¹³. Further the kinetics of N-methyl aniline has, already been studied by using different oxidants like hexacyanoferrate¹⁴, periodate¹⁵,

potassium peroxydisulfate¹⁶, N-bromosuccinimide¹⁷ by earlier workers.

The kinetics of chromic acid oxidation of some Nitrogenous organic compound (N-Methylaniline) have received no attention earlier. This therefore forms the subject matter of the present paper.

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 N-Methylaniline was distilled under reduced pressure using a trace 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 highest purity.

The progress of the reaction was followed by titrimetric procedure of Wiberg and Mill for the estimation of Cr (VI) eudiometrically using a starch end point in a measured aliquot of the reaction mixtures at various intervals.

Results and Discussion

Effect of Oxidant & Substrate

Kinetic investigation of the oxidation of N-methylaniline by chromic acid was made at several concentration by keeping [chromic acid] constant and varying [N-methylaniline] and also at varying [chromic acid] and constant [N-methylaniline].

The order of the reaction between chromic acid and N-Methylaniline is zero and one with respect to chromic acid and N-methylaniline respectively. Hence the total order of the reaction is (O+I) i.e. one the rate of the reaction increases with increase of chromic acid and N-methylaniline concentration.

Effect of acids :

The rate constant was found to depend upon the concentration of HCl and H_2SO_4 . With increase in $[\text{HCl}]$ and $[\text{H}_2\text{SO}_4]$ the rate was found to increase at initial stages only up to certain concentration of HCl and H_2SO_4 and the constant, thereafter decreased with further increase in $[\text{HCl}]$

and $[\text{H}_2\text{SO}_4]$, (Fig. 1). The results are recorded in Table 1. Added acids are exerting two opposing effects on one hand, acids are favouring the protonation of mines, while on the other, these acids are forming species like HOCrO_2Cl and $\text{HOCrO}_2\text{OSO}_3\text{H}$ with chromic acid. These are lesser oxidizing agents than chromic acid. It is likely that up to rate maxima, the former is predominant and after the mixima, the latter becomes predominant. Similar observations have also been reported by Bobtelsky *etal*¹⁸.

It was observed that HCl had greater influence on the rate of reaction as compared to H_2SO_4 .

Table No.-1 Effect of acids on the rate of Oxidation

$[\text{N-Methylaniline}] = 1.00 \times 10^{-2} \text{ M}$

$[\text{Chromic acid}] = 0.66 \times 10^{-3} \text{ M}$

Temperature = 25°C

$[\text{HCl}] \text{ M} \times 10^2$	$\text{Ko} \times 10^6 \text{ moles lit}^{-1} \text{ min}^{-1}$	$[\text{H}_2\text{SO}_4] \text{ M} \times 10^2$	$\text{Ko} \times 10^6 \text{ lit}^{-1} \text{ Min}^{-1}$
0.00	3.503	0.00	3.503
1.00	5.907	0.50	5.596
2.00	7.189	1.00	6.979
3.00	8.879	1.50	8.446
4.00	8.432	2.00	8.103
5.00	8.128	2.50	7.822
6.00	7.748	3.00	7.480

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 observation have been also observed by Arumugan *etal*¹⁹, Agrawal and Bhattacharya²⁰. The effects of salts are recorded in Table-2.

Table-2 Effect of Salts on the reaction rate

$[\text{N-Methylaniline}] = 1.00 \times 10^{-2} \text{ M}$ $[\text{Chromic acid}] = 0.66 \times 10^{-3} \text{ M}$

Temperature = 25°C

Salt	$[\text{Conc.}] \text{ M} \times 10^3$	$\text{Ko} \times 10^6 \text{ mole lit}^{-1} \text{ min}^{-1}$	Salt $\text{M} \times 10^3$	$[\text{Conc.}] \text{ Mole lit}^{-1} \text{ Min}^{-1}$	$\text{Ko} \times 10^6$
NaCl	0.00	3.503	Na_2SO_4	0.00	3.503
	4.00	3.559		1.00	3.581
	6.00	3.589		2.00	3.644
	8.00	3.609		3.00	3.702
KCl	4.00	3.543	K_2SO_4	1.00	3.559
	6.00	3.563		2.00	3.594
	8.00	3.585		3.00	3.652

Effect of catalyst :

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

Effect of the Solvent :

The rate of oxidation of N-methylaniline increases with increases in % of acetic acid (Table 3). 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 oxidizing agents than chromic acid alone²¹. Similar observations have been reported Sathyabhama, *et al.*²².

Table No.-3
Effect of solvent composition on the rate of oxidant

[N-Methylaniline] = $1.00 \times 10^{-2}\text{M}$

[Chromic acid] = $0.66 \times 10^{-3}\text{M}$

Temperature = 25°C

[Acetic acid] % V/V	$K_o \times 10^6 \text{ mole lit}^{-2} \text{ min}^{-1}$
10.00	6.023
20.00	7.225
30.00	8.325
40.00	9.054
50.00	10.211

Thermodynamic Parameters :

Various thermodynamic parameters such as activation energy, frequency factor, entropy of activation, free energy of activation of enthalpy of activation have been calculated, which are recorded in Table-4.

Table No. 4
Various Thermodynamic Parameters

[N-Methylaniline] = $1.00 \times 10^{-2}\text{M}$

[Chromic acid] = $0.66 \times 10^{-3}\text{M}$

Ea KJ mole ⁻¹	A 1 Sec ⁻¹ Mole ⁻¹	AH kJ mol ⁻¹	AG kJ mol ⁻¹	AS JK mole ⁻¹
46.16 ± 0.01	7.77 ± 0.14	68.99 ± 1.09	95.99 ± 0.16	-228.04 ± 0.27

Stoichiometry and identification of the oxidation product :

Stoichiometry of the reaction was determined. It was found that 3 mole of N-Methylaniline were consumed for each mole of the chromic acid. The end-product was identified to be NN dimethylbenzidine quinone dimine.

The overall reaction may be represented by empirical equation. $6\text{C}_6\text{H}_5\text{NHCH}_3 + 2\text{Cr}_2\text{O}_7 + 4\text{H}^+ = 3\text{C}_{14}\text{H}_{14}\text{N}_2 + 2\text{Cr}_2\text{O}_3 + 8\text{H}_2\text{O}$. The end product was identified by adopting the method described by Naylor and Saunders²³. Similar observations have been reported by Galus *et al.*²⁴

Mechanism :-

$\text{S} + \text{H}^+ \xrightleftharpoons{K_1} \text{SH}^+ \dots\dots\dots (\text{Slow}) (1)$
 $\text{SH}^+ + \text{H}_2\text{CrO}_4 \xrightarrow{k_2} \text{H}_2\text{CrO}_4 + \text{Product} \dots\dots\dots (\text{Fast}) (2)$
 $\frac{d}{dt} [\text{SH}^+] = k_1 [\text{S}] [\text{H}^+] - k_{-1} [\text{SH}^+] - k_2 [\text{SH}^+] [\text{H}_2\text{CrO}_4]$
 Applying stationary state approximate,
 $\frac{d}{dt} [\text{SH}^+] = 0$
 $[\text{SH}^+] = k_1 [\text{S}] [\text{H}^+] / k_{-1} + k_2 [\text{H}_2\text{CrO}_4]$
 $-\frac{d}{dt} [\text{H}_2\text{CrO}_4] = k_2 [\text{SH}^+] [\text{H}_2\text{CrO}_4] = k_2 k_1 [\text{S}] [\text{H}^+] [\text{H}_2\text{CrO}_4] / k_{-1} + k_2 [\text{H}_2\text{CrO}_4]$

Since the secondary and tertiary amines are more basic than anilines, the protonation of these will be more than that of aniline and it is likely that K_{-1} is small.

As $k_2 \gg k_{-1}$ than $-\frac{d}{dt} [\text{H}_2\text{CrO}_4] = K_1 [\text{S}] [\text{H}^+]$

The derived rate law explains all the observed experimental reacts.

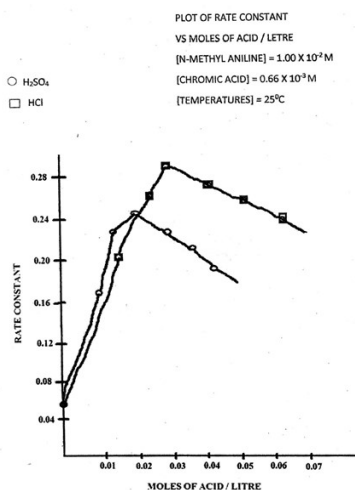


Fig. 1

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