Kinetics of Periodate Oxidation of Aromatic Amines – A Comparison of Effect of pH on Oxidation of Some Anilines

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The effect of pH on kinetics of oxidation of seven aromatic amines has been studied in acetone-water medium. The results have been compared and some of these have been found to differ from the trend reported in the earlier works.

INTRODUCTION

The studies on oxidation of aromatic amines by periodate ion as reported in literature are very few[1-7]. The kinetic studies made on these non Malaparadian oxidations are even fewer. The products formed are pH dependent[8-10]. Earlier reports[2-7, 11] suggest the reaction to be of ion-dipolar type or neutral molecule-ion type with stoichiometry of 2 mol of oxidant : 1 mol of substrate. Generally a first order dependence of rate on each of the reactants has been reported[2-7, 11]. The rate pH profiles reported in these studies do not follow a definite pattern. The present work is an attempt to investigate and interpret the effect of pH on rate of periodate oxidation of aniline, N-ethylaniline (EA), N,N′-dimethylaniline (DMA), N,N′-dimethylaniline (DEA), m-toluidine (m-Tol.), p-toluidine (p-Tol.), and N,N′-dimethyl-p-toluidine (DMT) in acetone-water medium.

EXPERIMENTAL

All chemicals and reagents used were of Loba G.R. or Merck A.R. grade. Amines were used after redistillationtion/recrystallization. Doubly distilled water was used to prepare the solutions. Thiel, Schultz and Koch buffer[12] was used to maintain the pH. The absorbances of reaction mixtures were recorded on Shimadzu double beam (UV-150-02) spectrophotometer. Initial rates were evaluated in terms of change in absorbance with time *i.e.* $(dA/dt)_i$. The reactions were studied under pseudo-first order conditions by taking one of the reactants in excess, and the studies were restricted to the period in which the λ_{max} did not change.

RESULTS AND DISCUSSION

The reaction mixtures developed are in brownish, violet, violet, yellow, reddish-voilet, violet and violet colours and λ_{max} were found to be 355, 560, 555, 472, 540, 470 and 565 nm in case of oxidation of aniline, EA, DMA, DEA, m-Tol., p-Tol. and DMT respectively. The $(dA/dt)_i$ values at different pH in these cases have been given in Tables 1–7.

TABLE- 1

[Aniline] = 5.0×10^{-3} M, [NaIO$_4$] = 5.0×10^{-4} M,

Temp. = $40 \pm 0.1°C$, $\lambda_{max} = 355$ nm Acetone = 1.265% (v/v)

pH	4.00	4.50	4.95	5.40	6.25	6.55	6.90	8.15
$\left(\dfrac{dA}{dt}\right)_i \times 10^3$	6.2	10.1	12.8	8.0	6.4	4.8	4.0	2.4

TABLE-2

[EA] = 1.0×10^{-2} M, [NaIO$_4$] = 1.0×10^{-2} M, Acetone = 10% (v/v),

Temp. = $30 \pm 0.1°C$, $\lambda_{max} = 555$ nm

pH	4.0	5.0	6.0	7.0	8.0	9.0
$\left(\dfrac{dA}{dt}\right)_i \times 10^3$	1.15	2.00	2.00	1.75	1.25	0.50

TABLE-3

[DMA] = 1.0×10^{-3} M, [NaIO$_4$] = 10.0×10^{-3} M, Acetone = 1.265% (v/v)

Temp. = $35 \pm 0.1°C$, $\lambda_{max} = 560$ nm

pH	4.16	4.63	5.10	6.10	6.96	7.30
$\left(\dfrac{dA}{dt}\right)_i \times 10^2$	3.8	5.2	6.0	5.2	5.0	3.6

TABLE-4

[DEA] = 1.0×10^{-4} M, [NaIO$_4$] = 1.0×10^{-3} M, Temp. = $30 \pm 0.1°C$,

Acetone = 1.265% (v/v), $\lambda_{max} = 472$ nm

pH	5.52	6.06	6.52	6.98	7.52	8.10
$\left(\dfrac{dA}{dt}\right)_i \times 10^3$	2.6	4.9	5.2	5.2	5.0	4.8

TABLE- 5

[m-Tol.] = 1.0×10^{-3} M, [NaIO$_4$] = 1.0×10^{-2} M, Acetone = 10% (v/v)

Temp. = $35 \pm 0.1°C$, $\lambda_{max} = 540$ nm

pH	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0
$\left(\dfrac{dA}{dt}\right)_i \times 10^3$	2.2	4.2	4.5	4.7	3.1	2.5	2.1	1.7

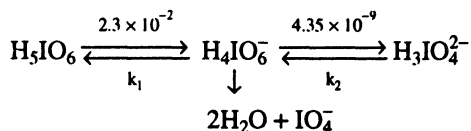### TABLE-6
[p-Tol] = 1.0×10^{-3} M, [NaIO$_4$] = 1.0×10^{-2} M, Acetone = 10% (v/v),
Temp. = $35 \pm 0.1°C$, $\lambda_{max} = 470$ nm

pH	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0
$\left(\dfrac{dA}{dt}\right)_i \times 10^3$	1.50	2.10	2.40	2.60	2.30	2.20	1.80	1.10

TABLE-7
DMT = 1.0×10^{-3} M, [NaIO$_4$] = 1.0×10^{-2} M, Acetone = 15% (v/v)
Temp. = $35 \pm 0.1°C$, $\lambda_{max} = 565$ nm

| pH	4.0	4.5	5.0	5.5	6.0	6.5	7.0
$\left(\dfrac{dA}{dt}\right)_i \times 10^3$	2.90	8.50	10.40	8.90	5.30	3.80	3.20

A perusal of the data reveals that for most of the amines the rate increases with an increase in pH and decreases on further increasing the pH. In this way a rate-maxima is obtained which corresponds to a definite pH value or range of pH. However, in case of the oxidation of aniline, rate goes on decreasing with an increase in pH.

This pH effect may be explained by the fact that the rate determining step in the expected mechanisms is a reaction between unprotonated amine and periodate monoanion, and thus the reaction rate will decrease when the concentration of either of these or both decreases. The concentration of periodate monoanion decreases with increasing pH after a pH of about 5.0 to 7.0 according to the following equilibria:

$$H_5IO_6 \xrightleftharpoons[k_1]{2.3 \times 10^{-2}} H_4IO_6^- \xrightleftharpoons[k_2]{4.35 \times 10^{-9}} H_3IO_4^{2-}$$
$$\downarrow$$
$$2H_2O + IO_4^-$$

after which dianion formation becomes predominant which is unreactive.

With the amines, the following equilibrium exists in the systems under study:

$$ArNR_2 + H_2O \rightleftharpoons Ar\overset{+}{N}RH + OH^-$$
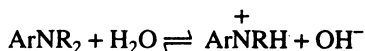
An increase in pH is expected to shift the equilibrium to right side and so the free [amine] is expected to increase which is probably the reason for an increase in the rate of reaction at comparatively lower pH values. The value of the pH, corresponding to the maximum rate observed, should shift to a lower value if the pK_a value of the amine is lesser. The results obtained in the case of aniline are in good agreement with this view as the pK_a for aniline is quite low in

comparison to the other amines. The same view is applicable to the behaviour shown by the other amines under present study as the value of maximum rate corresponds to higher pH value for the amines having higher pK_a value.

Periodate exists as IO_4^- around the pH $5-7^{2-7}$. Further, IO_4^- has been assumed to be the reactive species in some of these oxidation processes by earlier workers[3-7,11]. Hence, a decrease in the rate of reaction on increasing the pH after the rate maxima is observed, may be due to the fact that $[IO_4^-]$ goes on decreasing beyond these pH values..

The active species of periodate may be different at different pH values and so a number of reaction products are expected to be formed at different pH values. This is the fact which supports the earlier works of Tanabe[8-10].

It is important to note that the effect of pH on the rate of periodate oxidation of different aromatic amines under study has followed a common trend. The trend observed in the rate-pH profiles differs from earlier reports[2-6,11] on periodate oxidation of aniline, DMA, xylidines, and p-aminobenzoic acid. However, our studies are in good agreement with the results obtained by Pavolva et al[7]. Dolmanova et al.[13] also observed a similar effect for Mn catalysed and uncatalysed periodate oxidation of p-phenatidine.

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