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# Kinetics and Mechanism of Periodate Oxidation of N,N-Dimethylaniline and N,N-Diethylaniline

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The reaction was found to be second order being first order in each reactant *i.e.*, N,N-dimethylaniline (DMA) or N,N-diethylaniline (DEA) and the oxidant, periodate. The kinetics of the reaction has been followed by monitoring the increase in the absorbance of reaction intermediate, C. The rate law in accordance with the results under pseudo first order conditions, $[IO_4^-] >> [DMA \text{ or } DEA]$, is given by: $d[C]/dt = kKK_w [S] [IO_4^-]_0 [H^+]/\{K_2K_w + (K_w + K_bK_2) [H^+] + K_b[H^+]^2\}$, where kK = empirical composite rate constant, $K_w$ is ionic product of water, $K_2$ is acid dissociation constant of $H_4IO_6^-$, $K_b$ is base dissociation constant of aniline taken and $[IO_4^-]_0$ represents the concentration of periodate that has been taken in excess. In agreement with the rate law the $1/k_2$ *versus* $[H^+]$ profile passes through the minimum (where $k_2$ is second order rate constant). The rate of reaction remains unaffected by free radical scavengers and increases with increase in dielectric constant of the medium. Thermodynamic parameters evaluated are: Ea = 13.2 kcal $mol^{-1}$, A = $5.89 \times 10^9$ $dm^3$ $mol^{-1}$ $s^{-1}$; $\Delta S^\# = -16.2$ cal $mol^{-1}$ $K^{-1}$, $\Delta G^\# = 17.6$ kcal $mol^{-1}$ and $\Delta H^\# = 12.6$ kcal $mol^{-1}$ for DEA oxidation and Ea = 16.1 kcal $mol^{-1}$, A = $1.06 \times 10^{12}$ $dm^3$ $mol^{-1}$ $s^{-1}$; $\Delta S^\# = -6.32$ cal $mol^{-1}$ $K^{-1}$, $\Delta G^\# = 17.4$ kcal $mol^{-1}$ and $\Delta H^\# = 15.5$ kcal $mol^{-1}$ for DMA oxidation. Main reaction products of the periodate oxidation of DEA are O-ethylquinoneoxime and *p*-nitrosophenetole while these are O-methylquinoneoxime and *p*-nitrosoanisole for DMA oxidation.

**Key Words: Periodate oxidation, N,N-Diethylaniline, N,N-Dimethylaniline, O-Ethylquinoneoxime, *p*-Nitrosophenetole, O-Methylquinoneoxime, *p*-Nitrosoanisole.**

## INTRODUCTION

In continuation to our earlier reports[1-9], we are presenting the results of kinetics and mechanistic studies on periodate oxidation of N,N-dimethylaniline (DMA) and N,N-diethylaniline (DEA) in acetone-water medium including the unusual rate-pH profile observed.

## EXPERIMENTAL

Sodium metaperiodate (Loba Chemie), DEA and DMA (Sigma-Aldrich), acetone (E. Merck) and all other chemicals of analytical reagent/guaranteed reagent grade

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were used after redistillation/recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[10], consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH, measured on Systronics digital pH-meter-802. The reactions were studied in a spectrophotometric cell and initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing either DMA or DEA and buffer and maintained at the desired temperature (± 0.1 ºC).

**Procedure for kinetic studies:** The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV Pharmaspec-1700), at the $\lambda_{max}$ of the reaction mixture, 475 and 472 nm for DEA and DMA oxidation, respectively, only during the period in which it did not change. High precision thermostatically controlled water bath with an accuracy of ± 0.1 ºC was employed for maintaining the desired temperature.

**Product analysis:** The main reaction products were identified on the basis of UV-VIS and IR spectra and the earlier reports[2,11], as O-ethylquinoneoxime and *p*-nitrosophenetole for DEA oxidation and O-methylquinoneoxime and *p*-nitrosoanisole for DMA oxidation.

**Determination of stoichiometry of the reaction:** Stoichiometry of the reaction was determined by allowing a known excess of $NaIO_4$ to react with substrate. After completion of the reaction, the precipitated product was filtered out and in the filtrate, unconsumed $NaIO_4$ was determined iodimetrically. The results indicate the stoichiometry to be 1 mol DEA or DMA: 2 mol periodate for the initial part of the reaction.

## RESULTS AND DISCUSSION

On mixing the reactants in case of both, DEA and DMA, the solution becomes yellow which changes in to yellowish-green, than violet and than brown which changes in to a colourless solution. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. The rapid scan of the yellow solution showed the $\lambda_{max}$ of the intermediate C to be 475 and 472 nm for DEA and DMA oxidation, respectively. This yellow colour was not changing in to other colour during the period in which the kinetic studies were carried out in present studies. The UV-visible spectra of $IO_4^-$, DEA and DMA indicated these to show no absorption in visible region. Hence for following the kinetics the absorbance changes were recorded at 475 and 472 nm for DEA and DMA oxidation, respectively. Plane mirror and Guggenheim's methods, respectively were used for evaluation of initial rates in terms of change in absorbance with time and pseudo first order rate constants, $k_{obs}$.

The results of kinetic studies are given in Tables 1 and 2. The kinetics was studied under pseudo order conditions, *viz.*, $[IO_4^-]_0 >> [S]$ and $[S]_0 >> [IO_4^-]$ (where $[IO_4^-]_0$ and $[S]_0$ represent the initial concentrations of reactants in excess). Under

TABLE-1
EFFECT OF VARIATION OF CONCENTRATION OF REACTANTS, DIELECTRIC CONSTANT AND pH ON THE RATE OF OXIDATION OF DEA BY PERIODATE ION

| $[NaIO_4]$ (mol dm$^{-3}$) | [DEA] (mol dm$^{-3}$) | Acetone (v/v) % | Temp. ± 0.1 (°C) | pH | $k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|
| 0.0001 | 0.0010 | 10.0 | 30.0 | 7.0 | 3.84 |
| 0.0001 | 0.0015 | 10.0 | 30.0 | 7.0 | 3.58 |
| 0.0001 | 0.0020 | 10.0 | 30.0 | 7.0 | 3.45 |
| 0.0001 | 0.0025 | 10.0 | 30.0 | 7.0 | 3.38 |
| 0.0001 | 0.0030 | 10.0 | 30.0 | 7.0 | 3.33 |
| 0.0001 | 0.0035 | 10.0 | 30.0 | 7.0 | 3.29 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.92 |
| 0.002 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.86 |
| 0.003 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.79 |
| 0.004 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.72 |
| 0.005 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.69 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 5.5 | 0.42 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 6.0 | 0.62 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 6.5 | 1.12 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.92 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 7.5 | 4.80 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 8.0 | 2.64 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 8.5 | 1.39 |
| 0.001 | 0.0001 | 2.5 | 30.0 | 7.0 | 2.88 |
| 0.001 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.53 |
| 0.001 | 0.0001 | 7.5 | 30.0 | 7.0 | 2.27 |
| 0.001 | 0.0001 | 10.0 | 30.0 | 7.0 | 1.92 |

both these conditions the reaction displayed first order. The effect of pH was examined in the range 4.0-8.5. Rate-pH profile indicates a maximum at pH 7.5 and 6.5, which could be due to change in the nature of species and their relative reactivity when the pH is changed. An increase in dielectric constant increased the rate of reaction as indicated by a linear plot between log $k_2$ *versus* 1/D, where D = dielectric constant of the medium which indicates an ion-dipole type interaction in the rate-determining step and that the reacting ion is possibly an anion. Free radical scavengers acrylamide and allyl alcohol had no effect on the reaction rate.

Thermodynamic parameters as evaluated by studying the effect of temperature on reaction rate, are given in Tables 3 and 4.

**Rate law:** Before arriving at possible mechanism of the reaction between DMA or DEA and periodate ion, some of the observations have been considered. Initially, there is appearance of yellow colour which continues to darken with increase in the concentration of the intermediates, C and finally the product is formed on standing for long time. Obviously, the coloured intermediate is formed on a time scale of minutes and the final product on a time scale of hours. In reality the overall reaction involves several steps and possibly several transient intermediate in addition to comparatively stable one C, are formed during the oxidation of DEA or DMA (being commonly represented by DA here onwards) into products.

TABLE-2
EFFECT OF VARIATION OF CONCENTRATION OF REACTANTS, DIELECTRIC CONSTANT AND pH ON THE RATE OF OXIDATION OF DMA BY PERIODATE ION

| $[NaIO_4]$ (mol $dm^{-3}$) | [DMA] (mol $dm^{-3}$) | Acetone (v/v) % | Temp. ± 0.1 (ºC) | pH | $k_2$ ($dm^3$ $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| 0.0003 | 0.0030 | 5.0 | 30.0 | 7.0 | 1.05 |
| 0.0003 | 0.0035 | 5.0 | 30.0 | 7.0 | 1.01 |
| 0.0003 | 0.0040 | 5.0 | 30.0 | 7.0 | 0.99 |
| 0.0003 | 0.0045 | 5.0 | 30.0 | 7.0 | 0.97 |
| 0.0003 | 0.0050 | 5.0 | 30.0 | 7.0 | 0.94 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.61 |
| 0.0020 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.34 |
| 0.0030 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.18 |
| 0.0040 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.03 |
| 0.0050 | 0.0001 | 5.0 | 30.0 | 7.0 | 1.99 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 4.0 | 0.61 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 4.5 | 2.91 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 5.0 | 4.49 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 5.5 | 6.61 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 6.0 | 11.8 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 6.5 | 17.8 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.61 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.5 | 1.15 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 3.30 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 4.79 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 7.40 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 10.44 |
| 0.0010 | 0.0001 | 2.5 | 30.0 | 7.0 | 2.92 |
| 0.0010 | 0.0001 | 5.0 | 30.0 | 7.0 | 2.61 |
| 0.0010 | 0.0001 | 7.5 | 30.0 | 7.0 | 2.30 |
| 0.0010 | 0.0001 | 10.0 | 30.0 | 7.0 | 2.15 |

TABLE-3
ACTIVATION PARAMETERS FOR PERIODATE OXIDATION OF DEA IN ACETONE-WATER MEDIUM
$[DEA] \times 10^4 = 1$ mol $dm^{-3}$, $[NaIO_4] \times 10^3 = 1$ mol $dm^{-3}$,
acetone = 10 % (v/v), pH = 7, $\lambda_{max} = 475$ nm

| Temp. ± 0.1 (ºC) | $k_2$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | Ea (kcal $mol^{-1}$) | $A \times 10^{-9}$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | $-\Delta S^{\#}$ (cal $mol^{-1}$ $K^{-1}$) | $\Delta G^{\#}$ (kcal $mol^{-1}$) | $\Delta H^{\#}$ (kcal $mol^{-1}$) |
|---|---|---|---|---|---|---|
| 30.0 | 1.92 | 13.2 | 5.89 | 16.2 | 17.6 | 12.6 |
| 35.0 | 2.69 | | | | | |
| 40.0 | 3.80 | | | | | |
| 45.0 | 5.37 | | | | | |

Secondly, the kinetic order of one in periodate but requirement of the two periodate molecules for each DA molecule as per stoichiometry for the initial part of the reaction indicates the involvement of only one periodate ion in the rate determining step leading to the formation of intermediate C, whose kinetics has been followed in the study of this reaction. Obviously, second $IO_4^-$ ion is consumed in a fast reaction. It also indicates the yellow coloured intermediate is quite stable and its concentration is not in steady state. Had this been so, there should be no change in its concentration with time. On the contrary its concentration increases with time and reaches a limiting value. Thirdly $k_2$-pH profile indicates the presence of at least three different reactive reactant species in pH region chosen for study.

TABLE-4
Activation Parameters for periodate oxidation of DMA in acetone-water medium
$[DMA] \times 10^4 = 1$ mol dm$^{-3}$, $[NaIO_4] \times 10^3 = 4$ mol dm$^{-3}$,
acetone = 5 % (v/v), pH = 7, $\lambda_{max} = 472$ nm

| Temp. ± 0.1 (°C) | $k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$) | Ea (kcal mol$^{-1}$) | A × $10^{-12}$ (dm$^3$ mol$^{-1}$ s$^{-1}$) | $-\Delta S^\#$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta G^\#$ (kcal mol$^{-1}$) | $\Delta H^\#$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 30.0 | 2.61 | 16.1 | 1.06 | 6.32 | 17.4 | 15.5 |
| 35.0 | 4.07 | | | | | |
| 40.0 | 6.22 | | | | | |
| 45.0 | 9.12 | | | | | |

The stoichiometry for the initial part of the reaction (*i.e.*, upto the formation of quinoneimine 'C'), is given by eqn. 1.

$$C_6H_5(R)_2N + 2H^+ + 2IO_4^- \rightarrow C_6H_4ORN + ROH + 2HIO_3 \quad (1)$$

Assuming DA and $H_4IO_6^-$ as the reactive species and based on the observed kinetic data and pH-dependence, the following mechanism can be proposed:

$$DA + [IO_4^-] \xrightleftharpoons{K} [A] \quad (2)$$

$$[A] \xrightarrow{k} \text{Intermediate [B] (slow)} \quad (3)$$

$$[B] + IO_4^- \rightarrow \text{Intermediate [C] (fast)} \quad (4)$$

The intermediate, C, appear to undergo very slow reorganization/hydrolysis to yield the reaction product.

$$\text{Intermediate [C]} + IO_4^- \rightarrow \text{Product} \quad (5)$$

In the mechanism for simplicity, $H_4IO_6^-$ has been written as $IO_4^-$. Since the elementary reactions in liquid phase are a rareity, the formation of a transient intermediate [C], which could be a collisional complex/reactant pair in a rapid step having a low value of equilibrium constant, K, is assumed in the proposed gross mechanism.

The mechanistic steps (2-3) lead to the rate law:

$$d[C]/dt = k\,[A] \quad (6)$$

$$= kK[DA]\,[IO_4^-] \quad (7)$$

Since the observed kinetics shows first order in each of [DA] and $[IO_4^-]$, the value of K must be low. This can be proved as follows.

If $[IO_4^-]_0$ and $[S]_0$ represent the initial concentrations of reactants in excess, at a fixed pH, under the condition $[IO_4^-]_0 >> [S]$, the rate of formation of intermediate, C, is given by:

$$d[C]/dt = kK[IO_4^-]_{free}\ [S]_{free} \tag{8}$$

where $[IO_4^-]_{free}$ $[S]_{free}$ are the free concentration of two reactants. As $[IO_4^-]$ is in excess initially, its free concentration and initial concentration can be taken as almost the same.

$$d[C]/dt = kK[IO_4^-]_0\ [S]_{free} \tag{9}$$

If total concentration of substrate is represented by [S], then,

$$[S] = [S]_{free} + [S]_C \tag{10}$$

where $[S]_C$ = concentration used for formation of complex 'A'.

$$\text{Further, } [S]_C = [A] = K\ [S]_{free}\ [IO_4^-]_0 \tag{11}$$

From eqns. 10 and 11,

$$[S] = [S]_{free} + K\ [S]_{free}\ [IO_4^-]_0$$

or $$[S] = [S]_{free}\ (1 + K\ [IO_4^-]_0)$$

or $$[S]_{free} = [S]/(1 + K[IO_4^-]_0) \tag{12}$$

From eqns. 9 and 12,

$$d[C]/dt = kK[IO_4^-]_0[S]/(1 + K[IO_4^-]_0) \tag{13}$$

Likewise, under the condition $[S]_0 >> [IO_4^-]$

$$d[C]/dt = kK[IO_4^-]\ [S]_0/(1 + K[S]_0) \tag{14}$$

In eqns. 13 and 14, K must be very small to get $K[IO_4^-]_0$ or $K[S]_0$ negligible with respect to 1 and only then the order can be one in both reactants. As the order has been found experimentally one in each reactant, the value of K is very small.

Since the reaction shows first order in each of [S] and $[IO_4^-]$, the inequalities $K[IO_4^-]_0 << 1$ and $K[S]_0 << 1$ should operate in eqns. 13 and 14, respectively leading to the rate laws in eqns. 15 and 16.

$$d[C]/dt = k_2[IO_4^-][S]_0 \tag{15}$$

where $k_2$ is a pH-dependent second order rate constant and $k_{obs} = k_2[S]_0$.

$$d[C]/dt = k_2[IO_4^-]_0[S]\ (\text{where } k_{obs} = k_2[IO_4^-]_0 \tag{16}$$

**Complete rate law including [H$^+$] dependence:** The speciation of periodate and DA should be considered first.

Speciation of periodate ion:

$$H_5IO_6 \rightleftharpoons H_4IO_6^-, \qquad K_1 = 2.3 \times 10^{-2} \tag{17}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-}, \qquad K_2 = 4.35 \times 10^{-9} \tag{18}$$

Total concentration of periodate, $[IO_4^-]$ is sum of $[H_5IO_6]$, $[H_4IO_6^-]$ and $[H_3IO_6^{2-}]$, *i.e.*, $[IO_4^-] = [H_5IO_6] + [H_4IO_6^-] + [H_3IO_6^{2-}]$.

From equilibria (17) and (18)

$$[IO_4^-] = \{[H_4IO_6^-][H^+]/K_1\} + [H_4IO_6^-] + \{K_2[H_4IO_6^-]/[H^+]\} \tag{19}$$

$$[IO_4^-] = [H_4IO_6^-]\{[H^+]/K_1 + 1 + K_2/[H^+]\} \tag{20}$$

On substituting $[H^+] = 10^{-6}\text{-}10^{-9}$ (pH = 6-9) and $K_1 = 2.3 \times 10^{-2}$ in eqn. 20, we get

$$[IO_4^-] = [H_4IO_6^-][(4 \times 10^{-5}\text{-}4 \times 10^{-8}) + 1 + (4.35 \times 10^{-3}\text{-}4.35)].$$

So $[H^+]/K_1$ term is negligible in eqn. 20 as compared to two other terms. On neglecting $[H^+]/K_1$ in eqn. 20, we get

$$[IO_4^-] = [H_4IO_6^-]\ (1+ K_2/[H^+])$$

$$\text{or}\qquad [IO_4^-] = \{[H_4IO_6^-]([H^+] + K_2)\}/[H^+]$$

$$\text{or}\qquad [H_4IO_6^-] = [IO_4^-]\,[H^+]/([H^+] + K_2) \tag{21}$$

Speciation of DA:

$$DA + H_2O \rightleftharpoons DAH^+ + OH^- \tag{22}$$

($K_b = 14.1 \times 10^{-10}$ for DMA and $3.63 \times 10^{-8}$ for DEA[12])

Similarly from eqn. 22, the total concentration of the substrate, [S] is given by

$$[S] = [DA] + [DAH^+]$$
$$[S] = [DA] + K_b[DA]/[OH^-]$$
$$[S] = [DA]\,(1 + K_b/[OH^-])$$
$$[S] = \{[DA]\,([OH^-] + K_b)\}/[OH^-]$$

Reactive free [DA] is given by

$$[DA] = [S][OH^-]/\{[OH^-] + K_b\} \tag{23}$$

The rate is given by,

$$\text{Rate} = kK[DA][H_4IO_6^-]\ (\text{where } [H_4IO_6^-] = [IO_4^-]) \tag{7}$$

Under the condition when oxidant is taken in excess and on substituting the values of [DA] and $[H_4IO_6^-]$ from eqns. 21 and 23 in to eqn. 7,

$$\text{Rate} = kK\Big([S][OH^-]/\{[OH^-] + K_b\}\Big)\Big([IO_4^-]_0\,[H^+]/([H^+] + K_2)\Big) \tag{24}$$

$$\text{or}\qquad \text{Rate} = kK\{[S][OH^-]/[OH^-] + K_b\}\{[IO_4^-]_0\,[H^+]/[H^+] + K_2\}$$

$$\text{or}\qquad \text{Rate} = kK[S][OH^-][IO_4^-]_0[H^+]/\Big(\{[OH^-] + K_b\}([H^+] + K_2)\Big) \tag{25}$$

On putting, $K_w = [OH^-]\,[H^+]$ in numerator in eqn. 25,

$$\text{Rate} = kK\,K_w[S][IO_4^-]_0/\Big(([OH^-] + K_b)([H^+] + K_2)\Big) \tag{26}$$

$$\text{or}\qquad \text{Rate} = kKK_w[S]\,[IO_4^-]_0/\{[OH^-][H^+] + [OH^-]K_2 + K_b[H^+] + K_2K_b\}$$

Putting $[OH^-] = Kw/[H^+]$ and $[H^+]\,[OH^-] = K_w$ in denominator,

$$\text{Rate} = kKK_w[S]\,[IO_4^-]_0/\{K_w + (K_wK_2/[H^+]) + K_b[H^+] + K_2K_b\} \tag{27}$$

Multiplying by $[H^+]$ in numerator and denominator,

$$\text{Rate} = kKK_w[S][IO_4^-]_0[H^+]/\{K_w[H^+] + K_wK_2 + K_b[H^+]^2 + K_2K_b[H^+]\} \tag{28}$$

On rearranging eqn. 28,

$$\text{Rate} = kKK_w[S][IO_4^-]_0[H^+]/\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} \tag{29}$$

where kK is the empirical composite rate constant, $K_w$ is ionic product of water, $K_2$ is acid dissociation constant of $H_4IO_6^-$, $K_b$ is base dissociation constant of DA.

Comparing eqn. 29 with eqn. 16, we get,

$$k_2[IO_4^-]_0[S] = kKK_w[S][IO_4^-]_0[H^+]/\{K_wK_2 + [H^+]\,(K_w + K_2K_b) + K_b[H^+]^2\}$$

$$\text{or}\qquad k_2 = kKK_w[H^+]/\{K_wK_2 + [H^+]\,(K_w + K_2K_b) + K_b[H^+]^2\} \tag{30}$$

Eqn. 30 on rearranging becomes eqn. 31

$$1/k_2 = \{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\}/kKK_w[H^+] \tag{31}$$

$$\text{or}\qquad 1/k_2 = \{K_wK_2/kKK_w[H^+]\} + \{[H^+](K_w + K_2K_b)/kKK_w[H^+]\} + \{K_b[H^+]^2/kKK_w[H^+]\}$$

$$\text{or}\qquad 1/k_2 = \{K_2/kK[H^+]\} + \{K_w + K_2K_b)/kKK_w\} + \{K_b[H^+]/kKK_w\} \tag{32}$$

Putting $1/k_2 = L$, eqn. 32 reduces to the following form,

$$L = \{K_2/kK[H^+]\} + \{K_w + K_2K_b)/kKK_w\} + \{K_b[H^+]/kKK_w\}$$

Differentiating this eqn with respect to $[H^+]$,

$$dL/d[H^+] = -K_2/kK[H^+]^2 + 0 + K_b/kKK_w \quad (33)$$

For minimum or maximum value of L (*i.e.*, $1/k_2$), $dL/d[H^+] = 0$

Therefore, from eqn. 33 we have,

$$0 = -K_2/kK[H^+]^2 + K_b/kKK_w$$

or $$K_2/kK[H^+]^2 = K_b/kKK_w$$

or $$K_2/[H^+]^2 = K_b/K_w$$

or $$[H^+]^2 = K_2K_w/K_b$$

or $$[H^+] = [K_2K_w/K_b]^{1/2} \quad (34)$$

This is the desired equation for predicting the minima or maxima in $1/k_2$ *versus* $[H^+]$ plot. Now for finding out whether a minima or maxima will be obtained, the value of second derivative *i.e.*, $d^2[1/k_2]/d[H^+]^2$ should be obtained. If the value of second derivative is positive then the plot of $1/k_2$ *versus* $[H^+]$ shall pass through a minimum. The following treatment should be applied for getting the value of second derivative:

Differentiating the eqn. 33 again with respect to $[H^+]$,

$$d^2L/d[H^+]^2 = 2K_2/kK[H^+]^3$$

This value of $d^2L/d[H^+]^2$ is positive, so we will get minima at $[H^+] = [K_2K_w/K_b]^{1/2}$.

Or we can say that L (*i.e.*, $1/k_2$) is minimum when $[H^+] = [K_2K_w/K_b]^{1/2}$.

or $$[H^+]_{min.} = (K_2K_w/K_b)^{1/2} \quad (35)$$

On substituting the values of $K_2$, $K_w$ and $K_b$, we get

$$[H^+]_{min} = 3.46 \times 10^{-8} \text{ mol dm}^{-3} \text{ (for DEA oxidation)} \quad (36)$$

$$[H^+]_{min} = 1.93 \times 10^{-7} \text{ mol dm}^{-3} \text{ (for DMA oxidation)} \quad (37)$$

In present observations, the $k_2$-pH profile (Table-1) indicates a maxima at pH = 7.5 corresponding to $[H^+]_{min}$ of $3.16 \times 10^{-8}$ mol dm$^{-3}$ for DEA oxidation and at pH = 6.5 corresponding to $[H^+]_{min}$ of $3.16 \times 10^{-7}$ mol dm$^{-3}$ for DMA oxidation. Thus, the calculated values of $[H^+]_{min}$ are in excellent agreement with the experimental values. Present results are also in accordance with the earlier report by Gupta and Gupta[13] for other systems of this type.

**Molecular mechanism:** It is necessary to discuss the possible molecular mechanism of the reaction. The mechanism is similar to our earlier reports for other aromatic amines[5-9,16,17]. First step of mechanism can be assumed as a reversible bimolecular reaction between DA and $[IO_4^-]$. The formation of a charged intermediate complex [A] taking place by the attack of $[IO_4^-]$ on the nitrogen of anilino group and stabilization of positive charge on this nitrogen are well supported by our earlier studies related to the effect of substituents on reaction rate and isokinetic relationship for this type of reaction series[5,14,15]. The negative value of entropy of activation supports the involvement of solvation effects in this reaction. The formation of another intermediate [B] followed by its reaction with another $IO_4^-$ to form quinoneimine [C] in a fast step are the expected steps of the mechanism involved. The last step (5) seems to be the slow reaction of (C) with another periodate molecule to give final product (D)- a mixture of tautomers, that has been isolated, separated and characterized.

The proposed mechanism satisfies the observed kinetic data *i.e.*, order of reaction, high negative value of $\Delta S^{\#}$ which is suggestive of the involvement of solvent interactions and probability that the transition state is solvated. Earlier studies[5,14,15] suggesting the stabilization of positive charge on the activated complex, effect of dielectric constant of medium which suggests the ion-dipole interaction and stoichiometry of the reaction. $IO_4^-$ has been assumed as the oxidizing species in the light of the fact that the present studies were conducted at pH 7.0 and $IO_4^-$ is the reactive species[1-9] in the pH range 5-7.

It is important to point out that Pavolva *et al.*[11] have reported a free radical mechanism for the uncatalyzed periodate oxidation of N,N-diethylaniline in contrast to the conclusions on the basis of the present studies. As stated earlier, we have observed no effect of the free radical scavengers like acryl amide and allyl alcohol on the reaction rate. In addition, it is observed a clear negative effect of solvent in this reaction. Therefore, the ion-dipole type mechanism has been proposed in contrast to the work of Pavolva *et al.*[11]. The reason may be that if solutions of periodate are irradiated and not used a fresh, there is possibility of presence of free radicals that may alter the mechanistic pathway. Pavolva *et al.*[11] have studied the reaction in presence of light while in present case, the reaction vessels were painted black on outer surface to avoid the effect of light on the rate of reaction. Furthermore, the colour change observed by them, was initially yellow colour changing into yellowish green which finally converts into gray-black colour followed by precipitation. It is different from present observation in which initial yellow colour was found changing into yellowish green and than violet and finally changing into brown which becomes colourless after about 24 h. It is also suggestive of different mechanism being obeyed in present case.

It is also important to note that in the earlier report of Srivastava *et al.*[1], on kinetics and mechanism of the reaction between N,N-dimethylaniline and periodate, the studies were made at the absorption maxima of reaction mixture at 560 nm corresponding to the formation of violet coloured reaction product. As stated earlier, this colour formation represents the 2nd stage of the reaction under consideration. Therefore, Srivastava *et al.*, actually, reported the results of studies made on the second part of the reaction and not the initial part of the reaction which is impotant from kinetics point of view. We have been able to develop the conditions suitable for studying the kinetics of the initial part of this reaction represented by the formation of yellow coloured product (the absorption maxima of reaction mixture being 472 nm). This yellow coloured product changes into violet colour in later part of reaction that was not studied here as the later part of reaction is kinetically insignificant.

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