

Periodate oxidation of aromatic amines – Modelling for the effect of pH on reaction rate

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ABSTRACT

Using kinetic features and the product identification for the periodate oxidation of aromatic amines in general and o-anisidine in particular, the effect of pH on the reaction rate has been explained by kinetic modelling. An attempt has been made in this article to present the mathematical steps in a simple way clarifying all steps using basic mathematical equations so that a person with only basic knowledge of mathematics can understand the steps.

1. Introduction

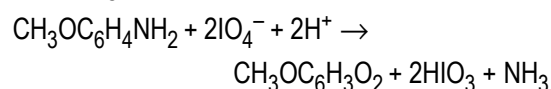
The oxidation of aromatic amines is important for degradation/removal of these pollutants from industrial effluents. There are many reports available for the oxidation of aromatic amines by periodate ion in catalyzed/uncatalyzed condition [1–13]. This article aims at providing knowledge about the modelling of these (uncatalyzed) reactions using kinetic and other features by taking the example of periodate oxidation of o-anisidine [12–13], with special attention to the unique rate-pH profile obtained in these non-Malapradian oxidation reactions.

2. Features of the reactions under consideration

The summary of features of this reaction as already worked out in separate experimental studies [1–13], is as follows:

1. The reaction is first order in substrate and oxidant each.
2. There is no effect of free radical scavengers on the reaction rate.
3. There is no appreciable effect of ionic strength and dielectric constant of the medium on the reaction rate.
4. The thermodynamic parameters like Entropy of activation, Activation energy, Free energy of activation, Arrhenius frequency factor and Enthalpy of activation suggest the solvation is playing important role in the reaction.
5. Taking the oxidation of o-anisidine as a representative

case, the stoichiometry has been found to be 1 mol amine: 2 moles periodate for the initial stage of the reaction given below.



6. The molecular mechanism is given in chart.
7. $1/k_2$ versus $[\text{H}^+]$ plot indicated a minima at a pH value that differs in case of different amines (Fig. 1). The value of minima relates to the Dissociation constant of the aromatic amine under consideration.
8. The reaction mixture shows colour changes followed by precipitation.
9. The main product of the reaction are quinoneimines and substituted benzoquinones.
10. The rate law, respectively for uncatalysed reactions, is given below:

$$d[\text{C}]/dt = kK_w[\text{S}][\text{IO}_4^-]_0[\text{H}^+]/\{K_2K_w + (K_w + K_bK_2)[\text{H}^+] + K_b[\text{H}^+]^2\}$$

where kK and kK_3K_4 are the empirical composite rate constants for uncatalysed and catalysed reactions, K_w is ionic product of water, K_2 is acid dissociation constant of H_4IO_6^- , S is the aromatic amine and K_b is base dissociation constant of aromatic amine.

In present article, we shall focus only on the uncatalyzed reactions.

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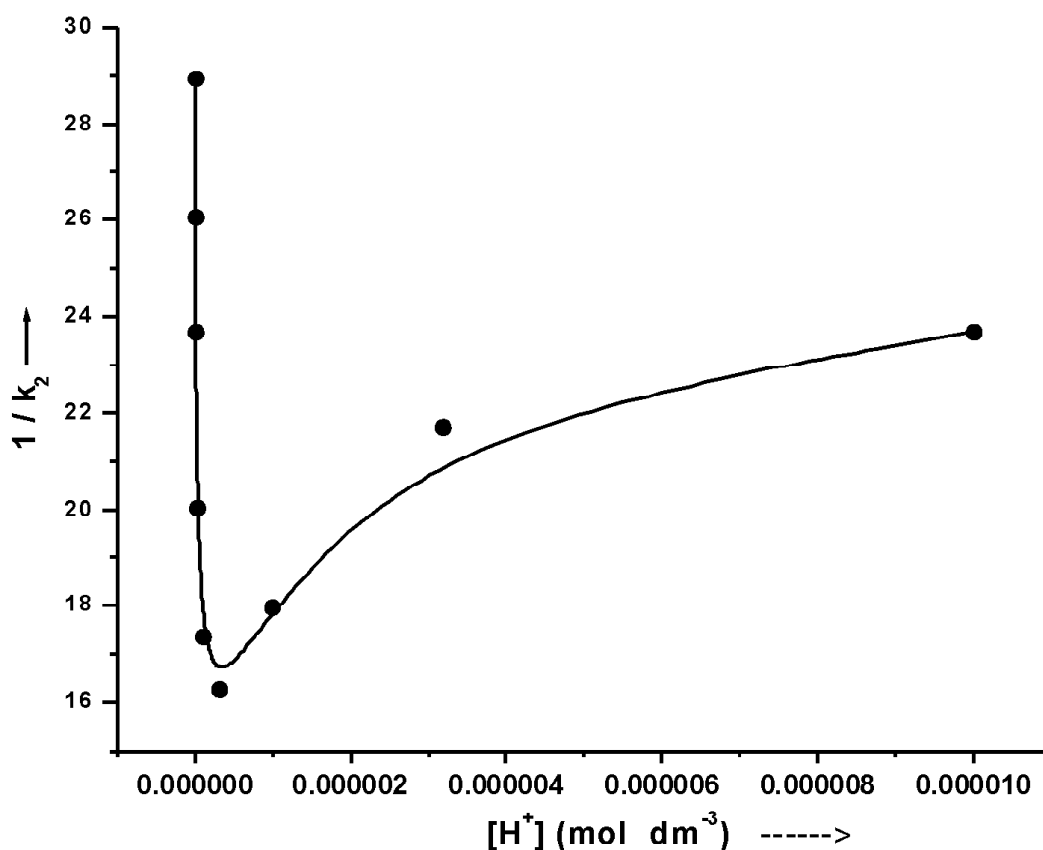
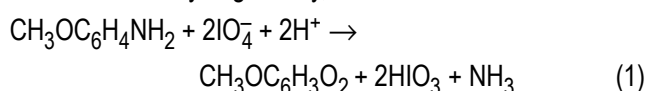


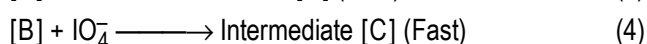
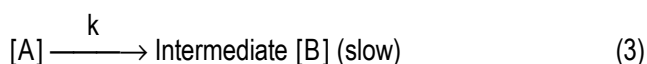
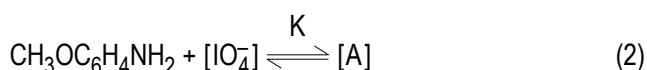
Fig. 1. Effect of $[H^+]$ on reaction rate at $[NaIO_4] = 0.001 \text{ mol dm}^{-3}$, $[OMA] = 0.01 \text{ mol dm}^{-3}$, acetone = 10% (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$.

2.1. Derivation of rate law:

The stoichiometry is given by,



Assuming $\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2$ and H_4IO_6^- as the reactive species and based on the observed kinetic data and pH-dependence, the following mechanism can be proposed:



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



In the mechanism for simplicity, H_4IO_6^- has been written as IO_4^- . Since the elementary reactions in liquid phase are a rarity, 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:

$$d[\text{C}]/dt = k[\text{A}] \quad (6)$$

$$= kK[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2][\text{IO}_4^-] \quad (7)$$

Since the observed kinetics shows first order in each of $[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2]$ and $[\text{IO}_4^-]$, the value of K must be low.

Since the observed kinetics shows first order in each of $[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2]$ and $[\text{IO}_4^-]$, the value of K must be low. This can be proved as described below.

If $[\text{IO}_4^-]_0$ and $[\text{S}]_0$ represent the initial concentrations of reactants in excess, at a fixed pH, under the condition $[\text{IO}_4^-]_0 \gg [\text{S}]$, the rate of formation of intermediate, C, is given by:

$$d[\text{C}]/dt = kK [\text{IO}_4^-]_{\text{free}} [\text{S}]_{\text{free}} \quad (8)$$

As $[\text{IO}_4^-]$ is in excess initially. Therefore, its free concentration and initial concentration can be taken as almost the same. Further representing the excess initial concentration of IO_4^- by $[\text{IO}_4^-]_0$, we get,

$$d[\text{C}]/dt = kK [\text{IO}_4^-]_0 [\text{S}]_{\text{free}} \quad (9)$$

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

$$[S] = [S]_{\text{free}} + [S]_{\text{C}} \quad (10)$$

where $[S]_{\text{C}}$ is the concentration used for formation of complex 'A'.

$$\text{Further, } [S]_{\text{C}} = [A] = K[S]_{\text{free}} [\text{IO}_4^-]_0 \quad (11)$$

From eqs. (9) and (10),

$$[S] = [S]_{\text{free}} + K[S]_{\text{free}} [\text{IO}_4^-]_0$$

Or

$$[S] = [S]_{\text{free}} (1 + K[\text{IO}_4^-]_0)$$

Or

$$[S]_{\text{free}} = [S] / (1 + K[\text{IO}_4^-]_0) \quad (12)$$

From eqs. (9) and (12),

$$d[C] / dt = kK[\text{IO}_4^-]_0 [S] / (1 + K[\text{IO}_4^-]_0) \quad (13)$$

Likewise, under the condition $[S]_0 \gg [\text{IO}_4^-]$

$$d[C] / dt = kK[\text{IO}_4^-] [S]_0 / (1 + K[S]_0) \quad (14)$$

In eqs. (13) and (14), K must be very small to get $K[\text{IO}_4^-]_0$ or $K[S]_0$ negligible w.r.t.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 $[\text{IO}_4^-]$, the inequalities $K[S]_0 \gg 1$ and $[\text{IO}_4^-] \gg 1$ should operate in eqs. (13) and (14), respectively leading to the rate laws in eqs. (15) and (16).

$$d[C] / dt = k_2 [\text{IO}_4^-] [S]_0 \quad (15)$$

where k_2 is a pH-dependent second order rate constant.

On the other hand, under the condition $[S]_0 \gg [\text{IO}_4^-]$, the rate was defined by eq. (iii) and k_{obs} was equal to $k_2 [\text{IO}_4^-]_0$.

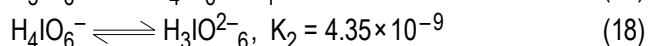
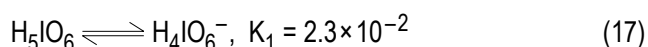
$$d[C] / dt = k_2 [\text{IO}_4^-] [S]_0 \quad (16)$$

The values of k_2 determined from k_{obs} values indicate a clear cut first order in each of periodate and aniline.

2.2. Derivation of complete rate law including $[H^+]$ dependence and explanation for the effect of pH on reaction rate:

Speciation of substrate and the oxidant are to be taken into consideration.

Speciation of Periodate ion:



Total concentration of periodate, $[\text{IO}_4^-]$ is sum of $[\text{H}_5\text{IO}_6]$, $[\text{H}_4\text{IO}_6^-]$ and $[\text{H}_3\text{IO}_6^{2-}]$, i.e.,

$$[\text{IO}_4^-] = [\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^-] + [\text{H}_3\text{IO}_6^{2-}]$$

From equilibria (17) and (18)

$$[\text{IO}_4^-] = \{[\text{H}_4\text{IO}_6^-] [\text{H}^+] / K_1\} + [\text{H}_4\text{IO}_6^-] + \{K_2 [\text{H}_4\text{IO}_6^-] / [\text{H}^+]\} \quad (19)$$

$$[\text{IO}_4^-] = [\text{H}_4\text{IO}_6^-] \{[\text{H}^+] / K_1 + 1 + K_2 / [\text{H}^+]\} \quad (20)$$

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

$$[\text{IO}_4^-] = [\text{H}_4\text{IO}_6^-] [(4 \times 10^{-5} \text{ to } 4 \times 10^{-8}) + 1 + (4.35 \times 10^{-3} \text{ to } 4.35)].$$

So $[\text{H}^+] / K_1$ term is negligible in eq. (4) as compared to two other terms. [Note: It will not be negligible even at pH 3, 4 or 5]

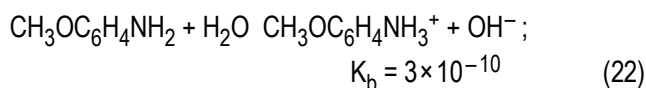
On neglecting $[\text{H}^+] / K_1$ in eq. (20), we get

$$[\text{IO}_4^-] = [\text{H}_4\text{IO}_6^-] (1 + K_2 / [\text{H}^+])$$

$$\text{Or } [\text{IO}_4^-] = \{[\text{H}_4\text{IO}_6^-] ([\text{H}^+] + K_2)\} / [\text{H}^+]$$

$$\text{Or } [\text{H}_4\text{IO}_6^-] = [\text{IO}_4^-] [\text{H}^+] / ([\text{H}^+] + K_2) \quad (21)$$

Speciation of Aniline:



Similarly from equilibrium (6), the total concentration of the substrate [S] is given by

$$[S] = [\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] + [\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_3^+]$$

$$\text{Or, } [S] = [\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] + K_b [\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] / [\text{OH}^-]$$

$$\text{Or, } [S] = [\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] (1 + K_b / [\text{OH}^-])$$

$$\text{Or } [S] = \{[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] ([\text{OH}^-] + K_b)\} / [\text{OH}^-]$$

Reactive free $[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2]$ is given by

$$[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] = [S] [\text{OH}^-] / \{[\text{OH}^-] + K_b\} \quad (23)$$

Complete rate law including $[H^+]$ dependence:

The rate is given by

$$\text{Rate} = kK[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2] [\text{H}_4\text{IO}_6^-] \quad (7)$$

where $[\text{H}_4\text{IO}_6^-] = [\text{IO}_4^-]$

Under the condition **when substrate is taken in excess**, and on substituting the values of $[\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2]$ and $[\text{H}_4\text{IO}_6^-]$ from eqs. (21) and (23) in to eqn. (7),

$$\text{Rate} = kK([\text{S}_0] [\text{OH}^-] / \{[\text{OH}^-] + K_b\}) ([\text{IO}_4^-] [\text{H}^+] / ([\text{H}^+] + K_2)) \quad (24)$$

Or

$$\text{Rate} = kK\{[\text{S}_0] [\text{OH}^-] / ([\text{OH}^-] + K_b)\} \{[\text{IO}_4^-] [\text{H}^+] / ([\text{H}^+] + K_2)\}$$

Or

$$\text{Rate} = kK[\text{S}_0] [\text{OH}^-] [\text{IO}_4^-] [\text{H}^+] / (\{[\text{OH}^-] + K_b\} ([\text{H}^+] + K_2)) \quad (25)$$

On putting, $K_w = [\text{OH}^-][\text{H}^+]$ in numerator in eq. (25),

$$\text{Rate} = kK_w[S]_0[\text{IO}_4^-] / (([\text{OH}^-] + K_b)([\text{H}^+] + K_2)) \quad (26)$$

Or

$$\text{Rate} = kK_w[S]_0[\text{IO}_4^-] / \{[\text{OH}^-][\text{H}^+] + [\text{OH}^-]K_2 + K_b[\text{H}^+] + K_2K_b\}$$

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

$$\text{Rate} = kK_w[S]_0[\text{IO}_4^-] / \{K_w + (K_wK_2 / [\text{H}^+]) + K_b[\text{H}^+] + K_2K_b\} \quad (27)$$

Multiplying by $[\text{H}^+]$ in numerator and denominator,

$$\text{Rate} = kK_w[S]_0[\text{IO}_4^-][\text{H}^+] / \{K_w[\text{H}^+] + K_wK_2 + K_b[\text{H}^+]^2 + K_2K_b[\text{H}^+]\} \quad (28)$$

On rearranging eqn. 28,

$$\text{Rate} = kK_w[S]_0[\text{IO}_4^-][\text{H}^+] / \{K_wK_2 + [\text{H}^+](K_w + K_2K_b) + K_b[\text{H}^+]^2\} \quad (29)$$

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 aniline and $[S]_0$ represents the concentration of aniline that has been taken in excess.

Comparing eqn. (29) with eqn. (15), we get,

$$k_2[\text{IO}_4^-][S]_0 = kK_w[S]_0[\text{IO}_4^-][\text{H}^+] / \{K_wK_2 + [\text{H}^+](K_w + K_2K_b) + K_b[\text{H}^+]^2\}$$

Or

$$k_2 = kK_w[\text{H}^+] / \{K_wK_2 + [\text{H}^+](K_w + K_2K_b) + K_b[\text{H}^+]^2\} \quad (30)$$

Equation (30) on rearranging becomes eqn. (31)

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

Or

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

Or

$$1/k_2 = \{K_2/kK[\text{H}^+]\} + \{K_w + K_2K_b\} / kK_w + \{K_b[\text{H}^+] / kK_w\} \quad (32)$$

The nature of the rate law (32) shows that a plot of $1/k_2$ versus $[\text{H}^+]$ shall pass through a minimum as discussed in a review by Gupta and Gupta [14].

2.3. Differentiation of $1/k_2$ with respect to $[\text{H}^+]$ as mentioned above for arriving at final relation $[\text{H}^+]_{\text{min}} = (k_2K_w / k_b)^{1/2}$ and obtaining the conditions of minimum in $1/k_2$ vs $[\text{H}^+]$ profile

Note: The formulas involved are as follows:

1. General formula is, $d/dx(x^n) = nx^{n-1}$

Therefore,

$$d/dx(1/x) = d/dx(x^{-1}) = -x^{-1-1} = -x^{-2} = -1/x^2$$

And

$$d/dx(1/x^2) = d/dx(x^{-2}) = -2x^{-2-1} = -2x^{-3} = -2/x^3$$

$$2. d/dx(a + bx + cx^3)^2 = \{d/d(a + bx + cx^3)\}$$

$$\{(a + bx + cx^3)^2 [d/dx(a + bx + cx^3)]\}$$

$$= [2(a + bx + cx^3)] [d/dx(a) + d/dx(bx) + d/dx(cx^3)]$$

$$= [2(a + bx + cx^3)] [0 + b + 3cx^2]$$

$$3. \lim_{x \rightarrow 0} \frac{1}{x} \text{ means } 1/x = \infty$$

$$x \rightarrow 0$$

$$4. x/y = 0 \text{ means, } x = 0$$

5. If differentiation coefficient is represented by d.c., Numerator by N, and denominator by D, then,

$$\text{d.c. of } (N/D) = \frac{D \text{ d.c. of } N - N \text{ d.c. of } D}{(D)^2}$$

Differentiation of $1/k_2$ with respect to $[\text{H}^+]$:

We have

$$1/k_2 = \{K_2/kK[\text{H}^+]\} + \{K_w + K_2K_b\} / kK_w + \{K_b[\text{H}^+] / kK_w\} \quad (32)$$

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

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

Differentiating this eqn. w.r.t. $[\text{H}^+]$,

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

For minimum or maximum value of L (i.e. $1/k_2$), $dL/d[\text{H}^+] = 0$
Therefore, from eqn. (33) we have,

$$0 = -K_2/kK[\text{H}^+]^2 + K_b/kK_w$$

Or

$$K_2/kK[\text{H}^+]^2 = K_b/kK_w$$

Or

$$K_2/[\text{H}^+]^2 = K_b/K_w$$

Or

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

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

Differentiating the eqn. (33) again w. r. t. $[H^+]$,

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

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

$$[H^+]_{\min} = 3.8 \times 10^{-7} \text{ mol dm}^{-3}$$

It is gratifying to note that the calculated value of $[H^+]_{\min}$ is in excellent agreement with the experimental value of $[H^+]_{\min}$ of $3.16 \times 10^{-7} \text{ mol dm}^{-3}$ obtained from $1/k_2$ versus $[H^+]$ plot (Fig. 1). Also, $1/k_2 - [H^+]$ profile will show a minimum.

2.4. Differentiation of k_2 with respect to $[H^+]$ as mentioned above for arriving at final relation $[H^+]_{\min} = (k_2k_w/k_b)^{1/2}$ and obtaining the conditions of maximum in $k_2 - [H^+]$ profile

Eqn. (30) is,

$$k_2 = kKK_w[H^+]/\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} \quad (30)$$

Differentiating w. r. t. H^+ , using formula – 5 as given earlier, $dk_2/d[H^+] =$

$$\frac{\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} kKK_w - kKK_w[H^+]\{(K_w + K_2K_b) + 2K_b[H^+]\}}{\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\}^2} \quad (36)$$

For getting minimum or maximum value of k_2 , The value of $dk_2/d[H^+]$ should be set equal to 0, and using formula – 4 (i.e. if $x/y = 0$, then the numerator is zero),

$$\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} kKK_w - kKK_w[H^+]\{(K_w + K_2K_b) + 2K_b[H^+]\} = 0 \quad (37)$$

Or

$$kKK_w[\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} - [H^+]\{(K_w + K_2K_b) + 2K_b[H^+]\}] = 0 \quad (38)$$

Or

$$[\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} - [H^+]\{(K_w + K_2K_b) + 2K_b[H^+]\}] = 0/kK_bK_w = 0 \quad (39)$$

Or

$$\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} - [H^+]\{(K_w + K_2K_b) + 2K_b[H^+]\} = 0 \quad (40)$$

Or

$$K_wK_2 + K_b[H^+]^2 - 2K_b[H^+]^2 = 0 \quad (41)$$

Or

$$K_wK_2 - K_b[H^+]^2 = 0 \quad (42)$$

Or

$$[H^+]^2 = K_2K_w/K_b \quad (43)$$

Or

$$[H^+] = [K_2K_w/K_b]^{1/2} \quad (44)$$

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

Eqn. (31) is,

$$\frac{\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} kKK_w - kKK_w[H^+]\{(K_w + K_2K_b) + 2K_b[H^+]\}}{\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\}^2}$$

Putting $K_wK_2 = a$, $kKK_w = b$, and $K_w + K_2K_b = c$

$$\frac{\{a + [H^+]c + K_b[H^+]^2\} b - b[H^+]\{c + 2K_b[H^+]\}}{\{a + [H^+]c + K_b[H^+]^2\}^2} \quad (45)$$

Or

$$\frac{ab + bc[H^+] + bK_b[H^+]^2 - bc[H^+] - 2bK_b[H^+]^2}{\{a + [H^+]c + K_b[H^+]^2\}^2} \quad (46)$$

Or

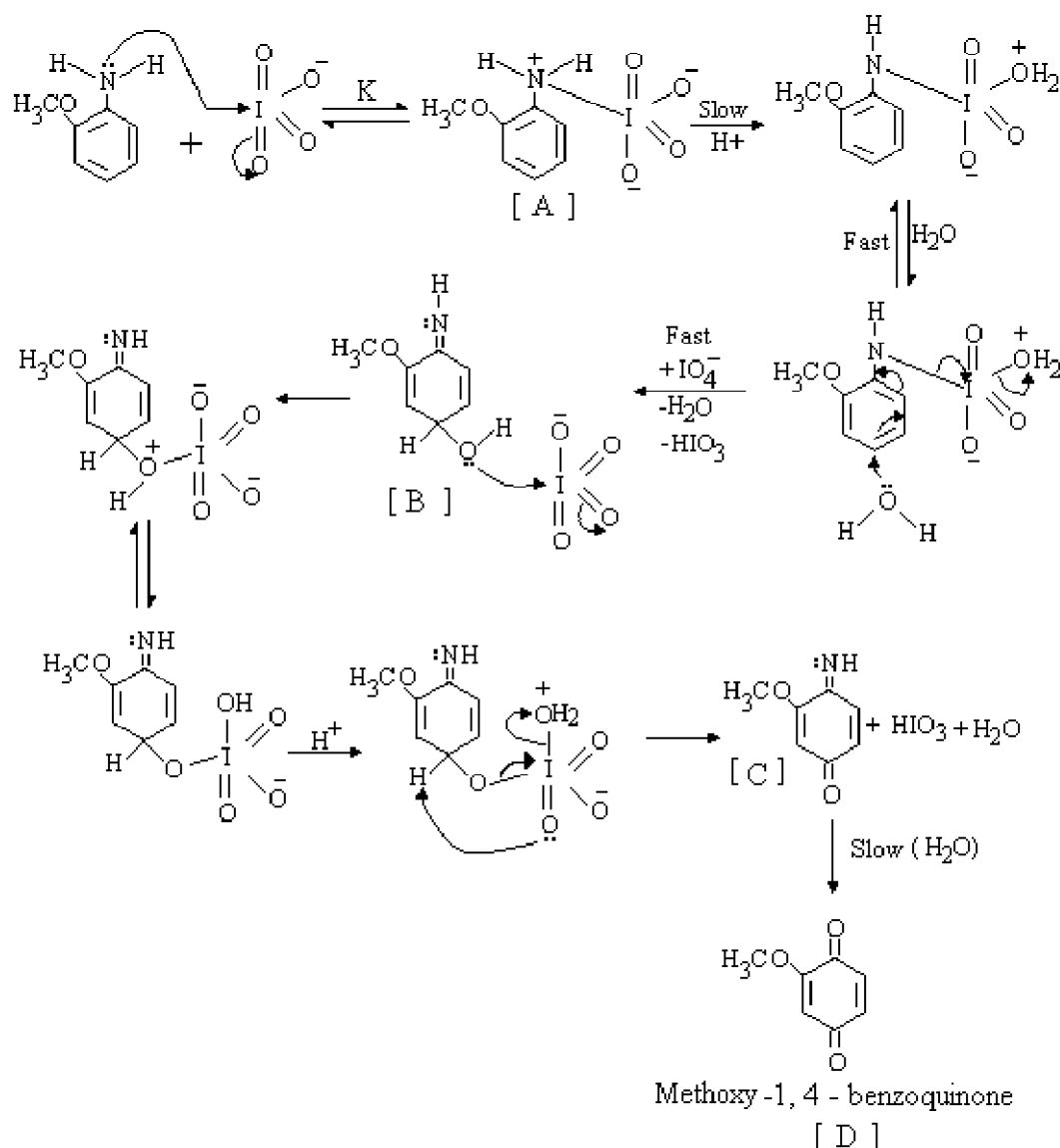
$$\frac{ab - bK_b[H^+]^2}{\{a + c[H^+] + K_b[H^+]^2\}^2} \quad (47)$$

Differentiating again w.r.t. $[H^+]$ (using formula –5 and 2),

$$\frac{0 - 2bK_b[H^+]\{a + c[H^+] + K_b[H^+]^2\}^2 - \{ab - bK_b[H^+]^2\}^2\{a + c[H^+] + K_b[H^+]^2\}}{\{0 + c + 2K_b[H^+]\} \{a + c[H^+] + K_b[H^+]^2\}^4} \quad (48)$$

Here in the numerator, in the term $-\{ab - bK_b[H^+]^2\}^2\{a + c[H^+] + K_b[H^+]^2\}$, the value of the term $ab - bK_b[H^+]^2$, can be obtained by putting the value of $[H^+]^2$ from eqn. (38) i.e. $[H^+]^2 = K_2K_w/K_b$.

$$ab - bK_b[H^+]^2 = ab - bK_b(K_2K_w/K_b)$$



Scheme 1

Or

$$ab - bK_b[H^+]^2 = ab - bK_b(a/K_b) = ab - ab = 0 \text{ (as, } K_2K_w = a)$$

As the term $ab - bK_b[H^+]^2$ in numerator of eqn. (43) is always zero, the numerator is always -ve. Hence, maxima will be obtained in the plot of k_2 vs $[H^+]$ at a point at which

$$[H^+] = [K_2K_w / K_b]^{1/2}$$

Or

$$[H^+]_{\max} = [K_2K_w / K_b]^{1/2} \quad (49)$$

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

$$[H^+]_{\max} = 3.8 \times 10^{-7} \text{ mol dm}^{-3}$$

It is gratifying to note that the calculated value of $[H^+]_{\max}$ is

in excellent agreement with the experimental value of $[H^+]_{\max}$ of $3.16 \times 10^{-7} \text{ mol dm}^{-3}$ obtained from k_2 versus $[H^+]$ plot. Also, k_2 - pH profile will show a maximum.

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