

Kinetics and Mechanism of Mn(II) Catalyzed Periodate Oxidation of 4-Chloro-2-methylaniline

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Kinetic-mechanistic studies made for periodate oxidation of 4-chloro-2-methylaniline (CMA) in acetone-water medium have been used for derivation of rate law and proposing mechanism which satisfy various observations like first order in each reactant and catalyst, stoichiometry (1 mol CMA : 2 mol periodate), kinetic parameters, main product identified (5-chloro-2-methyl-1,2-benzoquinone) and the effect of pH, dielectric constant, and ionic strength on reaction rate

Key Words: Kinetics, Mn(II) catalyst, Periodate oxidation, 4-Chloro-2-methylaniline.

INTRODUCTION

Reports on kinetic-mechanistic studies on the Mn(II) catalysed periodate oxidation of aromatic amines are very few¹⁻³. In continuation to our earlier communications on uncatalysed oxidations of such type⁴⁻⁶, the present paper deals with the kinetic studies on Mn(II) catalyzed periodate oxidation of 4-chloro-2-methylaniline (CMA) in acetone-water medium.

EXPERIMENTAL

Chemicals of E. Merck/CDH AR grade were used after distillation/recrystallization. Triply distilled water was used for preparation of the solutions. The progress of the reaction was followed spectrophotometrically⁵ by recording the absorbance at 490 nm, the λ_{\max} of reaction mixture in the duration in which the λ_{\max} did not change. The pH was maintained at 5.0 by using Thiel, Schultz and Koch buffer^{5,6} in all kinetic runs except when the effect of pH was studied. Plane mirror method and Guggenheim's method were used for evaluation of initial rates $[(dA/dt)_i]$ and pseudo first order rate constant k_1 or second order rate constant k_2 respectively. NaCl solutions were used for maintaining the ionic strength (μ) in the kinetic runs.

RESULTS AND DISCUSSION

1 mol CMA consumed 2 moles of periodate as determined iodometrically. The data (Table-1) indicated second order for the reaction, being first order in each reactant. Linear relation between concentration of the reactants and rate supported

the second order kinetics. In pseudo first order conditions (Table-2), the $[(dA/dt)]^{-1}$ or k_1^{-1} vs. $[S]^{-1}$ plots were linear with almost negligible intercept, suggesting the Michaelis-Menten type kinetics being followed with respect to both reactants with the possibility of formation of a fast decaying intermediate complex between reactants^{7,8}. Data in Table-3 established the first order in catalyst. Rate-pH profile showed a maxima at pH = 4.5 (Table-4). A linear relation between $\log (dA/dt)_i$ or $\log k_2$ and $1/D$ with negative slope (where D is the dielectric constant of the medium) and a primary linear type plot between $\log (dA/dt)_i$ or $\log k_2$ vs. ionic strength (μ) that were obtained from the data in Table-5, indicated an ion-dipole interaction in this reaction. Arrhenius plot was made between $35 \pm 0.1^\circ\text{C}$ to $50 \pm 0.1^\circ\text{C}$ and the values of different thermodynamic parameters evaluated taking $[\text{CMA}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{NaIO}_4] = 2.5 \times 10^{-3} \text{ M}$, $[\text{Mn}^{2+}] = 4.0 \times 10^{-6} \text{ M}$ and acetone = 10.0% (v/v), are $E_a = 4.67 \text{ kcal mol}^{-1}$; $A = 4.37 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$ $\Delta S^\ddagger = -43.58 \text{ eu}$; $\Delta F^\ddagger = 18.06 \text{ kcal mol}^{-1}$ and $\Delta H^\ddagger = 4.31 \text{ kcal mol}^{-1}$. Low value of energy of activation and high frequency factor are characteristic of a bimolecular reaction in the solution in which the reacting species are larger in size. A large negative value of ΔS^\ddagger suggests the formation of strongly solvated, charged and rigid transition state.

TABLE-1
DETERMINATION OF ORDER WITH RESPECT TO REACTANTS

$[\text{CMA}] \times 10^{-4} \text{ M}$	2.5	3.0	4.0	4.5	5.0	25.0	25.0	25.0	25.0	25.0	25.0
$[\text{NaIO}_4] \times 10^{-3} \text{ M}$	2.5	2.5	2.5	2.5	2.5	0.25	0.30	0.35	0.40	0.45	0.50
$(dA/dt)_i \times 10^2 (\text{min}^{-1})$	10.2	14.2	16.2	18.2	20.2	4.0	4.9	5.7	6.5	7.2	7.9

$\lambda_{\text{max}} = 472 \text{ nm}$; pH = 5.0; Acetone = 10.0% (v/v); Temp. = $3.5 \pm 0.1^\circ\text{C}$; $[\text{Mn}^{2+}] = 8.0 \times 10^{-6} \text{ M}$; $\mu = 2.66 \times 10^{-3}$

TABLE-2

$[\text{CMA}] \times 10^{-4} \text{ M}$	2.5	3.0	4.0	4.5	5.0	0.25	0.25	0.25	0.25	0.25
$[\text{NaIO}_4] \times 10^{-3} \text{ M}$	0.25	0.25	0.25	0.25	0.25	2.50	3.00	3.50	4.00	4.50
$(dA/dt)_i \times 10^2 (\text{min}^{-1})$	5.70	7.00	8.00	9.20	11.50	12.40	14.60	17.00	19.50	21.80
$k_1 \times 10^3 (\text{sec}^{-1})$	4.60	5.57	6.29	7.72	8.82	4.97	5.36	6.90	8.75	9.90

$\lambda_{\text{max}} = 472 \text{ nm}$; pH = 5.0; Acetone = 10.0% (v/v); Temp. = $3.5 \pm 0.1^\circ\text{C}$; $[\text{Mn}^{2+}] = 8.0 \times 10^{-6} \text{ M}$; $\mu = 2.66 \times 10^{-3}$

TABLE-3
DETERMINATION OF ORDER WITH RESPECT TO Mn^{2+}

$[\text{Mn}^{2+}] \times 10^{-6} \text{ M}$	8.0	16.0	24.0	32.0	40.0
$(dA/dt)_i \times 10^2 (\text{min}^{-1})$	3.4	6.5	9.0	11.2	13.5

$[\text{NaIO}_4] = 5.0 \times 10^{-3} \text{ M}$; $[\text{CMA}] = 5.0 \times 10^{-4} \text{ M}$; Temp. = $30.0 \pm 0.1^\circ\text{C}$; Acetone = 10.0% (v/v); $\mu = 5.16 \times 10^{-3}$

TABLE-4
RATE-pH PROFILE

pH	3.0	3.5	4.0	4.5	5.0	5.5	6.5	7.0	8.0	8.5
$(dA/dt)_i \times 10^3 (\text{min}^{-1})$	0.6	1.6	17.5	120.0	70.0	7.5	2.6	1.8	1.6	1.4

[CMA] = 2.5×10^{-4} M; [NaIO₄] = 2.5×10^{-3} M; λ_{max} = 472 nm; acetone = 10.0% (v/v);
Temp. = $35.0 \pm 0.1^\circ\text{C}$; [Mn²⁺] = 8.0×10^{-6} M

TABLE-5
EFFECT OF D AND μ ON REACTION RATE

D	71.0	69.7	68.4	66.8	-	-	-	-
$*\mu \times 10^3$	-	-	-	-	35.16	65.16	105.2	145.2
$(dA/dt)_i \times 10^2 (\text{min}^{-1})$	11.20	9.00	7.50	6.00	8.00	7.00	6.00	5.00
$k_1 \times 10^3 (\text{sec}^{-1})$	4.61	4.22	3.84	3.45	6.14	5.37	4.61	3.84
$k_2 (\text{L mol}^{-1} \text{sec}^{-1})$	1.84	1.68	1.53	1.38	2.46	2.15	1.84	1.54

[CMA] = 2.5×10^{-4} M; [NaIO₄] = 2.5×10^{-3} M; λ_{max} = 472 nm; *Acetone = 10.0% (v/v);
Temp. = $3.5 \pm 0.1^\circ\text{C}$; [Mn²⁺] = 8.0×10^{-6} M; $\mu = 2.516 \times 10^{-3}$

The increase in the rate from pH 3.0 to 4.5 that may be due to the decrease in the protonation of CMA from pH 3.0 to 4.5 (Table-4) which makes greater concentrations of CMA available for the reaction. This leads to the assumption that unprotonated CMA is the reactive species in the present case. Second part of this profile suggests that the periodate monoanion [IO₄⁻] is the reactive species of periodate⁹ whose concentration goes on decreasing with increase in pH beyond the value 4.5⁹ decreasing thereby the rate of reaction beyond pH 4.5.

Based on these results, the mechanism may be proposed (Chart-1) involving the lone pair of electrons on nitrogen atom of CMA for the coordinate bond formation between CMA and Mn²⁺ species in a reversible step to form complex C₁ [step (i)] which, in turn, interacts with IO₄⁻ in slow and rate determining step (ii) to give C₂. C₂ changes by fast hydrolysis into C₃. The formation of a charged intermediate complex C₂ by the attack of IO₄⁻ on the nitrogen of anilino group and stabilization of positive charge on nitrogen of this group, have also been observed and supported by LFER studies for the uncatalysed periodate oxidation of few aromatic amines¹⁰. In addition, a high negative value of entropy of activation and the effect of dielectric constant on the reaction rate support the involvement of solvation effects in this reaction.

It should also be noted that the initial part of the reaction is significant in the present case and the second molecule of IO₄⁻ reacting later to give C₄ is not significant. C₄ changes by fast hydrolysis to give C₅, *i.e.*, the main product of reaction that has been isolated and separated by employing the method reported earlier in case of other aromatic amines^{5,6}. It was characterized as 4-chloro-2-methyl-1,2-benzoquinone on the basis of test for quinone⁵, m.p.¹¹, UV-Vis, IR and ¹H-NMR spectra (showing characteristic bands for C—Cl¹² and *o*-benzoquinones¹³). The overall process may be represented as follows:

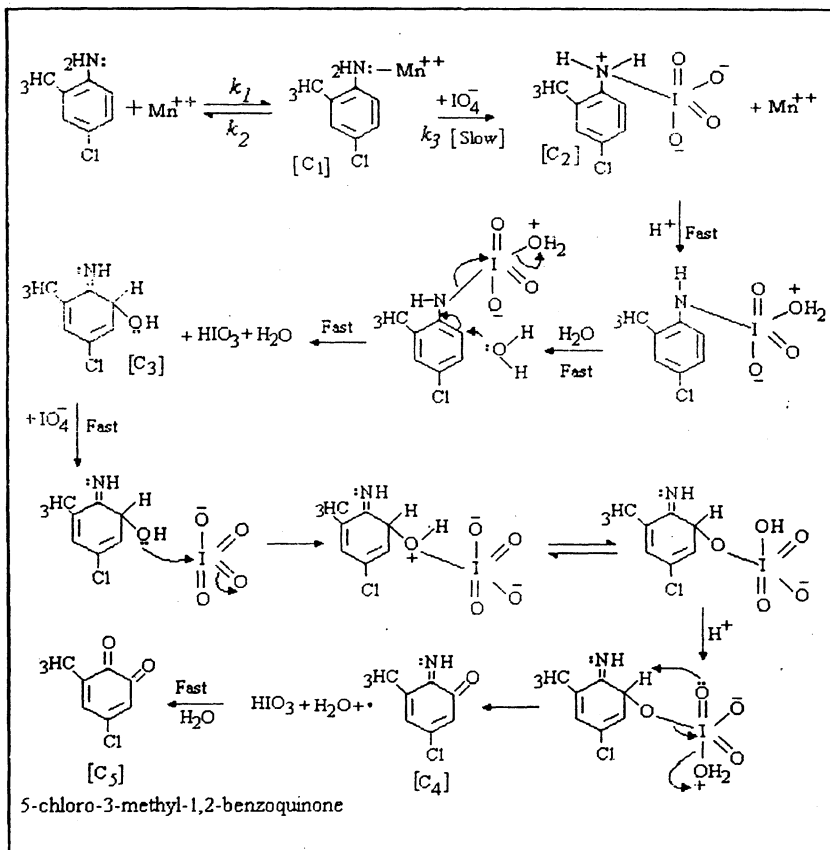
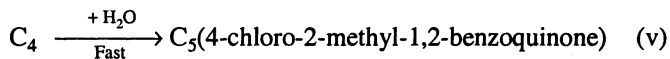
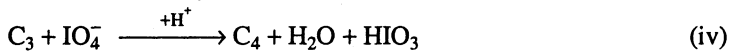
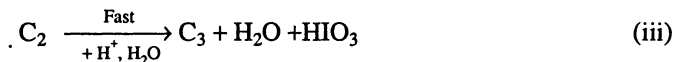


Chart-1



On applying steady state treatment to C₁, the rate law in terms of rate of loss of [IO₄⁻] may be derived as follows:

$$\begin{aligned} \text{Rate of loss of } [\text{IO}_4^-] \text{ or } -\frac{d[\text{IO}_4^-]}{dt} &= k_3[\text{C}_1][\text{IO}_4^-] \\ &= \text{Rate of loss of } \text{C}_1 \text{ or } -\frac{d[\text{C}_1]}{dt} \end{aligned} \quad (1)$$

$$\text{Rate of formation of } \text{C}_1 = +d[\text{C}_1]/dt = k_1[\text{CMA}][\text{Mn}^{2+}] - k_2[\text{C}_1]$$

$$\text{At steady state, } -\frac{d[\text{C}_1]}{dt} = +\frac{d[\text{C}_1]}{dt}$$

$$\text{Therefore, } k_3[\text{C}_1][\text{IO}_4^-] = k_1[\text{CMA}][\text{Mn}^{2+}] - k_2[\text{C}_1]$$

$$\text{or } [\text{C}_1]\{k_3[\text{IO}_4^-] + k_2\} = k_1[\text{CMA}][\text{Mn}^{2+}]$$

$$\text{or } [\text{C}_1] = \frac{k_1[\text{CMA}][\text{Mn}^{2+}]}{k_3[\text{IO}_4^-] + k_2} \quad (2)$$

$$\text{From (1) and (2), } -\frac{d[\text{IO}_4^-]}{dt} = \frac{k_3k_1[\text{CMA}][\text{Mn}^{2+}][\text{IO}_4^-]}{k_2 + k_3[\text{IO}_4^-]} \quad (3)$$

Since step (ii) is slow and rate determining step, hence $k_3[\text{IO}_4^-] \ll k_2$ may be assumed. Therefore, the rate law (3) may be written as rate law (4) which explains all the kinetic results.

$$-\frac{d[\text{IO}_4^-]}{dt} = k_{\text{obs.}}[\text{CMA}][\text{Mn}^{2+}][\text{IO}_4^-]$$

$$\text{where } k_{\text{obs}} = \frac{k_3k_1}{k_2}$$

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