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A kinetic-spectrophotometric study of Mn^{II} catalyzed oxidation of N,N-dimethylaniline by periodate ion

Ajay Kumar

Department of Applied Chemistry, Faculty of Engineering and Technology, Gurukul Kangri University, Haridwar (U.K.), India

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ABSTRACT

The present study deals with the kinetics and mechanism of Mn^{II} catalyzed periodate oxidation of N, N-dimethylaniline (DMA) in acetone-water medium at $30^{o}C$. The reaction was initiated by mixing previously thermostated $NaIO_4$ solution of known concentration to the reaction mixture containing the DMA, Mn^{II} and buffer. The kinetics was followed under pseudo first order conditions, $[IO_4^-] >> [DMA]$,

$$-d[IO_4^-]/dt = k_{obs} . [DMA][Mn^{++}][IO_4^-]$$

The stoichiometry of the reaction was observed to be 1:2 mole ratio of DMA to periodate ions. Free radical scavengers do not affect the reaction rate. The reaction products were identified and isolated using TLC separation techniques and characterized by IR, and GC-MS spectral studies. The reaction was found first order with respect to each reactant. The effect of pH, ionic strength and dielectric constants were also studied on the rate of reaction. A suitable mechanism is proposed based on the experimental results. The activation parameters were evaluated and found: $Ea = 6.98$ kcal mol^{-1}, $A = 10.98\times 10^5$ dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -35.43$ cal mol^{-1}, $\Delta F^{\#} = 17.34$ kcal mol^{-1} and $\Delta H^{\#} = 6.36$ kcal mol^{-1}.

Key words: Kinetics, oxidation, Mn^{II} catalysed, periodate, N, N-dimethylaniline, p-benzoquinone.

INTRODUCTION

Aromatic amines have known to be carcinogenic in humans [1-2]. They can be exposed into body through diet (e.g. pesticides), pharmaceuticals, hair dyes, smoking and industrial exposure e.g. textile, rubber and leather. N, N-dimethylaniline is one of the aromatic amine which causes unconsciousness, vomiting and dermatitis. It is a yellow color liquid having a characteristics odor, turns brown when exposed with air and decomposes on heating producing highly toxic fumes of aniline and nitrogen oxides. Few reports are published in literature on the kinetic studies of Mn^{II} catalyzed non-Malapradian periodate oxidation of aromatic amines [3-7]. Recent reports include the Mn^{II} catalyzed oxidation of acridine yellow by chloramine-T [8]. The purposes of the present study are: (1) to ascertain the reactive species of the reaction, (2) to elucidate the possible reaction mechanism, (3) to study the effect of various factors on reaction rate, (4) to calculate the activation parameters, (5) to predict the stiochiometry of the reaction and (6) product analysis.

MATERIALS AND METHODS

Reagents and Chemicals

Sodium metaperiodate and manganese sulphate monohydrate of CDH make (A.R. grade) were used after recrystallization. N, N-dimethylaniline of Sigma-Aldrich was used after zinc dust double distillation in a borosil glass assembly. Acetone, ether and chloroform were of CDH (AR) grade and were used after distillation. The pH of reaction mixtures was maintained by using Thiel, Schultz and Koch buffer [9], 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. Triply distilled water was used for preparation of the solutions.

Kinetic Procedure

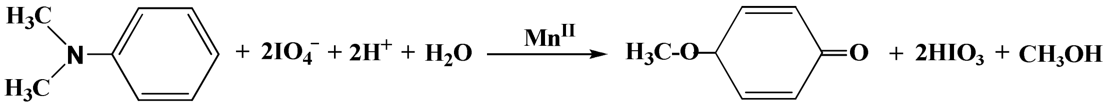
In all the experiments the pseudo first order kinetics with respect to N, N-dimethylaniline were monitored at 474 nm, i.e. the λ_{max} of the yellow color reaction mixture using Schimadzu double beam spectrophotometer (UV Pharmaspec-1700). λ_{max} was not found to change with change in time under experimental conditions. The reaction was studied in a spectrophotometric cell placed in the thermostatted compartment of Schimadzu double beam spectrophotometer and initiated by adding previously thermostated $NaIO_4$ solution of known concentration to the reaction mixture containing the DMA, Mn^{II} and buffer and the desired temperature was maintained with a high precision thermostatic water bath (±0.1°C).

Product Analysis

Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially the reaction mixture was yellow in color which turned into greenish color, thereafter violet color and finally the solid product settled down on standing. It was filtered and the filtrate was extracted with petroleum ether (40-60°C). The extract was evaporated at room temperature to get a sticky substance that was found to be TLC analysis (using 0.5 mm thick plate of silica gel ‘G’ as adsorbent, and chloroform, acetone and benzene in the ratio 40:60:40 ml used as eluent, and 30 minutes as the time for development). The yellowish-brown compound was not be recrystallized even though number of solvents were tried. It was characterized as p-benzoquinone on the basis of positive test for quinine [10] which suggested the presence of quinonoid structure in the compound. The IR spectrum (in KBr) showed a strong band at 1520 cm^{-1} (s) which is characteristic of nitroso group. Bands were obtained at 1230 and 1280 cm^{-1} which indicated the presence of aryl ether group. Further, the bands at 2920 cm^{-1} (s) may be due to $-OCH_3$ group. Bands obtained at 1450 and 1350 cm^{-1}(m) and 1091 cm^{-1}(m) may be due to anti-symmetric stretching of C−O−C structure and C−N stretching respectively. A band at 1730 cm^{-1} was indicated the presence of aryl ketonic group. The band at 940 and 1070 cm^{-1} were suggestive the presence of N−O (oxime) group of quinine monoxide. On the basis of IR data, this suggested that the final product was a mixture of the tautomers: O-methylquinoneoxime and p-nitrosoanisole as discussed in **Scheme-2**.

Stoichiometry

The stoichiometry of the reaction was determined iodimetrically by keeping $NaIO_4$ in excess to react with DMA. The reaction had gone to completion over a period of 24 h, the precipitated product was filtered out and in the filtrate unconsumed $NaIO_4$ was determined iodimetrically. A point of inflexion on the curve of log (a-x) versus time plot indicated the stoichiometry to be 1 mol DMA: 2 moles periodate for the reaction as in equation (1).



(1)

RESULTS AND DISCUSSION

Preliminary Observations

On mixing the reactants, the solution becomes light yellow which further changes into green and then violet in the later stages. On keeping for long time, it finally gives the product. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. The rapid scan of the light yellow solution showed the λ_{max} of the intermediate, C_4, to be 474 nm. The UV-visible spectra of IO_4^-, DMA and Mn^{II} indicated these to show no absorption in visible region. Hence, for following the kinetics the absorbance changes were recorded at 474 nm at which only the intermediate C_4 absorbs.

Effect of N, N-dimethylaniline and Periodate

Under pseudo first order conditions the plot of k_1^{-1} vs $[DMA]^{-1}$ and k_1^{-1} vs $[NaIO_4]^{-1}$ were found to be linear with a very little intercept (Table 1, Figure 1 & 2). This indicates that the intermediate formed between the periodate monoanion and the substrate is not stable.

Effect of Mn^{II}

The effect of Mn^{II} catalyst was studied on reaction rate using varied initial concentration of the Mn^{II}. The plot of $[Mn^{II}]$ vs rate has been found linear suggesting that order with respect to $[Mn^{II}]$ is one. The results are presented in Table 2.

Effect of pH

The effect of pH was examined in the range 4.0-6.5. Rate – pH profile indicates a maximum at pH = 5.5 (Table 1, Figure 3), which could be due to change in the nature of species and their relative reactivity when the pH is changed.

Effect of Ionic Strength

At constant concentrations of DMA, periodate and Mn^{II} catalyst with constant reaction conditions, the ionic strength was varied between 1.0×10^{-5} to 4.0×10^{-5} (mol. dm^{-3}) by varying the concentrations of a natural salt sodium chloride. The kinetic data of these runs are sited in Table 1. The plot between log k_2 and I (Figure 4) suggesting the salt effect was positive and primary linear type which indicated that the rate determining step may be a reaction between ion and dipole.

Effect of Dielectric Constant

The kinetic data in Table 1 suggested that the rate decreased with increased in dielectric constant. The plot of log k_2 vs 1/D was found to be linear with a negative slope (Figure 5), indicating that the rate determining step may be the reaction between a dipole and anion, which is a periodate monoanion.

Effect of Temperature

The rate constants were measured at four different temperatures (30 to 45°C) to find out the thermodynamic parameters. The results of these runs are given in Table 3 and Figure 6. A plot of log k_2 vs 1/T was found linear, indicating that the Arrhenius equation relating the temperature and specific rate, viz:

$$\log k_2 = [-Ea/2.303\ RT] + \text{Constant}$$

was followed. The energy of activation was then calculated from the slope of this curve. Results showed that the reaction is characterized by a large negative value of entropy of activation and a low value of activation, suggesting the formation of a charged and rigid transition state.

Effect of Free Radical Scavengers

Free radical scavengers, viz., acrylamide and allyl alcohol had no effect on the reaction rate. This suggests absence of free radical in the reaction mixture.

Mechanism of Reaction

Construction of a mechanism requires discussion on the speciation of DMA and periodate. In aqueous solutions, periodate exists in the three forms governed by the equilibria (2-3).

$$H_5IO_6 \rightleftharpoons H_4IO_6^{-} + H^{+} \qquad K_1 = 2.3 \times 10^{-2} \qquad (2)$$

$$H_4IO_6^{-} \rightleftharpoons H_3IO_6^{2-} + H^{+} \qquad K_2 = 4.35 \times 10^{-9} \qquad (3)$$

The value of K_1 indicates that in the pH range 4.5-9.0 species H_5IO_6 shall be practically non-existent and hence only species $H_4IO_6^{-}$ and $H_3IO_6^{2-}$ need be considered for explaining observed pH-dependence. For simplification, $H_4IO_6^{-}$ has been written as IO_4^{-} in the mechanism. In purposed mechanism **(Scheme-1)**, Mn^{++} plays an important role as a catalyst which justify due to the formation of a ternary complex, $[(DMA)Mn(H_4IO_6)]^{+}$, in which Mn acts as a conduit for electron transfer.

Based on the results, it assumes that the $C_6H_5N\,(CH_3)_2$ and $H_4IO_6^{-}$ to be the reactive species, the following plausible mechanism is hereby proposed:

$$C_6H_5N\,(CH_3)_{+}\,Mn^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [C_1] \qquad (4)$$

$$[C_1] + [IO_4^{-}] \xrightarrow{k_3} [C_2] + Mn^{2+} \quad \text{(Slow step)} \qquad (5)$$

$$[C_2] \longrightarrow [C_3] + CH_3OH + HIO_3 \ \text{(Fast step)} \qquad (6)$$

$$[C_3] + IO_4^{-} + H^{+} \longrightarrow [C_4] + CH_3OH + HIO_3 \qquad (7)$$

$$[C_4] \xrightarrow{[IO_4^-]} [C_5] \quad \text{(Product)} \quad \text{(Fast step)} \qquad (8)$$

On applying steady state treatment to C_1, the rate law in terms of rate of loss of $[IO_4^-]$ may be derived as follows:

Rate of loss of $[IO_4^-]$ or $-d[IO_4^-]/dt = k_3 [C_1] [IO_4^-] =$

Rate of loss of C_1 or $-d[C_1]/dt$ (9)

Rate of formation of $C_1 = +d[C_1]/dt = k_1 [DMA] [Mn^{++}] - k_2 [C_1]$

At steady state, $-d[C_1]/dt = +d[C_1]/dt$

Therefore, $k_3 [C_1] [IO_4^-] = k_1 [DMA] [Mn^{++}] - k_2 [C_1]$

Or $[C_1] \{k_3.[IO_4^-] + k_2\} = k_1 [DMA] [Mn^{++}]$

$$\text{Or } [C_1] = \frac{k_1 [DMA][Mn^{++}]}{k_3.[IO_4^-] + k_2} \qquad (10)$$

$$\text{From, (9) and (10), } -d[IO_4^-]/dt = \frac{k_3.k_1.[DMA][Mn^{++}][IO_4^-]}{k_2 + k_3.[IO_4^-]} \qquad (11)$$

Since equation (5) is slow step and rate determining step, hence it can be assumed that $k_3.[IO_4^-] << k_2$. Therefore, the rate law (11) may be written as rate law (12) which explains all of the observed kinetic data.

$$-d[IO_4^-]/dt = k_{obs} . [DMA][Mn^{++}][IO_4^-] \qquad (12)$$

Where, $k_{obs} = k_3.k_1 / k_2$

TABLE-1 Mn^{II} catalyzed periodate oxidation of N, N-dimethylaniline in acetone-water medium at 474 nm Values of k_{obs} and k_2 at 30± 0.1°C

$[NaIO_4]$ (mol dm^3)	[DMA] (mol dm^3)	$[Mn^{II}] \times 10^7$ (mol dm^3)	Acetone [%(v/v)]	[NaCl] $\times 10^5$ (mol dm^3)	pH	$k_{obs} \times 10^3$ (s^{-1})	k_2 (dm^6 mol^{-1} s^{-1})
0.00006	0.00066	80	5.0	-	4.0	6.45	9.77
0.00006	0.00072	80	5.0	-	4.0	6.91	9.60
0.00006	0.00078	80	5.0	-	4.0	7.49	9.60
0.00006	0.00084	80	5.0	-	4.0	8.06	9.60
0.00006	0.00090	80	5.0	-	4.0	8.64	9.60
0.00006	0.00096	80	5.0	-	4.0	9.10	9.48
0.00030	0.00003	8.0	5.0	-	4.0	3.07	10.24
0.00034	0.00003	8.0	5.0	-	4.0	3.45	10.16
0.00038	0.00003	8.0	5.0	-	4.0	3.84	10.10
0.00042	0.00003	8.0	5.0	-	4.0	4.22	10.05
0.00046	0.00003	8.0	5.0	-	4.0	4.61	10.01
0.00050	0.00003	8.0	5.0	-	4.0	4.99	9.98
	0.00003						
0.0005	0.00003	8.0	5.0	-	4.0	4.98	9.98
0.0005	0.00003	8.0	5.0	-	4.5	12.09	24.18
0.0005	0.00003	8.0	5.0	-	5.0	26.48	52.97
0.0005	0.00003	8.0	5.0	-	5.5	57.58	110.54
0.0005	0.00003	8.0	5.0	-	6.0	18.42	36.85
0.0005	0.00003	8.0	5.0	-	6.5	13.82	27.64
0.0005	0.00003	8.0	2.5	-	4.0	5.99	11.98
0.0005	0.00003	8.0	5.0	-	4.0	4.99	9.98
0.0005	0.00003	8.0	7.5	-	4.0	4.15	8.29
0.0005	0.00003	8.0	10.0	-	4.0	3.46	6.91
0.0005	0.00003	8.0	5.0	1.0	4.0	1.79	3.57
0.0005	0.00003	8.0	5.0	2.0	4.0	2.88	5.76
0.0005	0.00003	8.0	5.0	3.0	4.0	4.66	9.33
0.0005	0.00003	8.0	5.0	4.0	4.0	7.14	14.28

TABLE-2 Determination of Order with respect to Mn^{II} at 474 nm and 30± 0.1°C

[DMA] =3.0 × 10^{-5} mol dm^{-3}, [$NaIO_4$] = 5.0 × 10^{-4} mol dm^{-3}, Acetone = 5.0 % (v/v), pH = 4.0, Temp. = 30±0.1°C

[Mn^{II}] × 10^7 (mol dm^3)	3.0	4.0	5.0	6.0	7.0
$(dA/dt)_i \times 10^3$ (min^{-1})	26.0	35.0	43.0	52.0	61.0

TABLE-3 Activation Parameters with respect to slow step for Scheme 1 at 474 nm

[DMA] =3.0 × 10^{-5} mol dm^{-3}, [$NaIO_4$] = 5.0 × 10^{-4} mol dm^{-3}, [Mn^{II}] = 8.0 × 10^{-7} mol dm^{-3}, Acetone = 5.0 % (v/v), pH = 4.0

Temp. °C	**10^3 k_{obs} (s^{-1})**	**10^{-7} k_{cat} (dm^6 $mol^{-2}s^{-1}$)**	**Ea (kcal mol^{-1})**	**A×10^{-5} (dm^3 $mol^{-1}s^{-1}$)**	**$\Delta S^{\#}$ (cal mol^{-1})**	**$\Delta F^{\#}$ (kcal mol^{-1})**	**$\Delta H^{\#}$ (kcal mol^{-1})**
30	5.06	1.265	6.98	10.98	-35.43	17.34	6.36
35	5.98	1.495					
40	7.37	1.842					
45	8.75	2.188					

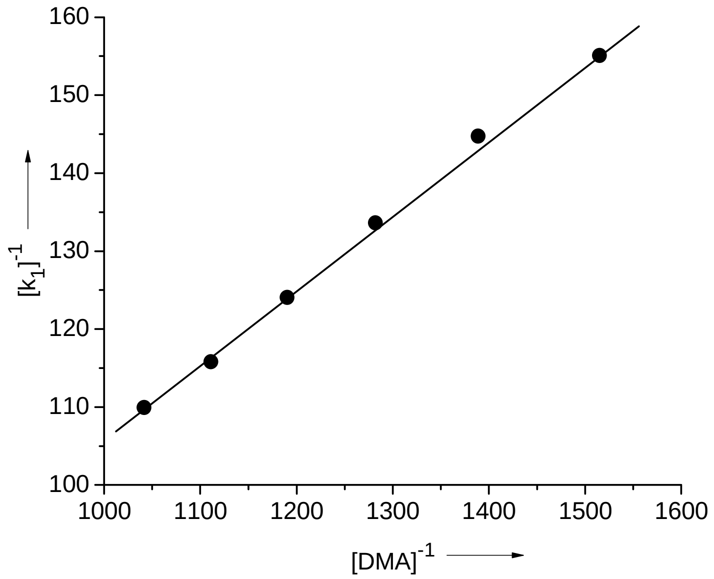


Figure 1 Variation of N, N-dimethylaniline at λ_{max} = 474nm, Acetone=5% (v/v), Temp. = 30±0.1°C, pH= 4.0, [$NaIO_4$] = 6.0 × 10^{-5} mol dm^{-3}, [Mn^{II}] = 8.0x10^{-6} mol dm^{-3}

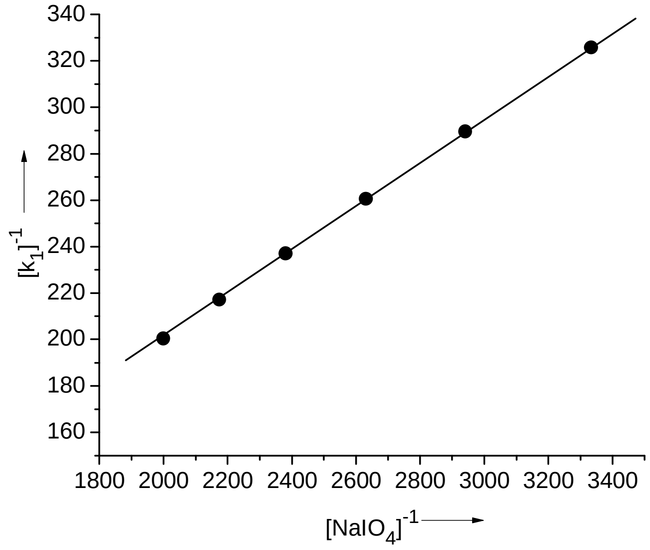


Figure 2 Variation of Periodate at λ_{max} = 474nm, Acetone=5% (v/v), pH= 4.0, Temp.= 30±0.1°C, [DMA] = 3.0 × 10^{-5} mol dm^{-3}, [Mn^{II}] = 8.0x10^{-7} mol dm^{-3}

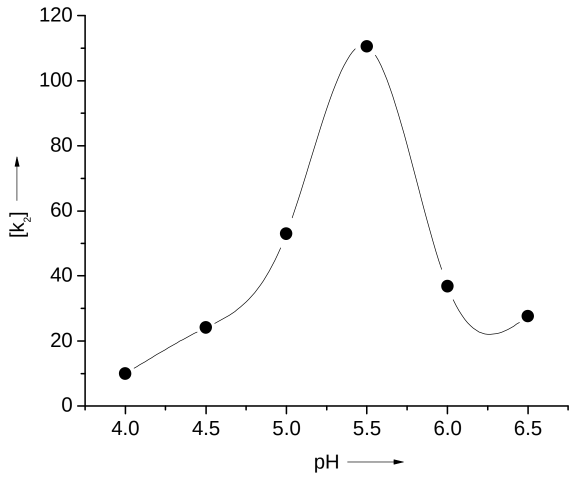


Figure 3 Effects of pH on the rate of Mn^{II} catalysed periodate oxidation of N, N-dimethylaniline in acetone-water medium at λ_{max} = 474nm, Acetone = 5% (v/v), Temp.= 30±0.1°C, [DMA] =3.0×10^{-5} mol dm^{-3}, [$NaIO_4$] = 5.0×10^{-4} mol dm^{-3}, [Mn^{II}] = $8.0x10^{-7}$ mol dm^{-3}

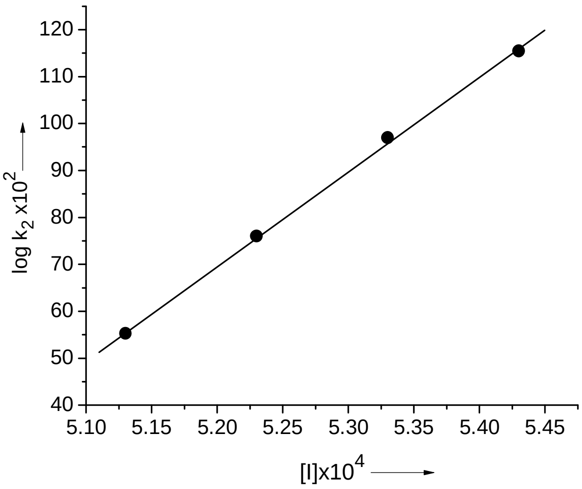


Figure 4 Effect of ionic strength on reaction rate of Mn^{II} catalysed periodate oxidation of N, N-dimethylaniline in acetone-water medium at λ_{max} = 474nm, Acetone = 5% (v/v), Temp.= 30±0.1°C, pH= 4.0, [DMA] = 3.0×10^{-5} mol dm^{-3}, [$NaIO_4$]= 5.0×10^{-4} mol dm^{-3}, [Mn^{II}]=$8.0x10^{-7}$ mol dm^{-3}

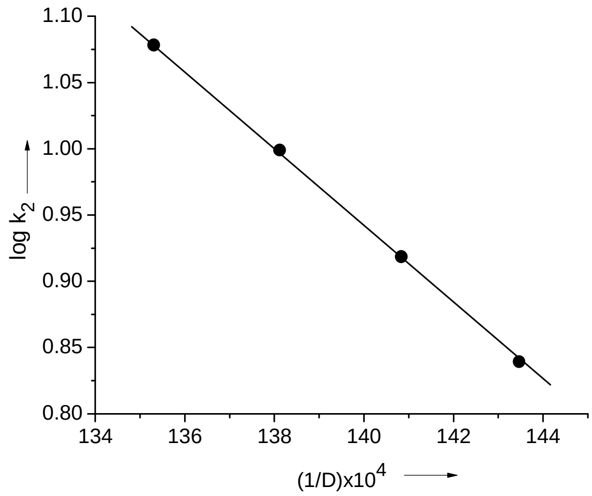


Figure 5 Effect of dielectric constant on reaction rate of Mn^{II} catalysed periodate oxidation of N, N-dimethylaniline in acetone-water medium at λ_{max}= 474nm, pH= 4.0, Temp.= 30±0.1°C, [DMA] = 3.0×10^{-5} mol dm^{-3}, [$NaIO_4$] = 5.0×10^{-4} mol dm^{-3}, [Mn^{II}] = $8.0 x10^{-7}$ mol dm^{-3}

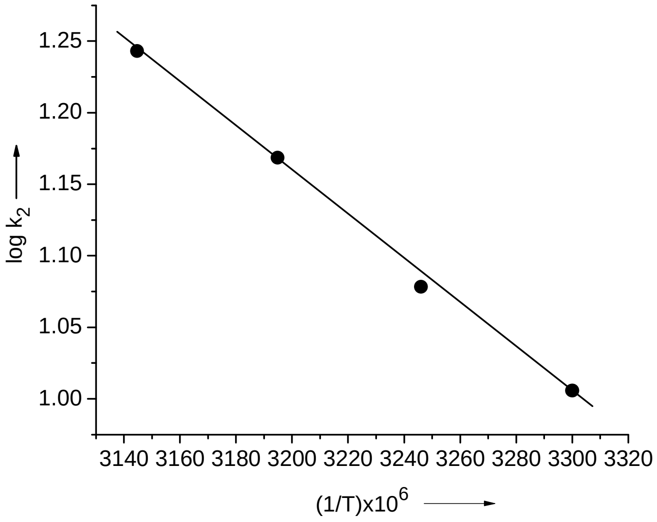
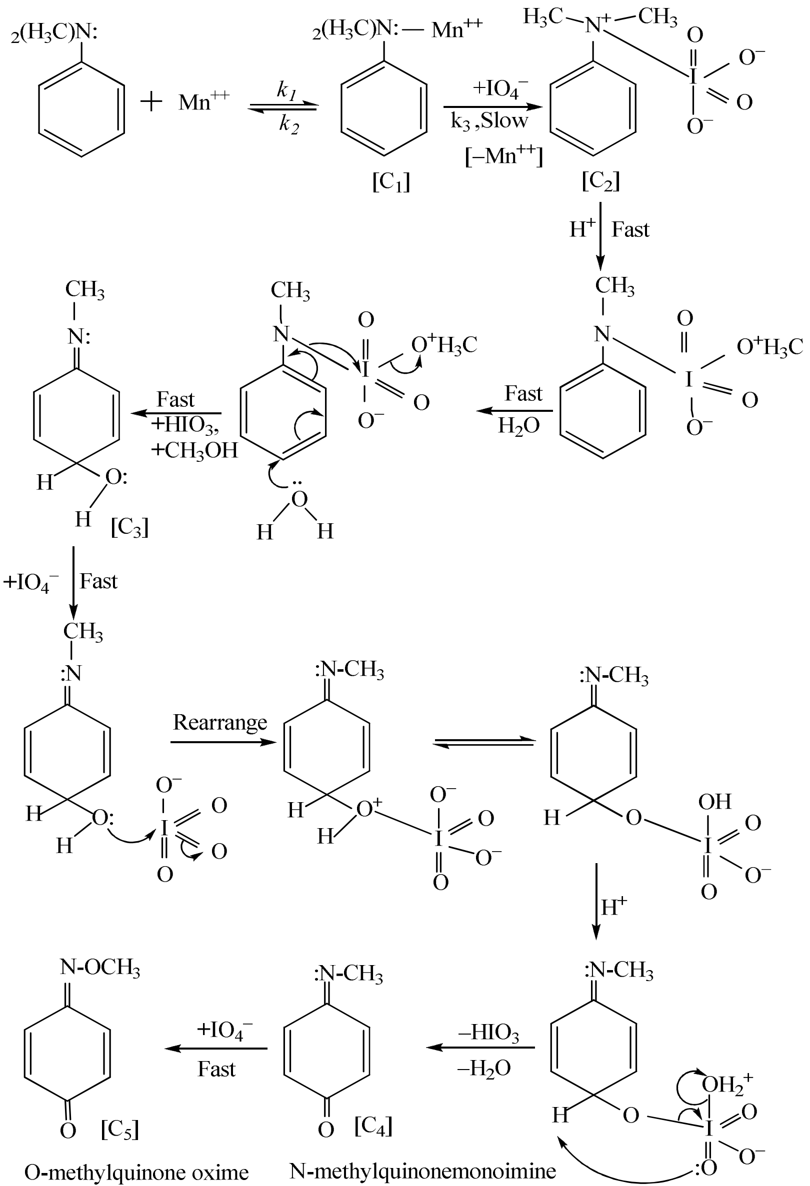
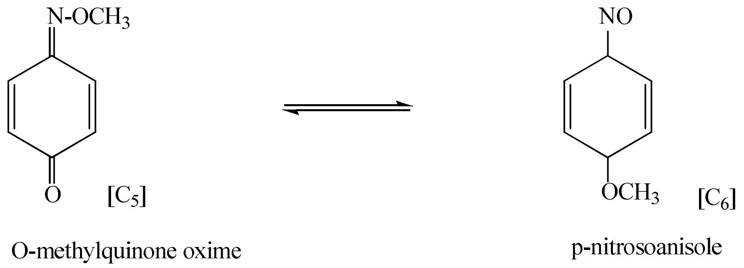


Figure 6 Effect of temperature on reaction rate of Mn^{II} catalysed periodate oxidation of N, N-dimethylaniline in acetone-water medium at λ_{max} = 474nm, Acetone =5% (v/v), pH= 4.0, [DMA] =3.0×10^{-5} mol dm^{-3}, [$NaIO_4$] = 5.0×10^{-4} mol dm^{-3}, [Mn^{II}] = 8.0×10^{-7} mol dm^{-3}



[SCHEME-1]



[SCHEME-2]

CONCLUSION

The kinetic-spectrophotimeric investigations of Mn^{II} catalyzed periodate oxidation of N, N-dimethylaniline showed the evidence of intermediate complex formation in this reaction. The salt effect was positive and primary linear type which indicated that the rate determining step may be a reaction between ion and dipole. Free radical scavengers test suggests the absence of free radical in the reaction mixture. The reaction of DMA with periodate ion showed a stoichiometry of 1:2.

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