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Research Article

Stopped Flow Kinetics of Mn[II] Catalysed Periodate Oxidation of 2,3-dimethylaniline - Evaluation of Stability Constant of the Ternary Intermediate Complex

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Abstract

The formation of ternary intermediate unstable complex during the oxidation of aromatic amines by periodate ion catalysed by Mn[II] has been proposed in case of some anilines. This paper is the first report on stopped-flow kinetic study and evaluation of stability constant of ternary complex forming in the Mn[II] - catalysed periodate oxidation of 2, 3-dimethylaniline (D) in acetone-water medium. Stop-flow spectrophotometric method was used to study the ternary complex formation and to determine its stability constant. The stop-flow trace shows the reaction to occur in two steps. The first step, which is presumably the formation of ternary complex, is relatively fast while the second stage is relatively quite slow. The stability constant evaluated for D - Mn[II] - IO$_4^-$ ternary complex by determining equilibrium absorbance is $(2.2 \pm 1.0) \times 10^5$. Kinetics of ternary complex formation was defined by the rate law $(\ln\{[C_2]_{eq}/([C_2]_{eq}-[C_2])\} = k_{obs}.t)$ under pseudo first order conditions, where, k_{obs} is the pseudo first order rate constant, $[C_2]$ is concentration of ternary complex at given time t, and $[C_2]_{eq}$ is the equilibrium concentration of ternary complex. © 2015 BCREC UNDIP. All rights reserved.

Keywords: Stopped flow kinetics; Stability constant; Ternary complex; Mn[II] catalysed; Periodate oxidation; 2,3-dimethylaniline

1. Introduction

Aromatic amines are used as intermediates in the manufacture of plastics, dyes, drugs, explosives, rubber, epoxy polymers, azo dyes, aromatic polyurethane products and pesticides [1]. These can come in contact with living organisms by inhalation, ingestion and skin contact and most of these are enlisted as carcinogenic and/ or toxic due to their genotoxic or cytotoxic properties [2,3]. It is of interest to study their new reactions for understanding their role in physiological activities and for developing methods for their detection, estimation and treatment. Aromatic amines have been subjected to oxidation reactions by using oxidants like peroxydisulphate ion [4], benzimidazolium fluorochromate [5] and periodate, etc.

The kinetics and mechanism of the uncatalysed and Mn[II] catalyzed non-Malapradian periodate oxidation of some aromatic amines has been the subject of study during the past few years. In these reports, a binary unstable intermediate complex formation between aromatic amine and periodate has been proposed in the

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reaction mechanism of uncatalysed reactions [6-16]. Also, there are some reports available which propose the ternary complex formation between periodate, aromatic amine and Mn^{II} in some reactions catalysed by Mn^{II} [17-23].

In continuation to our studies on periodate oxidation of 2,3-dimethylaniline catalyzed by Mn^{II} [23], and in order to make an attempt for the first time for evaluation of stability constant for the ternary intermediate complex being formed in this reaction, the results of stopped flow kinetic studies made on Mn^{II} -catalysed periodate oxidation of 2,3-dimethylaniline in acetone-water medium are being presented and discussed in this communication.

2. Experimental

2.1. Reagents and Chemicals

The principal reagents used were sodium metaperiodate (Loba Chemie) (CAS no. 7790-28-5), 2,3-dimethylaniline (Aldrich) (CAS no. 87-59-2) and manganese sulphate monohydrate (Aldrich) (CAS no. 10034-96-5) (here-to-after referred as I, D and Mn^{II}, respectively). All other chemicals of analytical reagent / guaranteed reagent grade were used after redistillation / recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer [24], used for maintaining the pH of reaction mixtures, was prepared by mixing desired volumes of 0.05 M oxalic acid (CAS no. 144-62-7), 0.02 M boric acid (CAS no. 10043-35-3), 0.05 M succinic acid (CAS no. 110-15-6), 0.05 M sodium sulphate (CAS no. 7757-82-6) and 0.05 M sodium tetraborate decahydrate (CAS no. 1303-96-4). Acetone (E. Merck) (CAS no. 67-64-1) was used for preparation of reaction mixtures.

2.2. Kinetic Procedure

All absorbance measurements were made on Shimadzu double beam spectrophotometer (UV-2450). The reaction was initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing D, Mn^{II} and buffer. The temperature of reaction mixture was maintained in the uv-vs spectrophotometer with the help of an in-built temperature control unit, Shimadzu TCC-
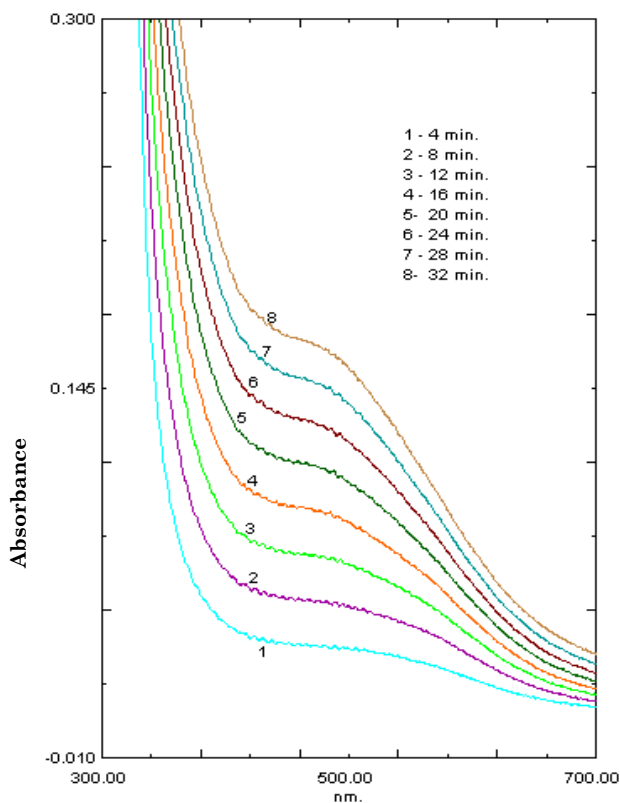

Figure 1. UV-VIS rapid scan at different time at [D] = 2.0×10^{-4} mol dm^{-3}, [I] = 2.0×10^{-2} mol dm^{-3}, pH = 6.0, Temp. = 35 ± 0.1 ºC, acetone =10.0 % (v/v), λ_{max} = 470 nm, time interval = 120 s
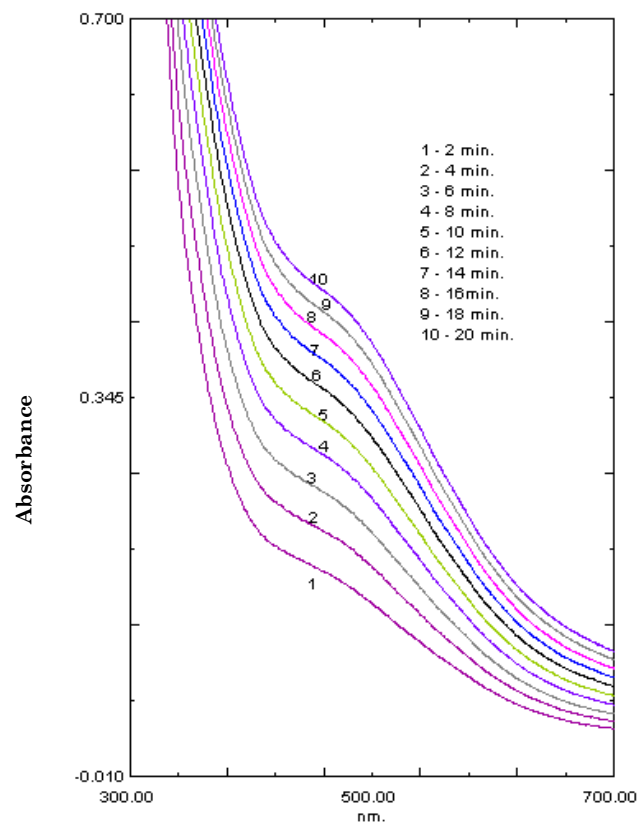
Figure 2. UV-VIS rapid scan at different time at [D] = 2.0×10^{-4} mol dm^{-3}, [I] = 2.0×10^{-2} mol dm^{-3}, [Mn^{II}] = 7.28×10^{-6} mol dm^{-3}, pH = 6.0, Temp. = 35 ± 0.1 ºC, acetone =10.0 % (v/v), λ_{max} = 470 nm, time interval = 60 s

240, with an accuracy of ± 0.1 ^{o}C. The absorption maximum (λ_{max}) of the reaction mixture was 470 nm. The value of λ_{max} remained unchanged during experimental conditions as shown in Figures 1, 2 and 3. For stopped flow kinetics study, the progress of the reaction was followed by recording the absorbance change with time at 470 nm on stopped flow apparatus (Applied Photophysics – Stopped Flow SX-20). Desired temperature (±0.01 ^{o}C) was maintained with the help of an automatic high precision thermostatic control (Thermo Scientific NESLAB RTE7).

Substrate solution was prepared by mixing known amounts of D (in acetone), Mn^{II}, acetone and buffer solution. After baseline setting to zero absorbance by emptying both syringes loaded with buffer solution, one of the syringes was loaded with periodate solution of known concentration, while other syringe was loaded with substrate solution. The reaction was initiated by emptying the syringes. Collected data were treated by the software (SX-20, Pro-data) for determining the pseudo-first order rate constants.
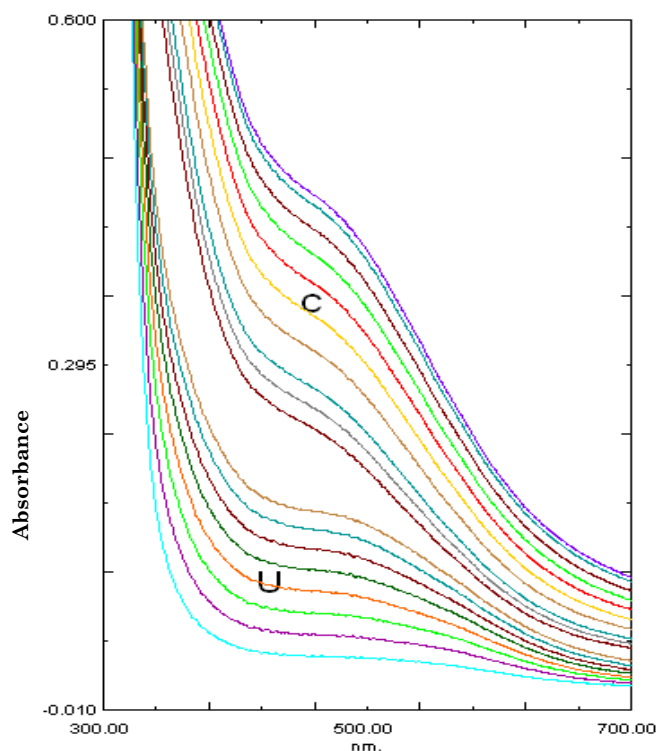

Figure 3. Compression of UV-VIS rapid scans of unanalyzed and catalyzed. Reaction at [D] = 2.0×10^{-4} mol dm^{-3}; [I] = 2.0×10^{-2} mol dm^{-3}, pH = 6.0, Temp. = 35 ± 0.1 ^{o}C, acetone =10.0 % (v/v), λ_{max} = 470 nm; [Mn^{II}] =7.28×10^{-6} mol dm^{-3} (for catalysed reaction only). U and C represent the scans for uncatalysed and catalysed reaction, respectively.

3. Results and Discussion

3.1. Preliminary Investigation

The absorption maxima of the reaction mixture containing Mn^{II}, D and I differed widely from that of the mixture containing only D and $NaIO_4$. Further, absorbance measurements indicated there to be no observable reaction between Mn^{II} and I or Mn^{II} and D. On mixing D and I, the solution turned light yellow and the nature of spectrum (Figure 1) was quite different from the individual spectra of D and I indicating the formation of complex or adduct, D - I. The λ_{max} of this adduct was found to be 470 nm, which did not change with time, as shown in Figure 1.

Our purpose was to study the kinetics of periodate oxidation of D in presence of Mn^{II}, which is known to be a catalyst for this system [23]. Therefore, the rapid scan spectra of the solution containing Mn^{II}, $NaIO_4$ and D were recorded and are shown in Figure 2. This mixture is yellow in colour, which deepens with progress of time. A comparison of spectrum of D - Mn^{II} - I system with that of I - D system indicates the formation of a ternary complex, Mn^{II} – D – I, when Mn^{II} is present. Although, λ_{max} is same (470 nm in Figure 3), but the molar extinction coefficient of ternary complex is high.

The reaction between periodate and D in presence of Mn^{II} has been shown to be first order in each reactant and catalyst as already reported [23]. So the kinetics was studied under pseudo first order conditions.

3.2. Stability Constant of D - Mn^{II} - I Ternary Complex

Stop-flow spectrophotometric method was used to study the ternary complex formation and to determine its stability constant. In all the experiments, both [I] and [D] were in large excess (at least ten times) over [Mn^{II}], and [I] was in excess over [D]. The stop-flow trace, as presented in Figure 4, shows the reaction to occur in two steps. The first step, which is presumably the formation of ternary complex, is relatively fast with 70% reaction occurring in ~200 s; the second stage is relatively quite slow. The ternary complex attained equilibrium in about 500 - 1500 s depending upon the reactant concentrations. The relatively faster rate of the first stage allowed us to assume maximum absorbance recorded in each stop-flow run to be equal to the equilibrium absorbance of the ternary complex. The values of equilibrium absorbance (A_e) are given in Table 1.
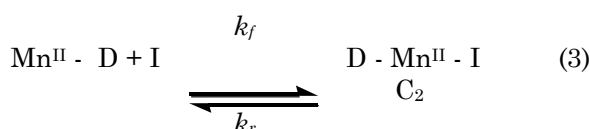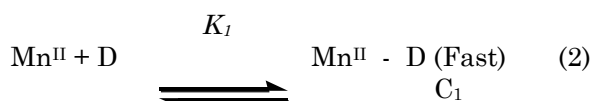
Ternary complex was formed in stop-flow

experiment, when a solution containing Mn^{II} and D was mixed with solution of $NaIO_4$. The formation of a complex can be written as in Equation (1).

$$Mn^{II} + D + I \overset{K}{\underset{}{\rightleftharpoons}} \underset{C_2}{D - Mn^{II} - I} \qquad (1)$$
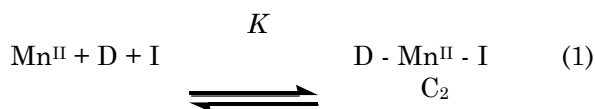
where C_2 represents the ternary complex, D - Mn^{II} - I.

The probable mechanism of the formation of ternary complex can be given in Equation (2).

$$Mn^{II} + D \overset{K_1}{\underset{}{\rightleftharpoons}} \underset{C_1}{Mn^{II} - D \text{ (Fast)}} \qquad (2)$$

$$Mn^{II} - D + I \overset{k_f}{\underset{k_r}{\rightleftharpoons}} \underset{C_2}{D - Mn^{II} - I} \qquad (3)$$

Subsequently, the ratio k_f/k_r has been used to represent K_2, the equilibrium constant of reaction (Equation (3)).

The spectra of D, I, Mn^{II} and reaction mixtures for catalysed / uncatalysed reactions show that the only principal species absorbing at 470 nm is ternary complex. At this wavelength, Mn^{II}, D, Mn^{II} - D and Mn^{II} - I display no significant absorbance. However, the D - I adduct absorb at 470 nm, but its absorbance is not sizable and, therefore, can be ignored.

Table 1. Equilibrium absorbance for [D- Mn^{II}-I] ternary complex formation. $[Mn^{II}]$ = 7.28×10⁶ mol dm⁻³, pH = 6.0, Temp. = 35 ± 0.01 °C, acetone = 10.0 % (v/v), λ_{max} = 470 nm

[NaIO₄] (mol dm⁻³)	[D] (mol dm⁻³)	Absorbance at equilibrium (Aₑ)
0.010	0.0002	0.082
0.015	0.0002	0.097
0.020	0.0002	0.102
0.025	0.0002	0.117
0.030	0.0002	0.125
0.010	0.0001	0.052
0.010	0.0002	0.082
0.010	0.0003	0.126
0.010	0.0004	0.156
0.010	0.0005	0.184

If the absorbance values at pre-selected wavelength, 470 nm, are measured in solutions containing different [D] and [I] but at fixed $[Mn^{II}]$, it can be shown that [25, 26]:

$$A_e = - (A_e - A_0) / K \text{ [D] [I]} + A_\infty \qquad (4)$$

where A_e is the absorbance of the ternary complex at equilibrium, A_∞ is the absorbance when Mn^{II} is fully present as ternary complex, and A_0 is the absorbance of Mn^{II} in the absence of D and I. K is the overall stability constant and based on Equation (1) is defined by Equation (5).

$$K = [Mn^{II} - D - I] / [Mn^{II}] \text{ [D] [I]} \qquad (5)$$

where, $[Mn^{II} - D - I] = [C_2]_{eq}$ = equilibrium concentration of ternary complex, $[Mn^{II}]$ = equilibrium concentration of uncomplexed Mn^{II}. [D] and [I] are initial concentrations of D and periodate, respectively.

On replacing $[Mn^{II} - D - I]$ by $[C_2]_{eq}$, Equation (5) becomes Equation (6) or (7).

$$K = [C_2]_{eq} / [Mn^{II}] \text{ [D] [I]} \qquad (6)$$
$$[Mn^{II}] = [C_2]_{eq} / K \text{ [D] [I]} \qquad (7)$$

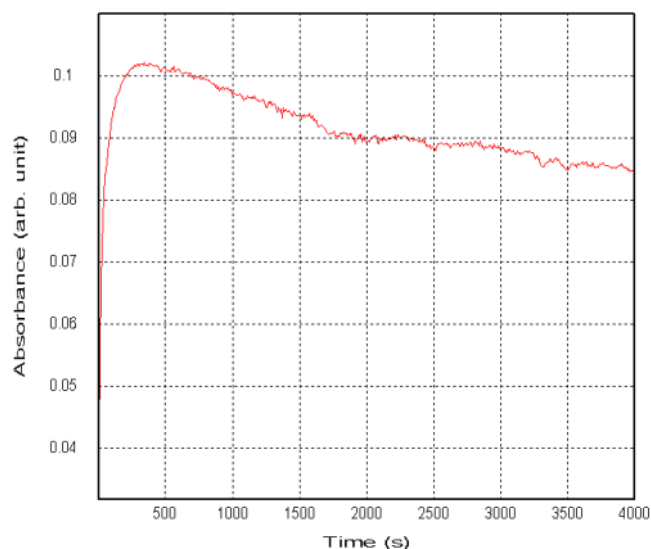By mass balance, total Mn^{II} concentration, $[Mn^{II}]_0$ is given by Equation (8):

Figure 4. The complete kinetic profile (in terms of stopped flow trace) for Mn^{II} catalyzed oxidation of D by $NaIO_4$ at [D] = 2.0×10⁻⁴ mol dm⁻³, pH = 6.0, [I] = 2.0×10⁻² mol dm⁻³, $[Mn^{II}]$ = 7.28×10⁻⁶ mol dm⁻³, Temp. = 35 ± 0.01 °C, acetone =10.0 % (v/v), λ_{max} = 470 nm

$$[Mn^{II}]_0 = [Mn^{II}] + [Mn^{II} \cdot D] + [Mn^{II} \cdot D \cdot I] \quad (8)$$
$$\qquad\qquad\qquad [C_1] \qquad\qquad [C_2]_{eq}$$

Since $[Mn^{II} \cdot D]$ is assumed to be very small, it can be neglected in Equation (8).

$$[Mn^{II}]_0 = [Mn^{II}] + [C_2]_{eq} \qquad (9)$$
or
$$[C_2]_{eq} = [Mn^{II}]_0 - [Mn^{II}] \qquad (10)$$

Putting the value of $[Mn^{II}]$ from Equation (7) into Equation (10), we get:

$$[C_2]_{eq} = [Mn^{II}]_0 - [C_2]_{eq}/ K [D] [I] \qquad (11)$$

As already mentioned in the section 3.1, absorbance measurements indicated no observable reaction between Mn^{II} and I or Mn^{II} and D. The experiments were conducted separately by
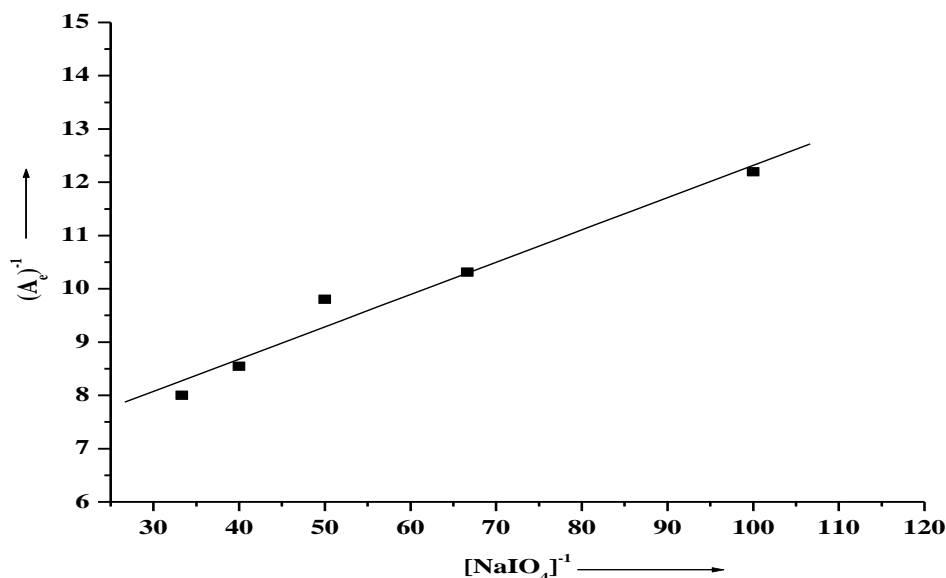
Figure 5. A plot $(A_e)^{-1}$ vs $[I]^{-1}$ at $[D] = 2.0\times10^{-4}$ mol dm^{-3}, pH = 6.0, $[Mn^{II}] = 7.28\times10^{-6}$ mol dm^{-3}, Temp. = 35 ± 0.01 °C, acetone = 10.0 % (v/v), $\lambda_{max} = 470$ nm
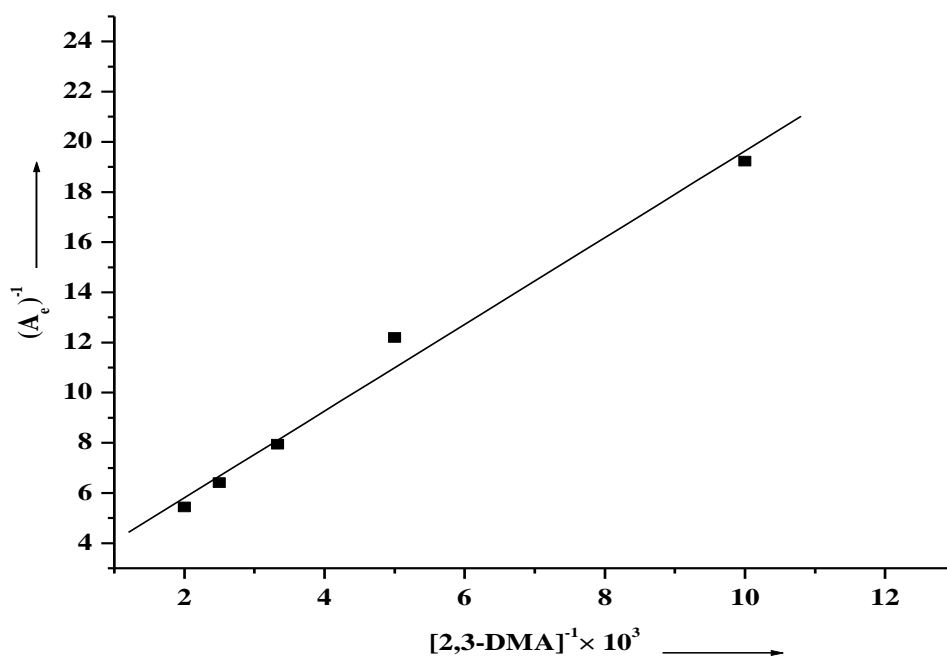
Figure 6. Plot $(A_e)^{-1}$ vs $[D]^{-1}$ at $[NaIO_4)] = 1.0 \times 10^{-2}$ mol dm^{-3}, pH = 6.0, $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, Temp. = 35 ± 0.01 °C, Acetone = 10.0 % (v/v), $\lambda_{max} = 470$ nm

mixing Mn^{II} and D and no absorbance was found at chosen wavelength i.e. 470 nm. Further, there was absorbance noted and recorded when all the three, i.e. I, Mn^{II} and D were mixed. Therefore, under the experimental conditions of this study, the binary complex, Mn^{II} – D, has no absorbance at chosen wavelength (470 nm). A_e can be assumed to be the absorbance due to ternary complex only.

If A_e is absorbance of ternary complex, C_2, and $\mathcal{E}$ is its molar absorptivity then for cell of path length 1 cm, we have:

$$A_e = \mathcal{E}\,[C_2] \tag{12}$$

where $[C_2]$ is the concentration of the ternary complex at time t. When whole of the manganese(II), i.e., $[Mn^{II}]_0$, is present as complex, then observed absorbance is equal to A_∞. So replacing the values of A_e by A_∞ and $[C_2]$ by $[Mn^{II}]_0$ in Equation (12), we obtain:

$$A_\infty = [Mn^{II}]_0 \cdot \mathcal{E}$$

or

$$[Mn^{II}]_0 = A_\infty / \mathcal{E} \tag{13}$$

Substituting the value of $[C_2]$ and $[Mn^{II}]_0$ into Equation (11) from Equations (13) and (12).

$$A_e / \mathcal{E} = A_\infty / \mathcal{E} - A_e / \mathcal{E}\,K\,[D]\,[I]$$

which on rearrangement becomes Equation (14):

$$1 / A_e = 1 / A_\infty\,K\,[D]\,[I] + 1/A_\infty \tag{14}$$

This equation assumes that no species other then ternary complex absorbs at chosen wavelength, 470 nm.

Table 2. Effect of variation of concentration of reactants on the reaction rate. $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, pH = 6.0, Temp. = 35 ± 0.01 °C, acetone = 10.0 % (v/v), λ_{max} = 470 nm

$[NaIO_4]$ mol dm^{-3}	[D] mol dm^{-3}	$10^2\,k_{obs}$ (s^{-1})
0.010	0.0002	2.64
0.015	0.0002	2.75
0.020	0.0002	2.83
0.025	0.0002	2.92
0.030	0.0002	3.02
0.010	0.0001	2.56
0.010	0.0002	2.64
0.010	0.0003	3.21
0.010	0.0004	3.68
0.010	0.0005	3.93

The values of A_e were determined first at different concentration of I and keeping [D] fixed. Under this condition Equation (14) becomes Equation (15).

$$1/A_e = 1/A_\infty + 1/ K_3\,[I]\,A_\infty \tag{15}$$

Equation (15) is equivalent to Equation (14) through $K_3 = K\,[D]$.

In another set of experiments, the values of A_e were determined at different concentration of [D] but at fixed concentration of [I]. Under this condition Equation (14) becomes:

$$1/A_e = 1/A_\infty + 1/K_4\,[D]\,A_\infty \tag{16}$$

A comparison of Equations (14) and (16) shows $K_4 = K\,[I]$.

As required by Equation (15), the plot of $1/A_e$ versus $1/[I]$ is a straight line as shown in Figure 5. This plot yields slope, $S_1 = 8.0 \times 10^{-2}$ and intercept, $I_1 = 6.25$. According to equation (15), $S_1 = 1/ K_3\,A_\infty$ and $I_1 = 1/A_\infty$. So from the ratio, I_1/ S_1, the value of K_3 was found to be 78.

Likewise, from Figure 6, we obtain, slope, $S_2 = 1.71 \times 10^{-3}$ and intercept, $I_2 = 2.07$. Equation (16) shows $K_4 = I_2/S_2$. From the values of S_2 and I_2, we obtain $K_4 = 1.2 \times 10^3$.

Now from the K_4 value of 1.2×10^3 (at [I] = 0.01 mol dm^{-3}), which is equal to $K\,[I]$, the value of K was found to be 1.2×10^5. On the other hand from the K_3 value of 78 (at [D] = 2×10^{-4} mol dm^{-3}), which is equal to $K\,[D]$, the value of K is found to be 3.1×10^5.
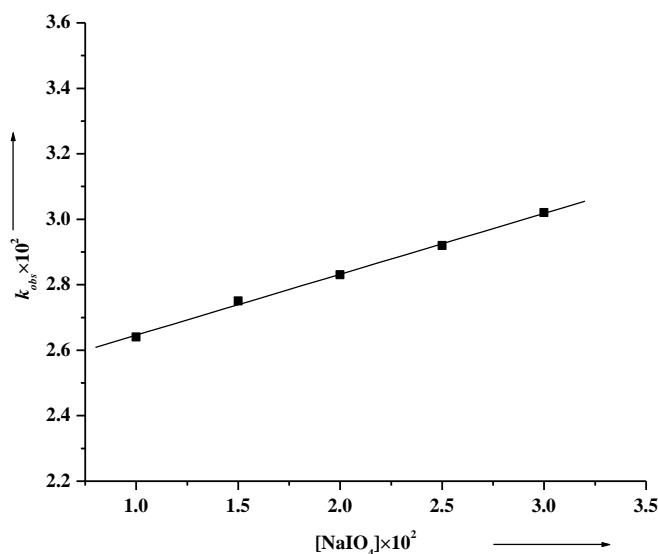

Fig. 7. k_{obs} vs [I] plot at [D] = 2.0×10^{-4} mol dm^{-3}, $[Mn^{II}]$ = 7.28×10^{-6} mol dm^{-3}, pH = 6.0, Temp. = 35 ± 0.01 °C, acetone = 10.0 % (v/v), λ_{max} = 470 nm

The excellent agreement between the K values, as determined from the [I] and [D] variations at fixed $[Mn^{II}]_0$, validates the hypothesis regarding the formation of ternary complex. The average value of K is $(2.2 \pm 1.0) \times 10^5$ at pH = 6.0, $[Mn^{II}]_0 = 7.28 \times 10^{-6}$ mol dm^{-3} and 35 °C.

3.3. Kinetics of Ternary Complex Formation

The complete profile of a kinetics run is shown in Figure 4. As indicated earlier, the reaction occurs in two stages the second stage is relatively slow. The first stage represents possibly the formation of ternary yellow complex, for which the stability constant determination has just been described.

In section 3.1, It has already been mentioned that the reaction has been shown to be first order in I, Mn^{II} and D as already reported [23]. Therefore, in present case, the kinetics was studied under pseudo first order conditions. The kinetics of the formation of the com-

plex was studied at 470 nm under pseudo first order conditions with [I] being in excess over [D] and $[Mn^{II}]_0$ both and [D] being in excess over $[Mn^{II}]_0$. Under these conditions, the ternary complex formation follows the pseudo first order kinetics and the values of pseudo first order rate constant, k_{obs}, are given in Table 2. Some first order plots are given in Figures 7 and 8.

The value of k_{obs} appear to be only dependent on [D] & [I] which were in excess as compared to $[Mn^{II}]$. k_{obs} may be defined by the Equation 17.

$$k_{obs} = k_f'[I] + k_r \qquad (17)$$

where k_f' and k_r are empirical rate constants as defined later. As required by Equation (17), the plot of k_{obs} versus [I] is linear as shown in Fig. 13. From this plot, the value of k_f' and k_r were found to be 0.19 l mol^{-1} s^{-1} and 2.5×10^{-2} s^{-1}, re-

Table 3. Data Analysis for [Mn^{II}-D-I] ternary complex formation

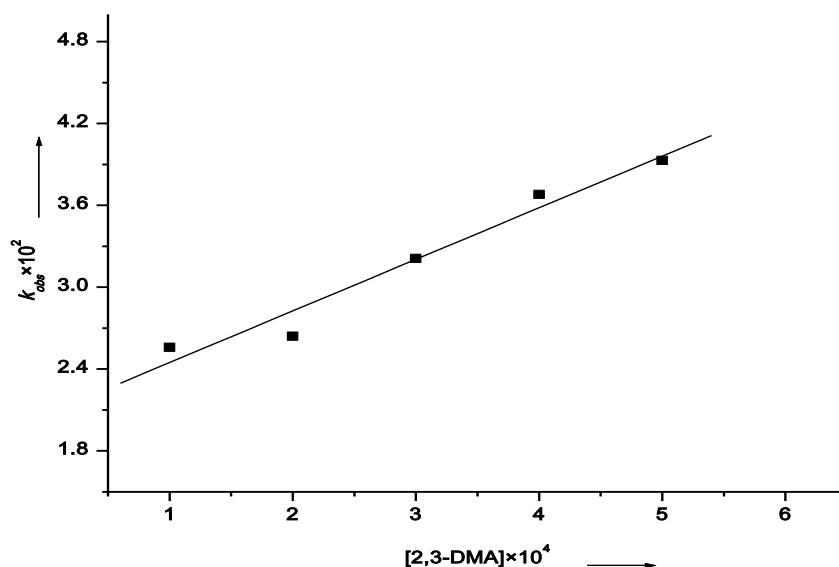| [I] mol dm^{-3}	[D] mol dm^{-3}	Plot	k_r (Intercept)	k_f' (slope) $= k_f K_1[D]$	k_f' (slope) $= k_f K_1[I]$	10^{-3} $k_f K_1$	10^{-5} $k_f K_1 / k_r$
variation	2×10^{-4}	k_{obs} vs [I]	2.46×10^{-2}	0.19	-	1.0	0.40
1.0×10^{-2}	variation	k_{obs} vs [D]	2.07×10^{-2}	-	37.69	3.8	1.80

Figure 8. k_{obs} vs [D] plot at [I] = 1.0×10^{-2} mol dm^{-3}, $[Mn^{II}]$ = 7.28×10^{-6} mol dm^{-3}, pH = 6.0, Temp = 35 ± 0.01 °C, acetone = 10.0 % (v/v), λ_{max} = 470 nm

spectively.

3.4. Mechanism of the Reaction

The kinetics results of ternary complex formation may be explained by the mechanism (Equations 2-3), which is decidedly not unique. It is possible to write one or more alternative mechanisms to explain the results obtained in this study.

The rate of formation of C_2 is given by:

$$d\,[C_2]/dt = k_f\,[Mn^{II}.D]\,[I] - k_r\,[C_2] \qquad (18)$$

where $[C_2]$ is the concentration of the ternary complex at time t.
By mass balance:

$$[Mn^{II}]_0 = [Mn^{II}] + [Mn^{II}.D] + [C_2] \qquad (19)$$

Assuming that the concentration of Mn^{II} - D is very small, and then on neglecting it, Equation (19) becomes Equations (20).

$$[Mn^{II}]_0 = [Mn^{II}] + [C_2] \qquad (20)$$

Assuming that equilibrium for the formation of the binary complex, Mn^{II} - D, is rapidly established then the value of concentration of Mn^{II} - D is given by Equation (21).

$$K_1 = [Mn^{II}.D]/[Mn^{II}][D] \qquad (21)$$

Substituting $[Mn^{II}$ - $D] = K_1\,[Mn^{II}][D]$ in Equation (18), we get:

$$d[C_2]/dt = k_f\,K_1\,[Mn^{II}][D]\,[I] - k_r[C_2] \qquad (22)$$

On substituting $[Mn^{II}] = [Mn^{II}]_0 - [C_2]$ from Equation (20) in Equation (22), we get:

$$d[C_2]/dt = k_f\,K_1[Mn^{II}]_0[D][I]\text{-}[C_2](k_fK_1[D][I] + k_r) \qquad (23)$$

If the ternary complex formation attains equilibrium then, $d[C_2]/dt = 0$ and $[C_2] = [C_2]_{eq}$, where $[C_2]_{eq}$ is the concentration of ternary complex at equilibrium. Under these conditions Equation (23) becomes Equation (24).

$$k_f\,K_3[Mn^{II}]_0[D][I] = [C_2]_{eq}(\,k_f\,K_1\,[D][I] + k_r) \qquad (24)$$

Now from Equations (23) and (24), we get:

$$d[C_2]/dt = (\,k_f\,K_1\,[D][I]+ k_r)(\,[C_2]_{eq} - [C_2]) \qquad (25)$$

which on modification becomes:

$$d[C_2]/dt = k_{obs}\,([C_2]_{eq} - [C_2]) \qquad (26)$$

where:

$$k_{obs} = k_f\,K_1\,[D][I] + k_r \qquad (27)$$
or
$$k_{obs} = k_f'\,[I] + k_r \qquad (17)$$

where $k_f' = k_f\,K_1\,[D]$. On integrating Equation (26), we get:

$$\ln\{[C_2]_{eq}/\,(\,[C_2]_{eq} - [C_2])\} = k_{obs}\,.\,t \qquad (28)$$

According to Equation (27) the plot of k_{obs} versus [I] (at constant [D]) is straight line with a intercept = k_r and slope = $k_f\,K_1[D]$ (Figure 7).

Likewise, from Equation (27) the plot of k_{obs} versus [D] (at constant [I]) is also straight line with intercept = k_r and slope = $k_fK_1[I]$ (Figure 8). The values of slopes and intercepts determined from these Figures are given in Table 3.

Using the values of intercepts and slopes of plots in Figures 7 and 8, the values of $k_f.K_1$ were found to be 1.0×10^3 and 3.8×10^3 dm^6 $mol^{-2}\,s^{-1}$ from periodate and 2,3-dimethylaniline variations, respectively. Likewise, the values of $k_f\,K_1/k_r$ determined from same figures were found to be 0.4×10^5 and 1.8×10^5 dm^6 mol^{-2}. The good agreement between the parameters determined from two different variations support the mechanism and the rate law proposed.

4. Conclusion

Stopped flow kinetics of Mn^{II} catalysed periodate oxidation of 2,3-dimethylaniline(D) in acetone-water medium and equilibrium absorbances have been used for the first time for evaluation of stability constant of the ternary intermediate unstable complex being formed in this reaction. The stability constant evaluated for D - Mn^{II} - IO_4^- ternary complex is $(2.2 \pm 1.0) \times 10^5$. Based on the proposed mechanism of formation of this complex, the rate law under pseudo first order conditions is: $\ln\{[C_2]_{eq}/\,(\,[C_2]_{eq} - [C_2])\} = k_{obs}\,.\,t$, where, k_{obs} is the pseudo first order rate constant, $[C_2]$ is concentration of ternary complex at given time t, $[C_2]_{eq}$ is the equilibrium concentration of ternary complex. The value of stability constant is in good agreement with that obtained from the proposed rate law.

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