Stopped flow kinetics of Mn$^{II}$ catalysed periodate oxidation of 3,5-dimethyl-aniline – Evaluation of stability constant of the ternary intermediate complex

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\begin{abstract}
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 kinetic study and evaluation of stability constant of ternary complex forming in the Mn$^{II}$-catalysed periodate oxidation of 3,5-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$_4^-$-ter-nary complex by determining equilibrium absorbance is $(4.5\pm0.1)\times10^5$. Kinetics of ternary complex formation was defined by the rate law (A) under pseudo-first order conditions.

\begin{equation}
\ln\left[\frac{[C_2]_{eq}}{([C_2]_{eq} - [C_2])}\right] = k_{obs}t \tag{A}
\end{equation}

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.

Keywords : Stopped flow kinetics, stability constant, ternary complex, Mn$^{II}$ catalysed, periodate oxidation, 3,5-dimethylaniline.
\end{abstract}

\section*{Introduction}
Aromatic amines are used as intermediates in the manufacture of plastics, dyes, drugs, explosives, rubber, epoxy polymers, azo dyes, aromatic polyurethane products and pesticide\textsuperscript{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\textsuperscript{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 peroxodisulphate ion\textsuperscript{4}, benzimidazolium fluoro-chromate\textsuperscript{5} and periodate\textsuperscript{5} 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 reaction mechanism of uncatalysed reactions\textsuperscript{7–11}. 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$^{II}$\textsuperscript{12–17}. In continuation to our studies on periodate oxidation of 3,5-dimethylaniline catalyzed by Mn$^{II}$\textsuperscript{18} 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 3,5-dimethylaniline in acetone-water medium are being presented and discussed in this communication.

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Experimental

Reagents and chemicals:

The principal reagents used were sodium metaperiodate (Loba Chemie), 3,5-dimethylaniline (Aldrich), manganese sulphate monohydrate (Aldrich) here-to-after referred as I, D and MnII, 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,\textsuperscript{19} used for maintaining the pH of reaction mixtures, was prepared by mixing desired 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.

Kinetic procedure:

All UV-Visible absorbance measurements were made on Shimadzu double beam spectrophotometer (UV-2450). The reaction was initiated by adding temperature equilibrated NaIO\textsubscript{4} solution of known concentration to the reaction mixture containing D, Mn\textsuperscript{II} and buffer. The temperature of reaction mixture was maintained in the UV-Vis spectrophotometer with the help of an in-built temperature control unit, Shimadzu TCC-240, with an accuracy of \(\pm 0.1 \, ^\circ\text{C}\). The absorption maximum (\(\lambda_{\text{max}}\)) of the reaction mixture was 530 nm. The value of \(\lambda_{\text{max}}\) remained unchanged during experimental conditions as shown in Figs. 1, 2 and 3. For stopped flow kinetics study, the progress of the reaction was followed by recording the absorbance change with time at 530 nm on stopped flow apparatus (Applied Photophysics – Stopped Flow SX-20). Desired temperature (\(\pm 0.01 \, ^\circ\text{C}\)) 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\textsuperscript{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.

Results and discussion

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 violet which later changes in to orange colour and the nature of spectrum (Fig. 1) was quite different from the individual spectra of D and I indicating the formation of complex or adduct, D-I. The $\lambda_{\text{max}}$ of this adduct was found to be 530 nm, which did not change with time, as shown in Fig. 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$^{18}$. Therefore, the rapid scan spectra of the solution containing Mn$^{II}$, NaIO$_4$ and D were recorded and are shown in Fig. 2. This mixture is orange 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, $\lambda_{\text{max}}$ is same (530 nm in Fig. 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$^{18}$. So the kinetics was studied under pseudo-first order conditions.

**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 Fig. 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 $\approx$ 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.
Table 1. Equilibrium absorbances for [D-MnII-I] ternary complex formation

| [NaIO₄] (mol dm⁻³) | [3,5-DMA] (mol dm⁻³) | [MnII]×10⁶ (mol dm⁻³) | Absorbance at equilibrium (Aₑ) |
|---------------------|-----------------------|------------------------|-------------------------------|
| 0.005               | 0.0002                | 7.28                   | 0.063                         |
| 0.010               | 0.0002                | 7.28                   | 0.108                         |
| 0.015               | 0.0002                | 7.28                   | 0.118                         |
| 0.020               | 0.0002                | 7.28                   | 0.130                         |
| 0.025               | 0.0002                | 7.28                   | 0.139                         |
| 0.010               | 0.0001                | 7.28                   | 0.069                         |
| 0.010               | 0.0002                | 7.28                   | 0.108                         |
| 0.010               | 0.0003                | 7.28                   | 0.118                         |
| 0.010               | 0.0004                | 7.28                   | 0.142                         |
| 0.010               | 0.0005                | 7.28                   | 0.160                         |
| 0.010               | 0.0002                | 3.28                   | 0.041                         |
| 0.010               | 0.0002                | 5.28                   | 0.065                         |
| 0.010               | 0.0002                | 7.28                   | 0.108                         |
| 0.010               | 0.0002                | 9.28                   | 0.113                         |

Ternary complex was formed in stop-flow experiment, when a solution containing MnII and D was mixed with solution of NaIO₄. The formation of a complex can be written as in eq. (1),

\[ \text{Mn}^{II} + \text{D} + \text{I} \xrightleftharpoons[K_{2}]{K} \text{C}_{2} \text{D-Mn}^{II-I} \]  

where C₂ represents the ternary complex, D-MnI⁻II-I.

The probable mechanism of the formation of ternary complex can be given as follows:

\[ \text{Mn}^{II} + \text{D} \xrightarrow[K_{1}]{K} \text{C}_{1} \text{Mn}^{II-D} \text{(Fast)} \]  
\[ \text{Mn}^{II-D} + \text{I} \xrightarrow[K_{2}]{K} \text{C}_{2} \text{D-Mn}^{II-I} \]  

Subsequently, the ratio \( k_{1}/k_{2} \) has been used to represent \( K_{2} \), the equilibrium constant of reaction (3).

The spectra of D, I, MnII and reaction mixtures for catalysed/uncatalysed reactions show that the only principal species absorbing at 530 nm is ternary complex. At this wavelength, MnII, D, MnII-D and MnII-I display no significant absorbance. However, the D-I adduct absorb at 530 nm, but its absorbance is not sizable and, therefore, can be ignored.

If the absorbance values at pre-selected wavelength, 530 nm, are measured in solutions containing different [D] and [I] but at fixed [MnII], it can be shown that

\[ A_{e} = - \frac{(A_{e} - A_{0})/K}{[\text{D}] [\text{I}]} + A_{\infty} \]  

where \( A_{e} \) is the absorbance of the ternary complex at equilibrium, \( A_{\infty} \) is the absorbance when MnII is fully present as ternary complex and \( A_{0} \) is the absorbance of MnII in the absence of D and I. \( K \) is the overall stability constant and based on eq. (1) is defined by eq. (5).

\[ K = \frac{[\text{Mn}^{II-D-I}]/[\text{Mn}^{II}]}{[\text{D}][\text{I}]} \]  

where, \([\text{Mn}^{II-D-I}] = [\text{C}_{2} \text{eq} = \text{equilibrium concentration of ternary complex, } [\text{Mn}^{II}] = \text{equilibrium concentration of uncomplexed MnII. And [D] and [I] are initial concentrations of D and periodate, respectively.} \]

On replacing \([\text{Mn}^{II-D-I}] \) by \([\text{C}_{2} \text{eq} \), eq. (5) becomes eqs. (6) or (7).

\[ K = \frac{[\text{C}_{2} \text{eq}]/[\text{Mn}^{II}]}{[\text{D}][\text{I}]} \]  
\[ [\text{Mn}^{II}] = [\text{C}_{2} \text{eq}]/K \]  

By mass balance, total MnII concentration, \([\text{Mn}^{II}]_{0} \) is given by eq. (8).

\[ [\text{Mn}^{II}]_{0} = [\text{Mn}^{II}] + [\text{Mn}^{II-D}] + [\text{Mn}^{II-D-I}] \]  

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

\[ [\text{Mn}^{II}]_{0} = [\text{Mn}^{II}] + [\text{C}_{2} \text{eq} \]  

or

\[ [\text{C}_{2} \text{eq} = [\text{Mn}^{II}]_{0} - [\text{Mn}^{II}] \]  

Putting the value of \([\text{Mn}^{II}] \) from eq. (7) into eq. (10), we get

\[ [\text{C}_{2} \text{eq} = [\text{Mn}^{II}]_{0} - [\text{C}_{2} \text{eq}]/K \]  

Under the experimental conditions of this study, the binary complex, MnII-D, has no absorbance at chosen wavelength (530 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 \( \varepsilon \) is its molar absorptivity then for cell of path length 1 cm, we have

\[ A_{e} = \varepsilon \times [C_{2}] \]
where \([C_2]\) is the concentration of the ternary complex at time \(t\). When whole of the manganese(II), i.e. \([\text{Mn}^{II}]_0\), is present as complex, then observed absorbance is equal to \(A_\infty\). So replacing the values of \(A_e\) by \(A_\infty\) and \([C_2]\) by \([\text{Mn}^{II}]_0\) in eq. (12), we obtain,

\[
A_\infty = [\text{Mn}^{II}]_0 \varepsilon
\]

or

\[
[\text{Mn}^{II}]_0 = A_e/\varepsilon
\]  

(13)

Substituting the value of \([C_2]\) and \([\text{Mn}^{II}]_0\) in eq. (11) from eqs. (13) and (12).

\[
A_e/\varepsilon = A_\infty/\varepsilon - A_e/\varepsilon \ K \ [D] \ [I]
\]

which on rearrangement becomes eq. (14)

\[
1/A_e = 1/A_\infty \ K \ [D] \ [I] + 1/A_\infty
\]

(14)

This equation assumes that no species other than ternary complex absorbs at chosen wavelength, 530 nm.

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

\[
1/A_e = 1/A_\infty + 1/K_3 \ [I] A_\infty
\]

(15)

Eq. (15) is equivalent to eq. (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 eq. (14) becomes,

\[
1/A_e = 1/A_\infty + 1/K_3 \ [D] \ A_\infty
\]

(16)

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

As required by eq. (15), the plot of \(1/A_e\) versus \(1/[I]\) is a straight line as shown in Fig. 5. This plot yields slope, \(S_1 = 5.4 \times 10^{-2}\) and intercept, \(I_1 = 4.77\). According to eq. (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 88.2.

Likewise, from Fig. 6, we obtain, slope, \(S_2 = 9.9 \times 10^{-4}\) and intercept \(I_2\) was found to be 4.58. Eq. (16) shows \(K_4 = I_2/S_2\). From the values of \(S_2\) and \(I_2\), we obtain \(K_4 = 4.62 \times 10^3\).

Now from the \(K_4\) value of \(4.62 \times 10^3\) (at \([I]\) = 0.01 mol dm\(^{-3}\)), which is equal to \(K \ [I]\), the value of \(K\) was found to be \(4.62 \times 10^5\). On the other hand from the \(K_3\) value of 88.2 (at \([D]\) = \(2 \times 10^{-3}\) mol dm\(^{-3}\)), which is equal to \(K \ [D]\), the value of \(K\) is found to be \(4.4 \times 10^5\).

The excellent agreement between the \(K\) values, as determined from the \([I]\) and \([D]\) variations at fixed \([\text{Mn}^{II}]_0\), validates the hypothesis regarding the formation of ternary complex. The average value of \(K\) is \((4.5 \pm 0.1) \times 10^5\) at \(pH = 5.0, [\text{Mn}^{II}]_0 = 7.28 \times 10^{-6}\) mol dm\(^{-3}\) and \(35.0 \pm 0.01^\circ C\).

**Kinetics of ternary complex formation:**

The complete profile of a kinetics run is shown in Fig. 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 orange complex, for which the stability constant deter-
mination has just been described. The kinetics of the formation of the complex was studied at 530 nm under pseudo-first order conditions with \[\text{[I]}\] being in excess over \[\text{[D]}\] and \[\text{[Mn}^{\text{II}}\] both and \[\text{[D]}\] being in excess over \[\text{[Mn}^{\text{II}}\] \(_0\). The ternary complex formation follows the first order kinetics and the values of first order rate constant, \(k_{\text{obs}}\), are given in Table 2. Some first order plots are given in Figs. 7 and 8.

**Table 2.** Effect of variation of concentration of reactants and \([\text{Mn}^{\text{II}}]\) on the reaction rate

| NaIO\(_4\) | [D] | \([\text{Mn}^{\text{II}}]\) \(\times 10^6\) | \(k_{\text{obs}}\) (s\(^{-1}\)) |
|-----------|-----|----------------|-----------------|
| (mol dm\(^{-3}\)) | (mol dm\(^{-3}\)) | (mol dm\(^{-3}\)) | |
| 0.005     | 0.0002 | 7.28 | 9.202 |
| 0.010     | 0.0002 | 7.28 | 11.222 |
| 0.015     | 0.0002 | 7.28 | 13.587 |
| 0.020     | 0.0002 | 7.28 | 15.781 |
| 0.025     | 0.0002 | 7.28 | 17.010 |
| 0.010     | 0.0001 | 7.28 | 10.674 |
| 0.010     | 0.0002 | 7.28 | 11.222 |
| 0.010     | 0.0003 | 7.28 | 12.006 |
| 0.010     | 0.0004 | 7.28 | 12.093 |
| 0.010     | 0.0005 | 7.28 | 12.368 |
| 0.010     | 0.0003 | 3.28 | 9.794  |
| 0.010     | 0.0002 | 5.28 | 10.526 |
| 0.010     | 0.0002 | 7.28 | 11.222 |
| 0.010     | 0.0002 | 9.28 | 12.793 |

Fig. 8. \(k_{\text{obs}}\) vs \([\text{I]}\) plot at \([D]=1.0 \times 10^{-2}\) mol dm\(^{-3}\), \([\text{Mn}^{\text{II}}]=7.28 \times 10^{-6}\) mol dm\(^{-3}\), pH = 5.0, Temp. = 35.0±0.01 °C, Acetone = 5.0% (v/v), \(\lambda_{\text{max}}=530\) nm. Slope = 4.259, Intercept = 0.01039.

The value of \(k_{\text{obs}}\) appear to be only dependent on \([\text{D}]\) and \([\text{I}]\) which were in excess as compared to \([\text{Mn}^{\text{II}}]\). \(k_{\text{obs}}\) may be defined by the eq. (17).

\[
k_{\text{obs}} = k_f' [\text{I}] + k_r
\]

where \(k_f'\) and \(k_r\) are empirical rate constants as defined later. As required by eq. (17), the plot of \(k_{\text{obs}}\) versus \([\text{I}]\) is linear as shown in Fig. 8. From this plot, the value of \(k_f'\) and \(k_r\) were found to be 0.40 L mol\(^{-1}\) s\(^{-1}\) and 0.72×10\(^{-2}\) s\(^{-1}\), respectively.

**Mechanism of the reaction**:

The kinetics results of ternary complex formation may be explained by the mechanism (eqs. (2) and (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 \(\text{C}_2\) is given by:

\[
d[\text{C}_2]/dt = k_f [\text{Mn}^{\text{II}}].\text{D} \cdot [\text{I}] - k_r [\text{C}_2]
\]

where \([\text{C}_2]\) is the concentration of the ternary complex at time \(t\).

By mass balance,

\[
[\text{Mn}^{\text{II}}]_0 = [\text{Mn}^{\text{II}}] + [\text{Mn}^{\text{II}}].\text{D} + [\text{C}_2]
\]

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

\[
[\text{Mn}^{\text{II}}]_0 = [\text{Mn}^{\text{II}}] + [\text{C}_2]
\]
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Table 3. Data analysis for [MnII-D-I] ternary complex formation

| [I] (mol dm⁻³) | [D] (mol dm⁻³) | k₁ | k₁ ′ | k₂ | k₂ ′ | 10⁻³ | 10⁻⁵ |
|----------------|----------------|----|------|----|------|------|------|
| Variation      | k₁obs vs [I]   | 0.72×10⁻² | 0.40 | 4.3 | 2.0  | 2.8  |
| 2×10⁻⁴         | k₁obs vs [D]   | 1.0×10⁻² | –    | 4.3 | 4.3  | 0.43 |

Assuming that equilibrium for the formation of the binary complex, MnII-D, is rapidly established then the value of concentration of MnII-D is given by eq. (21).

\[ K_1 = \frac{[\text{MnII}.D]}{[\text{MnII}].[D]} \]  

(21)

Substituting [MnII-D] = \( K_1 \) [MnII] [D] in eq. (18), we get,

\[ d[C_2]/dt = k_f K_1 [\text{MnII}].[D][I] - k_f [C_2] \]  

(22)

On substituting [MnII] = [MnII]₀ - [C₂] from eq. (20) in eq. (22), we get,

\[ d[C_2]/dt = k_f K_1 [\text{MnII}]_0 [D][I] - [C_2] (k_f K_1[D][I] + k_f) \]  

(23)

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

\[ k_f K_3 [\text{MnII}]_0 [D][I] = [C_2]_\text{eq} (k_f K_1[D][I] + k_f) \]  

(24)

Now from eqs. (23) and (24), we get,

\[ d[C_2]/dt = (k_f K_1[D][I] + k_f) \]  

(25)

which on modification becomes,

\[ d[C_2]/dt = k_{\text{obs}} ([C_2]_\text{eq} - [C_2]) \]  

(26)

where

\[ k_{\text{obs}} = k_f K_1[D][I] + k_f \]  

(27)

or

\[ k_{\text{obs}} = k_f ′[I] + k_f \]  

(17)

where \( k_f ′ \) = \( k_f K_1[D] \)

On integrating eq. (26), we get,

\[ \ln([C_2]_\text{eq} - [C_2])/[C_2]_\text{eq} = k_{\text{obs}} t \]  

(28)

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

Likewise, from eq. (27) the plot of \( k_{\text{obs}} \) versus \([D] \) (at constant \([I] \)) is also straight line with intercept = \( k_f \) and slope = \( k_f K_1[I] \) (Fig. 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 Figs. 7 and 8, the values of \( k_f K_1 \) were found to be \( 2.0×10^3 \) and \( 4.3×10^3 \) dm₆ mol⁻¹ s⁻¹ from periodate and 2,3-dimethylaniline variations, respectively. Likewise, the values of \( k_f K_1/K_f \) determined from same figures were found to be \( 2.8×10^5 \) and \( 0.43×10^5 \) dm₆ mol⁻². The good agreement between the parameters determined from two different variations support the mechanism and the rate law proposed.

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