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Studies on ternary intermediate complex formation in the Mn^{II} catalysed Periodate oxidation of *o*-Toluidine – Evaluation of Stability constant.

Jaspal Singh¹, RD Kaushik^{1*}, Nishant Khandelwal¹, Malvika Chawla¹ and Ekata Kumari².

¹Department of Chemistry, Gurukul Kangri University, Haridwar (Uttarakhand) India

²Uttaranchal College of Science and Technology, Dehradun (Uttarakhand), India

ABSTRACT

Although proposed in many cases, the ternary complexation during periodate oxidation of majority of anilines catalysed by metals like Mn^{II}, has not been thoroughly subjected to investigations particularly from point of view of evaluation of stability constant of the ternary complex formed and collecting the supporting evidences. In this paper, the formation of ternary intermediate unstable complex OT- Mn^{II} - IO₄⁻ during Mn^{II} catalysed reduction of periodate by *o*-toluidine (OT) has been explored and its stability constant has been evaluated. Its value of $(1.97 \pm 0.73) \times 10^7$ has been found to be in good agreement with that calculated from rate equation derived by us on the basis of kinetic studies made by using stopped flow method. As evidenced from the stopped flow trace, the formation of complex is comparatively faster than its decomposition into other reaction products. The kinetics of ternary complexation is given by the Eqn., $d[C_2]/dt = (k_f K_1 [OT][I] + k_r)([C_2]_{eq} - [C_2])$

where, $k_f / k_r = K_2$ i.e. equilibrium constant for the reaction of OT - Mn^{II} and IO₄⁻, K_1 equilibrium constant for formation of binary complex OT-Mn^{II}, $[C_2]$ 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, *o*-toluidine

**Corresponding author*

INTRODUCTION

Aromatic amines 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[1,2]. Being used as intermediates for plastics, drugs, rubber, explosives, polymers, pesticides etc, anilines can affect the living organisms by inhalation, skin contact and ingestion[3]. Their role in various physiological activities can be explored by studying their behavior when these come in contact with metals and oxidants. There are many reports that indicate the formation of binary or ternary complex formation as intermediates during metal catalysed/ uncatalysed oxidation of aromatic amines by periodate ion[4-30]. The detailed kinetic-mechanistic studies on Mn^{II} catalysed reduction of periodate by 2,3-xylydines and 3,5-xylydine[31,32] and studies on the ternary complex formation between these xylydines, Mn^{II} and periodate[33-34], are further continued in this communication. We have evaluated the stability constant of ternary complex while it is being formed between *o*-toluidine (OT), Mn^{II} , and periodate ion in acetone-water medium and the results along with the supporting evidences are being presented in this communication.

EXPERIMENTAL

Reagents and Chemicals

Solutions were prepared in triply distilled water. Redistilled or recrystallized chemicals like *o*-toluidine (OT) (GS Chemical), sodium metaperiodate(I) (Loba Chemie), manganese sulphate monohydrate(Mn^{II}) (Aldrich) and other chemicals of guaranteed reagent or analytical reagent grade were used. Buffers comprising of the prescribed concentrations of solutions of succinic acid, oxalic acid, boric acid, sodium sulphate and borax[35] were used for keeping pH of reaction mixtures at desired value.

Kinetic procedure

Shimadzu double beam spectrophotometer, UV-1800 was used for recording the absorption maxima(λ_{max}) of reactants, catalyst and reaction mixture in presence/ absence of catalyst. Spectrophotometer was coupled with Shimadzu TCC-240 temperature control unit with $\pm 0.1^\circ C$ accuracy. Experiments were conducted only during the time in which λ_{max} remained unchanged as shown in Fig. 1.

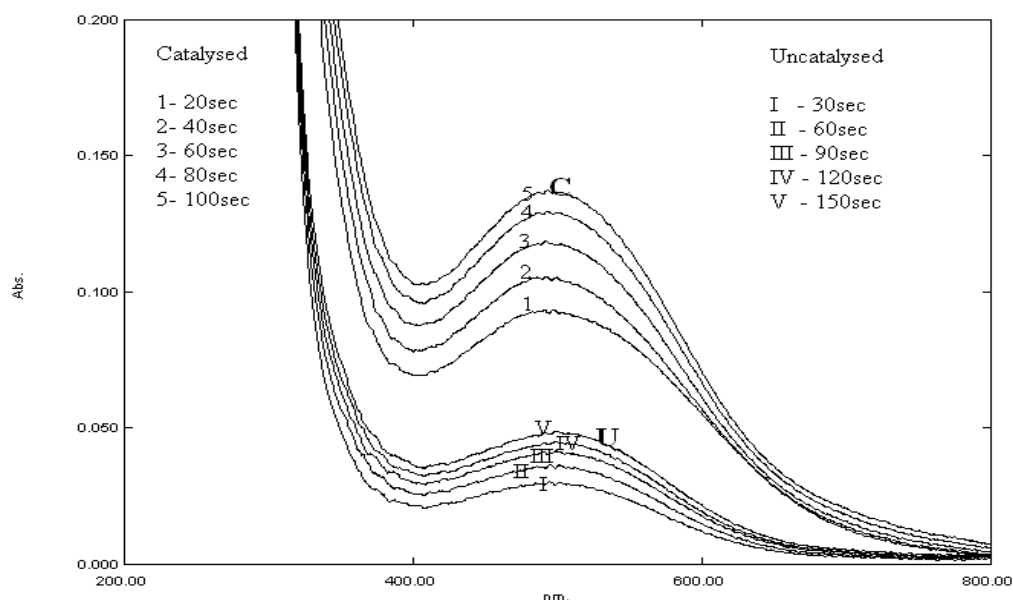


Fig.1: Compression of UV-VIS rapid scans of Uncatalyzed and Catalyzed reaction at $[OT] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[I] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), pH = 5.0, Temp. = $30 \pm 0.01^\circ C$, $\lambda_{max} = 500 \text{ nm}$, $[Mn^{II}] = 7.28 \times 10^{-7} \text{ mol dm}^{-3}$, (for Catalyzed reaction only). U and C represent the Uncatalyzed and Catalyzed reaction respectively.

As the λ_{\max} was 500 nm for the reaction mixture, the change in absorbance with time was recorded at this wavelength only using Applied Photophysics make stop flow SX-20 equipment coupled with Thermo Scientific NESLAB RTE7 thermostatic control unit with ($\pm 0.01^\circ\text{C}$ accuracy). Buffer solution was used for baseline setting to zero absorbance. After it, the reaction was started by unloading the two syringes – one loaded with periodate and the other loaded with substrate plus Mn^{II} solution. Pseudo first order rate constants were obtained by treatment of data with the software SX-20 Prodata.

RESULTS AND DISCUSSION

Preliminary observations

Following features were observed for the reaction under consideration:

1. No reaction could be observed between OT and Mn^{II} .
2. No reaction was observed between Mn^{II} and I.
3. λ_{\max} of reaction mixture (having Mn^{II} , OT and I) and same mixture without Mn^{II} , was 500 nm. However, the molar extinction coefficient is high in presence of Mn^{II} .
4. Reaction mixture turned pink which later changes in to brownish pink colour. After it, precipitation is observed in 24 hours.
5. Separate experiments showed the reaction to be first order w. r. t. OT, I and Mn^{II} . Therefore, pseudo first order conditions were adopted for following the kinetics of this reaction.

The reaction between periodate and OT in presence of Mn^{II} has been shown to be first order in each reactant and catalyst as already reported[6]. So the kinetics was studied under pseudo first order conditions.

Stability constant of OT - Mn^{II} - I ternary complex

In all experiments involving the stop-flow spectrophotometric for studying the ternary complex formation and for determining its stability constant, following conditions were maintained:

$$[\text{I}] \gg [\text{OT}] \gg \gg [\text{Mn}^{\text{II}}]$$

Fig. 2, presenting the stop-flow trace, spells out the fast formation of ternary complex (~200 s required for 70% reaction to take place). After it, a relatively slow step follows in which this complex decays. Equilibrium is attained in about 300-2000 s.

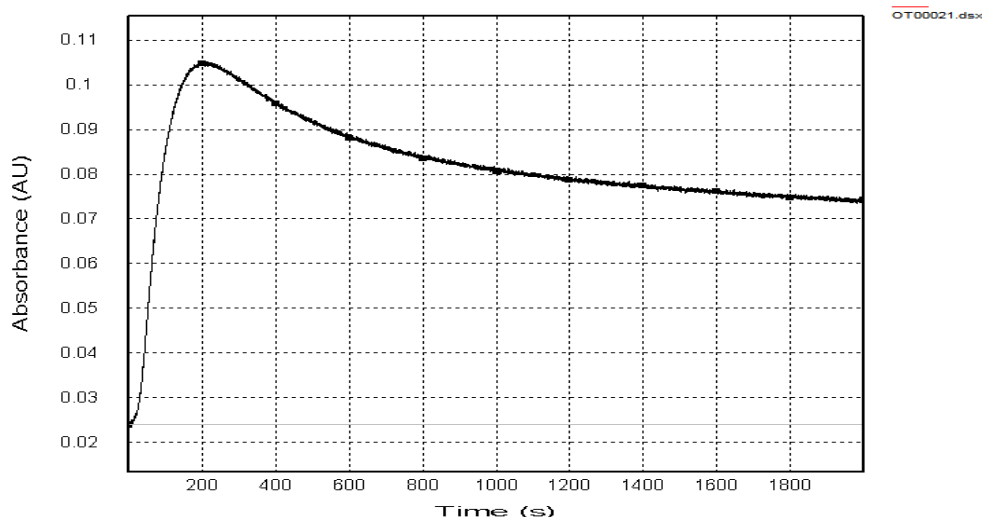


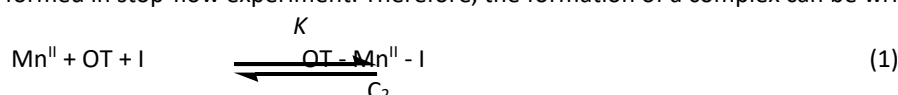
Fig. 2: The complete kinetic profile (in terms of stopped flow trace) for Mn^{II} catalysed oxidation of OT by NaIO_4 at $[\text{OT}] = 9.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\text{pH} = 5.0$, $[\text{I}] = 9.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] = 8.28 \times 10^{-6} \text{ mol dm}^{-3}$, $\text{Temp.} = 30.0 \pm 0.01^\circ\text{C}$, acetone = 5.0 % (v/v), $\lambda_{\max} = 500 \text{ nm}$.

Faster rate of formation and slower second stage, suggest that the maximum absorbance obtained in each stop flow set can be assumed to be the equilibrium absorbance (A_e) of ternary complex. A_e values are given in Table 1.

Table-1 A_e values for $[Mn^{II}-OT-IO_4^-]$ ternary complex at pH =5.0, $\lambda_{max} = 500$ nm, $[Mn(II)] \times 10^6 = 8.28$ mol dm^{-3} , Temp. = $30.0 \pm 0.01^\circ C$, Acetone = 5.0 % (v/v)

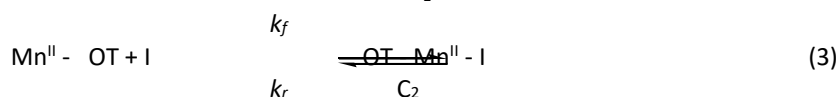
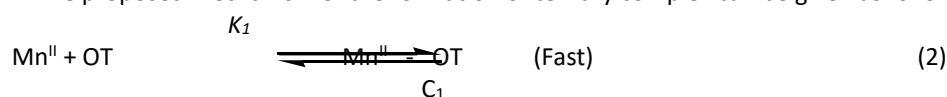
$[NaIO_4] \times 10^4$ mol dm^{-3}	$[OT] \times 10^5$ mol dm^{-3}	Absorbance at equilibrium (A_e)
7.0	9.0	0.095
8.0	9.0	0.099
9.0	9.0	0.103
10.0	9.0	0.106
11.0	9.0	0.101
9.0	7.5	0.093
9.0	8.0	0.097
9.0	8.5	0.100
9.0	9.0	0.103
9.0	9.5	0.105

When a solution containing Mn^{II} and OT was mixed with solution of I, the ternary complex was formed in stop-flow experiment. Therefore, the formation of a complex can be written as in Eq (1),



where C_2 is the ternary complex, $OT - Mn^{II} - I$.

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



Now onwards, the ratio k_f/k_r is being used to represent the equilibrium constant of reaction (3) i.e. K_2 .

The spectra of OT, I, Mn^{II} and reaction mixtures for catalysed/uncatalysed reactions show that only ternary complex absorbs at 500 nm. At this wavelength, Mn^{II} , OT, $Mn^{II} - OT$ and $Mn^{II} - I$ display no significant absorbance. However, the OT - I adduct absorb at 500 nm, but its absorbance can be ignored.

If the absorbance values at pre-selected wavelength, 500 nm, are measured in solutions containing different $[OT]$ and $[I]$ but at fixed $[Mn^{II}]$, it can be shown that [36,37]

$$A_e = - (A_e - A_0) / K[OT][I] + A_\infty \quad (4)$$

where A_e has already been defined earlier, 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 OT and I. K is the overall stability constant and based on Eq. (1) is defined by Eq. (5).

$$K = [Mn^{II} - OT - I] / [Mn^{II}] [OT] [I] \quad (5)$$

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

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

$$K = [C_2]_{eq} / [Mn^{II}] [OT] [I] \quad (6)$$

$$[Mn^{II}] = [C_2]_{eq} / K [OT] [I] \quad (7)$$

By mass balance, total Mn^{II} concentration, [Mn^{II}]₀ is given by Eq. (8)

$$[Mn^{II}]_0 = [Mn^{II}] + [Mn^{II} - OT] + [Mn^{II} - OT - I] \quad (8)$$

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

$$[Mn^{II}]_0 = [Mn^{II}] + [C_2]_{eq} \quad (9)$$

or

$$[C_2]_{eq} = [Mn^{II}]_0 - [Mn^{II}] \quad (10)$$

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

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

As the binary complex, Mn^{II} - OT, has no absorbance at chosen wavelength (500 nm) under the experimental conditions, the absorbance A_e can be safely assumed only due to ternary complex.

If A_e is absorbance of ternary complex, C₂, and ε is its molar absorptivity then for cell of path length 1 cm, we have

$$A_e = \epsilon [C_2] \quad (12)$$

where [C₂] 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 [C₂] by [Mn^{II}]₀ in Eq. (12), we obtain,

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

or

$$[Mn^{II}]_0 = A_\infty / \epsilon \quad (13)$$

Substituting the value of [C₂] and [Mn^{II}]₀ in equation (11) from equation (13) and (12).

$$A_e / \epsilon = A_\infty / \epsilon - A_e / \epsilon K [OT] [I]$$

which on rearrangement becomes Eq. (14)

$$1 / A_e = 1 / A_\infty K [OT] [I] + 1 / A_\infty \quad (14)$$

This equation assumes that no species other than ternary complex absorbs at chosen wavelength, 500 nm.

A_e values were determined at different concentration of I keeping [OT] fixed. In this condition, equation (14) leads to Eq. (15).

$$1 / A_e = 1 / K_1 [I] A_\infty + 1 / A_\infty \quad (15)$$

Comparison of Eqs. (14) and (15) gives $K_1 = K [OT]$.

A_e were also determined at different concentration of [OT] at fixed concentration of [I] I different experiments. This condition changes the equation (14) as follows,

$$1 / A_e = 1 / K_1 [OT] A_\infty + 1 / A_\infty \quad (16)$$

Eqs. (14) and (16) lead to $K_1 = K [I]$.

As required by Eq. (15), for the variation of I, the plot of $1/A_e$ versus $1/[I]$ is a straight line as shown in Fig. 3. This plot yields slope, $S_1 = 2.73 \times 10^{-3}$ and intercept, $I_1 = 6.63$. According to equation (15), $S_1 = 1/K_1 A_\infty$ and $I_1 = 1/A_\infty$. So from the ratio, I_1/S_1 , the value of K_1 was found to be 2428.6.

Likewise, from Fig. 3, for the variation of OT, we obtain, slope, $S_2 = 4.37 \times 10^{-4}$ and intercept I_2 was found to be 4.89. Eq. (16) shows $K_2 = I_2/S_2$. From the values of S_2 and I_2 , we obtain $K_2 = 1.12 \times 10^4$.

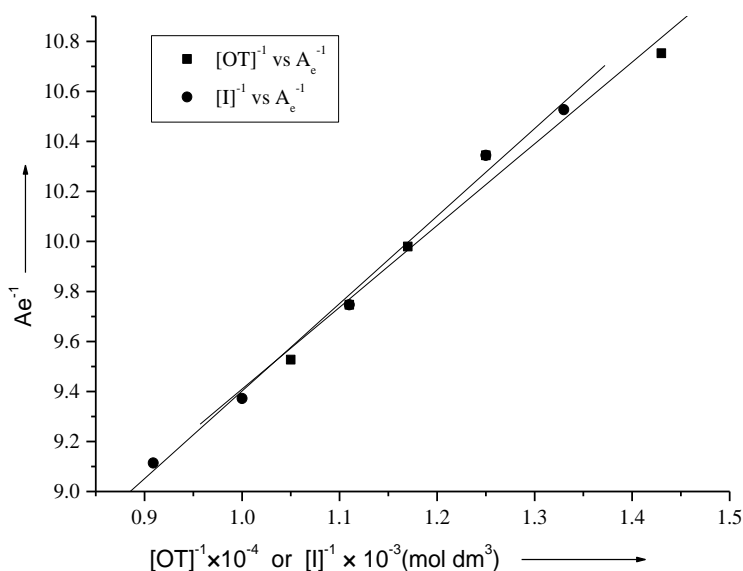


Fig.3: A_e^{-1} vs. $[NaIO_4]^{-1}$ or $[I]^{-1}$ plot $[Mn^{II}] = 8.28 \times 10^{-6} \text{ mol dm}^{-3}$, $pH = 5.0$, $Temp. = 30.0 \pm 0.01^\circ C$, $Acetone = 5.0 \%$ (v/v), $\lambda_{max} = 500 \text{ nm}$

From the K_1 value of 1.12×10^4 (at $[I] = 9.0 \times 10^{-4} \text{ mol dm}^{-3}$), which is equal to $K [I]$, the value of K was found to be 1.24×10^7 . On the other hand from the K_2 value of 2428.6 (at $[OT] = 9.0 \times 10^{-5} \text{ mol dm}^{-3}$), which is equal to $K [OT]$, the value of K is found to be 2.70×10^7 .

The excellent agreement between the K values, as determined from the $[I]$ and $[OT]$ variations at fixed $[Mn^{II}]_0$, validates the hypothesis regarding the formation of ternary complex. The average value of K is $(1.97 \pm 0.73) \times 10^7$ at $pH = 5.0$, $[Mn^{II}]_0 = 8.28 \times 10^{-6} \text{ mol dm}^{-3}$ and $30.0 \pm 0.01^\circ C$.

Kinetics of ternary complex formation

One of the complete kinetics profile is shown in Fig. 2. As discussed earlier, the second stage is relatively slow while the reaction occurs in two stages. The first stage is the formation of ternary brownish pink colour complex, for which the stability constant determination has just been undertaken.

The kinetics of the formation of the complex was studied at 550 nm under pseudo first order conditions, $[I] \gg [OT] \gg [Mn^{II}]$. For ternary complex formation the values of first order rate constant, k_{obs} , and overall rate constant (k_{cat}) are given in Table 2. Fig. 4 presents the first order plots. As expected, the value of k_{cat} is constant.

Table-2 Dependence of reaction rate on concentration of reactants at pH= 5.0, $\lambda_{\max} = 500 \text{ nm}$, Temp. = $30.0 \pm 0.01^\circ\text{C}$, Acetone = 5.0 % (v/v), $[\text{Mn}^{\text{II}}] \times 10^6 = 8.28 \text{ mol dm}^{-3}$

$[\text{NaIO}_4] \times 10^4$ (mol dm^{-3})	$[\text{OT}] \times 10^5$ (mol dm^{-3})	$k_{\text{obs}} \times 10^2$ (s^{-1})	$k_{\text{cat}} \times 10^{-7}$ ($\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$)
7.0	9.0	9.5	5.4
8.0	9.0	9.9	5.5
9.0	9.0	10.3	5.3
10.0	9.0	10.6	5.3
11.0	9.0	11.0	5.3
9.0	7.5	9.3	4.9
9.0	8.0	9.7	5.0
9.0	8.5	10.0	5.2
9.0	9.0	10.3	5.3
9.0	9.5	10.5	5.5

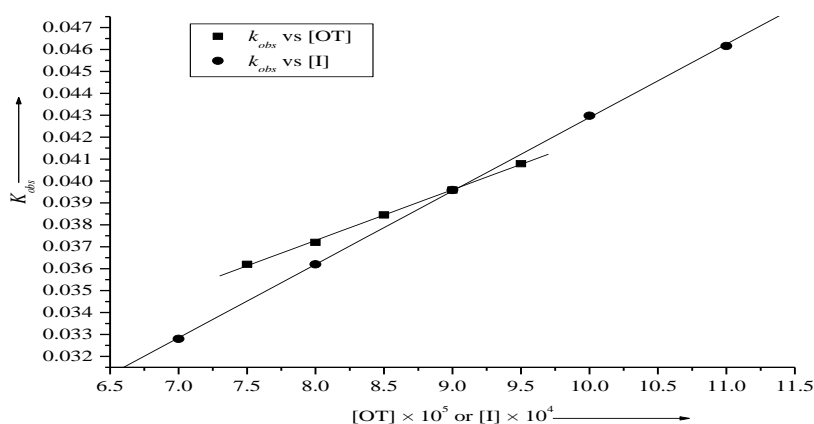


Fig.4: k_{obs} vs [I] or [OT] plots at $[\text{Mn}^{\text{II}}] = 8.28 \times 10^{-6} \text{ mol dm}^{-3}$, pH = 5.0, Temp. = $30.0 \pm 0.01^\circ\text{C}$, acetone = 5.0 % (v/v), $\lambda_{\max} = 500 \text{ nm}$

The value of k_{obs} appears to be only dependent on [I] and [OT] which were in excess as compared to $[\text{Mn}^{\text{II}}]$. k_{obs} may be given by the Eq.

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

where k_f' and k_r are empirical rate constants as defined later. In accordance to Eq. (17), a linear plot is expected between k_{obs} and [I] (Fig. 4). From this plot, the value of k_f' and k_r were worked out. Their values are respectively, $33.44 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ and $9.46 \times 10^{-3} \text{ s}^{-1}$.

Similarly, a linear plot is expected between k_{obs} and [OT] (Fig. 4). From this plot, the value of k_f' and k_r were worked out. Their values are respectively, $231.56 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ and $1.87 \times 10^{-2} \text{ s}^{-1}$.

Reaction Mechanism

The mechanism of ternary complex formation may be represented by the Eqs. 2-3. This mechanism is can not be taken as unique. One or more alternative mechanisms may possibly be written to explain the results obtained by us in this study. The rate of formation of C_2 is given by:

$$d[\text{C}_2]/dt = k_f [\text{Mn}^{\text{II}} \cdot \text{OT}] [\text{I}] - k_r [\text{C}_2] \quad (18)$$

where $[\text{C}_2]$ is the concentration of the ternary complex at time t . By mass balance,

$$[\text{Mn}^{\text{II}}]_0 = [\text{Mn}^{\text{II}}] + [\text{Mn}^{\text{II}} \cdot \text{OT}] + [\text{C}_2] \quad (19)$$

Assuming that the concentration of $\text{Mn}^{\text{II}} \cdot \text{OT}$ is very small, and negligible, Eq. (19) becomes Eq. (20).

$$[\text{Mn}^{\text{II}}]_0 = [\text{Mn}^{\text{II}}] + [\text{C}_2] \quad (20)$$

As already assumed, equilibrium for the formation of the binary complex, $\text{Mn}^{\text{II}} \cdot \text{OT}$, is rapidly established. Therefore, the value of concentration of $\text{Mn}^{\text{II}} \cdot \text{OT}$ is given by,

$$K_1 = [\text{Mn}^{\text{II}} \cdot \text{OT}] / [\text{Mn}^{\text{II}}] [\text{OT}] \quad (21)$$

Substituting $[\text{Mn}^{\text{II}} \cdot \text{OT}] = K_1 [\text{Mn}^{\text{II}}] [\text{OT}]$ in Eq. (18), we get,

$$d[\text{C}_2]/dt = k_f K_1 [\text{Mn}^{\text{II}}] [\text{OT}] [\text{I}] - k_r [\text{C}_2] \quad (22)$$

On substituting $[\text{Mn}^{\text{II}}] = [\text{Mn}^{\text{II}}]_0 - [\text{C}_2]$ from Eq. (20) in Eq. (22), we get,

$$d[\text{C}_2]/dt = k_f K_1 [\text{Mn}^{\text{II}}]_0 [\text{OT}] [\text{I}] - [\text{C}_2] (k_f K_1 [\text{OT}] [\text{I}] + k_r) \quad (23)$$

If the ternary complex formation attains equilibrium then Eq. (23) becomes Eq. (24).

$$k_f K_1 [\text{Mn}^{\text{II}}]_0 [\text{OT}] [\text{I}] = [\text{C}_2]_{\text{eq}} (k_f K_1 [\text{OT}] [\text{I}] + k_r) \quad (24)$$

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

$$d[\text{C}_2]/dt = (k_f K_1 [\text{OT}] [\text{I}] + k_r) ([\text{C}_2]_{\text{eq}} - [\text{C}_2]) \quad (25)$$

which on modification becomes,

$$d[\text{C}_2]/dt = k_{\text{obs}} ([\text{C}_2]_{\text{eq}} - [\text{C}_2]) \quad (26)$$

where

$$k_{\text{obs}} = k_f K_1 [\text{OT}] [\text{I}] + k_r \quad (27)$$

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

where $k_f' = k_f K_1 [\text{OT}]$

On integrating Eq. (26), we get,

$$\ln\{[\text{C}_2]_{\text{eq}} / ([\text{C}_2]_{\text{eq}} - [\text{C}_2])\} = k_{\text{obs}} \cdot t \quad (28)$$

Table – 3 : Data analysis for $[\text{Mn}^{\text{II}}\text{-OT-I}]$ ternary complex formation

[I] mol dm ⁻³	[OT] mol dm ⁻³	Plot	k_r (Intercept)	k_f' (slope) $= k_f K_1 [\text{OT}]$	k_f' (slope) $= k_f K_1 [\text{I}]$	10^{-5} $k_f K_1$	10^{-7} $k_f K_1 / k_r$
variation	9.0×10^{-5}	k_{obs} vs [I]	9.46×10^{-3}	33.44	-	3.71	3.93
9.0×10^{-4}	variation	k_{obs} vs [OT]	1.87×10^{-2}	-	231.56	2.57	1.37

According to Eq. (27) the plot of k_{obs} versus [I] (at constant [OT]) is straight line with a intercept = k_r and slope = $k_f K_1 [\text{OT}]$ (Fig.4). Also, the plot of k_{obs} versus [OT] (at constant [I]) is also straight line with intercept = k_r and slope = $k_f K_1 [\text{I}]$ (Fig. 4). Table 3 gives the values of slopes and intercepts determined from this figure. From I and OT variations respectively, using the values of intercepts and slopes of plots in Fig.4, the values of $k_f K_1$ were found to be 3.71×10^5 and $2.57 \times 10^5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Likewise, the values of $k_f K_1 / k_r$ determined from same figures were found to be 3.93×10^7 and $1.37 \times 10^7 \text{ dm}^6 \text{ mol}^{-2}$. Therefore, mechanism and rate law are

very well supported by the good agreement between parameters obtained from variation of o-toluidine and periodate.

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