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EVALUATION OF STABILITY CONSTANT OF TERNARY INTERMEDIATE COMPLEX FORMATION IN Mn^{II} CATALYSED PERIODATE OXIDATION OF 2, 5-XYLIDINE BY STOPPED FLOW METHOD

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ABSTRACT

Although proposed in many cases, the ternary complexation during periodate oxidation of majority of anilines catalyzed 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 2,5-XYL - Mn^{II} - IO_4^- during Mn^{II} catalyzed reduction of periodate by 2,5-xylidine(2,5-XYL) has been explored and its stability constant has been evaluated. Its value of (2.0 ± 0.66) × 10^6 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., $d[C_2]/dt = (k_f K_1 [2,5\text{-XYL}][I] + k_r)([C_2]_{eq} - [C_2])$,where, $k_f / k_r = K_2$ i.e. equilibrium constant for the reaction of 2,5-XYL - Mn^{II} and IO_4^- , K_1 equilibrium constant for formation of binary complex 2,5-XYL-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: 2, 5-xylidine, Stopped flow trace, Ternary complex, Mn^{II} catalyzed, Stability constant, Periodate oxidation

INTRODUCTION

Knowledge of stability constant of binary/ ternary complexation between amine, metals and oxidants can be useful for controlling the action of carcinogenic and/ or toxic aromatic amines which can cause genotoxicity and cytotoxicity[1,2]. 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, and 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 catalyzed/ unanalyzed oxidation of aromatic amines by periodate ion[4-30]. The detailed kinetic-mechanistic studies on Mn^{II} catalyzed reduction of periodate by 2,3-xylidines and 3,5-xylidine[31-32] and studies on the ternary complex formation between these xylidines, 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 2,5-xylidine (2,5-XYL), Mn^{II}, and periodate ion in acetone-water medium and the results along with the supporting evidences are being presented in this communication.

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EXPERIMENTAL

Reagents and Chemicals

Solutions were prepared in triply distilled water. Redistilled or recrystallized chemicals like 2, 5-xylidine (2,5-XYL) (E. Merck), 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 ± 0.1°C accuracy. Experiments were conducted only during the time in which λ_{max} remained unchanged as shown in Figures-1, 2 and 3.

As the λ_{max} was 535 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 (± 0.01°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 2,5-XYL and Mn^{II}.
2. No reaction was observed between Mn^{II} and I.
3. λ_{max} of reaction mixture (having Mn^{II}, 2,5-XYL and I) and same mixture without Mn^{II}, was 535 nm. However, the molar extinction coefficient is high in presence of Mn^{II}.
4. Reaction mixture turns pink initially, changing into wine red and then brown. After it, precipitation is observed in 24 hours.
5. Separate experiments showed the reaction to be first order w. r. t. 2,5-XYL, I and Mn^{II}. Therefore, pseudo first order conditions were adopted for following the kinetics of this reaction.

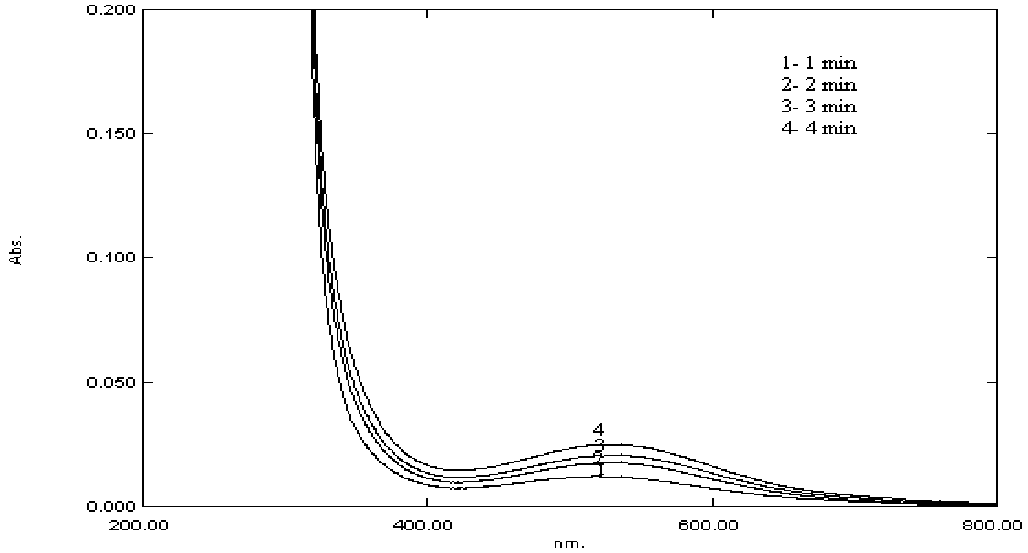

Fig.-1: Determination of Absorption maxima of periodate oxidation of 2,5-XYL
$[NaIO_4] \times 10^3 = 2.0$ mol dm^{-3},$[2, 5\ XYL] \times 10^4 = 4.0$ mol dm^{-3},
pH = 5.5, Temp. = 30.0 ±0.1 °C, acetone = 5.0 % (v/v)

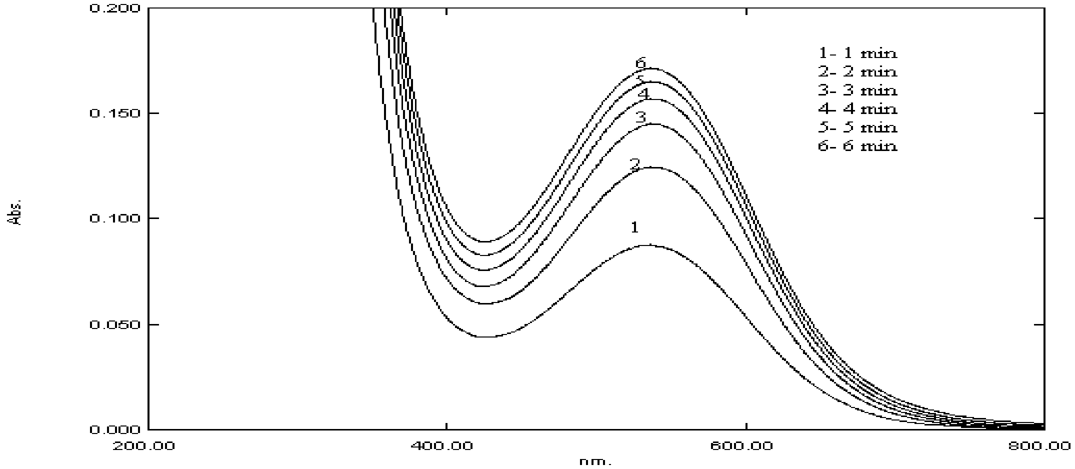

Fig.-2: Determination of Absorption maxima of Mn^{II} catalyzed periodate oxidation of 2, 5 –XYL $[NaIO_4] \times 10^3 = 2.0$ mol dm^{-3}, $[2,5\text{-}XYL] \times 10^4 = 4.0$ mol dm^{-3}, Acetone = 5.0 % (v/v), $[Mn^{II}] \times 10^6 = 3.28$ mol dm^{-3}, pH = 5.5, Temp. = 30.0 ±0.1 ºC

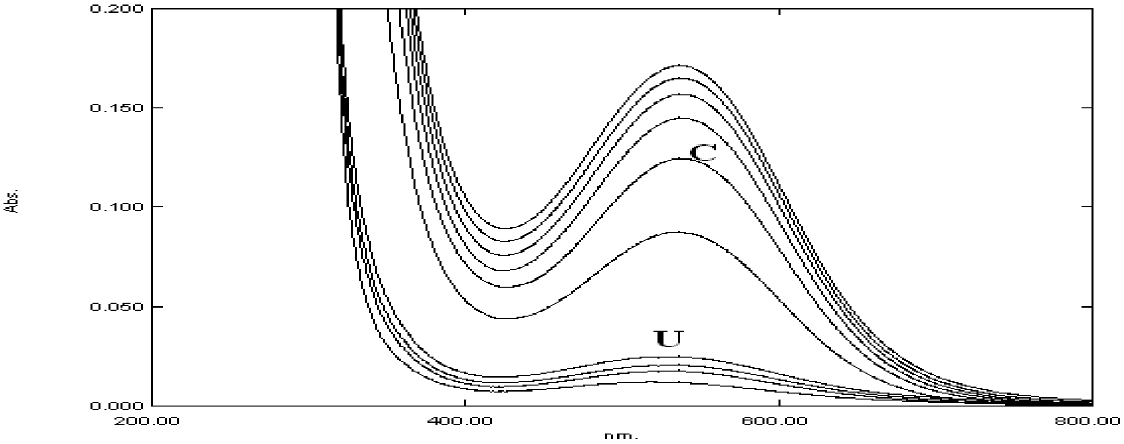

Fig.-3: Compression of UV-VIS rapid scans of unanalyzed and catalyze reaction at $[NaIO_4] \times 10^3 = 2.0$ mol dm^{-3}, $[2,5\ XYL] \times 10^4 = 4.0$ mol dm^{-3}, pH = 5.5, Acetone = 5.0 % (v/v),Temp. = 30.0 ±0.1 ºC, $[Mn^{II}] \times 10^6 = 3.28$ mol dm^{-3} (For catalysed reaction only). U and C represent the scans for unanalyzed and catalyzed reaction, respectively.

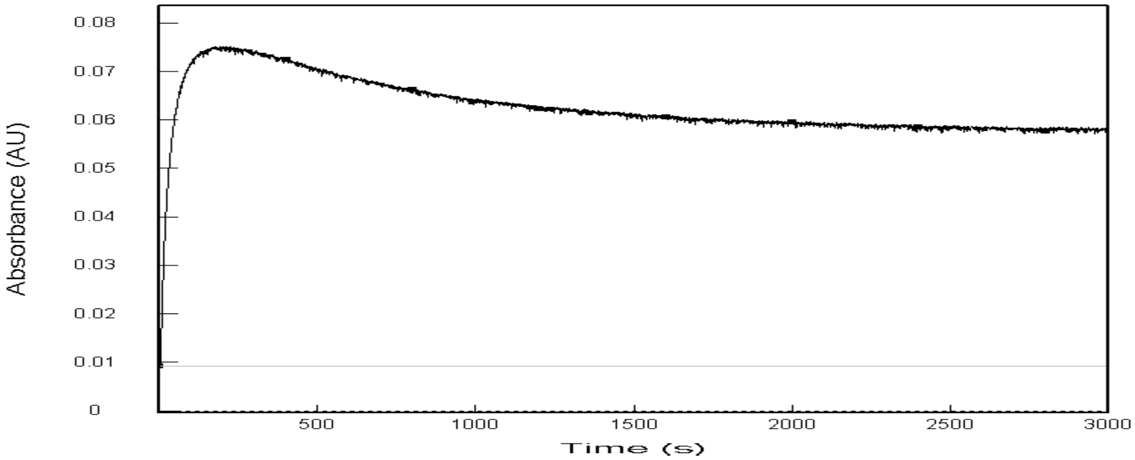

Fig.-4: The complete kinetics stopped flow trace for Mn^{II} catalyzed oxidation of [2,5-XYL] by $NaIO_4$ at $[2,5\ XYL] = 8.0 \times 10^{-5}$ mol dm^{-3}, pH = 6.0, $[I] = 8.0 \times 10^{-4}$ mol dm^{-3}, $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, Temp. = 30.0 ±0.01^0C, acetone = 5.0 %(v/v), λ_{max}= 535 nm

Stability constant of 2, 5-XYL - 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:

$$[I] >> [2,5\text{-XYL}] >>> [Mn^{II}]$$

Figure-4, 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 500-2000 s. 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 vales for [2,5-XYL-Mn^{II} - IO_4^-] complex $[Mn^{II}] \times 10^6 = 7.28$ mol dm^{-3}, pH = 5.5, Temp. = 30.0 ± 0.01°C, λ_{max} = 535 nm. Acetone = 5.0 % (v/v)

$[NaIO_4] \times 10^4$ mol dm^{-3}	$[2,5\text{-XYL}] \times 10^5$ mol dm^{-3}	A_e
8.0	8.0	0.042
8.5	8.0	0.044
9.0	8.0	0.047
9.5	8.0	0.049
10.0	8.0	0.051
8.0	5.0	0.027
8.0	6.0	0.034
8.0	7.0	0.037
8.0	8.0	0.042
8.0	9.0	0.046

Table-2: Dependence of reaction rate on concentration of reactants
$[Mn^{II}] \times 10^6 =$ 7.28 mol dm^{-3}, Acetone = 5.0 % (V/V), Temp. = 30.0 ± 0.01 °C, pH = 5.5, λ_{max} = 535 nm.

$[NaIO_4] \times 10^4$ mol dm^{-3}	$[2,5\text{-XYL}] \times 10^5$ mol dm^{-3}	$k_{obs} \times 10^2$ (s^{-1})
8.0	8.0	3.69
8.5	8.0	3.78
9.0	8.0	3.83
9.5	8.0	3.90
10.0	8.0	4.00
8.0	5.0	3.32
8.0	6.0	3.44
8.0	7.0	3.56
8.0	8.0	3.69
8.0	9.0	3.76

When a solution containing Mn^{II} and 2,5-XYL 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),

$$Mn^{II} + 2,5\text{-XYL} + I \xrightleftharpoons{K} \underset{C_2}{2,5\text{-XYL} - Mn^{II} - I} \quad (1)$$

Where, C_2 is the ternary complex, 2,5-XYL - Mn^{II} – I.

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

$$Mn^{II} + 2,5\text{-XYL} \xrightleftharpoons{K_1} \underset{C_1}{Mn^{II} - 2,5\text{-XYL}} \quad \text{(Fast)} \quad (2)$$

$$Mn^{II}\text{ - }2,5\text{-XYL} + I \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{C_2}{2,5\text{-XYL - }Mn^{II}\text{ - I}} \quad (3)$$

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 2,5-XYL, I, Mn^{II} and reaction mixtures for catalyzed/unanalyzed reactions show that only ternary complex absorbs at 535 nm. At this wavelength, Mn^{II}, 2, 5-XYL, Mn^{II} - 2, 5-XYL and Mn^{II} - I display no significant absorbance. However, the 2, 5-XYL - I adduct absorb at 535 nm, but its absorbance can be ignored.

If the absorbance values at pre-selected wavelength, 535 nm, are measured in solutions containing different [2,5-XYL] and [I] but at fixed [Mn^{II}], it can be shown that,[36,37]

$$A_e = -(A_e - A_0)/K[2,5\text{-XYL}][I] + A_\infty \quad (4)$$

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 2,5-XYL and I. K is the overall stability constant and based on Eq. (1) is defined by Eq. (5).

$$K = [Mn^{II}\text{-}2,5\text{-XYL - I}] / [Mn^{II}]\,[2,5\text{-XYL}]\,[I] \quad (5)$$

Where, [Mn^{II}-2,5-XYL -I] = $[C_2]_{eq}$ = equilibrium concentration of ternary complex, [Mn^{II}] = equilibrium concentration of uncomplexed Mn^{II}. And [2,5-XYL] and [I] are initial concentrations of 2,5-XYL and periodate, respectively.

On replacing [Mn^{II} – 2,5-XYL - I] by $[C_2]_{eq}$, Eq. (5) becomes Eq. (6) or (7).

$$K = [C_2]_{eq}/ [Mn^{II}]\,[2,5\text{-XYL}]\,[I] \quad (6)$$

$$[Mn^{II}] = [C_2]_{eq} / K\,[2,5\text{-XYL}]\,[I] \quad (7)$$

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

$$[Mn^{II}]_0 = [Mn^{II}] + \underset{[C_1]}{[Mn^{II}\text{ - }2,5\text{-XYL}]} + \underset{[C_2]_{eq}}{[Mn^{II} - 2,5\text{-XYL - I}]} \quad (8)$$

Since [Mn^{II} - 2,5-XYL] 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

$$[C_2]_{eq} = [Mn^{II}]_0 - [C_2]_{eq}/ K\,[2,5\text{-XYL}]\,[I] \quad (11)$$

As the binary complex, Mn^{II} – 2,5-XYL, has no absorbance at chosen wavelength (535 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, C_2, and ε is its molar absorptivity then for cell of path length 1 cm, we have,

$$A_e = \varepsilon\,[C_2] \quad (12)$$

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 Eq. (12), we obtain,

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

or

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

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

$$A_e/\varepsilon = A_\infty/\varepsilon - A_e/\varepsilon K\,[2,5\text{-XYL}]\,[I]$$

Which on rearrangement becomes Eq. (14)
$1/A_e = 1/A_\infty K[2,5\text{-XYL}][I] + 1/A_\infty$ (14)

This equation assumes that no species other then ternary complex absorbs at chosen wavelength, 535 nm. A_e values were determined at different concentration of I keeping [2,5-XYL] fixed. In this condition, equation (14) leads to Eq. (15).

$1/A_e = 1/K_I[I]A_\infty + 1/A_\infty$ (15)
A comparison of Eqs. (14) and (15) gives $K_I = K[2,5\text{-XYL}]$.
A_e were also determined at different concentration of [2,5-XYL] at fixed concentration of [I] I different experiments. This condition changes the equation (14) as follows,

$1/A_e = 1/K_I[2,5\text{-XYL}]A_\infty + 1/A_\infty$ (16)

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

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, $S_1 = 1.78 \times 10^{-3}$ and intercept, $I_1 = 0.191$. According to equation (15), $S_1 = 1/K_I A_\infty$ and $I_1 = 1/A_\infty$. So from the ratio, I_1/S_1, the value of K_I was found to be 107.
Likewise, from Fig. 6, we obtain, slope, $S_2 = 1.63 \times 10^{-4}$ and intercept, $I_2 = 0.345$. Eq. (16) shows $K_I = I_2/S_2$. From the values of S_2 and I_2, we obtain $K_I = 2.116 \times 10^3$.
From the K_I value of 107 (at $[2,5\text{-XYL}] = 8.0 \times 10^{-5}$ mol dm^{-3}), the value of K was found to be 1.34×10^6. Also the K_I value of 2.116×10^3 (at $[I] = 8.0 \times 10^{-4}$ mol dm^{-3}), leads to the value of K equal to 2.65×10^6.

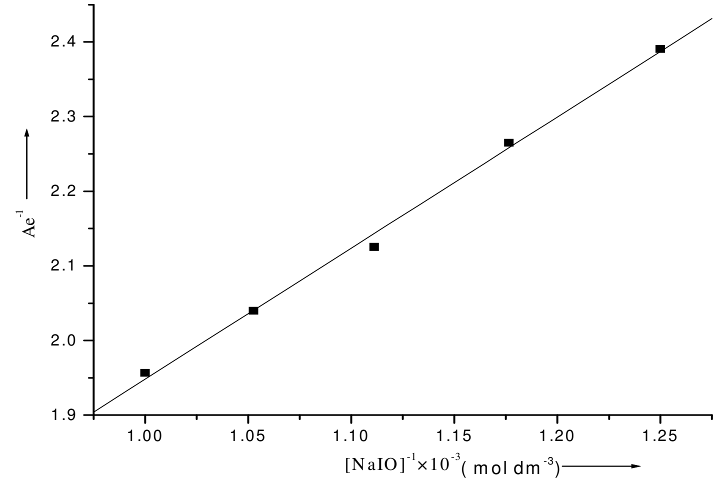

Fig.-5: Ae^{-1} vs. $[NaIO_4]^{-1}$ plot; $[2,5D]\times 10^5 = 8.0$ mol dm^{-3}, $[Mn^{II}]\times 10^6 = 7.28$ mol dm^{-3}, Acetone = 5.0 % (V/V), pH =5.5, Temp. =30.0 ± 0.01^{0}C; $\lambda_{max} = 535$nm

The good agreement between the K values, as determined from the variations of [I] and [2,5-XYL] at fixed $[Mn^{II}]_0$, supports the formation of ternary complex. The average value of K is $(2.0 \pm .66) \times 10^6$ at pH =5.5, $[Mn^{II}]_0 = 7.28 \times 10^{-6}$ mol dm^{-3} and 30.0 ± 0.01°c.

Kinetics of ternary complex formation
One of the complete kinetics profile is shown in Fig.-4. As discussed earlier, the second stage is relatively slow while the reaction occurs in two stages. The first stage is the formation of ternary pink complex, for which the stability constant determination has just been undertaken.

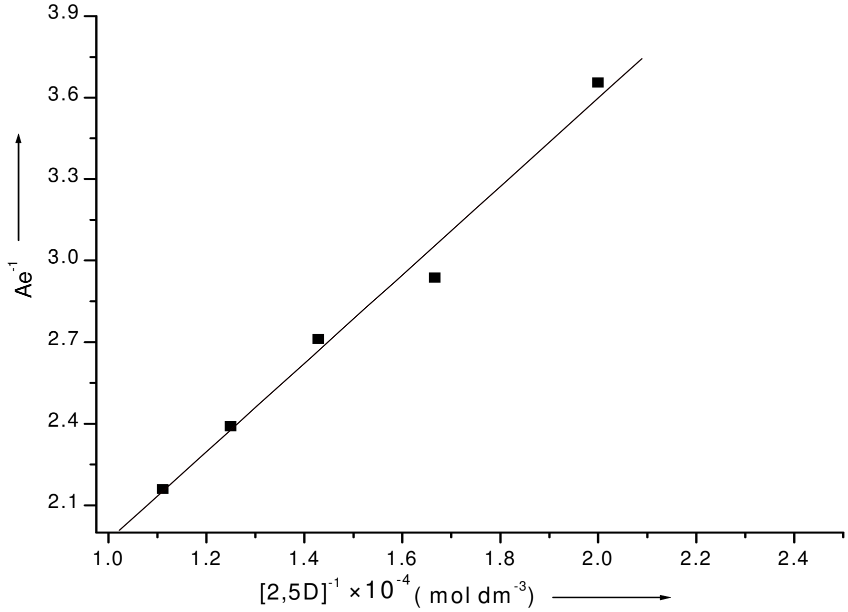

Fig.-6: Ae^{-1} vs. [2,5XYL]$^{-1}$ (or [2,5 D]$^{-1}$) plot; [NaIO$_4$]×10^4 =8.0 mol dm^{-3}, [Mn^{II}]×10^6 = 7.28 mol dm^{-3}, Acetone = 5.0 %(v/v), pH =5.5 , Temp. = 30.0 ± 0.01 ^{0}C, λ_{max} = 535nm

Table-3: Data analysis for [Mn^{II}-2,5-XYL-I] formation

[I] mol dm^{-3}	[2,5-XYL] mol dm^{-3}	Plot	k_r (Intercept)	k_f' (slope) = $k_f K_I$[D]	k_f' (slope) = $k_f K_I$[I]	10^{-5} $k_f K_I$	10^{-6} $k_f K_I/k_r$
variation	8× 10^{-5}	k_{obs} vs [I]	2.50 × 10^{-2}	1.48 ×10^2	-	1.9	7.4
8 × 10^{-4}	variation	k_{obs} vs [2,5-XYL]	2.79 × 10^{-2}	-	1.1 ×10^3	1.4	5.0

The kinetics of the formation of the complex was studied at 535 nm under pseudo first order conditions, [I] >> [2, 5-XYL] >>> [Mn^{II}]. For ternary complex formation the values of first order rate constant, k_{obs}, are given in Table-2. Figs.-7 and 8 present the first order plots.

The value of k_{obs} appears to be only dependent on [I] and [2,5-XYL] which were in excess as compared to [Mn^{II}]. k_{obs} may be given by the Eq.(17),

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

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.-7). From this plot, the value of k_f' and k_r were worked out. Their values are respectively, 1.48 × 10^2 L mol^{-1} s^{-1} and 2.5 × 10^{-2} s^{-1}.

Reaction Mechanism

The mechanism of ternary complex formation may be represented by the Eqs.-2 and 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:

$$d [C_2]/dt = k_f [Mn^{II}. 2,5\text{-}XYL] [I] - k_r [C_2] \qquad (18)$$

Where, [C$_2$] is the concentration of the ternary complex at time *t*.

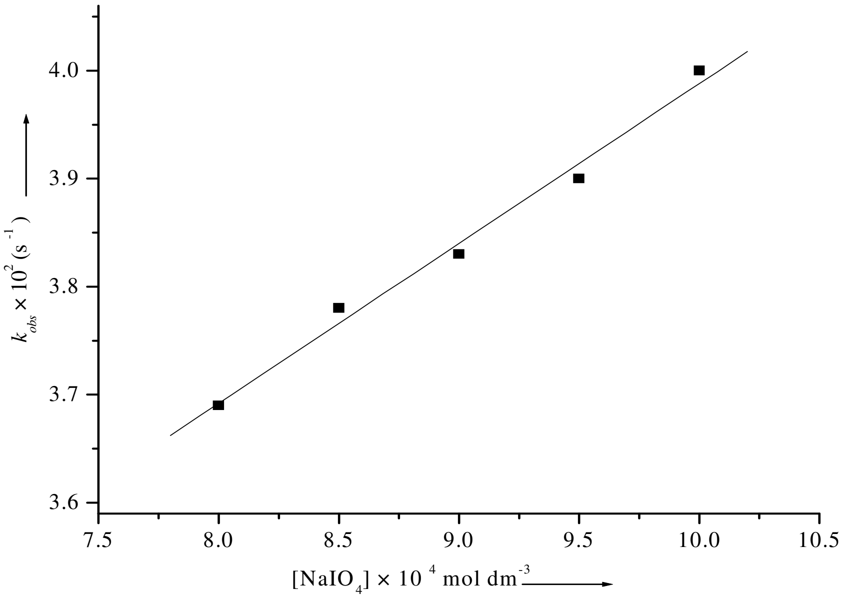

Fig.-7: k_{obs} vs. [NaIO$_4$] plot, [2,5-XYL]$\times 10^5$ = 8.0 mol dm^{-3}, [Mn^{II}]$\times 10^6$ = 7.28 mol dm^{-3}, Acetone = 5.0 %(V/V),pH = 5.5, λ_{max}= 535nm, Temp.= 30.0 ± 0.01^{0}C

By mass balance,

$[Mn^{II}]_0 = [Mn^{II}] + [Mn^{II}.\ 2,5\text{-}XYL] + [C_2]$ (19)

Assuming that the concentration of Mn^{II} - 2,5-XYL is very small, and negligible, Eq. (19) becomes Eq. (20).

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

As already assumed, equilibrium for the formation of the binary complex, Mn^{II} - 2,5-XYL, is rapidly established. Therefore, the value of concentration of Mn^{II} - 2,5-XYL is given by,

$K_1 = [Mn^{II}.\ 2,5\text{-}XYL]/ [Mn^{II}]\ [2,5\text{-}XYL]$ (21)

Substituting [Mn^{II} - 2,5-XYL] = K_1 [Mn^{II}][2,5-XYL] in Eq. (18), we get,

$d[C_2]/dt = k_f K_1 [Mn^{II}][2,5\text{-}XYL]\ [I] - k_r[C_2]$ (22)

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

$d[C_2]/dt = k_f K_1[Mn^{II}]_0[2,5\text{-}XYL][I]-[C_2](k_f K_1[2,5\text{-}XYL][I] + k_r)$ (23)

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

$k_f K_1[Mn^{II}]_0[2,5\text{-}XYL][I] =[C_2]_{eq}(k_f K_1 [2,5\text{-}XYL][I] + k_r)$ (24)

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

$d[C_2]/dt = (k_f K_1 [2,5\text{-}XYL][I]+ k_r)([C_2]_{eq} -[C_2])$ (25)

Which on modification becomes,

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

where

$k_{obs} = k_f K_1 [2,5\text{-}XYL][I]+ k_r$ (27)

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

where $k_f^{'}= k_f K_1 [2,5\text{-}XYL]$

On integrating Eq. (26), we get,
$\ln\{[C_2]_{eq} / ([C_2]_{eq} - [C_2])\} = k_{obs} . t$ (28)

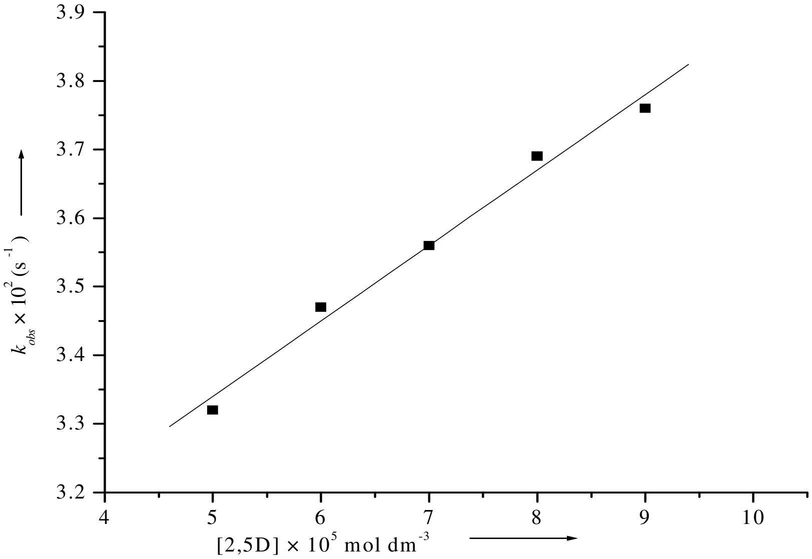

Fig.-8: k_{obs} vs. [2,5-XYL] or [2,5 D] plot, $[NaIO_4]\times10^4 = 8.0$ mol dm^{-3}, $[Mn^{II}]\times10^{6} = 7.28$ mol dm^{-3}, acetone = 5.0 %(V/V), pH = 5.5, Temp. = 30.0 ± 0.01 ^{0}C, $\lambda_{max} = 535$nm.

According to Eq. (27) the plot of k_{obs} versus [I] (at constant [2,5-XYL]) is straight line with a intercept = k_r and slope = $k_f\ K_I$[2,5-XYL] (Fig. 7). Also, the plot of k_{obs} versus [2,5-XYL] (at constant [I]) is also straight line with intercept = k_r and slope = $k_f\ K_I$[I] (Fig.-8). Table-3 gives the values of slopes and intercepts determined from these figures.

From I and 2,5-XYL variations respectively, using the values of intercepts and slopes of plots in Figures-7 and 8, the values of $k_f.K_I$ were found to be 1.9×10^5 and 1.4×10^5 dm^6 mol^{-2} s^{-1}. Likewise, the values of $k_f\ K_I/\ k_r$ determined from same figures were found to be 7.4×10^6 and 5.0×10^6 dm^6 mol^{-2}. Therefore, mechanism and rate law are very well supported by the good agreement between parameters obtained from variation of 2,5-xylidine and periodate.

REFERENCES

1. H.M. Pinheiro, E. Touraud and O. Thomas, *Dyes and Pigments*, **61**, 121 (2004)
2. J.M. Dupret, J. Dairou, F. Busi, P. Silar, M. Martins, C. Mougin, F.R. Lima and A. Cocaign, *InTech, Croatia*, 601 (2011)
3. S.K. Mortensen, X.T. Trier, A. Foverskov and J.H. Petersen, *J. Chromatogr. A.*, **40**, 1091 (2005)
4. V.K. Pavolva, Ya.S. Sevchenko and K.B. Yatsimiriskii, *Zh. Fiz. Khim.*, **44**, 658 (1970)
5. R.D. Kaushik, Amrita, M. Dubey and R.P. Singh. *Asian J. Chem.,***16(2)**, 831 (2004)
6. R.D. Kaushik, V. Kumar, R.K. Arya and D. Singh, *Asian J. Chem.,* **12**, 1123 (2000)
7. R.D. Kaushik, R.P. Singh and Shashi, *Asian J. Chem.,* **15**, 1485 (2003)
8. R.D. Kaushik, R. Malik and A. Kumar, *J. Indian Chem. Soc.,***87**, 317(2010)
9. R.D. Kaushik, Manila, D. Kumar and P. Singh, *Oxid. Commun.,* **33**, 519 (2010)
10. R.D. Kaushik, R. Kumari, T. Kumar and P. Singh, *Asian J. Chem.,* **22(10),** 7959(2010)
11. R.D. Kaushik, A.K. Chauby and P.K. Garg, *Asian J. Chem.,* **15**, 1655 (2003)
12. R.D. Kaushik, R.K. Arya and S. Kumar, *Asian J. Chem.,***12**, 1229 (2000)
13. R.D. Kaushik, S.D. Oswal and D. Singh, *Asian J. Chem.,* **12**, 1129 (2000)
14. R.D. Kaushik, V. Kumar and S. Kumar, *Asian J. Chem.,* **11**, 633 (1999)

15. R.D. Kaushik, D. Singh, R. Joshi and S. Kumar, *Asian J. Chem.,* **10**, 573 (1998)
16. R.D. Kaushik, R. Joshi and D. Singh, *Asian J. Chem.,* **10**, 567 (1998)
17. R.D. Kaushik and R. Joshi. *Asian J. Chem.,* **9,** 527 (1997)
18. R.D. Kaushik, P. Rathi, Manila, J. Singh, R. Yadav, *J. Chem. Pharm. Res.,* **6(7)**, 2752 (2014)
19. I.F. Dolmanova, V.P. Poddubienko and V.M. Peshkova, *Zh. Anal. Khim.*, **25**, 2146 (1970)
20. R.D. Kaushik, Shashi, Amrita and S. Devi, *Asian J. Chem.,* **16**, 818 (2004)
21. R.D. Kaushik, D. Kumar, A. Kumar and A. Kumar, *J. Indian Chem. Soc.,* **87(7),** 811(2010)
22. R.D. Kaushik, M. Kaur, R. Malik and A. Kumar, *Int. J. Chem. Sci.,* **8(3)**, 1379 (2010)
23. R.D. Kaushik, A. Kumar, T. Kumar and P. Singh, *React. Kinet. Mech. Cat.,* **101**, 13 (2010)
24. R.D. Kaushik, R. Malik, T. Kumar and P. Singh, *Oxid. Commun.,* **35(2)**, 316 (2012)
25. J. Singh, R. Malik, O. Singh, Sushma and R.D. Kaushik. *Int. J. Chem. Sci.,* **12(2)**, 445 (2014)
26. R.D. Kaushik, P. Sundriyal, P. Tyagi, P. Singh and J. Singh. *Int. J. Chem. Sci.,* **12(2)**, 600 (2014)
27. R.D. Kaushik, J. Singh, Manila, M. Kaur and P. Singh, *Bull. Chem. React. Eng. & Cat.,* **9 (3),** 182 (2014)
28. R.D. Kaushik, R. Malik, O. Singh, Manila and J. Singh, *Int. J. Chem.Tech. Res.,* **6(5)**, 2695 (2014)
29. R.D. Kaushik, R. Yadav, M.M. Tiwari, P. Rathi and J. Singh, *Der Pharmacia Lettre,* **6 (4)**, 78 (2014)
30. R.D. Kaushik, R. Malik, M.M. Tiwari, J. Singh, P. Singh, *Res. J. Pharma. Bio. Chem. Sci.,* **5(3),** 1963 (2014)
31. R.D. Kaushik, R. Malik, R. Agarwal and J. Singh, *Res. J. Pharma. Bio. Chem. Sci.,* **5(3),** 1644 (2014)
32. R. D. Kaushik, J. Singh, R. Agarwal and E. Kumari, *J. Indian Chem. Soc.,* **93(1),** 85(2016)
33. R.D. Kaushik, R. Aggarwal, P. Tyagi, O. Singh and J. Singh, *Bull. Chem. React. Eng. & Cat.,* **10 (1)**, 78 (2015)
34. R.D. Kaushik, R. Aggarwal, P. Tyagi, O. Singh and J. Singh. *J. Indian Chem. Soc., Accepted for publication* **94**, (2017).
35. H.T.S. Britton, "Hydrogen ions", D. Von Nostrand Co., p. 354 (1956)
36. M.H. Conklin, and M.R. Hoffmann, *Environ. Sci. Technol*., **22**, 899 (1988)
37. K.S. Gupta, U. Jain, A. Singh, Y. Dhayal and A. Rani, *J. Indian Chem. Soc*., **89**, 1035 (2012)

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