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Stopped flow kinetics of Mn^{II} catalysed Periodate Oxidation of *p*-Anisidine – Exploring the ternary Intermediate complex formation

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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. Stop-flow spectrophotometric method was used to study the ternary complex formation and to determine its stability constant. 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 *p*-Anisidine (PA) in acetone-water medium. 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 PA - Mn^{II} - IO₄⁻ ternary complex by determining equilibrium absorbance is $(2.45 \pm 1.28) \times 10^7$. Kinetics of ternary complex formation was defined by the rate law (A or B) under pseudo first order conditions.

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

or

$$\ln\{[C_2]_{eq} / ([C_2]_{eq} - [C_2])\} = k_{obs} \cdot t \quad (B)$$

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: Mn^{II} catalysed, Periodate oxidation, *p*-anisidine, Stopped flow kinetics, stability constant, ternary complex

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INTRODUCTION

It is of interest to study the new reactions of aromatic amines for understanding their role in physiological activities and for developing methods for their detection, estimation and treatment as 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]. These can be used as intermediates in the manufacture of plastics, dyes, drugs, explosives, rubber, epoxy polymers, azo dyes, aromatic polyurethane products and pesticides[3]. Various oxidants like peroxydisulphate ion[4] and benzimidazolium fluorochromate[5] etc have been employed for their oxidation. During the non-Malapradian periodate oxidation of some aromatic amines, a binary unstable intermediate complex formation between aromatic amine and periodate has been proposed in [6-19]. 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} [20-35].

In present communication, our earlier reported work on periodate oxidation of *p*-anisidine catalysed by Mn^{II} [30], has been extended and the reaction has been further explored to make an attempt for the first time for evaluation of stability constant for the ternary intermediate complex being formed in this reaction using the results of stopped flow kinetic studies made on Mn^{II} - catalysed periodate oxidation of *p*-anisidine.

EXPERIMENTAL

Reagents and Chemicals

Thiel, Schultz and Koch buffer[36] was used for maintaining the pH of reaction mixtures. Triply distilled water was used for preparation of the solutions. The principal reagents used were sodium metaperiodate (Loba Chemie), *p*-Anisidine (Loba Chemie), manganese sulphate monohydrate (Aldrich) here-to-after referred as I, PA and Mn^{II} , respectively. All other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization.

Kinetic procedure

All uv-visible absorbance measurements were made on Shimadzu double beam spectrophotometer (UV-2450). The reaction was initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing PA, Mn^{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 $\pm 0.1^\circ C$. The absorption maximum (λ_{max}) of the reaction mixture was 455 nm. The value of λ_{max} remained unchanged during experimental conditions as shown in Fig. 1, 2 and 3. For stopped flow kinetics study, the progress of the reaction was followed by recording the absorbance change with time at 455 nm on stopped flow apparatus (Applied Photophysics – Stopped Flow SX-20). Desired temperature ($\pm 0.01^\circ C$) 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 PA (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.

RESULTS AND DISCUSSION

Preliminary Investigation

The absorption maxima of the reaction mixture containing Mn^{II} , PA and I differed widely from that of the mixture containing only PA and I. Further, absorbance measurements indicated there to be no observable reaction between Mn^{II} and I or Mn^{II} and PA. On mixing PA and I, the solution turned yellow colour, thereafter brown followed by precipitation in about 24 hours (Fig. 1) was quite different from the individual spectra of PA

and I indicating the formation of complex or adduct, PA - I. The λ_{max} of this adduct was found to be 455 nm, which did not change with time, as shown in Fig. 1.

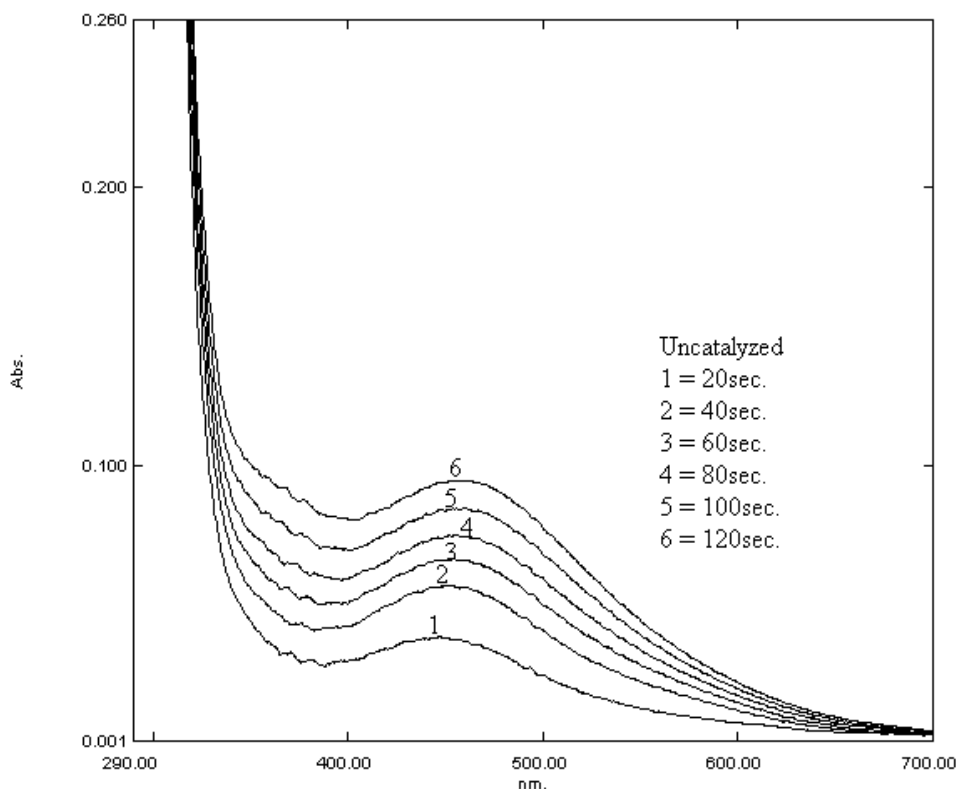


Fig 1: UV-VIS rapid scan at different time at [PA] = 3.0×10^{-5} mol dm⁻³, [NaIO₄] = 3.0×10^{-4} mol dm⁻³, Acetone = 5.0 % (v/v), pH = 7.0, Temp. = $30.0 \pm 0.01^\circ\text{C}$

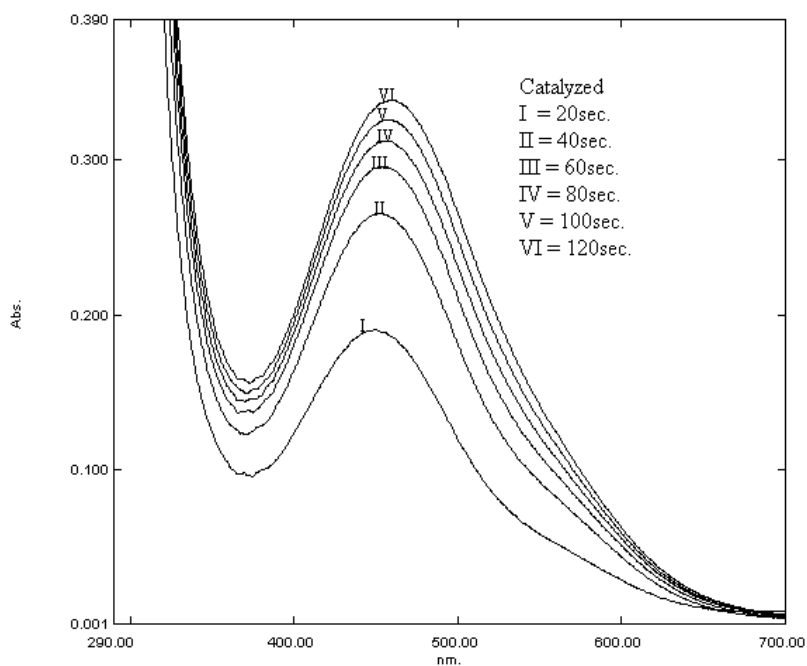


Fig 2: UV-VIS rapid scan at different time at [PA] = 3.0×10^{-5} mol dm⁻³, [NaIO₄] = 3.0×10^{-4} mol dm⁻³, [Mn^{II}] = 7.28×10^{-6} mol dm⁻³, Acetone = 5.0 % (V/V), pH = 7.0, Temp. = $30.0 \pm 0.01^\circ\text{C}$, λ_{max} = 455 nm.

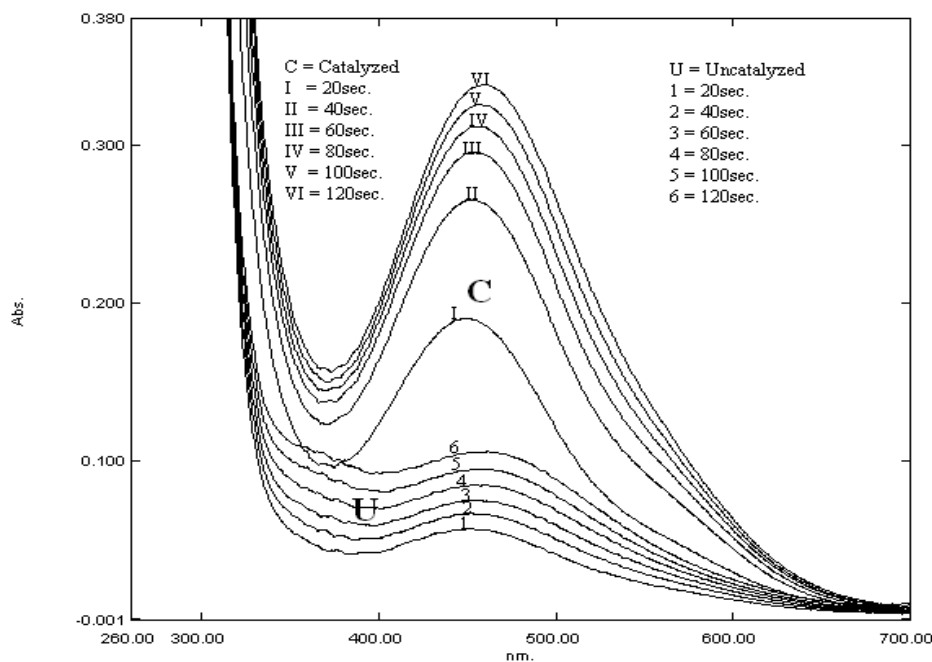


Fig 3: Compression of UV- VIS rapid scans of uncatalyzed and catalyzed Reaction at $[PA] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[I] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), pH = 7.0, Temp. = $30.0 \pm 0.01^\circ\text{C}$, (for catalyzed reaction only), $[Mn^{II}] = 7.28 \times 10^{-6} \text{ mol dm}^{-3}$, U and C represent the uncatalyzed and catalyzed reaction respectively

Our purpose was to study the kinetics of periodate oxidation of PA in presence of Mn^{II} , which is known to be a catalyst for this system. Therefore, the rapid scan spectra of the solution containing Mn^{II} , $NaIO_4$ and PA were recorded and are shown in Fig. 2. This mixture is reddish brown in colour, which deepens with progress of time. A comparison of spectrum of PA - Mn^{II} - I system with that of I - PA system indicates the formation of a ternary complex, $Mn^{II} - PA - I$, when Mn^{II} is present. Although, λ_{max} is same (455 nm in Fig. 3), but the molar extinction coefficient of ternary complex is high.

The reaction between periodate and PA in presence of Mn^{II} has been shown to be first order in each reactant and catalyst as already reported[30]. So the kinetics was studied under pseudo first order conditions.

Stability constant of PA - 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 $[PA]$ were in large excess (at least ten times) over $[Mn^{II}]$, and $[I]$ was in excess over $[PA]$. 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 90% reaction occurring in ~ 200 second; the second stage is relatively quite slow. The ternary complex attained equilibrium in about 400 - 2000 second 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 absorbance for $[Mn^{II}-PA-I]$ ternary complex at pH=7.0, Temp. = $30 \pm 0.01^\circ\text{C}$, Acetone = 5.0 % (v/v), $\lambda_{max} = 455 \text{ nm}$.

$[I] \times 10^4$ (mol dm ⁻³)	$[PA] \times 10^5$ (mol dm ⁻³)	$[Mn^{II}] \times 10^6$ (mol dm ⁻³)	Absorbance at equilibrium(A_e)

2.0	3.0	7.28	0.133
2.5	3.0	7.28	0.168
3.0	3.0	7.28	0.191
3.5	3.0	7.28	0.229
4.0	3.0	7.28	0.248
3.0	2.0	7.28	0.141
3.0	3.0	7.28	0.191
3.0	4.0	7.28	0.231
3.0	5.0	7.28	0.285
3.0	6.0	7.28	0.307

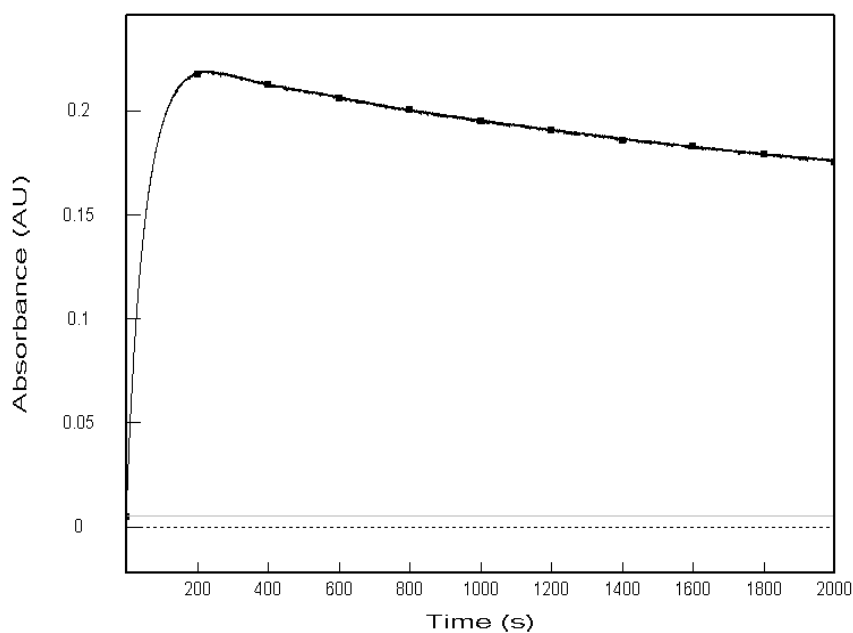
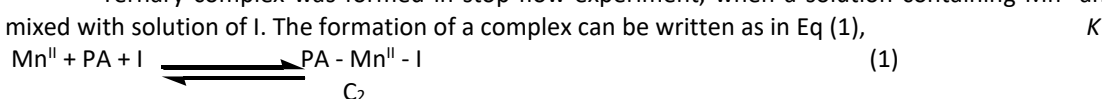


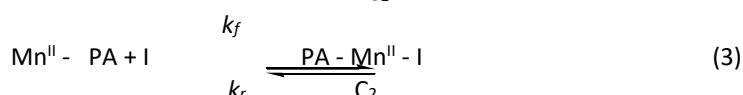
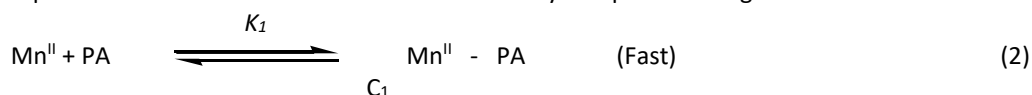
Fig 4: The complete kinetic profile (in terms of stopped flow trace) for Mn^{II} catalyzed oxidation of PA by I at [PA] = 3.0 × 10⁻⁵ mol dm⁻³, pH = 7.0, [I] = 3.0 × 10⁻⁴ mol dm⁻³, [Mn^{II}] = 3.0 × 10⁻⁴ mol dm⁻³, Temp = 30 ± 0.01°C, Acetone = 5 % (v/v), λ_{max} = 455 nm.

Ternary complex was formed in stop-flow experiment, when a solution containing Mn^{II} and PA was mixed with solution of I. The formation of a complex can be written as in Eq (1),



Where C₂ represents the ternary complex, PA - Mn^{II} - I.

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



Subsequently, the ratio k_f/k_r has been used to represent K₂, the equilibrium constant of reaction (3).

The spectra of PA, I, Mn^{II} and reaction mixtures for catalysed/ uncatalysed reactions show that the only principal species absorbing at 455 nm is ternary complex. At this wavelength, Mn^{II}, PA, Mn^{II} - PA and Mn^{II} - I

display no significant absorbance. However, the PA - I adduct absorb at 455 nm, but its absorbance is not sizable and, therefore, can be ignored.

If the absorbance values at pre-selected wavelength, 455 nm, are measured in solutions containing different [PA] and [I] but at fixed $[Mn^{II}]$, it can be shown that [37, 38],

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

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 PA and I. K is the overall stability constant and based on Eq. (1) is defined by Eq. (5).

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

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

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

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

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

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

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

$$\qquad \qquad [C_1] \qquad \qquad [C_2]_{eq}$$

Since $[Mn^{II} - PA]$ 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

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

Under the experimental conditions of this study, the binary complex, $Mn^{II} - PA$, has no absorbance at chosen wavelength (455 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 ϵ is its molar absorptivity then for cell of path length 1 cm, we have

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

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,

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

or

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

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

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

Which on rearrangement becomes Eq. (14)

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

This equation assumes that no species other than ternary complex absorbs at chosen wavelength, 455 nm.

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

$$1/A_e = 1/A_\infty + 1/K_1[I] A_\infty \tag{15}$$

Eq. (15) is equivalent to Eq. (14) through $K_1 = K [PA]$.

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

$$1/A_e = 1/A_\infty + 1/K_1 [PA] A_\infty \tag{16}$$

A comparison of Eqs. (14) and (16) shows $K_1 = K [I]$.

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, $S_1 = 1.39 \times 10^{-3}$ and intercept, $I_1 = 0.49$. 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 352.52.

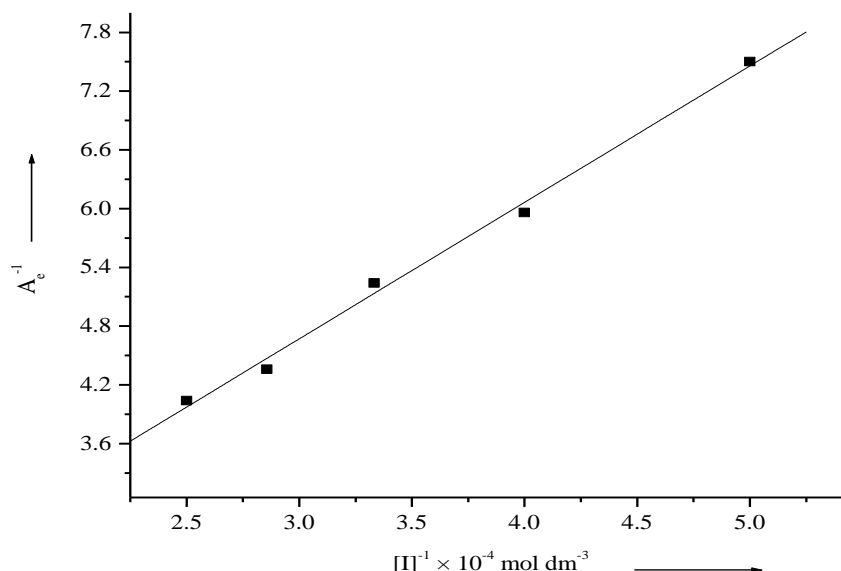


Fig 5: Plot $(A_e)^{-1}$ vs $[I]^{-1}$ at $[PA] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\text{pH} = 7.0$, $[Mn^{II}] = 7.28 \times 10^{-6} \text{ mol dm}^{-3}$, $\text{Temp.} = 30 \pm 0.01^\circ\text{C}$, $\text{acetone} = 5.0 \%$ (v/v), $\lambda_{\text{max}} = 455 \text{ nm}$

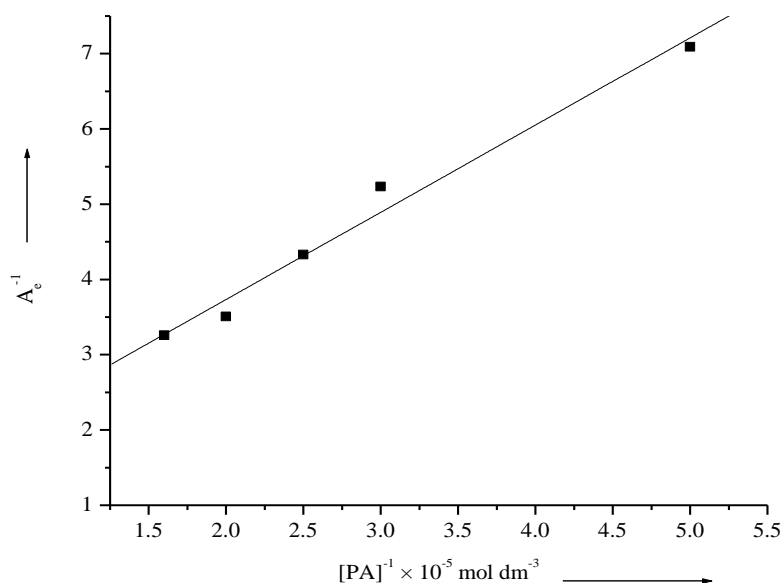


Fig 6: Plot $(A_e)^{-1}$ vs $[PA]^{-1}$ at $[I] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$, pH = 7.0, $[Mn^{II}] = 7.28 \times 10^{-6} \text{ mol dm}^{-3}$, Temp. = $30 \pm 0.01^\circ\text{C}$, Acetone = 5.0 % (v/v), $\lambda_{\text{max}} = 455 \text{ nm}$

Likewise, from Fig. 6, we obtain, slope, $S_2 = 1.17 \times 10^{-4}$ and intercept, $l_2 = 1.31$. Eq. (16) shows $K_1 = l_2/S_2$. From the values of S_2 and l_2 , we obtain $K_1 = 1.12 \times 10^4$.

Now from the K_1 value of 352.52 (at $[PA] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$), which is equal to $K [PA]$, the value of K was found to be 1.17×10^7 . On the other hand from the K_1 value of 1.12×10^3 (at $[I] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$), which is equal to $K [I]$, the value of K is found to be 3.73×10^7 .

The excellent agreement between the K values, as determined from the $[I]$ and $[PA]$ variations at fixed $[Mn^{II}]_0$, validates the hypothesis regarding the formation of ternary complex. The average value of K is $(2.45 \pm 1.28) \times 10^7$ at pH = 7.0, $[Mn^{II}]_0 = 7.28 \times 10^{-6} \text{ mol dm}^{-3}$ and 30°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 yellow complex, for which the stability constant determination has just been described. The kinetics of the formation of the complex was studied at 455 nm under pseudo first order conditions with $[I]$ being in excess over $[PA]$ and $[Mn^{II}]_0$ both and $[PA]$ being in excess over $[Mn^{II}]_0$. The ternary complex formation follows the first order kinetics and the values of first order rate constant, k_{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 $[Mn^{II}]$ on the reaction rate at pH = 7.0, Temp. = $30 \pm 0.01^\circ\text{C}$, Acetone = 5.0 % (v/v), $\lambda_{\text{max}} = 455 \text{ nm}$.

$[I] \times 10^4$ (mol dm ⁻³)	$[PA] \times 10^5$ (mol dm ⁻³)	$[Mn^{II}] \times 10^6$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^2$ (s ⁻¹)	$k_{\text{cat}} \times 10^{-7}$ (dm ⁶ mol ⁻² s ⁻¹)
2.0	3.0	7.28	2.65	1.8
2.5	3.0	7.28	2.75	1.5
3.0	3.0	7.28	2.88	1.3
3.5	3.0	7.28	3.01	1.2
4.0	3.0	7.28	3.11	1.1

3.0	2.0	7.28	2.75	1.3
3.0	3.0	7.28	2.88	1.3
3.0	4.0	7.28	3.04	1.4
3.0	5.0	7.28	3.21	1.5
3.0	6.0	7.28	3.31	1.5

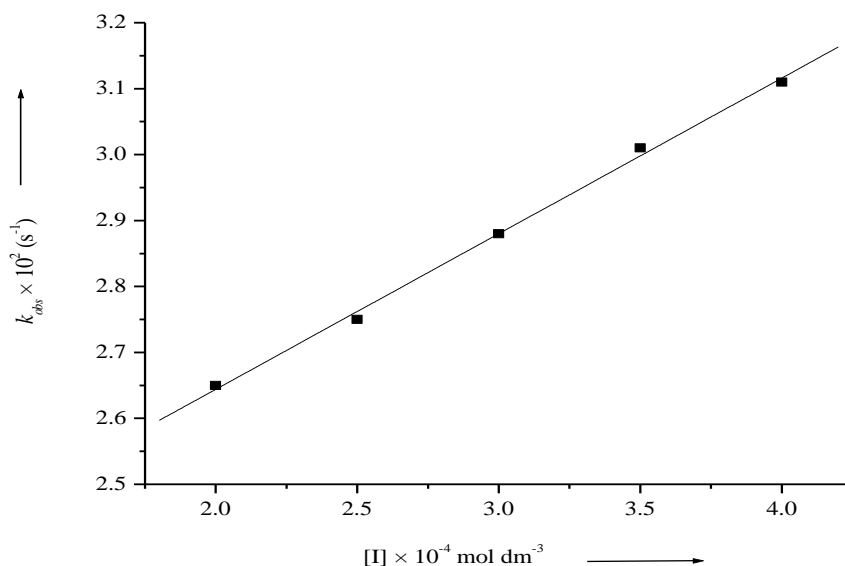


Fig 7: k_{obs} vs $[I]$ plot at, $[PA] = 3.0 \times 10^{-5}$ (mol dm⁻³), $[Mn^{II}] = 7.28 \times 10^{-6}$ (mol dm⁻³), Acetone = 5 % (v/v), pH = 7.0, Temp. = $30 \pm 0.01^\circ\text{C}$, $\lambda_{max} = 455$ nm.

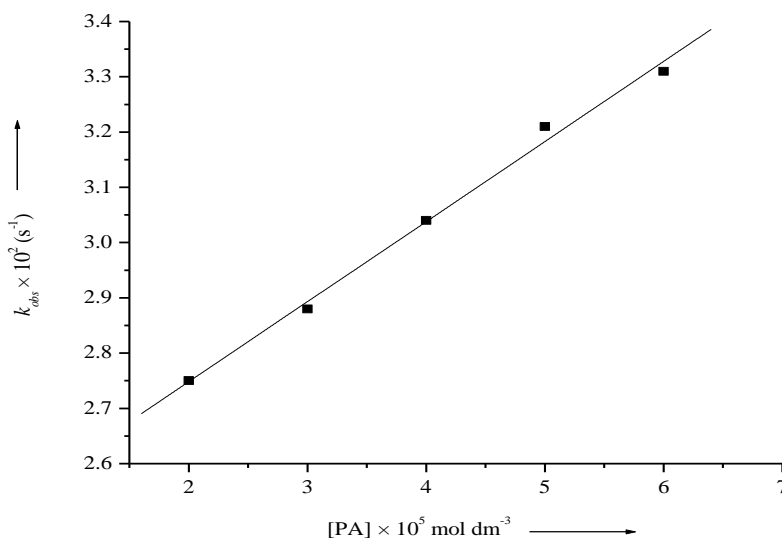


Fig 8: k_{obs} vs $[PA]$ plot at $[I] = 3.0 \times 10^{-4}$ mol dm⁻³, $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm⁻³, Acetone = 5 % (v/v), pH = 7.0, Temp. = $30 \pm 0.01^\circ\text{C}$, $\lambda_{max} = 455$ nm.

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

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

where k_f' and k_r are empirical rate constants as defined later. As required by Eq. (17), the plot of k_{obs} versus $[I]$ is linear as shown in Fig. 7. From this plot, the value of k_f' and k_r were found to be $23.6 \text{ L mol}^{-1} \text{ s}^{-1}$ and $2.17 \times 10^{-2} \text{ s}^{-1}$, respectively.

Mechanism of the reaction

The kinetics results of ternary complex formation may be explained by the mechanism (Eqs. 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:

$$d[C_2]/dt = k_f [Mn^{II} \cdot PA] [I] - k_r [C_2] \quad (18)$$

where $[C_2]$ is the concentration of the ternary complex at time t .

By mass balance,

$$[Mn^{II}]_0 = [Mn^{II}] + [Mn^{II} \cdot PA] + [C_2] \quad (19)$$

Assuming that the concentration of $Mn^{II} \cdot PA$ is very small, and then on neglecting it, Eq. (19) becomes Eq. (20).

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

Assuming that equilibrium for the formation of the binary complex, $Mn^{II} \cdot PA$, is rapidly established then the value of concentration of $Mn^{II} \cdot PA$ is given by Eq. (21).

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

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

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

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

$$d[C_2]/dt = k_f K_1 [Mn^{II}]_0 [PA] [I] - [C_2] (k_f K_1 [PA] [I] + k_r) \quad (23)$$

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 Eq. (23) becomes Eq. (24).

$$k_f K_1 [Mn^{II}]_0 [PA] [I] = [C_2]_{eq} (k_f K_1 [PA] [I] + k_r) \quad (24)$$

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

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

which on modification becomes,

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

Where

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

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

where $k_f' = k_f K_1 [PA]$

On integrating Eq. (26), we get,

$$\ln\{[C_2]_{eq} / ([C_2]_{eq} - [C_2])\} = k_{obs} \cdot t \quad (28)$$

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

Likewise, from Eq. (27) the plot of k_{obs} versus [PA] (at constant [I]) is also straight line with intercept = k_r and slope = $k_f K_1 [I]$ (Fig. 8). The values of slopes and intercepts determined from these Figures are given in Table 3.

Table 3: Data analysis for [Mn^{II}-PA-I] ternary complex formation

[I] mol dm ⁻³	[PA] mol dm ⁻³	Plot	k_r (Intercept)	k_f' (slope) = $k_f K_1 [PA]$	k_f' (slope) = $k_f K_1 [I]$	10^{-5} $k_f K_1$	10^{-7} $k_f K_1 / k_r$
variation	3.0×10^{-5}	k_{obs} vs [I]	2.17×10^{-2}	23.6	-	7.86	7.4
3.0×10^{-4}	variation	k_{obs} vs [D]	2.46×10^{-2}	-	145	4.83	1.97

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 7.86×10^5 and 4.83×10^5 dm⁶ mol⁻² s⁻¹ from I and PA variations, respectively. Likewise, the values of $k_f K_1 / k_r$ determined from same figures were found to be 7.4×10^7 and 1.97×10^7 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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